



TESE DE DOUTORAMENTO

**Testing, validation and optimization
of Surface-Enhanced Raman
Spectroscopy (SERS) sensors for the
detection of small molecules in
cultural heritage materials**

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**Testing, validation and optimization of Surface-Enhanced Raman
Spectroscopy (SERS) sensors for the detection of small molecules in
cultural heritage materials**

D. Massimo Lazzari

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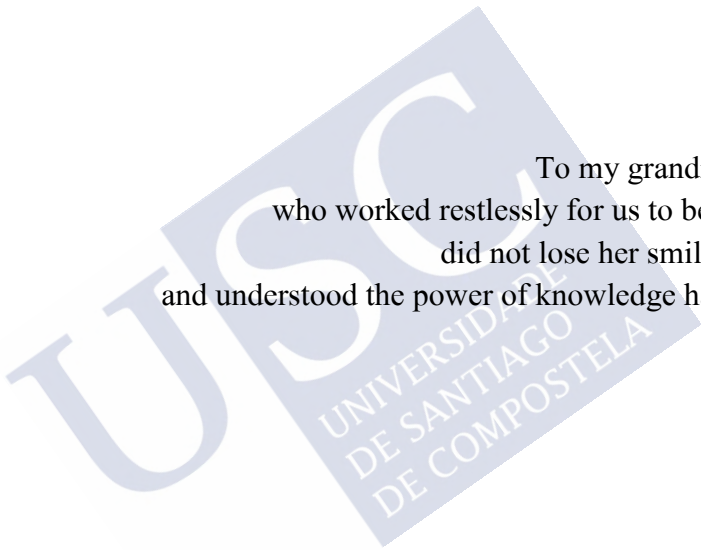


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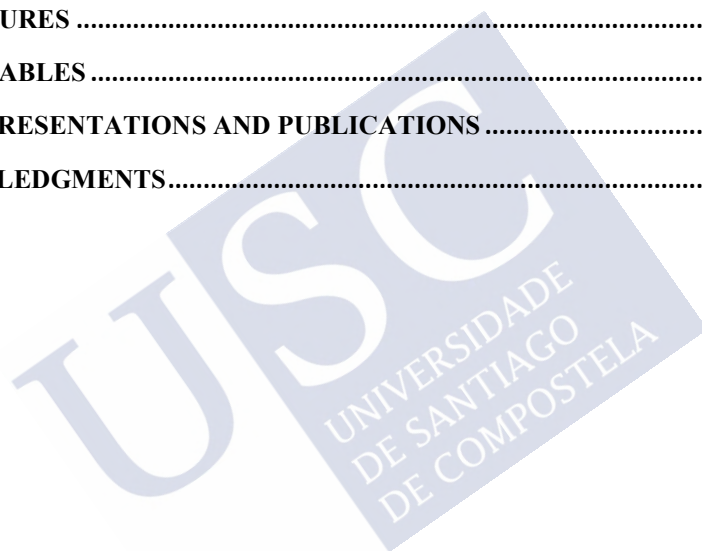
To my grandmother Antonia,
who worked restlessly for us to become educated,
did not lose her smile in bitter times,
and understood the power of knowledge having none of it.

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LIST OF THE JOURNAL ARTICLES FROM THE THESIS

Title	What Fate for Plastics in Artworks? An Overview of Their Identification and Degradative Behaviour (Review article)
Authors	M. Lazzari ^{1,2} & D. Reggio ^{1,2}
Affiliations	¹ Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela, 15701 Santiago de Compostela, Spain; ² Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Universidade de Santiago de Compostela, 15705 Santiago de Compostela, Spain
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Title	Characterization of contemporary and historical acrylonitrile butadiene styrene (ABS)-based objects: Pilot study for handheld Raman analysis in collections
Authors	D. Reggio ^{1,2} , D. Saviello ³ , M. Lazzari ^{1,2} & D. Iacopino ³
Affiliations	¹ Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela, 15701 Santiago de Compostela, Spain; ² Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Universidade de Santiago de Compostela, 15705 Santiago de Compostela, Spain ³ Tyndall National Institute, University College Cork, Nanotechnology Group, Dyke Parade, T12R5CP Cork, Ireland
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Impact factor	4.098
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Publisher	PERGAMON-ELSEVIER SCIENCE LTD
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PhD candidate's contribution	SERS platforms fabrication, all benchtop and SERS measurements, all data processing and graphs, research design, manuscript writing and editing.

Title Detection of degradation markers from polymer surfaces by a novel SERS-based strategy

Authors M. Gomez^{1,2*}, D. Reggio^{1,2*}, Massimo Lazzari^{1,2}

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PhD candidate's contribution All ageing experiments, spectroscopic measurements, validations on objects, data processing, manuscript editing.

Title Linseed oil as a model system for surface-enhanced Raman spectroscopy detection of degradation products in artworks

Authors M. Gomez^{1,2}, D. Reggio^{1,2}, Massimo Lazzari^{1,2}

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PhD candidate's contribution Spectroscopic measurements, data and graphs processing, background research, manuscript writing and editing.

ABBREVIATIONS

a.u.	arbitrary units
ABS	acrylonitrile-styrene-butadiene
Al	aluminum
ATR	attenuated total reflection
BR	butadiene rubber
CB	carbon black
CGAC	Centro Galego de Arte Contemporanea - Galician Contemporary Art Centre
CHCl ₃	chloroform
CICPs	complex inorganic colored pigments
CuPc	copper phthalocyanine
DeSC	derivative scanning calorimetry
DSC	differential scanning calorimetry
EtOH	ethanol
FTIR	Fourier transform infrared
GC/MS	gas chromatography/mass spectrometry
h	hour
LMW	low molecular weight
MALDI-ToF	matrix-assisted laser desorption - ionization - time of flight mass spectrometry
MA-XRF	macro X-Ray fluorescence spectrometry
min	minute
M_n	number average molecular weight
MPA	methylpropylphenone
MS	mass spectrometry
M_w	average molecular weight
NR	normal Raman
OIT	oxidative induction time
PCs	phthalocyanines
PDMS	polydimethylsiloxane
PFPE	perfluoropolyether
PI	polyisoprene
PVAc	poly(vinyl acetate)
PVD	physical vapor deposition
Py	Pyrolysis
SEC	size exclusion chromatography
s	second
SEM-EDS	scanning electron microscopy and energy dispersion system
SERS	surface-enhanced Raman spectroscopy
SOPs	synthetic organic pigments
T_g	glass transition temperature
UV-NIL	ultraviolet nanoimprint soft lithography

RESUMO

Os bens culturais están compostos por unha gran variedade de materiais, tamaños e técnicas de execución segundo as épocas nos que foron producidos e os lugares onde se conservan actualmente. O valor dos obxectos deriva da mensaxe cultural ou histórica que transmiten, aínda que a súa durabilidade está afectada pola calidade do material que os compón. *A ciencia da conservación* e, máis xeralmente, a disciplina da *ciencia do patrimonio*, adócanse plenamente á aplicación de métodos experimentais para o coñecemento dos materiais dos bens culturais. A salvagarda do obxecto e a súa integridade son prioritarias para a transmisión dos seus valores ás futuras xeracións e por este motivo se prefiren técnicas de análise non invasivas, como as técnicas hiperespectrais ou todas aquelas que non requiren toma de mostras. Do mesmo xeito, os instrumentos portátiles para a análise *in situ* estanse a adaptar constantemente ás peculiaridades dos bens culturais. No dominio da ciencia do patrimonio, no caso de requirir información adicional para cubrir un coñecemento axeitado dos materiais, priorízanse as técnicas analíticas non destrutivas, coas que se pode volver analizar a mostra e evitar novas tomas. Xeralmente, as análises químicas e fisicoquímicas xeran información compositiva, morfolóxica e estrutural.

INTRODUCCIÓN

En 2012, o Comité Europeo de Normalización (CEN) publicou o regulamento para a toma de mostras de bens culturais. O estándar fai fincapé nos danos que calquera mostraxe, por pequena que sexa, causa nos obxectos/edificios artísticos e históricos. En calquera caso, o peso, a concentración ou as dimensións das mostras a tomar non están exactamente definidas, deixando aos expertos científicos e aos xestores do patrimonio a avaliación se paga a pena sacrificar algún material cultural a cambio da información adquirida, e cando facelo.

A toma de mostras contribúe a garantir a salvagarda dos bens culturais a través da comprensión do seu estado de conservación e máis ben dos fenómenos de degradación que se traballan na superficie dos obxectos. Ademais de profundar no coñecemento do material, a análise de mostras admite a reconstrución da historia do obxecto e a súa técnica de execución con evidencias materiais, informando a historiadores de arte e arqueólogos a través de datos funcionais para responder ás súas preguntas de investigación. A sensibilidade da técnica analítica define o tamaño ou a concentración da mostra a analizar. Ademais, a especificidade da técnica permite discriminar entre o analito e as substancias interferentes. Con técnicas de análise ultrasensible, como a espectroscopia Raman mellorada en superficie (SERS), as mostras de pequeno tamaño (~ mg) son suficientes para obter sinais relativos á composición do material.

O traballo experimental presentado nesta tese contribúe ao desenvolvemento de dispositivos multiusos para a detección de moléculas de baixo peso (máximo 1.5 kDa) procedentes da superficie de obxectos culturais. Os sensores empregados son substratos de

espectroscopía mellorada en superficie (SERS) do tipo "plataforma plana" con *nano* e *micro* estruturas para a amplificación do sinal. No presente traballo, as plataformas SERS foron recubertas de aluminio como o metal plasmónico. O método de microextracción antecedente da transferencia de analitos a substratos SERS baséase no uso de tiras de silicona (polidimetilsiloxano - PDMS) que por presión directa sobre a superficie do obxecto atraen moléculas polares ou apolares por fisisorción. Despois, disolventes con diversas características de polaridade e solubilidade favorecen a mostraxe selectiva de moléculas libres. A recolección destas moléculas e a súa transferencia aos sensores SERS con pipetas/capilares nunha soa etapa forman parte do protocolo analítico SERS proposto e optimizado nesta tese. A complexidade da extracción, baseada no uso de ácidos fortes citados na literatura sobre SERS aplicada ao patrimonio cultural, puido ser reducida coas optimizacións presentadas nesta tese.

O presente proxecto de investigación cuestiona a mostraxe *minimamente invasiva*, imprescindible no dominio da ciencia do patrimonio. A motivación xeral da tese consiste no desenvolvemento de novas ferramentas para unha mellor protección dos bens culturais e estratexias para a súa conservación preventiva, impulsado inicialmente como parte do proxecto europeo NanoRestArt (Nanomateriais para a Restauración de obras de Arte). O estudo consta de varias etapas, destinadas á optimización e validación do que se define como mostraxe **nanodestrutiva** con dispositivos de detección SERS. Anteriormente ao comezo desta tese, no grupo de investigación da USC Lazzari foi obtida unha estimación de peso: trasladáronse moléculas estándar de cumarina e rodamina con unha concentración coñecida previamente á superficie das plataformas, para calcular o peso dos analitos e relacionalo coa sensibilidade da técnica analítica. Con esa estimación tamén se calculou o **factor de mellora** do sinal Raman con réplicas de pirámide invertidas na orde de magnitude 10^9 - 10^7 . Tales analitos xeraron excelentes impresións dactilares con espectroscopia Raman e o seu peso foi estimado en aproximadamente 10^{-10} g.

En 1974, Martin Fleischmann observou un fenómeno de intensificación do sinal Raman dunha molécula de piridina sobre unha superficie rugosa dun eléctrodo de prata. Outros experimentos independentes de metais nobres confirmaron estas observacións en 1977. O fenómeno de **amplificación do sinal en SERS** débese á absorción de moléculas na superficie do metal. O efecto SERS prodúcese cando a interacción con láseres no rango do infravermello cercano (NIR) e visible cumpren condicións de **resonancia localizada**. Os **plasmóns** son oscilacións colectivas de electróns de condución que emiten un dipolo en resonancia cun campo óptico. A proximidade da molécula ao metal, a rugosidade e periodicidade da estrutura, o tipo de metal e a lonxitude de onda do láser contribúen á intensificación do sinal. O campo eléctrico de entrada combínase co campo dipolar electromagnético xerando a superficie plasmónica. A mellora do sinal pode ser baixa e homoxénea, ou altamente localizada e con elevada amplificación. No caso de que se use **aluminio** como **metal plasmónico**, as moléculas poden detectarse no rango UV-Vis (100-750 nm). O volume da dispersión inelástica de Raman varía dependendo da adhesión dos analitos ao metal e pode cambiar se o substrato é plano ou resulta da agregación de nanopartículas coloides.

PLANTEXAMENTO E OBXECTIVOS

O plantexamento da tese ten como obxecto demostrar a aplicabilidade das plataformas SERS *nano* e *micro* estruturadas recubertas de aluminio en asociación cun novo método de microextracción con tiras de silicona e cun disolvente apropiado no marco da ciencia do patrimonio. A tese divídese en **tres liñas de investigación** con obxectivos analíticos concretos e progresivos. A primeira liña refírese á fabricación de dispositivos de detección (plataformas SERS e tiras de PDMS), e presenta os experimentos de optimización na fase de **fabricación**. A segunda trata o tema da detección de produtos de baixo peso en obras de **arte contemporáneas** feitas con plástico. Esta liña pretende ampliar o debate sobre os criterios para o desenvolvemento de **ferramentas de diagnóstico para a conservación preventiva** e protección mellorada do patrimonio cultural. A terceira liña presenta experimentos para demostrar a aplicabilidade dos sensores SERS a unha gran variedade de pequenas moléculas, como novas ferramentas **multiusos**, de utilidade, aínda que non exclusivamente, para expertos que operan no dominio da ciencia do patrimonio.

Os **obxectivos** concretos da tese son os seguintes: 1) optimizar os procesos de fabricación por litografía branda de nanoimpresión con distintos polímeros fluorados e fotoiniciadores; 2) probar os efectos de **fisisorción** das tiras de PDMS, a afinidade con analitos estándar, a **solubilidade** e **polaridade** dos disolventes; 3) aplicar o método analítico a polímeros modelo para avaliar a capacidade de detección de **moléculas marcadoras** da **degradación oxidativa**; 4) **validar** o método analítico con obras de arte contemporáneo feitas con plástico; 5) extender a aplicación dos sensores SERS á detección de **colorantes naturais/sintéticos** con adaptación dos protocolos de microextraccións; 6) validar as microextraccións SERS en superficies de gravados, pinturas murais e coiro histórico que conteñen pigmentos orgánicos sintéticos e inorgánicos minerais, e posibles produtos de tratamentos previos de conservación. Ao longo do proxecto, leváronse a cabo probas de concepto para combinar o método analítico á **instrumentación portátil** de espectroscopía Raman para análises *in situ* en ambiente museal. Para isto empregáronse coleccións históricas e contemporáneas de obxectos de deseño industrial (ladrillos LEGO®).

METODOLOXÍA EXPERIMENTAL E MATERIAIS

Os dispositivos de detección SERS fabricáronse mediante litografía branda de nanoimpresión con FLUOROLINK® MD700 (PFPE-uretano acrilato de metilo) de Solvay™ e fotoiniciadores (fenonas) de Darocur™ y Ciba™. A lámpara UV utilizada é a Midas System MDA modelo 400LJ. A copia mestra dos substratos con pirámides invertidas (~400 x 400 nm) son réplicas do dispositivo comercial KLARITE® de Renishaw Diagnostics Limited. No caso das réplicas de nanoestruturas con columnas tubulares (~50 nm ø), empregáronse películas de SOKEN® FleFimo™ para a fabricación da copia mestra. Producíronse moldes feitos de PDMS con réplicas negativas das estruturas para a reprodución en serie dos dispositivos SERS. O recubrimento de aluminio foi fabricado por deposición física de vapor (PVD) con unha evaporadora con raio de electróns BALZERS BALTEC™ BAE 250. De feito, os ciclos de condensación/evaporación a alta presión e temperatura permiten a supersaturación do

ambiente. As capas de aluminio resultantes deste procedemento miden ~150 nm que ao entrar en contacto co aire se transforman inmediatamente en óxido pasivante (Al_2O_3).

As tiras producíronse con SYLGARD™ 184 de Dow Corning por cura térmica en estufa durante 2 horas a 80°C con pretratamento baixo bomba de baleiro durante 10 minutos. Foron empregados varios moldes para dar formas diferentes aos dispositivos de mostraxe: vasos desbotables en polipropileno (~1.5 cm $\varnothing$), ou tiras de separación/embalaxe lisas e rugosas en polipropileno. A calidade e a morfoloxía das réplicas dos dispositivos de detección foi monitorizada con microscopía electrónica de barrido (SEM). Ademais, a solubilidade das tiras de PDMS foi estimulada con varios disolventes a distintas polaridades (H_2O , EtOH, acetona, CHCl_3 , THF). Os extractos analizáronse con GC/MS para avaliar posibles residuos e contaminación da mostraxe. Empregáronse estándares para cromatografía por separación de tamaño (SEC) con distribución estreita de pesos moleculares de polietilenglicol e poliestireno para simular respectivamente moléculas polares e apolares. As medidas de espectroscopia de masas (MALDI-ToF) permitiron unha estimación do límite superior (1.5 kDa) de extracción por fisiorción de moléculas de baixo peso de ambas polaridades.

Os materiais para o envellecemento artificial foron aceite de linaza purificado de Titan™, acrilonitrilo-butadieno-estireno (ABS) extrudo de MAGNUM™ 3404 de Dow Chemicals, poliacetato de vinilo (PVAc) de Rayt™, e cis-1,4 polisopreno (PI) de SEMPERIT™. Os experimentos de fotoxidación foron executados en cámaras climáticas e de intemperie acelerada SUNTEST® de Atlas. A oxidación térmica a baixas temperaturas ($\leq 150^\circ\text{C}$) foi en estufa. Aparte da espectroscopía infravermella con transformada de Fourier (FTIR) e a SEC, outras técnicas robustas se empregaron para a caracterización dos produtos de degradación dos materiais poliméricos como: GC/MS, DSC, e reflectancia para corroborar finalmente os datos obtidos con varios espectrómetros Raman (InVia Flex de Renishaw e alpha300 de WITec).

Para validar o sistema de mostraxe proposto na tese, foron caracterizados outros materiais coas mesmas técnicas mencionadas arriba. Esculturas e pinturas dos artistas contemporáneos galegos Andrés Pinal e Manuel Eiris puideron ser analizadas grazas á colaboración co Centro Galego de Arte Contemporánea (CGAC). Ademais, analizáronse gravados xaponeses da época tardía Edo, tal como obxectos de deseño industrial (ladrillos LEGO®), coleccións de colorantes naturais de cochinilla, kermes e laca de carmín, coiro histórico e pinturas murais do Dolmen de Antelas en Portugal. Algunhas medidas de fluorescencia de raios X foron executadas para proveer información adicional sobre a composición de algúns pigmentos minerais (Micro XRF M4 Tornado de Bruker™).

A selectividade da mostraxe depende da versatilidade da tira de silicona como dispositivo apto ao contacto con varios materiais e a do disolvente elixido en canto que sexa capaz de maximizar a extracción en varios sistemas sólido-líquido. Deste xeito, é posible extraer compoñentes diferentes de matrices complexas das superficies de obxectos arqueolóxicos, históricos ou modernos envellecidos naturalmente. Por outra parte, o SERS en sí é unha técnica altamente específica onde a resonancia localizada de plasmóns superficiais produce un efecto de intensificación do sinal, ata poder producir unha pegada dactilar de calquera sistema

molecular. A afinidade dos analitos pola superficie plasmónica afecta á amplificación do sinal e á sensibilidade do método.

RESULTADOS E DISCUSIÓN

Os experimentos de litografía branda de nanoimpresión con luz UV levaron á conclusión de que o protocolo óptimo para a fabricación dos sensores SERS consta dos seguintes parámetros: prepolímero fluorado FLUOROLINK[®] MD700 con 5% en peso de fotoiniciador de fenona (651 de Ciba[™]), irradiación UV durante 40 s con tratamento previo en atmosfera de nitróxeno durante 5 min. As tiras de PDMS foron producidas con ratio 10:1 de SYLGARD[™] 184 e iniciador de fábrica.

Algunhas moléculas marcadoras informan sobre os procesos de degradación que están ocorrendo na superficie de materiais poliméricos e permiten predicir o comportamento degradativo dos obxectos a curto prazo. A fotoxidación acostuma monitorearse observando a formación de compostos gaseosos e sólidos como ácidos carboxílicos ou aldehídos, entre outros. O aumento de grupos carbonilos en tales compostos obsérvase con técnicas clásicas, como a espectroscopía FTIR. O SERS e o método analítico presentado nesta tese permitiron a redución do límite de detección de moléculas marcadoras sólidas de baixo peso. Ademais, os dispositivos de PDMS permitiron o traslado de moléculas de baixo peso ás plataformas de SERS que de xeito normal non se detectan coa SEC. A cantidade mínima de mostra para ambas técnicas clásicas é da orde de miligramos. Pola contra, o SERS permite a discriminación ultrasensible e selectiva de oligómeros invisibles durante o acto de toma da mostra.

Os materiais modelo de aceite de linaza, ABS, PVA, e PI envellecéronse artificialmente para simular fenómenos de degradación oxidativa. As reaccións oxidativas en estruturas poliméricas tipo olefinas son secuenciais e radicalarias, como por exemplo a escisión β . Os fenómenos de ruptura das cadeas e formación de oligómeros de baixo peso poden ocorrer á vez que os fenómenos de entrecruzamento das cadeas con aumento do peso molecular. Xeralmente, nas primeiras etapas de degradación do material é cando se forman na superficie pequenas cantidades de sólidos de baixo peso útiles para a detección temperá da oxidación. Tales marcadores proporcionan unha información diagnóstica para a prevención do decaemento rápido da obra, sen necesidade de recoller mostras de tamaño visible.

O sistema modelo do aceite de linaza serviu para validar a detección de marcadores en películas fotoenvellecidas artificialmente durante máis de 2,000 h. Na literatura, o marcador de oxidación do aceite de linaza máis fiable é o ácido azelaico, que nas mostras usadas no presente estudo se detectaron con GC/MS. A información foi corroborada coa SEC, observando fraccións solubles de baixo peso nas mostras máis oxidadas. Ademais, a espectroscopía FTIR permitiu correlacionar o aumento das bandas de carbonilos e hidroxilos, e a diminución dos enlaces C=C, coas horas de envellecemento das mostras. Algo similar ocorreu con películas de ABS fotoenvellecidas durante ~400 horas. A heteroxeneidade do terpolímero, que sofre degradación diferencial debido á presenza de nódulos nanométricos de PB máis susceptibles a oxidarse respecto ás compoñentes enxertadas de SAN, causou a formación de fotoproductos de baixo peso. Ademais, os cambios de peso molecular e

amarelamento afectaron a mostras de ABS. No caso do PVAc, observouse que o comezo da formación de produtos de baixo peso ten lugar a temperaturas máis baixas e en menos horas de oxidación térmica (~300 h) comparado co que sostén a literatura. O PI tamén demostrou ser un excelente material modelo para simular a escisión das cadeas poliméricas e para detectar produtos de baixo peso (fotoenvellecemento de 120 h). A sensibilidade e especificidade do SERS, combinada coa versatilidade do método analítico con PDMS e disolventes adecuados, permitiron identificar pegadas dactilares de moléculas que se poden asociar a varios produtos de oxidación, tal como se esperaba. Este sistema foi suficientemente probado ata ser validado con éxito na superficie da obra feita con PI de Andrés Pinal *Traxe de home* que se atopa actualmente no almacén do CGAC.

A parte da tese que abarca a aplicación dos sensores SERS como dispositivos multiusos para a detección de moléculas pequenas de colorantes comezou coa proba de concepto de identificación de pigmentos sintéticos orgánicos e inorgánicos en dúas coleccións de ladrillos LEGO®. Os resultados do experimento pódense estender a obxectos de deseño industrial feitos de plástico que se encontran en ambientes museais. Foi utilizada instrumentación portátil de espectroscopia Raman e comparada a súa resolución coa do Raman de laboratorio usado para crear unha base de datos sobre a composición dos colorantes sintéticos. O obxectivo foi averiguar se o método SERS adaptado se pode usar como alternativa ao espectrómetro portátil cando a súa baixa resolución non permite a discriminación de sinais en matrices complexas con colorantes pouco concentrados. De feito foron detectados ftalocianinas de cobre, titania, hematita e carbón negro sintéticos en varios cores e tons.

No marco da colaboración coa Universidade de Vigo, un kit de tiras de PDMS foi enviado a Antas en Portugal, sede do famoso dolmen prehistórico. Isto deu a oportunidade de validar o uso dos dispositivos de mostraxe entre os non expertos. As antas de granito pintado do dolmen, entre os máis antigos e mellor conservados da Península Ibérica, foron mostreadas co método proposto nesta tese para averiguar información molecular sobre aglutinantes e produtos de conservación que as técnicas de microscopía óptica e electrónica non puideron proporcionar. A toma de mostra foi feita polos investigadores da Universidade de Vigo, demostrando así a sinxeleza no uso do sistema. Tralo seu uso as tiras foron devoltas aos laboratorios da USC. Ademais de detectar a hematita e o carbón negro, dous típicos pigmentos de orixe natural en uso dende a prehistoria, detectouse PVAc en zonas da superficie amarelentas. De feito, o sistema de mostraxe proposto nesta tese permitiu detectar a presenza de adhesivos e podería valer para outros tratamentos de conservación a miúdo non documentados na historia dos obxectos.

Ademais colaboracións co Instituto Superior de Restauración e Conservación de Italia permitiron averiguar a calidade da resposta analítica das plataformas SERS, con estándares históricos de colorantes naturais e dunha mostra de coiro procedente dun calzado litúrxico de época tardía medieval. As extraccións de microorganismos de cochinilla e kermes, ademais da laca de carmín, serviron para crear referencias de calibración do sistema. Os cromóforos de ácidos carmínico e kermésico puideron ser detectados coas plataformas fabricadas ao longo do presente estudo. Tras facer isto aplicouse o método con tiras de PDMS ao fragmento de coiro (~2 mg) chegando a detectar residuos de coláxeno de varios tipos. O método de extracción foi

adaptado para chegar a maximizar a información. O seguinte paso foi rascar delicadamente con bisturí grans debilmente adherentes ao soporte de coiro. Os grans de repetidas rascaduras foron sometidos a distintas extraccións con solventes polares, apolares e misturas (H_2O , EtOH , CHCl_3). Despois os microextractos foron trasladados ás plataformas SERS e concentrado para la detección. As mellores amplificacións foron rexistradas co láser a 488 nm, a pesar de ter probado varios. No caso da extracción con disolventes polares, a pegada dactilar do ácido carmínico puido ser detectada nas microextraccións SERS. Por outra parte, o CHCl_3 confirmou os residuos de coláxeno e fenilalanina, pero neste caso, o sinal do carmín era moito máis débil. Ao rematar as extraccións dos grans rascados, o fragmento de coiro histórico foi sometido a extracción completa con NH_4OH 28% en H_2O . Esta última parte dos experimentos permitiu confirmar a información obtida coas anteriores microextraccións SERS. En xeral, a adaptación do método SERS demostrou ser moi útil nas análises de cromóforos e compoñentes proteicas en coiro histórico, o cal é un resultado novidoso.

Seis partes dun gravado xaponés Ukio-e foron sometidas a unha validación posterior co método SERS combinado coas tiras de PDMS usando H_2O e acetona como disolventes para o traslado das moléculas libres de baixo peso. A investigación permitiu definir algúns puntos de referencia da transición á época industrial Meiji (1868-1912) a través da reconstrución da historia dos colorantes e pigmentos detectados. Nove agrupacións de cores permitiron discriminar as compoñentes de misturas de compostos sintéticos e minerais típicamente en uso nesta época. Os grupos vermellos e violetas foron os que resultaron máis complicados de investigar, e ao mesmo tempo os que revelaron aspectos máis novidosos no uso das tintas nos gravados Ukio-e. Detectouse **disazo β -naftol** en varias zonas vermellas e alaranxadas, xunto ao clásico **bermellón** na roupa dos personaxes máis importantes dos debuxos. O ion bario xunto ao β -naftol que produce un vermello vívido escuro, foi detectado en amplias zonas dos debuxos, como as columnas. A presenza desta tintura é a demostración dunha enxeñosa experimentación ocorrida na época Meiji. Os azo-pigmentos comezon a ser sintetizados por primeira vez, e algúns deles seguen en uso como tinturas para impresoras (por exemplo o Sunbrite 60:1). Para o grupo violeta (claro e escuro) detectáronse **anilinas** (e xofre cristalino) que son compostos sintéticos inéditos no campo dos gravados xaponeses. As anilinas son propensas a fotodegradarse, e de feito varios desprazamentos de bandas e unha baixa intensidade espectral Raman e SERS distinguen este grupo de cor. Nas zonas azuis e verdes, identificouse o composto organometálico sintético **azul de Prusia** baseado en ferrocianuro de hierro, inventado en 1704. Este representara a revolución da época anterior Edo, cando aínda se encontraba misturado con índigo e outros compostos de orixe natural nos gravados. Pero é na época Meiji, na que se encontra só. O amarelo procede dun pigmento de vidro sintético baseado en minerais de **sulfato de arsénico amorfo**. A pegada dactilar en espectroscopía Raman de este pigmento, baseado en varios minerais, é inconfundible. As bandas satélites axudaron a discriminar o uso de xofre cristalino engadido para aumentar o brillo. O sulfato de arsénico foi detectado no verde misturado co azul de Prusia e no rosa. Este último resultou misturado con **hematita** en algúns tons, isto nunca tivera sido referenciado en publicacións anteriores sobre a análise de gravados Ukio-e. Como era de esperar, a hematita foi detectada

tamén no marrón, pero misturada co negro carbón e o azul de Prusia. Da mesma forma, o negro foi identificado como **negro carbón**.

CONCLUSIÓNS

As conclusións xerais de esta tese demostran que incluso con baixas concentracións de analitos é posible obter información química fiable sobre sistemas multimateriais complexos, que tal vez foran envellecidos naturalmente. A presente investigación optimizou e validou a aplicabilidade de sensores multiusos SERS, do tipo plataformas planas recubertas con aluminio, asociados a tiras de silicona que por fisisorción se adheren ás moléculas libres de baixo peso (≤ 1.5 kDa) presentes nas superficies de bens culturais. A capacidade do sistema microextractivo a ser modificado baséase na selectividade dos disolventes escollidos en función da súa solubilidade, polaridade e afinidade co analito.

A tese cuestionou a definición de método de análise non invasivo e mostraxe non destrutivo e nanodestruutivo, profundizando os aspectos específicos do dominio da ciencia do patrimonio. A estimación de 10^{-10} g en peso das moléculas mostreadas co sistema proposto aquí considérase unha cantidade máis que aceptable como mostra a analizar a cambio da especificidade da información obtida coa espectroscopía Raman.

A fabricación dos dispositivos de análise foi optimizada ao principio do proxecto, e na primeira fase de validación foron utilizados materiais modelo para simular e corroborar os límites da mostraxe. Os dispositivos demostráronse funcionais ao detectar produtos de oxidación en superficies de materiais plásticos e en obras de arte contemporáneo. Ademais, a finalidade desta tese extendéuse a aplicación dos dispositivos a outras moléculas de baixo peso de colorantes, pigmentos e produtos con conservación.

De cara a futuras investigacións, o método analítico proposto podería ser aplicado a outros dominios, como por exemplo a detección de contaminantes medioambientais (microplásticos) ou narcóticos nos controles de seguridade. Sen embargo, serán necesarios máis experimentos para entender mellor a influencia da fisisorción durante a toma das mostras con PDMS.

1. INTRODUCTION

‘Sampling¹ is invasive and invariably causes damage, however small. It should be undertaken if there is a strong justification for it and in the closest consultation with those having responsibility for the object and those who will be studying the samples. The consultation should consider whether the same information could be obtained by non-invasive methods’ (European Committee for Standardization, 2012) [2].

The current thesis is based on principles commonly accepted in heritage science about the removal of samples from the surface of objects for research purpose. First, the priority is to preserve the integrity of the object, disregarding the prestige of the researchers conducting the investigations [3–5]. Second, the scientific tools for the analysis of cultural heritage materials are at service of experts of other disciplines, such as archaeologists, historians and conservators [6,7]. Research questions on the identification materials, technology of production of objects, and conservation conditions are the most common among heritage experts. A multidisciplinary approach distinguished the current research in the attempt to transfer the knowledge available in the fields of chemistry and materials science to applications for cultural heritage. In this perspective, ultrasensitive analytical methods developed for precision medicine/biotechnology [8–10] inspired this research. Reducing the limits of detection of sensing devices will help to integrate scientific tools in routine monitoring of cultural objects/buildings.

Surface-enhanced Raman spectroscopy (SERS)-based sampling will be following introduced. Aluminum (Al)-coated platforms have been combined with polydimethylsiloxane (PDMS) strip samplers and solvents to transfer very small molecular fragments from the surface of objects to SERS platforms. At first, the research focused on the detection of degradation products from polymeric materials used in contemporary art. Accelerated aging tests on model polymers were conducted to understand their behavior and the sampling method proposed was built upon the evidence of the simulations. Then, object-based validation tests were conducted to anticipate possible challenges posed by complex composite materials in collections. Further, the sensitivity of handheld Raman instruments was compared to that of benchtop instruments, and SERS sampling was adapted for routine screenings of museums objects. The current research fostered the application of *in situ* tools for heritage science purposes, providing backup evidence on the reliability of the analytical tools. Through time, the focus of the research shifted to establish validity in different application fields. The

¹Sampling, in analytical chemistry, is the process in which a representative piece of material is extracted from a larger amount and used for analysis [1].

optimized SERS-sampling served different purposes, not only for the detection of early markers of degradation in polymers, but also for the identification of synthetic organic pigments (SOPs), natural dyes, unwanted conservation products, among others materials.

1.1 PREREQUISITE: MINIMALLY-INVASIVE ANALYSIS IN HERITAGE SCIENCE RESEARCH

The European Committee for Standardization in the *methodology for sampling from materials of cultural property* (CEN EN 16085:2012) [2,11] describes sampling as a threat causing potential damage to cultural objects. The following preliminary clarifications aim to present the ethical and scientific framework in which the current research was conducted.

Broadly speaking, an *ethical* sampling scenario for collaborative research in science and technology applied to the cultural heritage comprises: 1) articulating research questions and aims, and 2) proposing analyses and tests with an adequate language for owners/managers of the objects [3,7]. Although the statistical representativeness of the samples is crucial to draw meaningful conclusions on the analysis conducted, in this thesis it will not be debated, being out of the scope of the research. Of course, the mere growth of the researcher's reputation is not a justification for pursuing sampling on unique objects [3]. Instead, scientific investigations are tools to provide tailored services to preservation stakeholders and to foster technological transfer based on fundamental knowledge conceived in academic contexts (e.g., materials science, chemistry, and engineering).

As stated in the EN 16085:2012 standard: '*Only a minimum but sufficient amount of material should be taken. The amount of material depends on the type of cultural property, the nature of the material, and the kind of scientific investigation to be employed*'. Point 8 of the standard is extremely generic on how small a sample is meant to be; hence, heritage scientists are called to narrow down what is a *minimum but sufficient* amount of sample for each analytical technique.

In this perspective, the overall motivation of this thesis is built upon the following research questions: are we able to detect low molecular weight (LMW) compounds from polymeric surfaces reducing the risks to damage cultural or artistic objects during sampling? Why SERS sensors are an optimal choice to detect small molecules at low concentrations? How the outputs of the research will impact the overall preservation cultural heritage materials?

The current thesis began within a HORIZON 2020 European Union (EU) funded project promoting material-based research named Nanomaterials for the Restoration of Works of Art (NanoRestArt). Several research questions were posed within the wider project, involving 29 partners from different EU and associated countries. Partners worked on complex multidisciplinary issues, from industry to museum validation tests with inputs from academic institutions. NanoRestArt lasted four years, ending in November 2018, and generating publications and collaborative initiatives, as well as dissemination events through numerous workshops and conferences. Eight work packages (WP) were conceived to address the following conservation challenges:

- cleaning of contemporary painted and plastic surfaces;
- stabilization of canvases and painted layers in contemporary art;
- removal of unwanted modern materials;
- enhanced protection of artworks in museums and outdoors.

The University of Santiago de Compostela (USC) was involved in two WPs: WP4, on the protection of surfaces, active protection of polymer-based materials with metal coatings, and WP5 on the ‘development of SERS-active substrates for the detection of art materials and degradation products. The research herein presented is mainly based on WP5. However, several tangential collaborations within the project led to conduct further tests, including one to evaluate the performance of new formulations of passive coatings for contemporary art plastics (the results are reported in annex 3.1, 3.2, 3.4).

1.1.1 Structure of the thesis

The current thesis is divided into four chapters:

- In Chapter 1 **Introduction**, SERS principles are outlined focusing on the enhancement factor of Al-coated platforms. Then, the photooxidative and thermoxidative behavior of polymers is explored. Artificial aging tests of model materials are presented, focusing on linseed oil, acrylonitrile-styrene-butadiene (ABS), poly(vinyl acetate) PVAc and polyisoprene (PI). Object-based validation is presented by introducing a variety of materials later analyzed: contemporary artworks, LEGO® bricks collections, and woodblock prints, among other materials investigated.
- In Chapter 2 **Experimental Methodology and Materials**, preparation and fabrication of the SERS substrates is explained in detail with insights on the characterization techniques used to follow their replication. Similarly, the fabrication of the PDMS strip samplers is presented. Accelerated aging of materials is detailed. The preparation of micro-extracts with the different solvents is eventually addressed.
- In Chapter 3 **Results and Discussion**, the first section on sensing and sampling devices fabrication presents how the optimal conditions for the fabrication of the substrates and PMDS strip samplers were reached. Then, further sections about detecting degradation markers in polymeric materials are presented. Finally, various sections argue the suitability of one-step method proposed for small molecules in heritage objects (multipurpose approach). Handheld and benchtop Raman spectrometers were combined to the SERS method to extend the findings in museum collections.
- In Chapter 4 **Concluding Remarks** summarize the findings and show the potentials for future research.

1.2 SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS) AS A TOOL FOR THE DETECTION OF LOW MOLECULAR WEIGHT (LMW) COMPOUNDS

Several heritage science publications report SERS as a sensitive and selective analytical method to identify cultural materials, like pigments, dyes, binders and further preparatory layers in paints [12–18]. Additionally, woodblock prints, illuminated manuscripts and other archival materials have been extensively characterized through variations of SERS settings, tailoring excitation wavelengths, power of the lasers, preparation of different colloidal nanoparticles among other optimizations [18–20]. Usually in these studies, SERS provides reliable molecular information on micrometric samples of few grams from museum objects, and it is associated to other spectroscopic techniques, such as Fiber Optic Reflectance Spectroscopy (FORS), Fourier transform infrared (FTIR) spectroscopy, X-Ray fluorescence (XRF) spectrometry and scanning electron microscopy and energy dispersion system (SEM-EDS) [21–25]. These methods do not enable to reach the specificity and limits of detection of Raman spectroscopy in molecular identification, although they are essential features to obtain meaningful information to address preservation research questions. In addition, portable and handheld versions of the spectrometers have been extensively tested to foster *in situ* analytical work, indispensable when large-size or immovable objects are under analysis, *i.e.* wall paintings [22,26,27].

In the last 40 years, SERS had a rather successful trajectory in advancing the potentials of molecular sensing in a variety of fields, including biomedicine, environmental and security [8,28–35]. Cultural heritage scientists have contributed to lower the detection limits of SERS-based methods to prioritize the integrity of cultural objects during sampling. Nonetheless, tailored adaptations encompassing the peculiarities of cultural materials are still necessary to expand the application of SERS. Generally, SERS analytical procedures rely on strategies that put more emphasis on the outcomes of the analyses, or on the enhancement factors, rather than on the size of the samples [12,36,37]. In this thesis, not only the sampling strategy was crucial to build the evidence, also for the first time SERS sensors were employed to detect LMW products from oxidized surfaces of plastic materials, not detectable with traditional methods [38]. Solid molecular fragments from degraded polymers are usually accomplished with size exclusion chromatography (SEC). This thesis discussed the relevance to switch from SEC to SERS for the detection of LMW compounds lowering the detection limits as an achievement for heritage and polymer science applications.

SERS foundations will be briefly, and not exhaustively, presented in the next section. Basic concept on Al plasmonics will justify why this metal was preferred to gold and silver, known as ideal for plasmonic enhancement [29,39–49].

1.2.2 Raman scattering and SERS principles

The Raman effect is based on the inelastic scattering of light in the interaction with matter. Photons can lose or gain energy through vibrational excitations and the change produces a shift in the frequency of the scattered light. Each molecular structure shows

specific vibrational features associated with the energy of bonds allowing its identification. Another way to define the Raman scattering refers to the ability of a photon source of known energy to change the polarizability of a molecule. IR-active molecules are those with a permanent dipole induced by an asymmetric stretching mode. Complementarily, symmetric stretching modes make molecules Raman-active [50]. Integrating the information from both vibrational spectroscopies can provide valuable information on compounds in different phases of aggregation [51,52].

Raman scattering is a weak effect depending, among other factors, on the cross-section of the analyte molecule ($\sigma_R [m^2]$ total Raman cross-section integrating scattered light from all directions) [53]. Experimental and theoretical determination of the cross-section varies according to the type of molecule, the concentration and the intensity of the peaks from the analyte. Reference molecules with known cross-sections can be used to derivate the relative cross-section of unknown samples (Eq. 1.1) [53]:

$$\left(\frac{d\sigma_R}{d\omega}\right)_{sample} = \left(\frac{d\sigma_R}{d\omega}\right)_{ref} \frac{I_{sample}}{I_{ref}} \frac{c_{ref}}{c_{sample}} \quad 1.1$$

where c is the concentration and I the measured integrated intensities of the Raman peak under study. Interestingly, large molecule cross-sections occur when the frequency of the excitation light matches the electronic transitions within the molecule (*resonance*). Such condition generates an electromagnetic enhancement, derived from the interference of the Raman scattered light and the magnification of the incident light.

In 1974, Martin Fleischmann [54] observed an anomalously high Raman signal from a pyridine molecule on the surface of a roughened silver electrode. Similar findings were confirmed independently later by other scholars in 1977 [55]. Up to date, gold, silver and copper are the most used metals for the fabrication of SERS active substrates [39,47,49,56–59]. In fact, noble metals, if excited with the NIR or green lasers, fulfill the resonance conditions. SERS phenomenon is about amplifying the Raman signal by several orders of magnitude. Molecules absorbed on the surface of the metal interact. *Plasmon resonance* is a large amplification of the laser field resulting from the electromagnetic interaction of the light with the metal. *Plasmons* are collective oscillations of conduction electrons and they emit a dipolar field in resonance with the optical field. The proximity of the molecule with the metal boosts the efficiency of those interactions, also depending on the type of metal, the roughness, size and shape of crystals/clusters. Further, the incoming electric field combined with the dipolar electromagnetic field generates the *plasmonic surface* [53].

Another definition of *plasmons* is *polaritons*, quasi-particles that arise from the strong coupling of IR or visible electromagnetic waves traveling along a metal dielectric or metal air interface. *Polaritons* affect the efficiency of the SERS substrate. In fact, a good SERS substrate is either one that can provide a low, but uniform enchantment, or one that shows a large variation of the surface enchantment with very highly localized amplifications (*hot spots*). The former is best suited for single-molecule detection [60].

Plasmon resonances are highly dependent on the metal nanostructure, geometry, roughness and size. Further, SERS substrates are usually designed to function in the range 400-1000 nm. In the Vis/NIR range most Raman active molecules can be detected. However, as in the case of Al, molecules can be also detected in the ultraviolet (UV) [45]. To further comprehend the mechanism, it is worth mentioning that the molecule to be detected has to attach to the surface of the metal substrate. Thus, the transfer of the molecule from a volume to the surface can affect the resonance. The scattering volume changes, if the substrate is plane or resulting from the aggregation of metal clusters, *i.e.* colloids. Drawbacks of the sample preparation include the presence of negatively charged species, either in the colloidal solution or from the analyte, which generate electrostatic repulsion hence reducing the enhancement [53].

Furthermore, based on the enhancement phenomenon there are various differences between normal Raman (NR) and SERS signals. Plasmon resonances are highly wavelength dependent and can affect one part only of the spectrum due to the dilution of the analyte [53,60]. In addition, the orientation of the molecule can also affect the surface selection rules [61]. Both result in a change of the relative intensities of the peaks. Usually, the cross-sections of molecules remain the same in NR and SERS, but in some instances new vibrational modes can appear. In addition, the light polarization is dependent on the plasmon resonances inert to the interaction of the substrate and with the analyte, generating slightly different spectra compared to NR. Furthermore, metal complexes can form at the interface, slightly shifting the signal or broadening the peaks, through what is called *chemical enhancement* [28].

Among other classifications [12,53,60–62], SERS substrates can be broadly divided as follows:

- aggregated metallic colloidal nanoparticles in solution (*e.g.* pastes);
- assembled nanoparticles on surfaces;
- **structured surfaces (*e.g.* 2D planar substrates, ordered arrays, platforms, etc.);**
- metallic electrodes (not currently in use).

Colloidal nanoparticles are by far the most used SERS substrates, facilitated by the fact that silver and gold nanoparticles are stable in water. The scattering volume of colloids is determined by the instrument wavelength, and the particles concentration and motion. On the other hand, in planar substrates the wavelength of excitation has a larger influence on the amplification of the Raman signal. The contact between the substrate and the analyte might be either dipping the substrate into the solution or dropping the solvent/analyte onto the substrate. In any case, the estimation of the molecules being absorbed onto the metal surface is difficult. An accurate estimation of the number of molecules in the volume of interaction can be provided by working with solutions at known concentration to preliminarily calibrating the substrate. A further parameter affecting the absorption efficiency is the molecular density that varies with to the sample preparation. Spin coating, for example, increases the analyte area, while lowering the density, which reduces the absorption [53].

KLARITE[®] Renishaw Diagnostic[™] and SOKEN[®] FleFimo replica substrates fabricated through UV-nanoimprint soft lithography (UV-NIL) were used in the current research project. Al-coating was performed by Physical Vapor Deposition (PVD), applying a layer of about 150 nm on the platforms. Plasmon activity in the UV-VIS region was previously demonstrated in similar Al-coated platforms [42]. Lastly it is worth mentioning, the formula of the average *Enhancement Factor* (EF) (Eq. 1.2.) [53]

$$AEF = \frac{I_{SERS}/c_{SERS}}{I_{RS}/c_{RS}} \quad 1.2$$

Average EF equals the ratio between SERS signal I_{SERS} and molecule concentration c_{SERS} on the SERS substrate, and NR signal I_{RS} and molecule concentration c_{RS} . A crucial condition is that, the c_{SERS} is affected by the molecular absorption of the analyte on the covered surface, and it forms sub-monolayers and multilayers of molecules. Average standard EFs span from 10 - 10^3 for non-optimized conditions to 10^7 - 10^8 for very efficient SERS substrates [53].

Overall, SERS scattering is a complex phenomenon comprehending optical, electromagnetic, chemical, and electro-chemical aspects, as well as experimental evidence through applications, especially in the biological, medical and environmental fields^{20,35-42}. Heritage science research has still to fully explore the potentials of the technique and this thesis offers an opportunity to do so.

1.2.1 Aluminum (Al) plasmonics

Al is the metal used to coat the SERS platforms: *why gold or silver were not used?*

As anticipated, the plasmon resonance of Al in the visible region (2.0 - 3.0 eV/ λ = 400 - 700 nm) was explained through a model of Bragg optical activity combined with localized surface plasmon resonances (LSPR)s of Al nanoparticles [29,40,42-45,47]. The optical activity is due to the geometry and roughness of the structures, and the LSPR to the scattering in the UV-VIS region of randomly oriented Al nanocrystals [45]. The parameters affecting the enhancement were: the aspect ratios of the arrays, the size of the nanocrystals, and the periodicity of the nanovoids coated with the plasmonic metal [41]. The Raman transition moment of the molecules absorbed on the metal surface is, however, the main contributor to the SERS effect. McClain and co-workers [45] demonstrated that ordered 2D Al nanodisks assemblages show plasmon resonances in the UV range (4.95 - 1.95 eV/ λ = 250 - 630 nm). The content oxygen attenuates the LSPRs, and the increased size of the nanocrystals shifts the resonance from the UV to the visible range. Opposite to what expected, the thin layer of Al_2O_3 , naturally forming on the Al nanocrystals, provides stability to the substrates [45]. Equally, Gómez *et al.* [42] characterized freshly fabricated Al coated substrates with electron energy-loss spectroscopy (EELS), extrapolating the energy maxima with a Gaussian fitting (Annex Figure 1.1). The sample profile was compared to that of commercial layers obtained from pure metallic Al and Al_2O_3 : the spectrum of the sample matches more closely the one of pure Al than that of Al_2O_3 , as a further evidence of the negligible effect of the oxide layer on the plasmonic resonance. For the current research, fabricating the Al-coated SERS platforms

following the method tested by previous researchers of the same group was an evidence-based decision, although further testing, optimization and validation were pursued.

In various studies, Al-coated platforms have shown LSPRs peaks from 5.3 to 1.6 eV: the range of resonance reported in the literature spans from deep UV to NIR, and it has been respectively associated to small spheres and larger structures [68,70]. Gómez *et al.* [42] demonstrated that Bragg diffraction combined with LSPRs extends the SERS enhancement within a wider frequency range than previously thought possible. Accordingly, PFPE derivatives have been used to fabricate elastomeric substrates through NIL replicating large scale periodical structures of KLARITE[®] exhibiting Bragg diffraction in the NIR region. The size of the nanoparticles measured between 10-50 nm with average height of 5.4 nm, overall features affecting the ability of the substrates to exhibit resonance in the range of interest. To avoid fluorescence from the polymeric background, 150 nm-thick layer of Al was deposited on the platforms, providing sufficient room for heat accumulation during laser/metal/analyte interaction. Furthermore, reflectance spectroscopy ($\lambda = 360\text{-}740\text{ nm}$) was performed to show the differences between coated and uncoated replicas of KLARITE[®] (Figure 1.1).

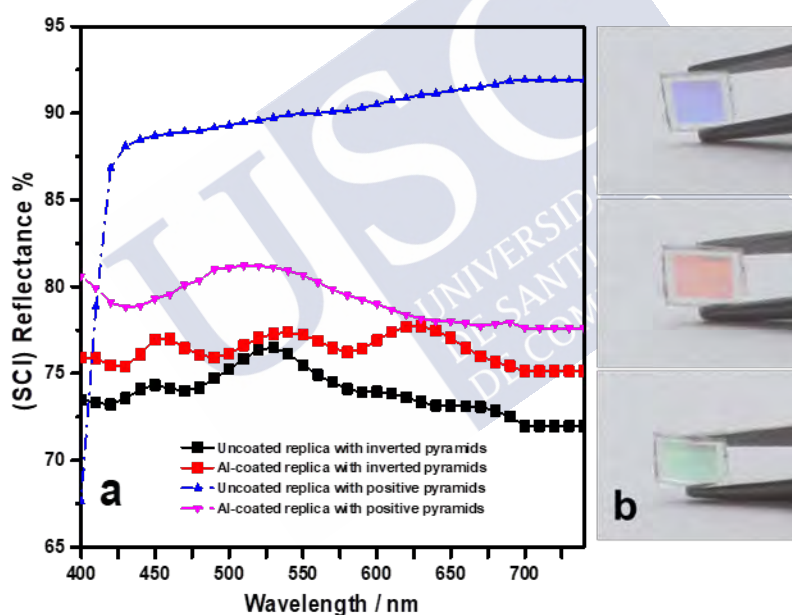


Figure 1.1: reflectance spectra. (A) specular component included (SCI) of coated and uncoated replicas of squared array structures with positive ($\blacktriangle$) and inverted pyramids ($\blacksquare$) obtained with a Konica Minolta CM700-d spectrophotocolorimeter; (b) uncoated replicas photographed under natural light with different tilt angles. CIE L*a*b* color space D65 illumination, 10° observer. Adapted with permission from ref. [42]. Copyright Royal Chemical Society.

Spectra point at extending Al plasmonic resonance in the visible region, opposite to gold and silver that do not show such an optical activity [47,56,68]. Reflectance % provides an indication of the influence of the surface morphology on the optical properties of the object under analysis. The Al-coated platforms show a periodical reflectance frequency, compared to uncoated platforms that show almost none (Figure 1.1 a). This allows hypothesizing that the

periodically modulated structures favor the propagation of the surface polaritons corresponding to the appearance of the localized dips of the pyramids. Those generate a non-constant reflectivity profile, opposite to what expected for Al, a highly specular reflective metal [46]. Figure 1.1 b shows the photographs of uncoated substrates with inverted pyramids manifesting different colors (namely blue, red and green) in the visible region changing with the tilt angle of light source/detector (*e.g.* photo camera). SEM and photographs of coated substrates will be presented in Figure 2.2, section 2.2.1. Further evidence has allowed inferring the plasmonic nature of Al through high spatial resolution EELS and finite difference time domain (FDTD) simulation measurements (the latter is in Annex Figure 1.2). Figure 1.2 is extracted from Gómez's *et al.* [42] publication and it shows EELS tests on substrates fabricated with the same materials and procedures as those used in the research herein presented.

Al plasmonic properties combined with the Bragg diffraction show in EEL spectra that the inverted pyramids dips exhibit strong plasmonic signals at approximately 1.35 and 2.25 eV (NIR and visible range respectively). EEL intensity maps in the corresponding ranges have been integrated accordingly in an energy window of 0.3 eV. For maximum signal enhancement, the excitation wavelength of the laser should match the plasmonic signal, namely 785 and 514 nm. Nonetheless, the intensity maps have shown how the structure periodicity affects the polaritons propagation, resonating through a diagonal direction at 1.35 eV. The roughness of the Al nanoparticles influences the signal at 2.25 eV (Figure 1.2 d). In addition, the maps show that LSPRs occur preferentially in dips rather than in flat areas, even when the surface roughness is comparable. Subsequently, a matching irradiation wavelength with energy between 1.2-1.6 eV (~ 785 nm) can trigger the polaritons resonance at the edges of the Al nanoparticles throughout the periodic structure. Instead, the same structure appears to behave differently when the excitation wavelength is set at higher energies 2.35 – 2.65 eV (~ 514 nm), possibly due to the hybrid resonance Bragg and surface roughness resonance showing a non-oriented enhancement, but only on the Al particles edges Figure 1.2 f.

Similarly, FDTDs simulations of the electric field have provided hints of the NIR phenomena contributing to the enhancement (Annex Figure 1.2, profiles obtained with 514 and 785 nm excitation wavelengths and rhodamine as analyte). They confirm the EELS results on inverted pyramids with continuous Al-platforms, showing the highest signal in the dips and edges of the Al-nanoparticles.

Given the random distribution and orientation of Al nanoparticles, the LSPRs could not be easily, however molecular detections with standard compounds have been handy to assess the fabricated as to those used for in the current research. Rhodamine 6G (R6G) and coumarine 440 standards from Sigma Aldrich™ have been diluted at different concentrations with pure ethanol, dropped with a micropipette on a controlled area (~ 0.02 μ L on 0.2 mm²) and illuminated with a laser of 60 μ m² $\varnothing$ in the center to avoid aggregates. Some of the results on coumarine 440 are reported in Figure 1.3

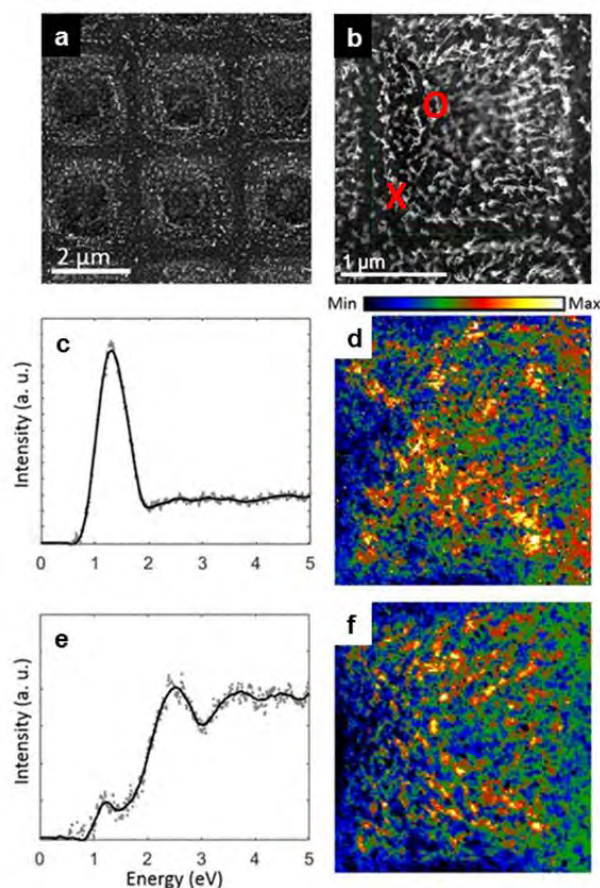


Figure 1.2: high angle annular dark-field imaging.
 HAADF STEM image of the Al layer with inverted pyramids (a). The electron energy loss spectroscopy (EELS) measurements were recorded from a single pyramid (b). EEL spectra showing intense surface plasmon signals at 1.35 eV (c) and 2.5 eV (e), as collected from the points with red X and O marks, respectively, in image (b). Corresponding intensity maps with integrated intensity in the energy range of 1.2-1.5 eV (d) and 2.35-2.65 eV (f), respectively. Adapted with permission from ref. [42]. Copyright Royal Chemical Society.

The concentration of the analytes spanned from 1×10^{-6} to 1×10^{-15} M and distinctive bands for both analytes have been consistently recorded with the Raman spectrometer ($1511\text{--}1162\text{ cm}^{-1}$ for RG6, $1235\text{--}1162\text{ cm}^{-1}$ for coumarine 440). However, changes in the relative intensities of some spectral features occurred, especially at lower concentrations. They were attributed to the random orientation of the Al grains, implying differential local enhancement. Further data on the performance of the SERS substrates used for the present thesis have confirmed that replicas of inverted pyramids show the best noise signal ratio [42]. Finally, to be mentioned that EFs calculated on the distinctive bands yield 5.5×10^9 factor for R6G and 3.6×10^7 for coumarine 440 with $\lambda_{\text{exc}} = 514\text{ nm}$, and 2.2×10^7 for R6G and 3.6×10^7 for coumarine 440 with $\lambda_{\text{exc}} = 785\text{ nm}$.

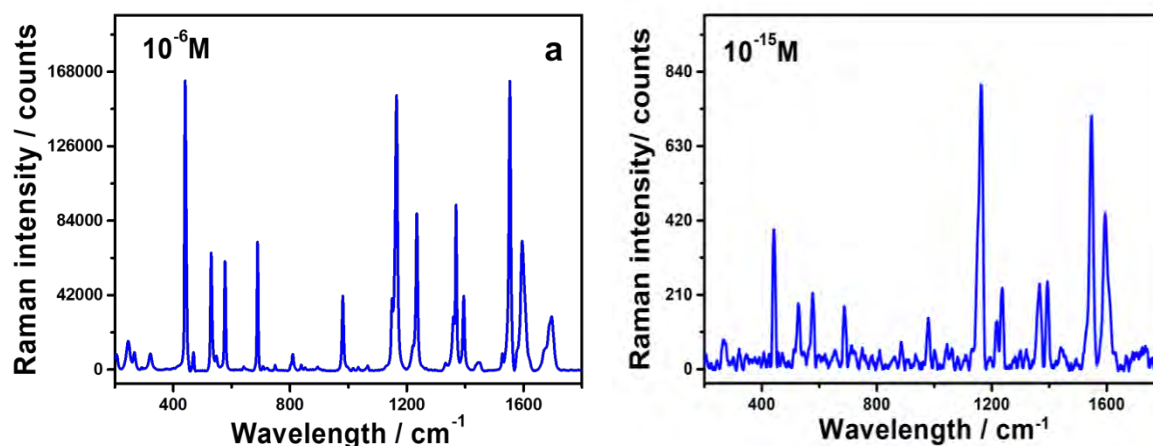


Figure 1.3: SERS spectra of coumarine 440 at (a) 10^{-6} M and (b) 10^{-15} M with $\lambda_{\text{exc}} = 785$ with an inVia™ confocal Raman spectrometer. Distinctive bands at 1235 and 1162 cm^{-1} have been used to calculate the enhancement factor (EF) of the Al-coated continuous 2D structures with inverted pyramids.

1.2.2 Summary

- The motivation of the thesis was introduced, providing preliminary scientific and ethical framework on sampling of cultural heritage materials.
- NanoRestArt EU project gave the chance to focus on developing disposable sensors for the enhanced protection of polymer-based contemporary artworks.
- Early detection of degradation markers (LMW compounds from oxidized surfaces) can inform us on the preservation conditions of heritage objects, previous conservation treatments, and ongoing mechanisms of degradation.
- Principles of Raman inelastic scattering and hybrid UV-Vis plasmonic resonance of Al (Bragg and LPRSs) were introduced.

1.3 BEHAVIOR OF POLYMERS

After having provided background information, some aspects about polymers identification and degradation will be introduced. Within the NanoRestArt project, a selection of underexplored polymers used as contemporary art materials was defined (*e.g.* ABS, PI). If cellulose esters and other early plastics have been commonly researched, the materials selected by NanoRestArt experts required further research targeted to address heritage science questions [71–79].

In general, polymers are substances made of long sequences of repeating units of atoms or group of atoms linked together through covalent bonds. The linked molecules in each chain are between 1,000 and 100,000 approximately (macromolecules) [80,81]. The monomer is not the repeating unit, but the small molecule from which the polymer is synthesized (Figure 1.4 a). The degree of polymerization is indicated by the subscription n and it refers to the number of repeating units linked together. Polymers can be classified in two broad categories: thermoplastic and thermosetting (Figure 1.4 b, c), and further subcategories include elastomers and gels.

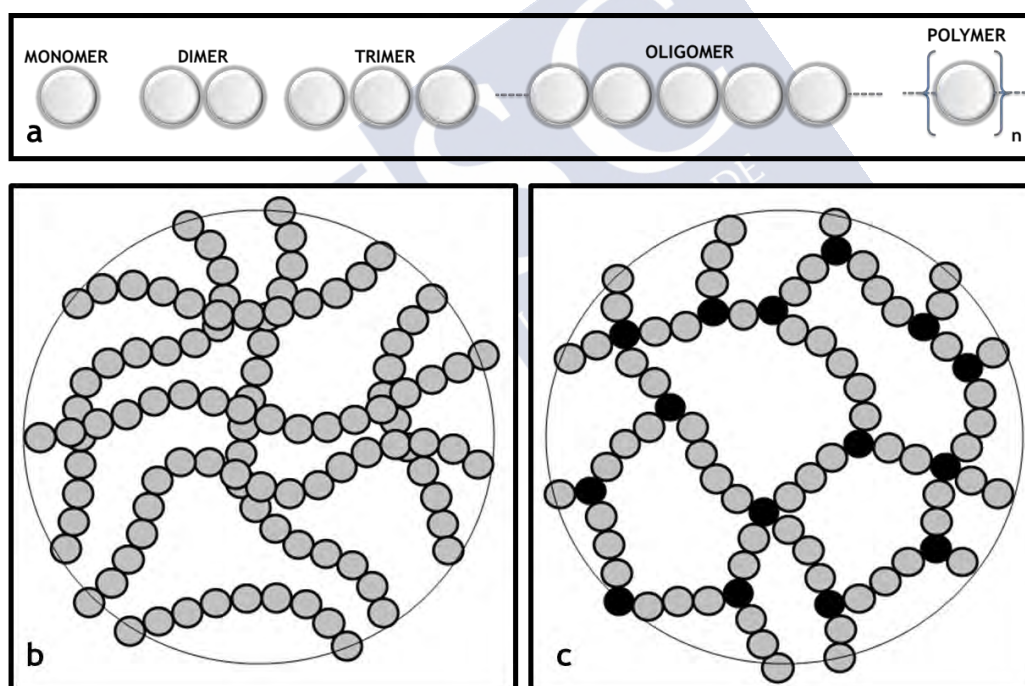


Figure 1.4: representation of monomer and repeat unit of a polymer (a); linear chains of macromolecules (b); a three-dimensional macromolecule (c). *Crosslinking nodes* are represented in black (example of a thermoset). The dimension monomer unit is approximately 1 ångström (Å). Adapted from free media repository [82].

A relevant concept to understand the behavior of polymers is the melting temperature (T_m), which is a range of temperatures depending on the polymer polydispersity. It consists of a transition from solid to liquid associated to the chemical structure of the polymer. The crystalline portion of the polymer is a non-equilibrium distribution of crystallites of different size melting at different times. However, for the current thesis the most relevant concept is the glass transition temperature (T_g). It is a crucial parameter with practical implications and it

depends on the 1) density of the crosslinks, 2) free chains-ends, 3) rigidity of segments, and 4) concentration of unreacted groups. Further factors affecting the T_g include the addition of plasticizers, for example, that separate the polymer chains, reducing the interactions and lowering the transition temperatures. Similarly, at increasing molecular weights the T_g drops linearly. Molecular chains absorb heat from the environment and increase their mobility, shifting from a glassy state to a rubbery one or vice versa, (Figure 1.5 summarizes polymer behaviors based on heat transitions). Structural features changing with the temperature affect the molecular rotations. The specific mobility restrictions due to the inert nature of the bonds and the proximity with different chain-ends affect the transitions. T_g is a second order transition expressed as a range of temperatures, and reflecting a change in heat capacity of the material with no latent heat occurring, for example, in crystallization transitions [80,81,83,84]. Overcoming certain energy barriers allows bonds to initiate movements. For example 2 kcal/mol for a simple hydrocarbons as ethane is the energy necessary for motion [81]. Furthermore, the proximity with chain charges generates dipolar repulsion or attraction, creating localized crystallinity. Rotational energy levels can also be considered as a function of substituents, such as carboxylic functional groups, that favor chain attraction.

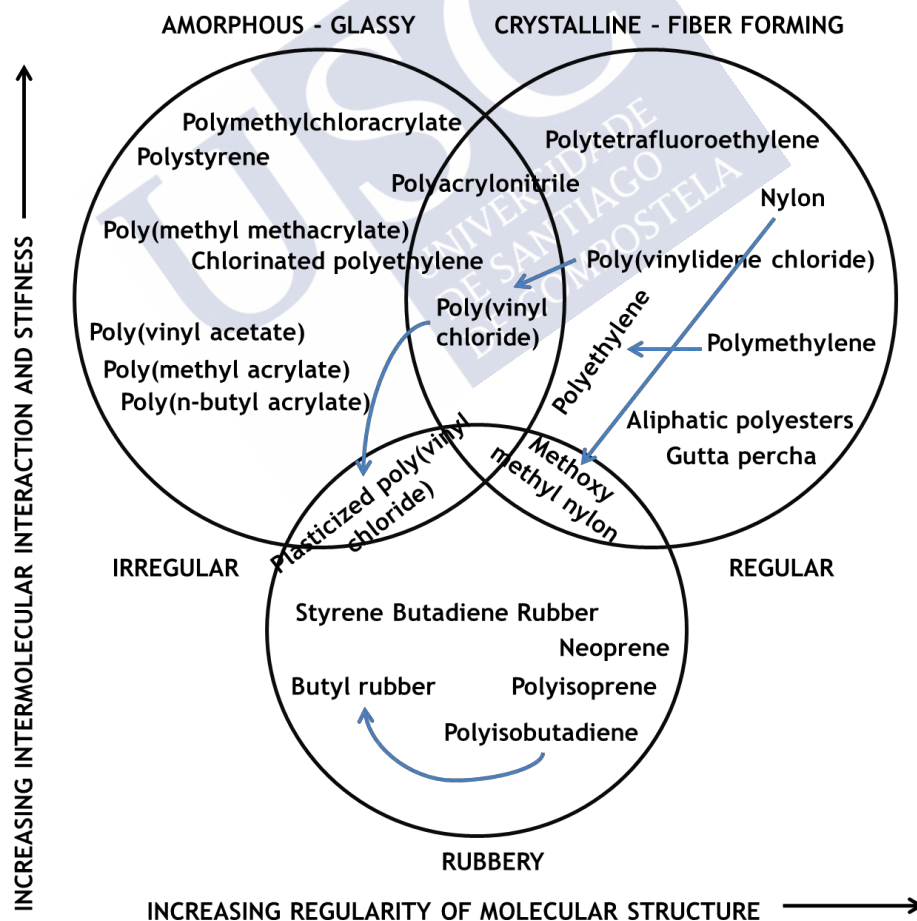


Figure 1.5: Schematic grouping of polymers according to the molecular structure and the effects on properties. Adapted with permission from ref. [81]. Copyright Elsevier Science & Technology Journals.

Overall, the greater is the stability of the molecule, the greater is the energy necessary to break the bonds. Chains based on aliphatic bonds, as C-C and C-O, are more flexible than those with rings. Additional stiffness in the structure is provided by the presence of double bonds. Furthermore, some authors connected transition temperature to thermodynamic transitions, and T_g is considered the temperature at which the configurational entropy tends to zero [81].

1.3.1 Classification of polymers

Thermoplastics are polymeric materials used below their T_g and they are characterized by supermolecular interactions. Above certain temperatures, they transition from rigid to viscoelastic, being molded and remolded in any shape through extrusion and/or injection. Although they are considered non-crosslinked, the strength of the intermolecular interaction is high enough to provide the materials with stable performances. *Thermosets* are obtained by irreversibly curing (crosslinking) a prepolymer with heat or irradiation. They work below their T_g . *Elastomers* are connected through covalent bonds, as thermoplastics, but they are used above their T_g uncovering different properties [85]. Figure 1.5 shows the effects of the structural regularity, molecular stiffness and molecular interactions and how these influence the properties of the polymeric material.

Polymers can be synthetic and semi-synthetic and contain additives to enhance their performance towards thermal, chemical, biological, and mechanical stresses. Natural polymers contain impurities working as additives. Behavior of polymers has been widely investigated at industrial level to enhance processing and service life of plastics [81,86]. For example, additives, plasticizers and fillers, are usually tested for the specific purposes of the end-product [80]. As far as the fabrication techniques are concerned, polymers can be transformed into plastic objects by foaming, molding (injection and extrusion), sheething, castings, laminating, fiber forming, carving, and their properties change accordingly [87]. The effect of plastic processing on the behavior of polymers will be disregarded in the present work, being out of the scope of research.

Additives are divided physically into four groups: solid, liquid, rubbers and gases. The most important classification, however, refers to the functionality that each additive provides to the polymer. In this perspective, additives can be classified as, 1) plasticizers, 2) flame retardants, 3) lubricants, 4) impact modifiers, 5) antioxidants and stabilizers, 6) colorants, 7) initiators and cross-linkers, 8) solvent and diluents [81,86]. Additives constitute up to 50 % wt. of the polymer composition, but the greater effect on weathering is connected to the inert properties of the matrix polymer [83,86]. This explains why the majority of studies on polymers degradation focus on the polymer behavior, rather than on the additives [86,88,89]. Similarly, the current thesis will deepen the study of the few polymers and copolymers selected within the NanoRestArt disregarding the contribution of additives. Since later in the thesis, the role of colorants in complex polymeric matrices will be discussed, few fundamental concepts are herein introduced.

Colorants can be grouped based on how they are applied to the polymer base: painted as coatings, added as surface dyes, and added to the mass of the matrix polymer as

chromophores or pigments. Colorants can be roughly divided into organic and inorganic (either dyes and pigments) based on their solubility within the polymer matrix. However, the two-group separation might present limitations of applicability in case of composite materials [90,91]. Overall, the influence of colorants on the degradative behavior of polymeric materials is dual, accelerating the rate or improving the protection of the matrix polymer [92,93]. As an example, titanium dioxide (TiO_2) is widely studied for its contribution to the formation of hydroxides and perylhydroxyl radicals, causing interactions within the polymer matrix, hence increasing the degradation [94]. Another example of degradation promoted by colorants is represented by iron-containing pigments or copper organometallic pigments dispersed in ABS or acrylic resins [95,96]. Evidence shows that in ABS the loss of toughness and ductility are favored comparing to other pigments within the same polymer matrix [96]. However, if pigments are treated with coatings and inert particles, like silica and zinc oxide, they might have a stabilizing effect on the polymer. They reduce the light penetration towards the polymer bulk, like carbon black (CB), hence reducing the rate of photo-degradation.

1.3.2 Chemistry of degradation: tackling the formation of LMW compounds

This section lays the foundations to understand the mechanisms of formation of LMW products of oxidation in polymeric materials. Phenomena leading to oxidative degradation are hereby put into context and they will be reiterated in the section of the results and discussion (Chapter 3).

Weathering is the term comprising the several changes leading to the decay of the polymers exposed to outdoor conditions [97]. Factors affecting the degradation of polymers are heat, oxygen, UV, moisture, ionizing radiations (γ and X rays), biodeterioration due to bacteria and mold, and mechanical stress. A combination of two or more factors can occur: for example, as a result of UV and oxygen diffusion, light initiated chemical reactions, acting on free radicals within the polymer matrix lead to *photooxidation*. However, degradation due to oxygen penetration in absence of light also occurs through a series of similar radical chain reactions (*oxidative degradation*) taking place at room temperature. On the other hand, *thermooxidative* phenomena combining heat and oxygen can take place. Overall, concurrent effects of degradative processes might coexist; therefore, it is not straightforward to predict the behavior of the polymer and the mechanisms of formation of LMW products [81,86]. As anticipated, all polymers during and after processing show low stability and additives are necessary to transform them into service plastics.

Accelerated aging studies have been designed at industrial level to prolong the service life of plastics and to adapt the processing technologies. Performance and durability of the polymers are tested under artificial conditions of light, temperature and humidity. The inert properties of the polymer network, such as number average molecular weight (M_n), average molecular weight (M_w), and repeating unit interactions influence substantially the degradation mechanisms. The ratio between M_w/M_n average numbers is called index of polydispersity, and it is functional to monitor changes of molecular weight due to degradation.

Oxidative degradation is a slow process influenced by the oxygen diffusion within the material. Oxygen diffuses preferentially through the amorphous areas of the material, and

rates are higher in those polymers like PI compared to more crystalline ones, as high density polyethylene (HDPE) or polycarbonate (PC). The diffusion mechanism is expressed with the following development of Fick's second law (Equation 1.3):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - r \quad 1.3$$

C = concentration of the reactant; t = time; x = depth of penetration of the reactant; D = diffusion coefficient; r = rate of diffusion. The diffusion coefficient can be determined as a classic sorption and permeation mechanism ($\text{cm}^2 \text{s}^{-1}$), as a constant parameter independent of depth, time and concentration of the reactant. In case of aging, the superficial layers change their oxygen permeability and the plastic becomes heterogeneous, due to possible chemical reactions as crosslinking [98].

Oxidation in polymers is usually an auto-accelerating process, slow at the beginning and then accelerating fast to a constant rate. Oxygen uptake is consistently reduced by the presence of antioxidants, meaning that *oxidative induction time* (OIT) before oxygen is absorbed increases. *Photo-degradation* is the kind of deterioration initiated by sunlight in absence of oxygen. The wavelength of radiation is approximately from 700-300 nm ($170\text{-}390 \text{ kJ mol}^{-1}$). C-C and C-H have energies of 420 and 340 kJ mol^{-1} , respectively, but in proximity of aromatic and unsaturated structures they break at lower energies. Chromophoric groups favor the absorption of light, hence initiating a transfer of energy to the bond resulting in its scission right after. The reaction of bond scission is attenuated during propagation throughout the bulk of the polymer, while being faster in the outer layers of the polymer. Following, the radical chain scission for oxidation and photooxidation based on Bolland and Gee are presented in Table 1.1 [99,100]:

Table 1.1: Sequence of reactions of radical scission in polymeric materials

	Oxidation	Photo degradation
Initiation:	Polymer $\rightarrow$ R•	RH $\rightarrow$ (hv) R• + H•
Propagation:	R• + O ₂ $\rightarrow$ ROO•	H + RH $\rightarrow$ H ₂ + R•
	ROO• + RH $\rightarrow$ ROOH + R•	R• + H• $\rightarrow$ H ₂ + unsaturations
Termination:	R• + R• $\rightarrow$ R-R	H• + H• $\rightarrow$ H ₂
	R• + ROO• $\rightarrow$ ROOR	R• + R• $\rightarrow$ R-R (crosslinking)
	ROO• + ROO• $\rightarrow$ ROOR + O ₂	

In initiation reactions, impurities and chromophoric groups in the polymer associated with the decomposition of hydroperoxides from processing form radical species (R•). Homolytic bond scission leads to the formation of free radicals as well. Radicals usually react quickly with the oxygen present in the environment and in the polymer. Hydrogen abstraction

is the common mechanism to transfer hydrogen from molecule to radical species in the system. The primary dissociation of C-C bonds forms reactive radical species that propagate through the polymer chain with different mechanisms. One of them is the unzipping, as above mentioned, a depolymerization and fragmentation resulting in the monomeric unit with C-C double bond. A second mechanism is the intermolecular transfer that leads to a random (statistical) chain scission of the polymer forming smaller reactive fragments and leaves LMW compounds. Finally, the third mechanism is the intramolecular transfer of radical species occurring throughout the polymer chain and forming oligomeric fragments, units containing dimers or trimers of the original polymer. Highly relevant to notice that in photo-degradation and photooxidation, carbonyl groups are among the most photo-labile species undergoing to Norrish type I and type II cleavage (Figure 1.6). Norrish type I is a radical reaction, while Norrish type II is non-radical, both leading to chain scission. Carbonyl groups and hydroperoxides precursors are decomposed by light (hv) preferentially on the tertiary C-H bond.

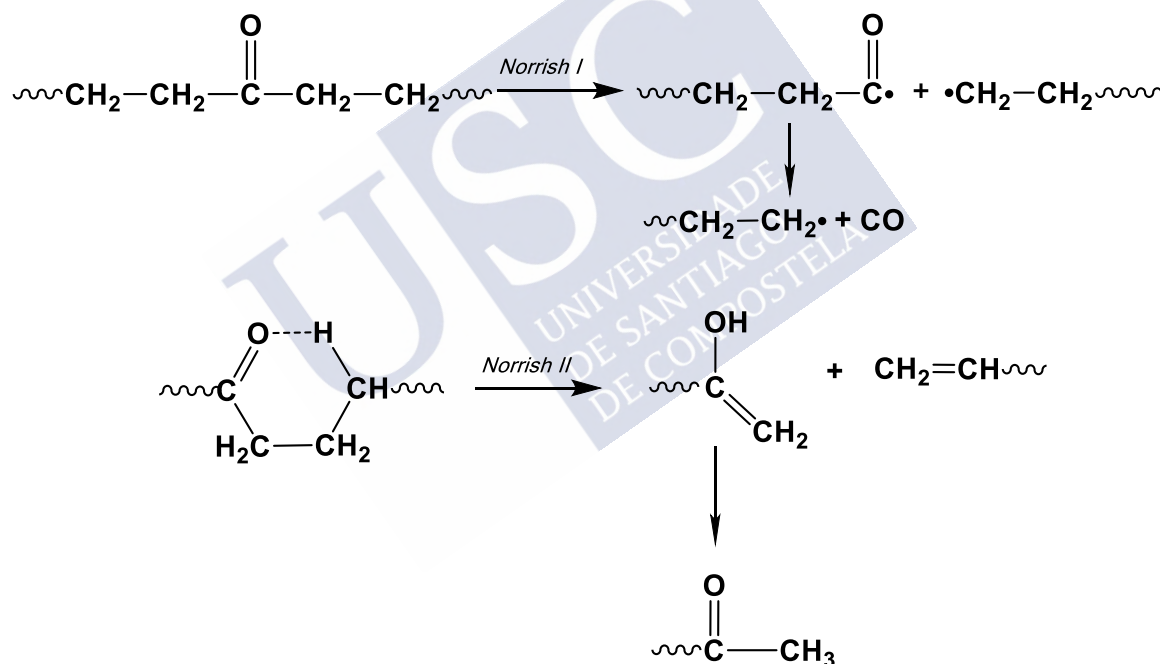


Figure 1.6: photo-degradative chain scission reactions of Norrish type (I, II) based on chain scission of polypropylene (PP) polymer network. Norrish I leads to the direct formation of radical species next to carbonyl groups, whereas Norrish II to methyl ketones and vinyl unsaturations from ring transition state. Adapted with permission from ref. [88]. Copyright Elsevier Science & Technology Journals.

Propagation reactions in oxidative degradation are faster than those in photo-degradation [88]. Alkyl species react very quickly forming alkylperoxyl radicals ($\text{ROO}\cdot$). Then, an auto-accelerating process in presence of diradicals or singlet oxygen favors auto-initiation of the oxidation mechanism. Radical chain reactions involve ground state oxygen, which is absorbed progressively on weak C-H bonds and leads to the formation of hydroperoxides (ROOH). C-H bond breaking ($\text{ROO}\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$) requires higher energy of activation and

yields high concentrations of alkylperoxyl radicals. Determining the rate of this step of the radical chain helps evaluating the overall rate of oxidation in most kind of polymers. Bond dissociation energy in saturated polymers varies in a range of 10 to 65 kJ mol⁻¹ (e.g. PP, PE, PVC, PVAc, PU, PMMA), whereas is lower in unsaturated polymers (e.g. PS, PET). Nonetheless, H abstraction is not a thermodynamically favorable phenomenon, and furthermore if the formed radical center is conjugated with an adjacent C=C, or stabilized by C=O groups and nitrogen/oxygen lone pairs, the propagation is spontaneous [88]. However, the presence of defects in the polymer structure or internal double bonds in the backbone makes the autoxidation more likely to occur in polyesters and polyolefin. On the contrary, in peptides bearing α C-H bonds the formation of peroxides takes place in the side chains.

In termination reactions, more stable species form and crosslinking is favored. Oxygen concentration affects the removal of radical species. Secondary reactions lead to decomposition of hydroperoxides, main product of oxidation. Under the action of light (h ν), ROOH decompose forming RO• (alkoxyl radical) and OH• (hydroxyl radical) that propagate in nonpolar media and can react with metal ions (redox and catalysis). Alkoxyl and hydroxyl radicals are efficient hydrogen abstracting species generating new radicals within the reaction chain, and therefore re-initiating the degradative cycle.

Domains of concentration of the oxygen have a huge impact on the rate of oxidative degradation. In case the concentration of oxygen is low, not all radicals react, if not in the termination phase. On the other hand, when oxygen concentration is high, the reaction of radical species is instant and almost all radicals react forming radical oxides. Afterward, the hydrogen abstraction reaction, leading to the formation of hydroperoxides or cyclic peroxides, is much slower. These compounds easily decompose in secondary reactions forming small molecules, which may be volatile, or remain onto the polymer surface as LMW compounds. They contain different functional groups as ketones, carboxylic, and vinyl groups. As anticipated, also in secondary reactions, the presence of metal ions and other impurities from processing, boost the oxygen uptake. This thesis will focus on the detection of the non-volatile fraction of LMW products, as exceptionally reliable markers of degradation in the early stages. Usually, polymeric oxidation is followed by FTIR spectroscopy determining carbonyl, hydroxyl and unsaturated groups. The conversion to concentration units is expressed by the Lambert-Beer equation (Equation 1.4):

$$A = \varepsilon L C \quad 1.4$$

A = absorption; L = optical path length; ε = excitation coefficient (mol⁻¹cm²); C = concentration (mol cm⁻³). The most useful bands to monitor the degradation of hydrocarbon polymers through FTIR spectroscopy are in the region 1710-1735 cm⁻¹: 1735 cm⁻¹ for aldehydes, 1720 cm⁻¹ ketones, 1710 cm⁻¹ for carboxylic acids progressively dominating during different phases of degradation. Hydroperoxides species at 3550 cm⁻¹ are usually monitored at the beginning of the degradation [88]. Experiments of artificial photoaging are necessary to tackle some unknown aspects of the mechanism leading to chemical transformations. In any case, the reactions have to be the same as those occurring in natural

conditions, and the resulting products of accelerated aging have to be the same as natural ones to validate the accelerated tests. Furthermore, long-term behavior of the material can be predicted according to irradiation times and doses. To this aim, Xenon lamps filtered to limit $\lambda < 300$ nm were used to irradiate model samples presented later in this chapter. The average experimental conditions applied for the photoaging tests were 50-200 Klx, 20-45°C, and 40-60% relative humidity. Thermoxidative aging experiments were conducted in mild conditions ($\sim 150^\circ\text{C}$) in the oven.

Overall, different types of degradative phenomena can lead to the formation of LMW products: radical reactivity, lateral substitutions, scission, elimination, or cyclization among the most relevant. Small molecules from the environment are involved in the reaction with the polymer (e. g. H_2O , O_2 , O_3). The reaction rate and the thickness of the oxidized layer are the critical parameters that can affect the overall process of oxidation. We assumed that for the type of plastic objects under study, the process is kinetically controlled by diffusion mechanisms, and the degradation we are observing is heterogenous.

1.3.3 Polymers in art: peculiarities of contemporary art materials

Polymeric materials found in collections comprise 3D objects (art and design), as well as paintings, lacquers, and photographic materials [76,101–112]. The focus of NanoRestArt project WP5 was to develop disposable sensing devices for the detection of early degradation products from the surface of **plastic artworks**. With this objective in mind, further parallel investigations on design objects (e.g. LEGO[®] toys) and colorants were conducted. Further, collaborations with artists and conservators also contributed to contextualize the use of knowledge envisaged through the thesis. The parallel studies enriched the overall understanding of the behavior of polymers and helped integrating background information to address issues related to molecular sensing through SERS platforms.

1.3.3.1 Outline of synthetic materials, fabrication techniques and plastic history

Plastics durability is an especially relevant requisite for collectability. To date the majority of plastics collected, hence potentially researched by material scientists, are design objects [76,77,110,113]. Traditionally to be collectible, the object has to be rare, which is in contradiction with the mass production of plastics. Then, the impactful design, the use of color, the technical precision, the variety of shapes and functions associated should be rather unique [101,108]. The artistic components and elegance brought by the object and its resulting innovations make it more desirable for collection. However, advancing knowledge about objects with a greater artistic and economic value, such as sculptures, could have a higher impact on societal concerns for their transmission to future generations [110,114].

Private and public collectors keep investing considerable amounts of money in contemporary art objects, and certainly synthetic materials have a prominent role in the fabrication of such works. Artprice.com most recent report shows that in the last 20 years the international market of contemporary art had a turnover multiplied by 20 [115]. Contemporary art is indeed among the healthiest sectors of modern economy, and even in times of global financial crisis has shown exponential growth. Therefore, heritage scientists

and conservators urge to upgrade their knowledge about emerging materials (*e.g.* 3D printing polymers) to fully understand long-term behaviors of synthetic polymers and to respond to upcoming losses [116–118]. The report also confirms that masterpieces and monumental works fabricated with more durable supports have higher turnovers on sales (*e.g.* return of +1000% from Basquiat's canvases over +4% on his printed drawings sold in 20 years) [119].

Table 1.2 presents a timeline polymers and fabrication methods for art and design objects. Artists mixed resins with dyes or other poor studio means, causing shrinkage and cracks to the sculptures, being not usually concerned about technical requirements for durability [120]. Regardless stability, most artists' choices respond to aesthetic needs, rather than to functional ones. In this respect, Newman [87,121,122] described plastics as the new art medium, and lists thoroughly and chronologically polymers, their workability along with their aesthetic properties explored by the artists.

Polymers can be worked to plastic objects by foaming, molding, sheething, castings, laminating, carving, and their properties change accordingly. Fillers and pigments are added to achieve specific visual effects. In some instances, the color can help identifying the production method, for example phenolic formaldehyde produced by compression molding is usually dark fawn, whereas cast phenolic is amber [87].

Table 1.3 reports the types of polymers with corresponding artists registered in museums and collections catalogues, some with no analytical evidence, others resulting from articles published in the heritage science literature. In brackets, there is the date of birth of the artist to deduce the approximate working period of. British researchers developed an early interest in plastic collections. In 1977, Sylvia Katz wrote the catalogue of the exhibition 'Plastic Antiques' sponsored by the British polymer manufacture company British Petroleum BIP [76,108]. Two inputs profoundly influenced the evolution of polymeric materials during the 20th century; the first is *internal*, and the second *external*. They respectively refer to the massive technological advances in plastic processing, associated with the necessity to imitate existing materials through less costly and easy-to-work materials (*e.g.* wood, textiles, ivory). The mimetic features of plastics provided a solution to economic, social and aesthetic demands, beyond the advent of macromolecular chemistry [76, 101]. Early plastics, especially cellulose esters, (1850 - 1950) have been extensively researched in many aspects, from the production techniques to the degradation mechanisms [76, 77, 111, 116]. They constitute the majority of the design objects in plastic collections and photographic archives[78, 123, 124]. They are semi-synthetic and natural polymers, as cellulose esters, gutta percha, vulcanite, casein, shellac, bois durci and cast phenol-formaldehyde [87,123]. In late 19th century, industry invested on adapting existing technologies and patenting new ones, as for example calendering and extruding machines, to process natural and semisynthetic polymers [87]. Concurrently, well-established technologies in use since the antiquity to fabricate glass or metal, such as casting, blowing, and carving, were being applied.

Table 1.2: Timeline of artists, materials and fabrication techniques of plastic artworks and design objects.

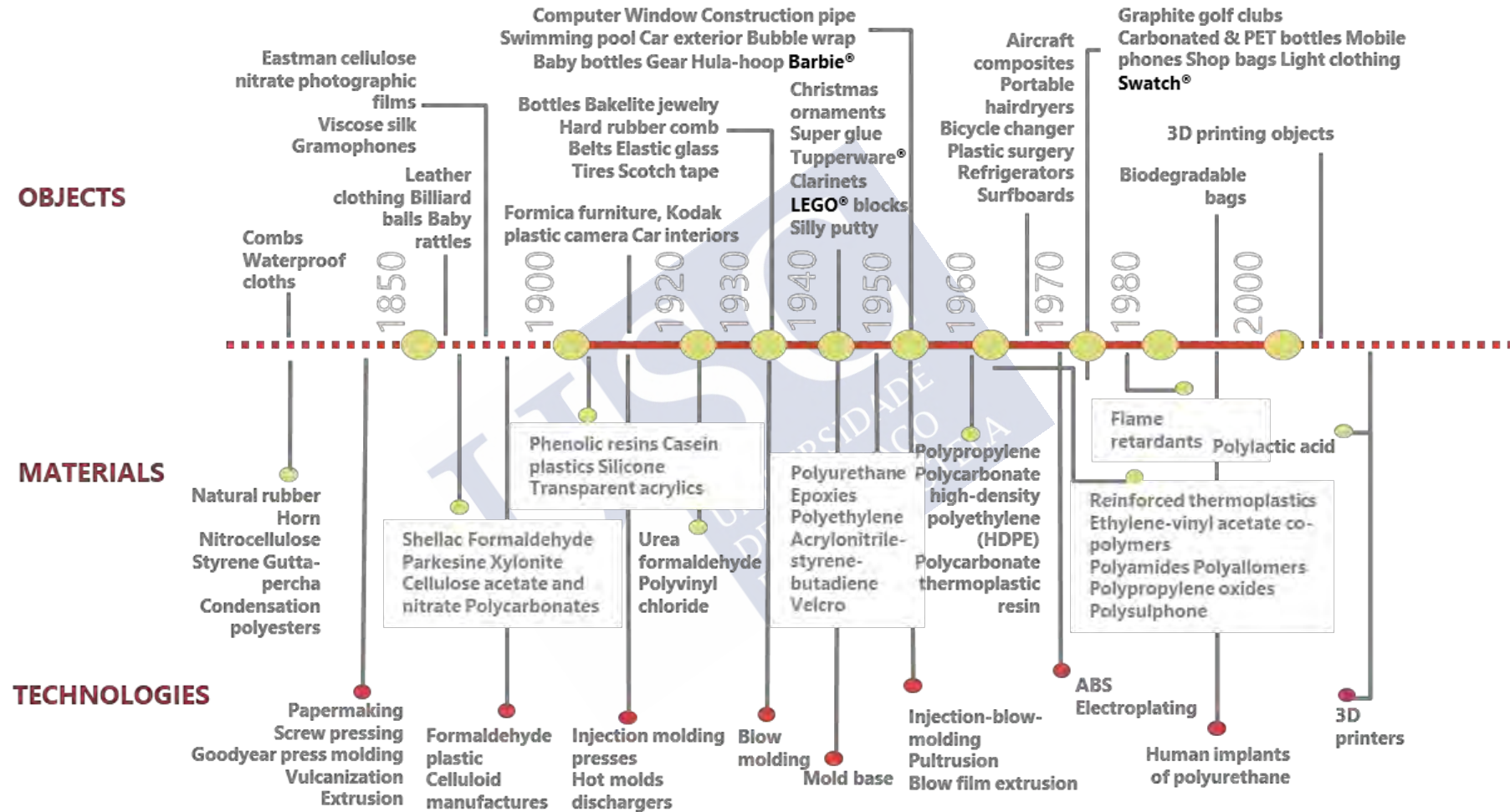


Table 1.3: Synthetic polymers used in contemporary art sculptures*

Polymers	Artist (date of birth)
ABS, PS	Joseph Konzal (1905), Claudia Hart (1955), Roselyne Erutti (n.a.)
EP	Karin Sander (1957), Edward Higgins (1930), Francois Xavier Lalanne (1927)
MF	Sergio Lombardo (1939)
PA	Naum Gabo (1890)
PE	Massimo Zuppelli (1939)
PI	Andrés Pinal (1968), Eva Hesse (1936)
PMMA	Angelo de Sousa (1938), John McCracken (1934), Larry Bell (1939), Robin Irwin (1928), Fred Dreher (n.a.), William Reimann (1935), Ted Hallman (1933), Freda Koblick (1920), Donald Judd (1928), Jesús Rafael Soto (1923), Fernandez Arman (1928), Naum Gabo (1890), Vasa Velizar Mihich (1933)
PP	Pino Pascali (1935)
PUR (ether/ester)	Pietro Gilardi (1942), Lorenzo Quinn (1966), Gaetano Pesce (1939), Thelma Newman (1925), Loris Cecchini (1969), Ted Hallman (1933), Giulio Turcato (1912), Sante Monachesi (1910), Urs Fischer (1973)
PVC	Alberto Burri (1915), Christo and Jeanne Claude (1935, 1935), Duck-Bong Kang (1979)
UP (unsaturated polyester resins)	Alberto Burri (1915), Cracking Art Collective (1993), Tony Cragg (1949), Jess Koon (1955), Niki de Saint Phalle (1930), Naum Gabo (1890), Robert Mallary (1917), Yves Klein (1938), Thelma Newman (1925), John de Andrea (1941), Etienne Bossut (1949), Martine Orsoni (1959), Francois Xavier Lalanne (1927), César Baldaccini (1921), Maurizio Cattelan (1960), Roselyne Erutti (n.a.), Claudia Hart (1955).

*Catalogues of collections of museums, auction galleries and specialized libraries have been accessed to build the upper list of artists using synthetic polymers: plastic.syr.edu, artprice.net, artsy.net, saatchiart.com, Sotheby's, Christie's, Judd Foundation, americanswedish.org, Archive of American Art, The Museum of Modern Art, Guggenheim Museum, Tate Modern Gallery, Los Angeles County Museum of Art, Galleria Nazionale d'Arte Moderna e Contemporanea Roma.

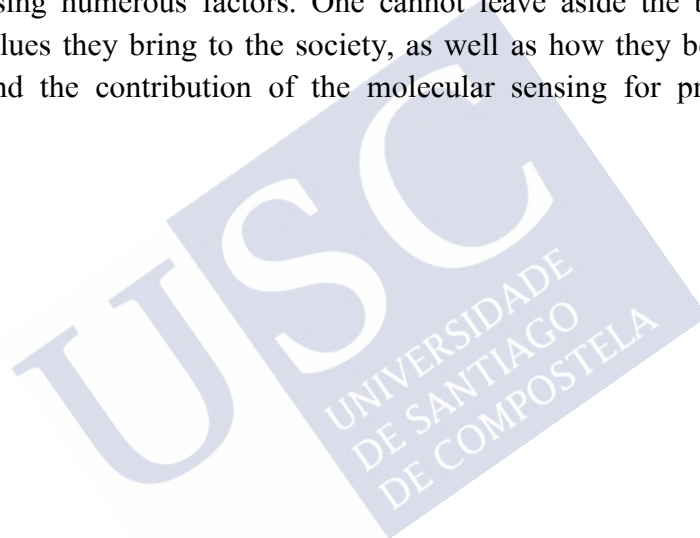
Later, during World War II, as a result of the increased demand for smart materials, plastics manufacturing shifted to scale production in the US and Europe, and compression molding was the first method used to produce PF objects [77]. After the war, due to the shortage of resources for the population, plastics started to be used for the production of basic goods, such as shoes soles, cloths, and household products. Later in wealthier times, plastic aesthetics had penetrated the society, and not surprisingly artists shifted from artisanal to serial fabrication methods using industrial raw materials and technologies [108,125].

In the 1960's in the US, west coast visual artists developed an increasing interest in materials and methods used for manufacturing cars and surfboards, as acrylic resins and polyurethanes. Craig Kauffman admitted to have disengaged from the traditional creative processes to adopt industrial techniques, such as vacuum-forming to mold acrylic plastics [125]. Larry Bell used thin films vacuum deposition to coat his sculptures, handling himself industrial machineries. Robert Irwin and Peter Alexander as well produced sculptures by molding polyesters and acrylic resins, and polishing them to exploit at the best all the features of light. McCracken was using polyester resins and acrylic lacquers to finish his sculptural surfaces with extreme obsession for the interaction of plastic with light (*Finish Fetish*) [125].

In general, plastics were no less means to humans' ends than other materials were in human history. In fact, eras have been named after materials and technologies predominating the social interactions, and it is not surprising that the 20th century was defined the 'Plastic Age' [102,125,126]. During the *plastic age*, the standards of art and architecture have changed radically, similarly to the ages of *stone* and *bronze*.

Although non-linearly, the mechanisms of introduction of new materials into art repeat themselves in human history. First, functional objects of every-day-use start being produced with a material that seems more functional, cheaper or aesthetically pleasant than the previous one. Then, once for a few decades such material becomes of common use, some artists might attempt to convey artistic, conceptual, and symbolic contents to the public using it. The behavior of the material becomes known enough for experimentations beyond artisanal and serial production, and concurrently its abundance or lack thereof determine its success.

Finally, some of objects make it through history, ending up in collections and museums, after having acquired different meanings and values for a group of people or for the whole humanity (*e.g.* world heritage sites). As reiterated earlier in this section, any material revolution was anticipated by technological advancements serving specific practical needs identified in productive societies (*e.g.* producing kilns that enable to melt raw materials at higher temperatures). Transition of materials in art and design should be thought as a complex event encompassing numerous factors. One cannot leave aside the behavior of polymeric materials, the values they bring to the society, as well as how they became art materials to deeply understand the contribution of the molecular sensing for preventive conservation purposes.



1.4 MODEL MATERIALS AND ARTIFICIAL AGING

In polymer science research, model materials are used to simulate processing reactions, limiting the waste and cutting the costs of production [81,86,127–131]. In academia as in industrial research centers, small scale experiments allow to predict the long-term behavior of plastics and to understand their degradation pathways. Usually, mechanical tests of loading and strain are also performed [132]. Early degradation products are diagnostic of the identification of polymeric material, as well as of the ongoing weathering mechanisms. In heritage science, efforts to develop effective preservation strategies benefit from early detection tools to provide rapid information on the pristine stages of the decay objects. As in medicine, rapid detection allows to act on external accelerating factors and to reduce the rate of damage (*e.g.* changing light exposure). Linseed oil, ABS, PVAc, and PI were tested to validate the sampling method with the PDMS strip sampler. Selectivity and sensitivity towards LMW oxidation products transferred to the Al-coated SERS platforms was tested. It is the first time that SERS was used to detect LMW products from weathered plastic objects².

1.4.1 Linseed oil: pristine research model

A short explanation on why linseed oil was selected as a model material is necessary. Research conducted prior to the beginning of the current project in the same research group comprised experimental tests on purified linseed oil samples. Photoaged and naturally aged films of linseed oil were available to test the method with the PDMS strip sampler method, in addition to FTIR spectroscopy, SEC and Py-GS/MS. Linseed oil seemed an optimal model material, since its aging behavior is comparable to that of polyolefins. Linseed oil is easy to access as a drying oil for paints and food supplement. Linseed oil has been extensively studied in several fields, including nutrition and painting conservation [134–138].

Linseed oil is a triglyceride, resulting from the mixture of saturated and unsaturated fatty acids that in few hours dry through a crosslinking mechanism, which is surpassed by the competitive mechanism of chain scission during subsequent aging [138,139]. Spectroscopic observations of artificially-aged samples allow confirming the processes of autoxidation and formation of a variety degradation products, such as carboxylic acids, aldehydes and ketones [138,140,141]. Linseed oil is particularly prone to crosslinking when in contact with oxygen due to its high degree of unsaturation. In particular, α -linolenic and linoleic unsaturated acid residues are the main components contributing to the polymer-bearing behavior.

Additionally, palmitic, stearic saturated acid residues are also present in the mixture, together with oleic monosaturated acid (Figure 1.7). Among other uses, this natural oil is employed as a binding medium and varnish in paints due to its ability to form a transparent glossy protecting film that hardens over time [137,139,142–145]. Throughout aging, azelaic acid is the diagnostic marker searched for with robust benchtop techniques as evidence of the ongoing autoxidation (*e.g.* pyrolysis). Traces of unsaturated diacidic methyl esters prove the process. Such dicarboxylic acid and further carbonyl products reflect in the Raman spectral features as broadening of the peak at 1745 cm^{-1} , even more evident in FTIR spectra [139].

² One exception is the poster published Krish *et al.* [133]. SERS continuous substrates were placed in bags containing PVC objects for 24-h monitoring of VOCs. Results, however, were not conclusive.

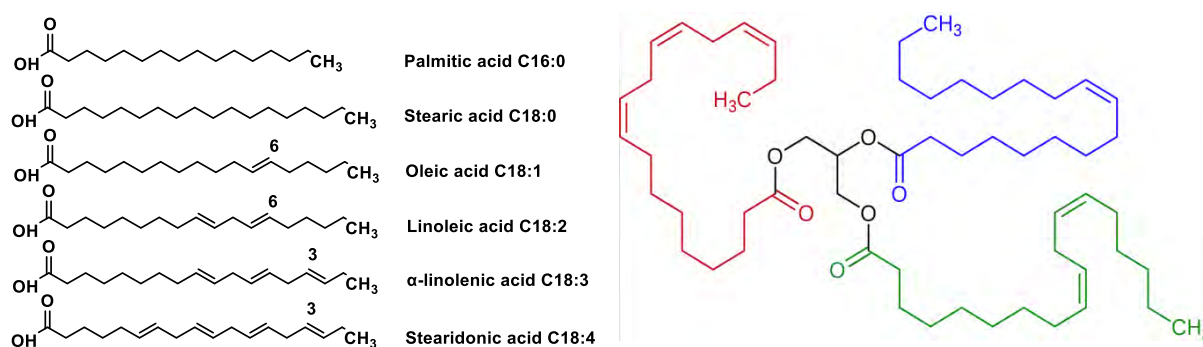


Figure 1.7: chemical structure of linseed oil triglyceride. Average composition comprises unsaturated α -linolenic acid (52 - 55 %); saturated palmitic and stearic acid, 7 and 3 - 5% respectively; monounsaturated oleic acid (18 - 23%), unsaturated linoleic acid (14 - 17%). Right-hand structure image adapted from wikipedia free repository.

As introduced earlier, FTIR spectroscopy is the method of choice to analyze polymers. Similarly, for linseed oil, the spectral changes observed comparing fresh, touch-dry and aged linseed oil films summarized below conclude this part of the introduction:

- hydroperoxides formation on linolenic and linoleic chains;
- hydroperoxides decomposition and formation of alkoxy radical species (more reactive);
- hydrogen abstraction and β -scissions, formation of LMW products, as alcohols and carboxylic species;
- secondary mechanisms of alkoxy radical addition to $C=C$ bearing species leading to the formation of high molecular weight triglycerides (*e.g.* crosslinking).

1.4.2 Acrylonitrile-styrene-butadiene (ABS): omnipresent plastic

Styrene-based plastics were introduced on the market in 1930 by BASFTM and from 1934 up to the end of the Second World War Dow ChemicalsTM fabricated various styrene-based electrical insulators and cables. In 1942, Japan banned the plantation and export of rubber trees to the US, increasing demands to investigate new synthetic routes. Since then, many styrene and polystyrene polymers served as general purpose or high impact thermoplastics, being cheap and versatile materials. ABS is one of the most complex styrene copolymers produced in a quantity of 3×10^6 tons per annum [81]. ABS is also used in many art installations, and more recently in 3D printed design objects [117].

ABS is a grafted copolymer with thermoplastic properties widely used as an industrial plastic for its improved mechanical and impact performances (Figure 1.8). ABS degradative behavior has been widely studied through chemical characterization (*e.g.* FTIR and Raman spectroscopies) [146–150]. Plasticizers commonly used in ABS are hydrocarbon processing oils, phosphate esters, long-chain fatty acids and aromatic sulfonamides [81]. Their influence on the structure is complex and there are limited studies clarifying how they improve impact and tensile strength. They certainly have an effect on the elongation of the chains and, in different formulations, they impact melt flow and flame retarding properties [151].

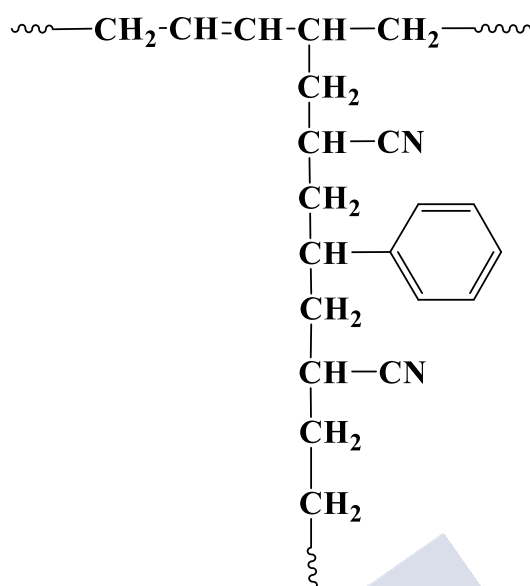


Figure 1.8: chemical structure of acrylonitrile-styrene-butadiene (ABS).

ABS is extremely photo-sensitive. Different components of ABS suffer from differential degradation kinetics: photooxidation begins with the crosslinking of the rubbery phase (BR polybutadiene), that leads to the reduction of the elastomeric properties. The styrene-acrylonitrile (SAN) component shows changes to a much lower degree. In addition, aromatic chromophores might initiate color change reactions leading to the well-known poor photo-sensitive performance [148–150]. Yellowing and reduction of transparency are among the most relevant macroscopic effects of ABS photo-degradation. Roughly 20% wt. of the copolymer is constituted of BR nodules 400 nm in diameter dispersed in a SAN matrix. On those nodules the reactions of crosslinking initiate [150]. Carbonyl and hydroxyl indexes accompanied with weight loss data are generally reported. The FTIR spectral features that manifest upon photooxidation are the following:

- in the $\text{C}=\text{O}$ region the band at 1697 cm^{-1} disappears shortly after; while the maximum at 1721 cm^{-1} broadens and shifts initially to 1717 cm^{-1} and later to 1725 cm^{-1} , similarly for the bands at $1775\text{--}1785\text{ cm}^{-1}$;
- in the OH region the absorption shifts from 3410 to 3440 cm^{-1} ;
- in the C-H region a band at 2731 cm^{-1} appears in the initial phase of aging, forming an α,β -unsaturated aldehyde;
- in the C-O region the band at $1000\text{--}1400\text{ cm}^{-1}$ increases as a result of formation of lactone structures, crosslinking, α,β -unsaturated alcohols (saturated secondary alcohols and saturated ethers).

Comelli *et al.* [152] demonstrated the use of multispectral imaging techniques to extend the comprehension of ABS degradation in design objects. Complementary use of FTIR spectroscopy, emission fluorescence, fluorescence lifetime imaging and time resolved photo-

luminescence allowed to picture object-based degradation patterns on naturally weathered objects. Similarly, Saviello *et al.* [153] analyzed ABS model samples together with Italian design objects from the 1960's. Synchrotron-based FTIR spectroscopy was used to observe the presence of ketones, aldehydes, esters and unsaturated carbonyl compounds. Mapping the object layers allowed demonstrating a selective degradation behavior upon oxygen diffusion combined to a passivation layer formed on the surface. UV-stabilizers and proteinaceous inclusions were detected and mapped for the first time. Andersen *et al.* [96] studied the interaction of eighteen pigments with ABS, exploring the potential catalyzing effect on the rate of degradation. Pigments with iron and copper oxides increase the rate of thermal degradation, even at mild conditions, in addition to reducing four times the resistance to impact of the plastic.

In the current thesis, FTIR spectroscopic information helped to identify newly formed species, such as ketones and aldehydes. DSC was performed to identify structural changes. Complementary spectrophotocolorimetry allowed measuring the reflectance % on a variety of films. Chromatographic techniques, such as SEC and GC/MS, detected LMW oxidation products. Finally, optimized SERS confirmed the presence of LMW products (*e.g.* dimeric fractions from β -scission) with the PDMS strip sampler method at much lower concentration than other traditional techniques.

1.4.3 Poly(vinyl acetate) (PVAc): adhesive, binder, and unwanted conservation product

PVAc-based materials are used in conservation treatments as adhesives, stabilizers, consolidants, and binders (Figure 1.9). However, they can be used also as base materials to make objects [154]. Accelerated thermo and photooxidative experiments have shown that the degradation of PVAc is mostly an autocatalytic process forming acetic acid [155–158].

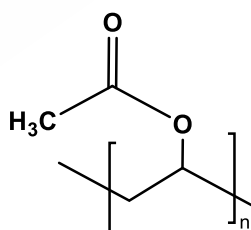


Figure 1.9: chemical structure of PVAc repeat unit.

Deacetylation is the loss of the acetyl group ($\text{CH}_3\text{C}=\text{O}$) and it is reported as the primary degradation mechanism in PVAc, followed by the competitive mechanisms of depolymerization and crosslinking [155,157,159]. In both mechanisms, Norrish II type mechanisms of degradation take place, as follows:

- hydrogen abstraction from the polymer backbone by an acyl radical, followed by the formation of aldehydic species in photooxidation;
- formation of volatile acetic acid, followed by intramolecular hydrogen abstraction, and subsequent C=C bonds formation on the polymer backbone in thermal oxidation;
- chain scission and formation of oligomeric fragments in mild photooxidative conditions.

Thermal degradation and thermo-oxidative degradation of PVAc have been compared by Rimez *et al.* [160,161]. The two main differences highlighted were: 1) the endset temperature of deacetylation is higher in thermo-oxidative degradation than in thermal degradation; 2) a third step is introduced in thermoxidative degradation. Along with acetic acid, the formation of CH-CH-CH, benzene, toluene, naphthalene was reported [160,161]. The identification of solid residues formed during degradation was achieved by solid state NRM [161].

FTIR spectroscopy and DSC have been extensively used to assess the degradative behavior of PVAc [155,160,162,163]. Toja *et al.* [154,164] report that up to 1500 h of accelerated thermoxidative aging, FTIR spectral features increase, while deacetylation proceeds. For longer periods, competing degradation mechanisms occur due to the heterogeneity of the new formed degradation products. In general, plasticized PVAc shows better aging performances with longer OIT of the onset of deacetylation highlighted by the increase of the band at 3020 cm⁻¹ [154].

Surveying museum objects, acetic acid has been consistently reported as a detrimental agent of decay in cellulose esters, especially in photographic archives [78,165]. Rock art, paints, or textiles from museum objects are usually stabilized with PVAc as a binder [166–172]. PVAc adhesives are present in artworks and ubiquitous in many types of surfaces that received conservation treatments, possibly because long term-effects of aging were not thoroughly researched in the past. If adhesives have suffered from degradation, not only they yellow, but they also lose their viscoelastic properties, as a consequence of their change in solubility. Given the spread often undocumented use of PVAc, it seemed indispensable to test its degradative behavior for potential encounters as an unwanted conservation material on the surface of heritage objects during the sampling with the PDMS sampler method.

1.4.4 Polyisoprene (PI): rubber and plastic artwork

PI is naturally occurring latex and derives from 2500 rubber-producing plants, including the *Hevea brasiliensis* tree. Uses of natural PI rubbers (*cis*) and gutta percha (*trans*) have been multiple. It can be transformed into an elastomer, shaped into rigid objects (*e.g.* tires and furniture), or used as a coating/binder in paints [173–176]. The most successful processing treatment of PI rubber is vulcanization, which consists of adding sulfur under heating to harden it [177]. CB and zinc oxides might be also added as catalysts or anti-oxidants in semi-synthetic PI rubbers. Synthetic PI is made by solution polymerization of isoprene (2-methyl-1,3-butadiene) [80,81].

Conformational isomers of PI (1,2-*vinyl*, 3,4-*vinyl*, 1,4-*trans* and 1,4-*cis*) are distinguishable with Raman and FTIR spectroscopies [178] (Annex Table 1.3). Further,

Santos (dos) *et al.* [179] noticed that natural *cis* and *trans* isomers present different OIT and they suggest FTIR bands at 837 and 800 cm^{-1} are more reliable than C=C bonds to follow the degradation processes. Few differences were highlighted between the oxidation products of natural versus synthetic (non-vulcanized) isomers [99,100,176]. The relative concentration of oxidation products in PI isomers differs slightly, as well as the resulting products of photo and thermal oxidations. In general, in degradation of 1,4-*cis* PI hydroperoxides concentration is higher than in other isomers, making it ideal for accelerated aging tests. In fact in the current research, vulcanized 1,4-*cis* PI was used as a model material for the photooxidative experiments (Figure 1.10). Extensive formation of LMW compounds in PI oxidation was reported [150,180].

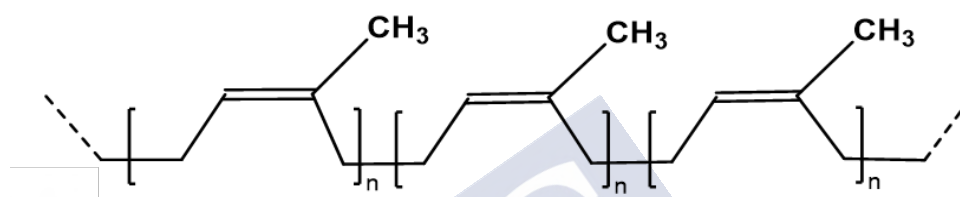


Figure 1.10: chemical structure of 1,4 *cis* polyisoprene.

Cyclic peroxides and carbonyl species form along with VOCs, while C=C double bonds decrease. The most likely route of PI breakdown is β -scission of the alkoxy radical in the methylenic position [88,150,176,180–182]. The β -cleavage of the macromolecular alkoxy radical leads to the formation of saturated end-chain ketones.

In photooxidation, the hydroxyl-stretching region result in a broad band with a shoulder at 3225 cm^{-1} appearing at the initial stages of exposure. An intense band at 3440 cm^{-1} is also observed. In the carbonyl-stretching region, the band at 1722 cm^{-1} shifts to 1717 cm^{-1} while that at 1693 cm^{-1} remains stable. C=C bonds at 1665 and 1645 cm^{-1} decrease, while a shoulder at 1775 cm^{-1} appears. In the deformation region, the band at 874 cm^{-1} , assigned to the epoxy groups appears, while a band at 835 cm^{-1} decreases [179,181]. Overall, in oxidative conditions the mechanisms of degradation are:

- hydrogen abstraction from the allylic position in 1,4-*cis* unit;
- tertiary macro-radical association to the newly formed tertiary hydroperoxide;
- ketonic groups (α,β saturated and unsaturated) forming followed by observing bands at 1637-1726 cm^{-1} with FTIR spectroscopy;
- β -scissions and lowering of average molecular weight followed with SEC;
- addition reactions predominance in long-term aging;
- alcohols, acids, esters and epoxides forming.

In museum collections, PI-based materials have been reported either as contemporary artworks, design objects or paints (Figure 1.11) [118,163,173,174,178,183]. Vibrational spectroscopies have been used to identify degradation products in historical and re-made design objects, such as the icon chaise longue ‘Mies’ at the Vitra Design Museum, Germany

[184]. Connors S.A. *et al.* [185] reported studies of degradation of historical vulcanized rubber museum artifacts, comparing natural and artificially aged samples. Similarly, Lazzari *et al.* [186] characterized the degradation products of PI-based sculptures by Andrés Pinal through comparison of naturally degraded artworks and accelerated photoaging of model samples. Šuštar [187] inserted PI in the predictive statistical model on the identification of historical polymers. Over 500 NIR spectra from portable instrumentation were used to validate the model on museum objects. Kehelet *et al.* [163] addressed the depth of degradation of natural rubber objects by Licio Isolani with unilateral Profile NMR Mouse[®]. Data was supported with benchtop ¹H and ¹³C solid-state NMR spectra that allowed identifying esters and hydroperoxides, as expected degradation products.



Figure 1.11: PI-based contemporary artworks. On the left, *Contingent* 1969 by Eva Hesse, made of fiberglass and latex. Source from 'The Estate of Eva Hesse' image courtesy© from Hauser & Wirt from 'The Estate of Eva Hesse'. On the right, *Capitello* 1971 by Studio65, made of polyurethane foam and latex rubber coating. Image© Studio 65 photo: Jürgen Hans, with permission from the Vitra Design Museum, Germany.

1.5 OBJECT-BASED VALIDATION

Several museums and galleries were involved in the NanoRestArt partners to ensure the validation of analytical methods, cleaning procedures, and formulation of new products. Moreover, *in situ* monitoring and protocols were adapted in collaboration with several conservation experts [26,27,188–193].

In the context of heritage science, the importance of validation studies lies in the awareness that long-term behaviors of (model) materials not necessarily correspond to long-term behaviors of objects. Chemical reactions taking place at *nano* and *micro* scale combined with mechanical damages and variable environmental conditions affect the object stability in complex interactions. Sculptures, paint layers, prints and design objects are composite materials; hence, their stability is *dynamic*. The variables affecting the rate of degradation must be studied separately (e.g. light, moisture). To achieve a fulfilling knowledge of the object-system interaction, understanding of the material and of the object are both essential.

Meaningful sampling strategies focus on various parameters, like the analytical method (e.g. molecular elemental information, destructive/non-destructive), the statistical representativeness of the area sampled, the availability of condition reports with the history of previous treatments, the existence of mock-ups and spectral databases on similar objects. Not surprisingly, several platforms are currently attempting to integrate imaging, chemical and conservation data from heritage objects/built heritage [194–196]. However, complex events, such as cross-infection of collections, and limited selectivity and sensitivity of portable instruments can make the transfer of knowledge gained with simulations somewhat unpredictable [197,198].

Few museum research programs work in collaboration with artists to create databases of contemporary art materials. For example, the Whitney Museum in New York, US documents artists' choices through interviews [199]. Combining databases and archival research with instrumental analysis is the first step toward an improved knowledge of the materials/objects [200,201]. Further, the most comprehensive collection of reference samples for plastic in collections is the **SamCo** kit, achievement of the PopArt European funded project [202]. SamCo derives from the analysis of commercially available ResinKit™, Woonsocket, US [203]. The database comprises 100 samples of unaged and naturally aged plastics, respectively standard and objects. Each polymeric sample is present in its pure form and in combination with dyestuff, pigments and anti-oxidants. Among polymeric standards/naturally aged polymers there are: PMMA, ABS, CA, CN, PA, PC, PE, PP, PS, PUR ester, PUR ether, PVC, and silicone rubber³.

In this research, various attempts to validate the analytical method with the strip sampler, solvent and SERS-active substrate were pursued on contemporary artworks from the Contemporary Art Centre of Galicia (CGAC). In addition, woodblock prints, toys, historical leather, natural dyes collections, and rock art paintings were analyzed with the purpose to detect small coloring molecules. The most pertinent and successful results will be presented in Chapter 3, whereas fewer are in the attached information.

³ PMMA (polymethyl methyl acrylate); CA (cellulose acetate); CN (cellulose nitrate); PA (polyamide); PE (polyethylene); PP (polypropylene); PC (polycarbonate); PS (polystyrene); PUR ester or ether (polyurethane); PVC (polyvinylchloride).

1.5.1 Collaborating with the *Centro Galego de Arte Contemporánea* (CGAC)

From 2005 up to now, several opportunities for collaboration between the CGAC Department of Conservation and Lazzari's research group arose [186,204–207]. Since the gallery opening in 1993, artworks in display and storage presented moderate/severe signs of weathering, such as yellowing, cracking and loss of gloss. During explorative campaigns, different polymers were identified analyzing loose fragments from various objects, initially mostly with FTIR spectroscopy. Polymers identified were PUR, PI, vinyl ester EP, aliphatic EP, PVAc, and alkyd resins, respectively in the artworks by Loris Cecchini, Andrés Pinal, Francisco Leiro, Karin Sanders, Dario Villalba and Manuel Eiris [204,206–208]. In parallel, aging studies on similar model materials were being conducted at the research facilities of Center for Research on Biological Chemistry and Molecular Materials (CiQUS).

Data obtained allowed a thorough identification of polymers and plasticizers, while degradation mechanisms were proposed. As part of the validation protocol, the experimental results were compared to naturally aged artworks to establish the reliability of the analytical procedures. Chromatography and thermal analysis were performed to extend the spectroscopic data obtained with UV-Vis, FTIR, and Raman spectroscopies [186].

Rodriguez-Mella *et al.* [207] identified epoxy vinyl ester resins used as a base in a series of sculptures by Francisco Leiro. Artificial tests of thermal and photooxidation allowed the authors to propose *a posteriori* a mechanism of inter-crossing oxidation coherent with the spectral information collected on naturally aged artworks. During the current project, a collaboration with the visual artist Manuel Eiris was held. An interview, a poster and a short publication with the results of the analytical work conducted on the use of materials is in annex (Annex 1.4). In addition, PI loose fragments from *Traxe de Home* by Andrés Pinal were further studied with SERS platforms to validate the PDMS analytical method.

1.6 FOCUS SHIFT ON COLORING MEDIA

The optimization of the SERS platforms reached a satisfactory level of progress toward the end of the third year of the PhD project [209,210]. The validation on model materials and objects from collections extended the understanding of the potentials of the analytical method. The applicability of the PDMS strip sampler method on small molecules was tested beyond the detection of degradation products. A multipurpose approach was explored by the end of the third year throughout the fourth year of PhD. In heritage science, cross-disciplinary research questions often arise (*e.g.* technical art history, conservation science); however, not always the analytical tools available are sufficiently versatile: ***why not using the same diagnostic tool to resolve different issues?***

In 2019, different objects were investigated to establish the suitability of the sampling method to detect coloring media. LEGO[®] building bricks were received from a private collector based in Ireland. A previous attempt to test handheld instrumentation for *in situ* measurements of ABS objects was held at the Tyndell Institute in Cork, Ireland. The unsatisfactory resolution of the instrumental settings was overcome by new SERS-based strategies combined to benchtop tests held as a pilot study [211]. Further, a collaboration with the managers of the Dolmen of Antelas (Portugal) arose. An inexpensive box, named *rapid toolkit*, containing the PMDS strip samplers and a labeling system was sent to the site. Fellow researchers from the University of Vigo, Spain, were in charge of the dolmen survey and sampling on the wall paintings. Further, natural dyes reference materials and historical leather were made available through a collaboration with the Higher Institute for Conservation and Restoration in Rome, Italy. Further, Japanese woodblock prints were received from a paper conservator based in Paris, France. The technology of production and the materials of the prints were thoroughly characterized with SERS platforms and additional imaging methods.

Selected solvents in agreement with the polarity and solubility of the expected analytes were used in the various validation tests. In this perspective, using the SERS platforms to detect dyes, pigments and further conservation products, upgraded the purpose of the thesis. New contributions to analytical strategies for cultural heritage materials will be discussed during the presentation of the validation tests⁴.

The following two sections will introduce the pilot study conducted on contemporary and historical LEGO[®] bricks, and the SERS validation tests on dyes and lakes in the Japanese woodblock prints. The option of combining minimally-invasive SERS with handheld instrumentation for *in situ* analysis in museum environments lead to conceive general recommendations for the detection of colorants in complex polymeric matrices. Further, the study on Japanese prints allowed extending the spectral evidence available on pigments and dyes used during the transition from the Edo⁵ to the Meiji era in Japan.

⁴Rock art paints from the dolmen of Antelas will be summarized in a short note. The limited amount of sample available, with no option to repeat the sampling, and the need to share the method with non-experts researchers lead to achieve only preliminary results.

⁵The Edo or Tokugawa era is from 1603 to 1867; the Meiji era is from 1868 to 1912.

1.6.1 LEGO[®] toys: pilot study for *in situ*, non-destructive and non-invasive analyses⁶

In heritage settings handheld instrumentation is often preferred to preserve the integrity of the objects under examination for research or treatment purposes [188,212–218]. As well-known, the characterization of museum objects requires the use of sensitive analytical techniques with minimal invasiveness and/or *in situ* measurement capabilities [12,18,36]. Additional requirements should be low cost and ease of use to facilitate routine surveys prior to conservation treatments. The potential of portable Raman instrumentation for the investigation of pigment content in polymers was highlighted by Carron and Cox [219]. The impact of in-depth Raman investigations on ABS-based objects can be extrapolated to a broader variety of historical and artistic plastics.

Analytical evidence from benchtop instrumentation is often considered more reliable than that from portable instruments to address condition state of the objects, conservation treatments, ongoing weathering mechanisms, and optimal preservation strategies [220,221]. Scientists face the challenge to address research questions on materials, while being held back by ethical limitations to sampling and instrumental availability to analyze those materials [3,7]. Further, opposite to classic art materials (e.g. stone, metals and pigments), the lack of experimental research on relatively new materials used in art, as synthetic polymers, justified the need of a pilot study to establish the foundations for the interpretation of handheld instrumental results.

Plastic artifacts from collections have been extensively investigated with FTIR spectroscopy, less so with Raman and its portable versions [21,189,222,223]. In the last decades, Raman and SERS have been extensively used in museum contexts, especially to address questions on pigments and dyes in paintings and paper media [221,224–227]; however, the pilot study conducted is a unique example of identification of synthetic organic pigments (SOPs) and complex inorganic colored pigments (CICPs) in polymeric matrices. LEGO[®] bricks seemed an ideal choice to pursue a systematic study on colored ABS for a dual reason: first, having easy access to contemporary and historical pieces with a variety of colors at low costs. Second, LEGO[®] bricks have had such a huge cultural impact on society, that even renowned contemporary artists, as Nathan Sawaya, Ai Weiwei and Olafur Eliasson, use them as an art medium (Figure 1.12) [228,229].

It is anticipated that for the historical bricks from the 1970's sampling was not considered essential for the aim of the study. Such choice resembles a real museum decision-making scenario: the knowledge gained through the analyses of contemporary bricks was considered extendable to other historical colored ABS objects. Therefore, the integrity of the bricks was completely preserved by analyzing them only with non-destructive and non-invasive handheld and benchtop Raman instruments, as it should be preferred by analysts in museum contexts.

⁶ Introduction and results from this section of the thesis have already been published as: Reggio, D.^{ab}, Saviello, D.^c, Lazzari, M.^{ab} & Iacopino, D.^c. Characterization of contemporary and historical acrylonitrile butadiene styrene (ABS)-based objects: Pilot study for handheld Raman analysis in collections. *Spectrochim Acta A Mol Biomol Spectrosc* **242**, 118733 (2020) [211].

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Contemporary LEGO® objects were comparatively examined with three instrumental settings: non-invasive handheld Raman spectrometer for initial screening, non-invasive benchtop Raman spectrometer to obtain finer spectral features, and finally minimally-invasive SERS as method alternative to handheld Raman.



Figure 1.12: LEGO® building bricks used as art media by contemporary artists. On the left, sculpture by Nathan Sawaya from the global exhibition ‘The art of brick’. Image courtesy© of Nathan Sawaya. On the right, the *collectivity project 2005* by Olafur Eliasson. With permission of the copyright holders Nathan Sawaya and Olafur Eliasson.

1.6.1.1 Outline of LEGO® building brick materials and technology

In 1908, wooden building toys were patented in the US by Charles Frost (patent n° US879455) [230], followed in 1916 by improvements to the interlocking system patented by Stanley Finch (patent n° US1191884) (Figure 1.13) [231]. In 1932, Ole Christiansen founded the LEGO® factory producing wooden toys in Billund, Denmark [232]. In 1939, the British Hilary Page patented self-locking building blocks toys made of CA and fabricated through injection molding machines [233]. Unfortunately for him, the patent and its several succeeding improvements were only recognized by the regulations of United Kingdom. Thirsty for innovation, Ole Christiansen constantly wanted to upgrade the technology of his factory and happened to visit a fair of injection molding machineries where a British vendor showed him Page’s CA blocks for the first time in 1946 [232]. By 1953, the whole production in Billund had switched from wood to CA, while sales had enormously improved through new LEGO® assemblages, like towers, castles and many new challenging learning creations for kids.

The real turning point for the success of LEGO® bricks is represented by Gotfried Kirk Christiansen’s patent (US/Denmark, 1958) on the invention of tubular studs to connect the parallelepipeds with following improvements [234]. This invention added a *clutching* power to the bricks that allowed versatility of the constructions, as well as mechanical stability and impact resistance [235–237]. While the patent was assigned to the Swiss Interlego factory in the same year, an international airport was built in Billund for exports to the US. Upon the suggestion of the Swiss engineer Hans Schiess, LEGO® began using ABS to produce the bricks in 1962. This newly synthesized copolymer was relatively inexpensive, easy to mold

accurately in small measures, much more colorfast and durable than its predecessor CA, and it showed better friction behavior [238].

LEGO® toys are iconic cult objects part of numerous private and museum collections and having a dedicated museum in Denmark, the Lego House. The color palette of LEGOs also considerably widened from the original seven colors (white, gray, black, red, blue, yellow and green) to the fifty-seven colors used in contemporary formulations. Unsupported data suggest that MACROLEX™ thermoplastic colorants are currently the constituents of twenty-five colors currently being produced by LEGO® [236]. Elsewhere, Laxess Chemicals™ dyes and INEO Styrolution ABS pellets are mentioned [239–241]. However, to date no systematic scientific literature is available on the chemical composition of contemporary and historical LEGO® objects.

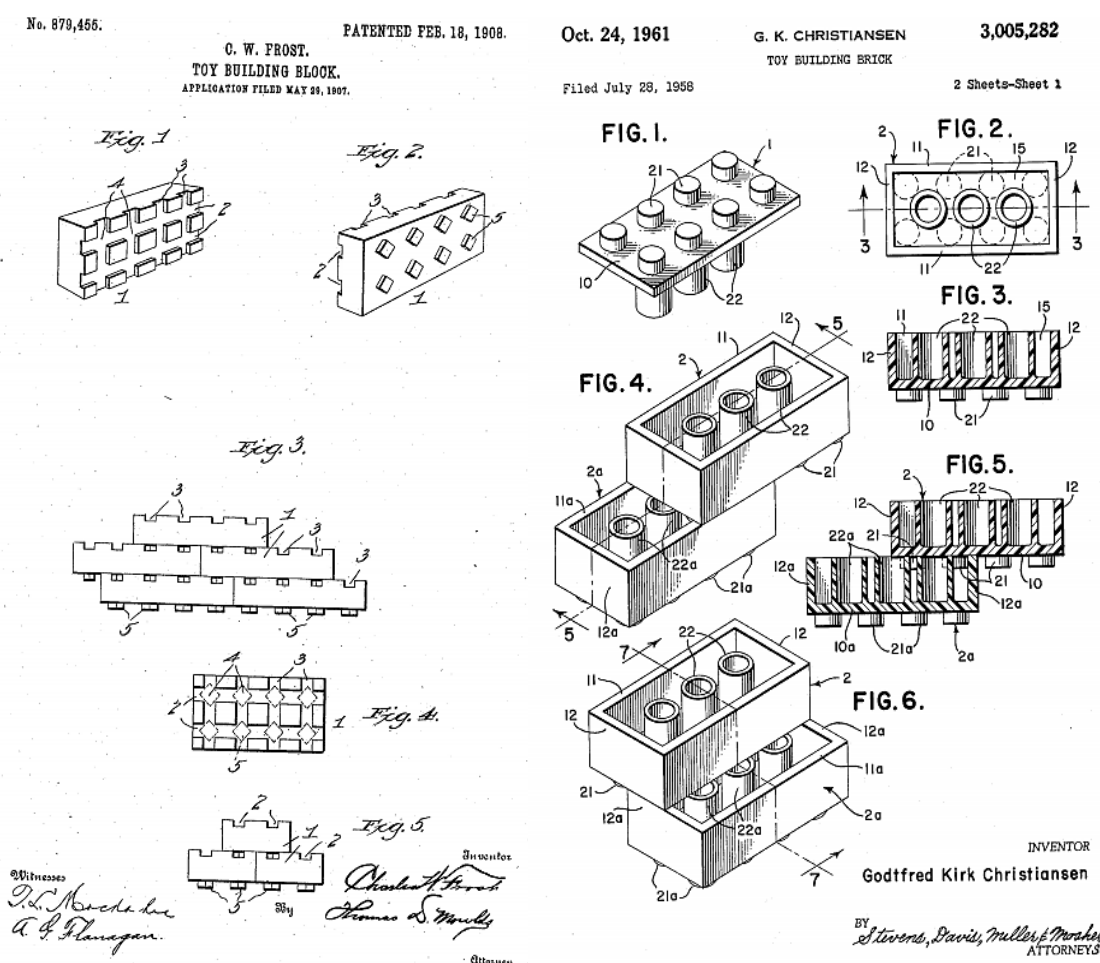


Figure 1.13: Drawings from the patents filed in the United States Patents Office. On the left the first interlocking toy building block patented in 1908 by Charles Frost. On the right, the clutching interlocking toy block made of ABS. LEGO® production was global by 1961 with Kirk Christiansen patent. Images from the free repository of Google Patents (n° US879455 and 3005282).

1.6.1.2 Coloring media in plastics

A number of coloring media were identified through Raman spectroscopy in the collections of historical and contemporary LEGO® bricks. In Chapter 3, spectral features will

be discussed in detail, however in this section chemical background information is provided to anticipate a thorough understanding of the materials behavior during SERS sampling.

SOPs and CICPs are classified by the Color Index International (CI) with Color Index Generic Name (*e.g.* Pigment Yellow 10 - PY10) and Color Index Constitution Name (CI 12710). Lightfastness, structure and behavior when combined with polymeric components of the matrix are highly valued in the selection of the coloring media, as well as thermal and chemical resistance during processing [240]. It is anticipated that colors unequivocally identified analyzing the bricks with handheld, benchtop and SERS spectroscopy were the following:

- carbon black (PBk6 CI 77266, CB);
- titanium dioxide (PW6, CI 77891 - (TiO_2));
- Pigment Brown 29 (PBr29, CI 77,500 - (Cr, Fe) $_2\text{O}_3$);
- Pigment Blue 15 (copper phthalocyanine (CuPc), PB15:0, PB15:3 CI 74160);
- Pigment Green 7 and 36 (CuPc, PG7, CI 74260 – PG36, CI 74265).

CB (PBk6 CI 77266) is a synthetic carbon used for many purposes including coloring elastomers (*e.g.* tires), additive to enhance the electrical conductivity and UV screen [242]. CB provides solid color according to its concentration. It is highly compatible with other plastic components. CB is also defined as a paracrystalline carbon formed by thermal and thermoxidative decomposition of petroleum residues, wood, charcoal, and coke. In particular, primary particles of CB (<100 nm) are held together to form aggregates (<500 nm) that with weak forces form agglomerates (<1 μm) (Figure 1.15). Its narrow particle size distribution makes CB suitable as filler. Increasing particle size affects the tint darkness and hue. CB has been widely used to dye paints, inks, and varnishes [242–244].

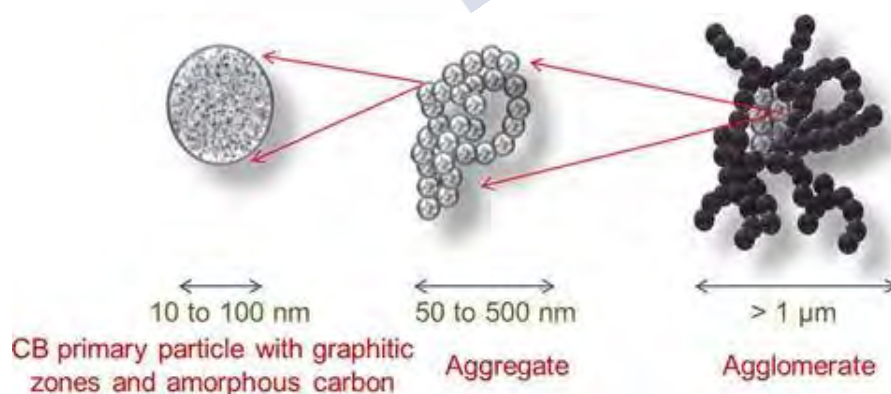


Figure 1.14: representation of carbon black (CB) particles graphitic, aggregate and agglomerate types. Adapted with permission from ref. [243]. Copyright Taylor & Francis.

TiO_2 is a white pigment extracted from several natural occurring minerals, among which the most important are ilmenite (hexagonal), anatase and rutile (tetragonal) (examples in Figure 1.15) [242,244]. TiO_2 is classified as Pigment White 6 (PW6, CI 77891). Crystalline

structures are stable at different temperatures and composition varies according to the content of iron oxide in the ore (Figure 1.15). It is considered the whitest among white pigments provided its excellent opacity (high refractive index), ease of dispersion in the matrix, thermal and chemical stability and non-toxicity. TiO_2 is produced by acid dissolution of the ores, followed by precipitation of the iron oxides (through the sulfate 46% and chloride 54% routes) and hydrolization. Micro-crystalline particles are subsequently grinded, floated and dried before entering the market. Similarly to CB, TiO_2 has the ability to improve light performance of materials as UV screen. It is a highly durable material used to dye plastics, prints, coatings, wood, built materials and glass [94].

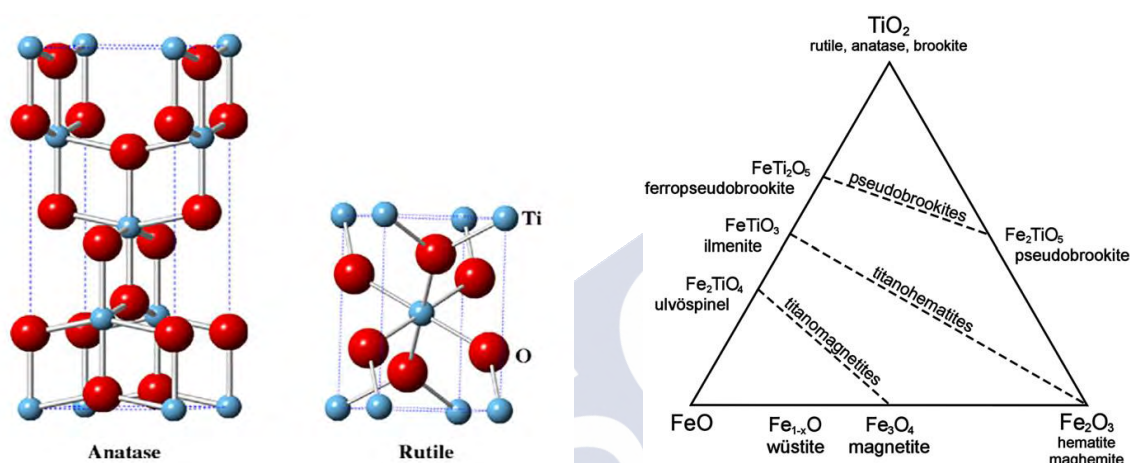


Figure 1.15: structure of anatase and rutile on the left; triangular plot of FeO - Fe_2O_3 - TiO_2 showing high temperature solid solution series. Adapted with permission from ref. [245,246]. Copyright Elsevier.

Pigment Brown 29 (PBr29, CI 77500) is a chromium and iron oxide ($(\text{Cr}, \text{Fe})_2\text{O}_3$) that can be classified as hematite, among industrial CICPs. It is compatible with most polymers and has excellent lightfastness, high opacity and heat resistance up to 300°C [92]. The color range of PBr29 spans from black to brown and is specifically designed for IR reflectance. Opposite to inorganic mineral pigments, PBr29 reflects NIR radiation conferring a different hue to the color perceived [90]. In building materials, windows structures in PVC, PBr29 reduces the deformations due to heat build-up [247]. It is considered a mixed phase pigment based on chromium-oxide iron oxide (Figure 1.16) [248].

Phthalocyanines (PCs) are a large group of synthetic blue and green macrocyclic ligand complexes heavily exploited as pigments, but not only, since 1930s' (Figure 1.17) [249]. The central void of the structure allows chelating a metal/hydrogen atom. Copper constitutes the main metal ion used to synthesize such macrocyclic complexes (CuPc) and a variety of peripheral substituents determine their absorbance, hence the color and the intensity of the pigment. Chlorine and bromine are commonly used substituents with Cu, although over 5000 PCs polymorphs, including those with hydrogen, zinc and iron as central atoms, have been identified. It is anticipated that the CuPc identified through Raman spectroscopy in the LEGO® bricks were PB15:0, PB15:3, PG7, and PG36. PB15:0 and PB15:3 [211]. They are unstabilized non-halogenated α -form and β -form of CuPc [250]. On the contrary, PG7 and

PG36 are chlorinated and halogenated forms, respectively [92]. Overall CuPc have high heat and solvent resistance, while exhibiting high lightfastness [91,92].

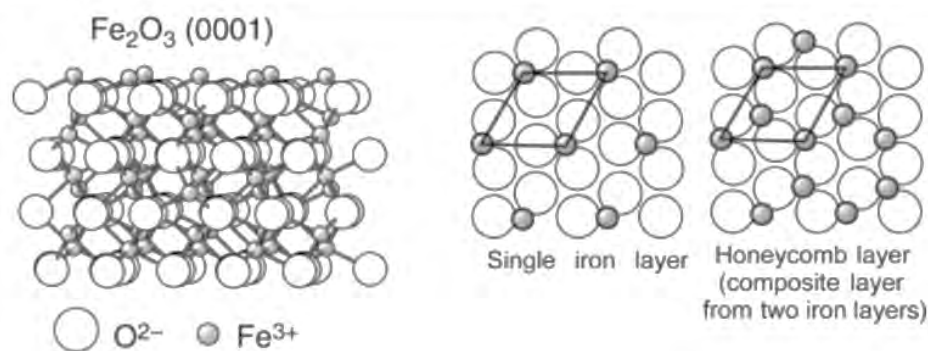


Figure 1.16: hematite atomic structure, left to right side view of hematite terminated by a single iron layer and top $\alpha\text{-Fe}_3\text{O}_4$ (0001), views for the surface terminated by a single and a honeycomb layer. The iron is substituted with Cr in some lattice layers of Pigment Brown 29. Adapted with permission from ref. [249] Copyright Royal Society of Chemistry.

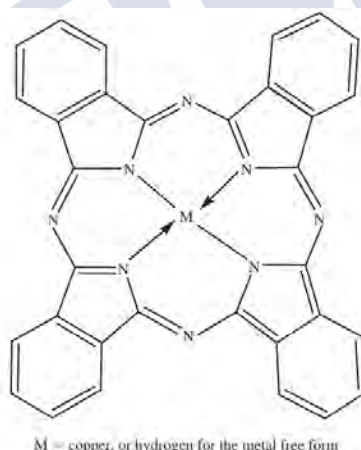


Figure 1.17: structure of macrocyclic ligand complexes (phthalocynine). Adapted with permission from ref. [251] Copyright Springer.

1.6.2 Japanese woodblock prints: Ukiyo-e technological issues

Materials and technologies of production of Japanese woodblock prints were researched as a complementary activity within the NanoRestArt project. Mr. Antonio Mirabile, a paper conservator based in Paris, shared a number of panels from a private collection. The aim of the research was to investigate the coloring media of the prints testing merits and limitations of the PDMS strip sampler method and newly developed tools for the enhanced protection of artworks. Alternative minimally-invasive analytical tools were validated and optimized with the idea in mind to share them with museum research managers in the future.

1.6.2.1 Technology and materials for the production of the prints

The success of the *Ukiyo-e* woodblock prints worldwide was due to their increasing popularization among upper class westerners in the late 19th century. Nowadays virtually, everyone recognizes iconic prints such as *The Great Wave* by Hokusai (1830) (Figure 1.18). Two classifications help distinguishing the major styles of the Japanese woodblock prints: Edo (1603-1868) and Meiji (1868-1912), named after the eras of different rulers. The former prints depict any sort of images, including erotic scenes and animals, using **light hues**. The latter focus on private scenes, landscape and war scenes, using **symbolic strong tints**, inadmissible earlier [252].



Figure 1.18: woodblock print *The Great Wave (Kanagawa oki nami ura)* from the series *Thirty-six Views of Mount Fuji (Fugaku sanjūrokkei)* by Katsushika Hokusai 1830-32. Image from the free repository of Google Arts and Culture [253].

Pure cellulose was pressed onto woodblocks previously prepared with a rice starch heated before application to favor gelatinization between coloring media and paper. Furthermore, mica powder was added to provide a metallic glitter to some hues (e.g. grey/silver), concurrently functioning as a thickener of the gel. When the print dried, the excess of powder was brushed off and the fine grains enhanced the light reflection. Further, the presence of uneven patterns obtained rubbing the surface preferentially in white and black areas of high-status characters' cloths was ascribed to the *Kirazuri* technique. Carved patterns on the surface provided interesting light effects to be ascribed to the *Shomenzuri* technique (Figure 1.19) [254].

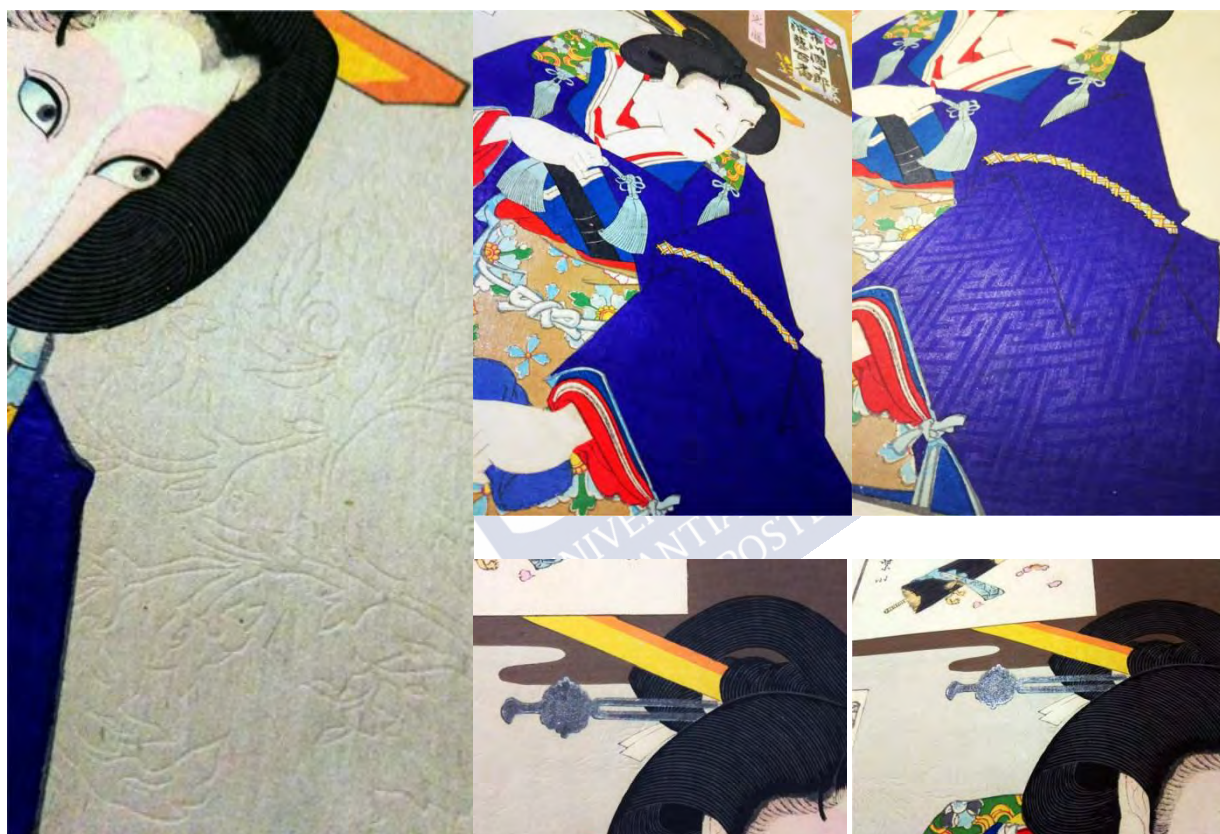


Figure 1.19: early Meiji woodblock print from the 'The Series One Hundred Roles of Ichikawa Danjūrō' by Toyohara Kunichika (1891). On the left, uneven pattern carved on the white area (*Kirazuri*). Upper row in the center and right, uneven patterns carved on the dress hit from different light angles with opaque or shiny effects (*Shomenzuri*). Lower row in the center and right, used of mica for glittery effect of silver color. The license from the copyright holders for the use of images could not be obtained [254].

1.6.2.2 Coloring media in Japanese woodblock prints

The range of molecular weights of the colorants identified varied between 200 and 800 Da, which made these small molecules ideal for the validation of the one-step SERS method applied for the study of LEGO[®] bricks. In-depth SERS spectral assignments from minimal-invasive removal of small molecules through PDMS samplers with various solvents will be presented in Chapter 3. It is anticipated that SERS detection was combined in this instance with non-invasive macro X-Ray Fluorescence (MA-XRF) spectrometry that completed the identification with elemental mapping for a greater understanding of the prints.

Colorants found in the six panels will be divided in macro-groups of reds and purples, and smaller groups of blue, green, yellow, pink, brown and black. Within each group, usually more than one hue was detected, as well as mixtures of water-soluble organic dyes, metal salt lakes, and inorganic mineral pigments.

The macro-groups of reds and purples generated the most relevant research inputs for the current project. Without a doubt, the end of 19th century was a period of great experimentation in formulating dyes and synthetic organic pigments. Special needs were arising in the textile sector and chemists were required to be up-to-date with the manufacturing processes, finding new solutions to old problems of solubility, tinctorial strength and coupling of coloring materials [255]. Similarly, the printing industry had begun mass-producing all sorts of cheap/disposable paper-based materials. In this context, the traditional woodblock printing methods were gradually substituting natural dyes and inorganic mineral pigments with newly formulated azo and aniline dyes. In this respect, the Meiji period was a time of perfecting technological experimentations, such as the *Kirazuri* and *Shomenzuri*, and mixing well-established coloring media from the Edo period with new materials [256].



1.7 AIMS AND OBJECTIVES OF THE THESIS

The overall aim of the present research is to optimize a novel SERS-based analytical method for the detection of LMW degradation products/small molecules collected from heritage objects. The first objective is to control and optimize the replication of *nano* and *micro* structures with different fluorinated UV-curing polymers through nanoimprint soft lithography. The second objective is to test the PDMS strip samplers enabling the removal of molecular fragments by physisorption and in combination with different solvents, tuning polarity and solubility according to the affinity with the analyte under study. The third objective is to apply the method on polymer model materials to assess its potential for the detection of early markers of degradation in contemporary plastic artworks. The fourth objective is to validate the analytical method with museum objects. The fifth objective is to optimize SERS microextractions on historical reference natural dyes and lakes. The sixth objective is to address synthetic colorants and technology of production of Japanese woodblock prints in the phase of transition to the Meiji era. The focus shift toward the identification of coloring media will help to establish sound evidence for the multipurpose potentials of the SERS-based analytical method proposed. Further along the project, the silicone samplers were made available to non-specialized personnel to validate its ease of use on site. Comparison of portable, benchtop and SERS microextracts is a tangential methodological approach to foster the *in situ* application of the method proposed.



2. EXPERIMENTAL METHODOLOGY AND MATERIALS

Most of the experiments presented in this work were carried out in the facilities of the CiQUS at the USC. Instruments used for sample preparation and characterization include nanoimprint soft lithography UV-lamps, ATR-FTIR spectroscopy, spectrophotometry, DSC, SEC, high speed exposure unit for photo-oxidation, ovens for thermal oxidation and optical microscopes.

Further specialized equipment was provided by the USC Network of Infrastructures Supporting Research and Technological Development and comprised instruments such as Raman benchtop spectrometer, SEM-EDS, MA-XRF, Py-GC/MS and MALDI-time-of-flight mass spectrometry (MALDI-TOF MS). PVD equipment to coat the SERS substrates was provided by the Department of Optics at USC.

Different materials served specific purposes, namely fabrication of devices, detection of small molecules and validation of the analytical method on actual objects from collections. Collaborations and subsequent exchange of samples with the NanoRestArt partners, along with parallel exchanges with researchers during other training opportunities allowed analyzing a wide variety of materials. The following lists summarize materials purchased or obtained to accomplish the different thesis objectives.

- **Fabrication of SERS devices and PDMS strip samplers:**

- i. UV-curing polymers for nanoimprinting FLUOROLINK[®] MD700 PFPE-urethane methacrylate by Solvay[™]; radical photoinitiators by Darocur[™] and Ciba[™];
- ii. Master molds of micro and nanostructures by Renishaw[®] Diagnostics Limited and tape FleFimo[™] by SOKEN[®] Mold Solution;
- iii. PDMS replica molds with thermally cured SYLGARD[™] 184 by Dow Corning;
- iv. PDMS strip samplers with thermally cured SYLGARD[™]184 by Dow Corning casted on webnet molds or polypropylene circular disposable containers.

- **Model polymers and other materials:**

- i. Liquid linseed oil and PVAc drying films in pristine, naturally, thermally and photo-aged conditions (purified linseed oil by Titan[™] and PVAc emulsion by Rayt[™]);
- ii. Solid ABS and PI films in pristine, naturally, thermally and photo-aged conditions (extruded ABS pellets by MAGNUM[™] 3404 Dow Chemicals and 1,4 *cis* PI, double sided, smooth and coarse, by SEMPERIT[™]);

- iii. Solid ABS coated films in pristine and photoaged conditions, water-borne WB6 (polyurethane) and WB9 (acrylic) coatings;
- iv. Solid ABS coated films in pristine and photoaged conditions, water-borne WSP grade 1 and grade 2 oxygen barrier coatings developed at CEA.

- **Object-based materials:**

- i. Contemporary art: PI fragments from *Traxe de Home* by Andrés Pinal, Manuel Eiris's twins gold paints.
- ii. Design objects: historical and contemporary collection LEGO[®] bricks (ABS, PMMA).
- iii. Rock art paints from the dolmen of Antelas in Portugal.
- iv. Reference materials of cochineal, kermes and carmine with historical leather from liturgical footwear
- v. *Ukiyo-e* Japanese woodblock prints from the Meiji period.

2.1. SERS SUBSTRATES FABRICATION

Among other classifications [12,53,60–62], SERS substrates can be broadly divided as follows:

- aggregated metallic colloidal nanoparticles in solution;
- assembled nanoparticles on surfaces;
- **structured surfaces (2D planar substrates, ordered arrays, platforms, etc.);**
- metallic electrodes (outdated).

The ease of functionality of structured surfaces is undeniable, especially when dealing with very limited amounts of analytes at unknown concentrations (e.g. LMW fragments from surface sampling). However in the literature, colloidal nanoparticles are reported more frequently than continuous planar arrays [257–261]. Although for the sake of collecting evidence, a comparative study of different SERS-active substrates with standard analytes would be necessary, it was ruled out being out of the scope of this thesis.

Prior to the beginning of this research, Gómez & Lazzari published several papers on the fabrication of planar SERS-active substrates [42,262,263]. Replicas of squared and hexagonal arrays of micro and nanostructures were consistently fabricated on glass supports and coated with different plasmonic metals, including copper, silver and aluminum. Different PFPE polymers were functionalized to optimize the performance of replicas at the nanoscale to achieve high resolution and reproducible structures. Meanwhile, ORMOCER[™] polymers, initially used for soft lithography, ended up out of production and FLUOROLINK[®] MD700 by Solvay[™] became the fluorinated polymer of election to pursue this research. Additionally, since the present study began, replicas of micro and nanostructures have been fabricated either as self-supporting substrates, or on polyethylene (PE) supporting sheets, and aluminum has been the only metal coating utilized (150±10 nm thick layer).

FLUOROLINK[®] MD700 is a fluoropolyether derivative (difunctional methacrylic PFPE oligomer) designed to pretreat or coat surfaces of glass, ceramics and metals for the application of paints. It is activated with a variety of photoinitiators, including 2-Hydroxy-2-methyl-1-phenyl-propan-1-one by Darocur[®] BASF. Conversion rates, weight % of a variety of photoinitiators in different experimental conditions are discussed in Chapter 3.

2.1.1 Ultraviolet Nanoimprint Soft Lithography (UV-NIL) and Physical Vapor Deposition (PVD)

Nanoimprinting is a highly regarded low-cost technology deriving from microelectronic applications that enables to replicate nanopatterns; nonetheless optics, cellular biology and energy fields, among others, have been exploiting its potentials in the last decades [257–260]. Overall, it comprises thermal and photo imprinting processes for the fabrication of high resolution, reproducible and continuous structures.

In the current thesis, the fabrication procedure included three steps: 1) PMDS mold fabrication; 2) master mold replica through PDMS mold (stamp); 3) UV-cured replica of micro and nanopatters (resist). A preliminary fabrication step consisted of producing molds to support the PMDS stamp. They were 3D-printed with a LPKF ProtoMat PCBs model S64 with different materials, as anodized aluminum, fiber glass, and polylactic acid with 5x5 mm and 0.5 mm thick cavities. During phases 1 and 2, SYLGARD[™] 184 prepolymer was mixed with a curing agent (10:1) and poured onto the master mold. Air entrapment was prevented by pretreating the viscous liquid for 10 min with vacuum at room temperature, followed by 2 h isothermal treatment at 80°C with the oven model VacuTherm by Thermo Fisher. A detailed discussion about the relative components of SYLGARD[™] 184 is provided in Chapter 3. Steps 1) and 2) are schematically represented in Figure 2.1.

Figure 2.2 summarizes the step of replication of the substrates through soft lithography. When an elastomeric mold is involved, we speak of soft lithography, opposite to common photo-lithography that relies on rigid masks (photo-resists) [257]. In both cases, multiple copies of the patterned structures can be replicated. For the present study, UV-curable fluorinated polymers (resist) are pressed in a sandwich-like structure between a PE support (*quasi* non-UV absorbent) and the stamp prior to irradiation. Drops of approximately 10 μ L of viscous PFPE derivative fill the negative cavities of the stamp. The UV-lamp system used was from Midas System MDA model 400LJ with beam wavelength filtered for i-line=365 nm of 20 mW cm⁻² intensity and variable exposure times (1 s to 10 min) in atmospheres of N₂ or air.

The contact process between stamp and resist is highly relevant to ensure the replication of the patterns; similarly, the release phase (demolding) requires crucial operator's skills. An air layer has to form between stamp and resist. Surface energy of the stamp has to be low enough to allow the prompt release of the resist while ensuring no fractures of the newly thin polymerized layer. For batch production of substrates, the residues of unpolymerized PFPE derivative in the stamp were carefully removed with mildly polar solvents, namely 2-isopropanol and ethanol, to avoid swelling and deformation of PDMS in combination with occasional ultrasonic baths for 10-30 min.

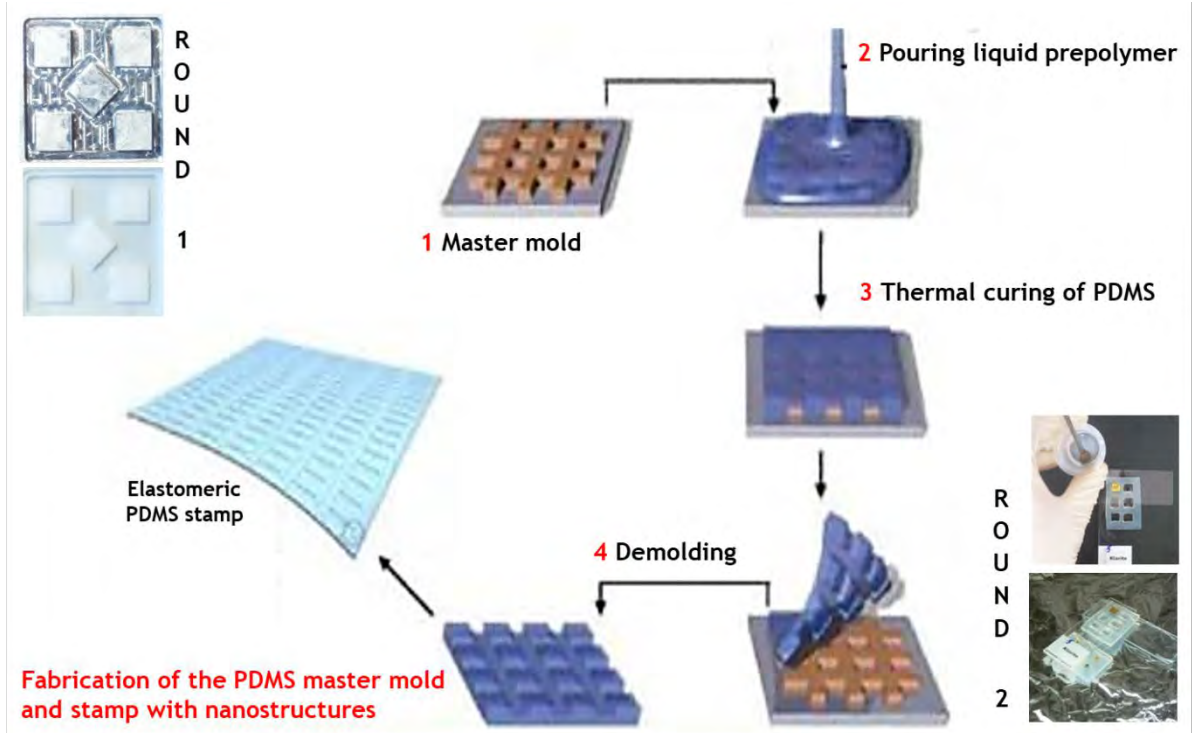


Figure 2.1: Representation of the procedure of fabrication of elastomeric mold and replica of structured master mold through thermal curing of PDMS. Photo inset Round 1 shows 3D printed aluminum and PLA molds; photo inset Round 2 shows the replication of KLARITE® microstructures inside PDMS cavities. The procedure for both replicas of PDMS mold and stamp is the same and involves liquid prepolymer mixed with curing agent 10:1, thermal curing with vacuum pretreatment and demolding. *Adapted with permission from Penn State Materials Research Institute, NanoFabLab, Dr. Eichfeld's image courtesy.*

PVD was used to coat the structured surfaces. Specifically, a BALZERS BALTEC™ BAE 250 electron beam evaporator was used to produce the metal thin films. The system comprises of a TT-3 electron gun and a turbo pumped vacuum chamber (0.0001 Pa); the acceleration voltage range is 4-7 kV and the maximum current 750 mA. High vacuum was obtained with a Pfeiffer Balzers Tpg-300 vacuum gauge controller running for 6 h before plasma formed. In general, e-beam evaporation can be performed with metals (Au, Cu, Ag, Al etc.) and insulators (AlO_x , SiO). In any case, an oxidation process between the evaporations is taking place. The walls of the chamber are heated/cooled through water circulation. Sensors monitor the thickness of the deposit.

Various processes are involved in PVD thin film fabrication: most relevant for this research, pure aluminum passed through cycles of condensed/vapor/condensed phases. The equipment allowed a super-saturation of the vapor phase in the inert atmosphere working at high temperature and pressure, hence enabling the condensation of the metal nanoparticles and instant formation of a passivation aluminum oxide layer at air contact. A rotating lid held the substrates placed upside-down during the formation of plasma. The average thickness of the Al-coating for the substrates used in this work was 150 ± 10 nm.

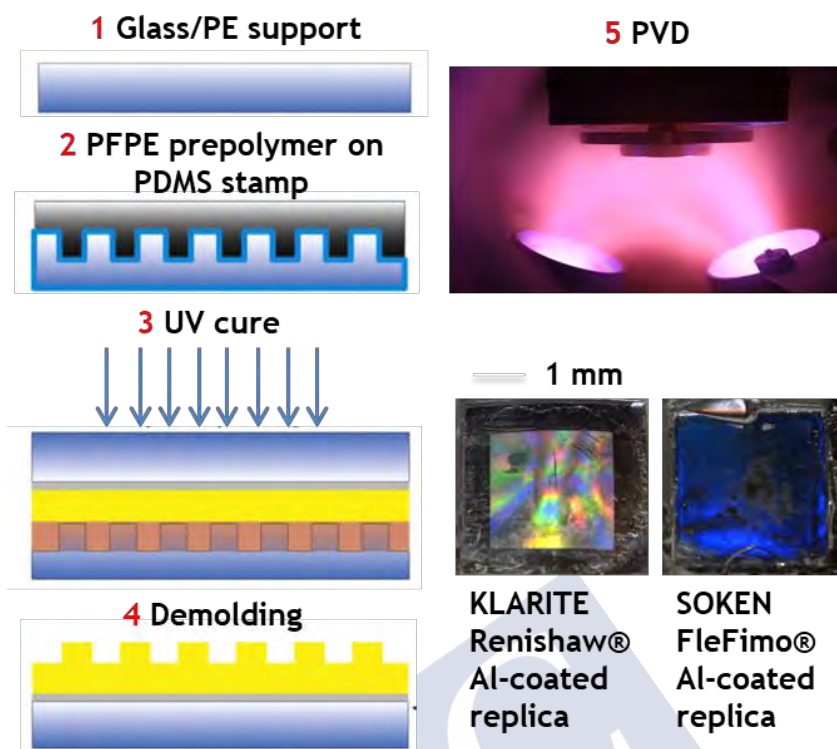


Figure 2.2: Representation of the procedure of fabrication of elastomeric SERS substrate with PFPE derivative. Steps consist of 1) holding a glass or polyethylene support; 2) placing the PFPE prepolymer onto the PDMS mold with the transparent support on the top; 3) irradiating with UV light; 4) demolding the structures substrate; 5) coating the substrate with aluminum with physical vapor deposition system. Photo insets down to the right show replicas of the two *micro* and *nano* structures replicas. Adapted with permission from ref. [264]. Copyright Elsevier.

2.1.2 Characterization methods

Optical observations and stereo microscopy allowed assessing the quality of the fabrication. However, to deepen the information at *micro* and *nano* scale SEM imaging was necessary. In general, the different parameters affecting the SERS resonance are contact surface, size and distribution of the metal nanoparticles. Additionally, lateral resolution of the replicas, assessed with SEM, as well as deterioration of the elastomeric stamps undergoing several batches of production are crucial parameters.

2.1.2.1 Scanning Electron Microscopy (SEM)

Advanced imaging control was necessary during the fabrication of the substrates. In SEM, electrons travel in a vacuum atmosphere, hit and interact with the matter, thereby exciting the atoms and producing characteristic emissions generating the image. In the current research, two instruments were utilized: 1) Zeiss FESEM Ultra Plus equipped with EDS for high magnification images; and 2) Zeiss Evo Ls 15 equipped with variable pressure probe. The acceleration voltage ranged between 1.5 to 20 kV, the beam current was at 50 nA, and the

working distance ranged (WD) 3-10 mm. Detectors of backscattered (BSE) and secondary electron (SE) were used to collect the images.

SERS substrates were coated with Al during the PVD process and no further coating prior to SEM observations was carried out. Further, **elastomeric stamps** and **uncoated substrates** were also observed by SEM to assess the replica defects throughout the various steps (Figure 2.3 top and intermediate rows). Preventing electrostatic charge buildup on insulating polymeric materials is not straightforward; in fact, surface electron conduction was not optimal and the image reported for control could not be improved further. To overcome this issue, variable pressure equipment and low-speed electron beam have been used and provided slightly blurred images, yet also this image was indispensable to observe features and defects of the structures. On the contrary, to confirm the Al-coated structures, high-speed electron beam were used and images obtained were much clearer than those of PMDS stamps and uncoated FLUOROLINK[®] replicas (Figure 2.3 down row).

KLARITE[®] Renishaw replica substrates display a squared array of inverted pyramids with approximate pit size 1.5 x 1.5 μm and pitch 2 μm . FleFimo SOKEN[®] replicas from embossed PET of nanopillars display a hexagonal array with diameter 145 ± 30 nm, height 250 ± 30 nm, and pitch 250 ± 30 nm. The resulting roughness of the surface in combination with the lateral dimensions of the pits, as well as the residues of unpolymerized PFPE derivative have played a huge role in batch fabrication of the substrates and in their eventual sensitivity. PDMS molds preliminarily fabricated also took a large amount of time to ensure minimal residues of unpolymerized fractions and planarity of the surface to host the plasmonic surfaces. Overall, the reproducibility of the fabrication process, irrespective of switching from glass to PE supports and from ORMOCER[®] to less viscous FLUOROLINK[®], was satisfactory for the aims of research.

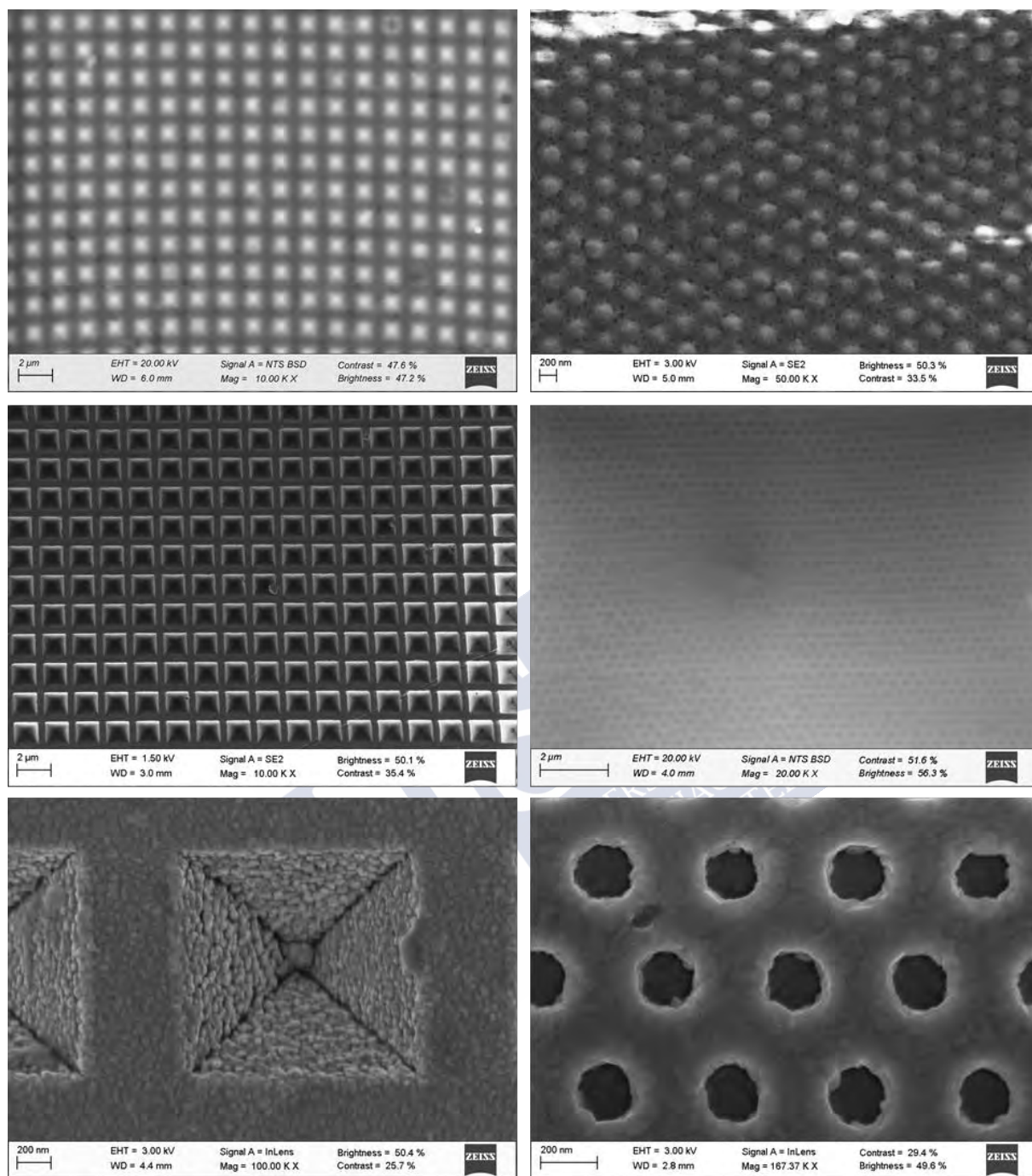


Figure 2.3: SEM microphotographs of KLARITE® (left) and SOKEN® (right): PDMS stamps, positive pyramids on the left and pillars on the right (top row); PFPE uncoated replica substrates (middle row); and Al-coated SERS substrates (lower row).

2.2 PDMS STRIP SAMPLERS FABRICATION

Combining the use of Al-coated platforms with the PDMS strip sampler method enabled to collect LMW compounds, or otherwise small molecules, for ultrasensitive Raman detection. The strip samplers were fabricated by casting and thermally curing a liquid prepolymer (SYLGARD® 184 by Dow Corning™) under vacuum at 80° C for 2 h, as for the elastomeric master molds mentioned earlier. Coarse nylon webbing strips and smooth disposable polypropylene (PP) circular containers were used to cast the samplers, while testing different shapes to improve the sampling performance (Figure 2.4).

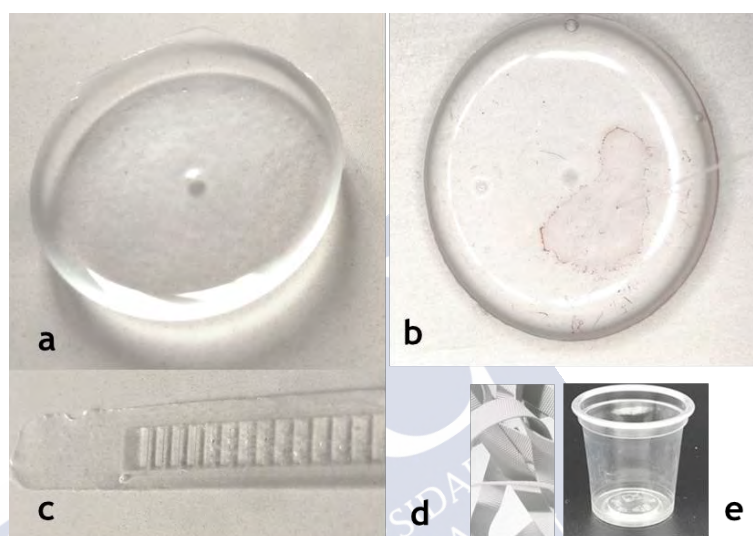


Figure 2.4: PDMS strip samplers: a) circular sampler with a slight cavity and smooth surfaces, approximate thickness 7 mm; b) circular sampler under use with capillary glass tube on the right and reddish dye inside the cavity; c) strip sampler molded from nylon webbing tape; d) nylon webbing tape; e) circular PP container.

Although further explanations are provided in several sections of the thesis, it is hereby significant to introduce the sampling steps in detail before Raman results are discussed. Samplers support the mixture of medium (solvent) and molecular fragments (analyte) for transportation to the SERS platforms. The collection of such solvent/analyte mixture was efficient, either using glass capillary tubes, though an additional step on a glass slide was necessary, or directly dropping the solvent onto the strip sampler and collecting the molecules with a micropipette for deposit to the SERS platform.

A number of tests were run to ensure that the release of solubilized siloxanes from the sampler was negligible and would not interfere with the low concentrations of analytes from the surface of the objects. Mass spectrometry techniques were selected as the best option to provide backup evidence in this respect.

2.2.1 Characterization methods

Although the amount of solvent used to wash the samplers out varied between 50 mL to 2 μ L, the probability of solubilizing the sampler was likely to take place in case of repeated extractions or prolonged permanence on the sampler (*e.g.* min), especially with good solvents (*e.g.* THF and CHCl_3). The extractive procedure of the molecules and the subsequent transfer to the platforms were usually below a minute time; however, to obtain the actual amount of PDMS residues during sampling, a variety of samplers (smooth and coarse) were left soaking in THF, CHCl_3 , acetone, EtOH and H_2O and controls with FTIR spectroscopy at different times were collected. Those routine controls are not reported, as they were merely functional to compare and correlate the samplers shape with the influence on the amount of the PDMS released at different time ranges. As far as shape and solubilization were concerned, no positive correlation was recorded.

On the other hand, more sophisticated analyses were necessary to address the lower limits of detection for PDMS release during sampling. Microextractions were simulated with the typical amounts of solvent involved and using standard compounds with certified molecular weights of polyethylene glycol (PEG) and polystyrene (PS). A detailed explanation of the results of extractions on certified polymers is provided in Chapter 3. Additional microextracts with model materials, namely linseed oil, were optimized studying LMW degradation products from films exposed to accelerated photooxidation. PDMS residues in *quasi* actual conditions were also determined with mass spectrometry techniques.

2.2.1.1 Gas chromatography/mass spectrometry (GC/MS): studying the influence of PMDS residues

Different ratios of SYLGARD[®] 184 prepolymer and curing agent were tested to optimize the release of siloxanes, while guaranteeing the flexibility of the strip during sampling, namely 10:1, 50:1; 100:1. Therefore, further GC/MS measurements were conducted on the microextracts with capillary tubes from PDMS samplers up to 5 mL for each ratio. A chromatograph model 320-MS GC/MS Triple Quadrupole Mass Spectrometer from Agilent Technologies, equipped with a Bruker 450 GC chromatograph, with universal capillary injector PTV 1079 and with mass range 10-2000 Da was employed.

2.2.1.2 MALDI-ToF MS: determining the thresholds of physisorption

Films of blends of various molecular weights and narrow distributions of PS and PEG (SEC calibration standards) were prepared to mimicking polar and nonpolar polymers, respectively. This initial study of evaluation of the thresholds of LMW compounds removed with the sampler allowed building evidence about physisorption and affinity of PDMS with a variety of molecules. It helped to ensure that PDMS would be a suitable elastomeric material for multipurpose applications of the sampling method (*e.g.* dyes and polymers). Molecular weights ranged between 2.5 kDa for the upper limit and down to 0.5 kDa for the lower limit of detection.

A Bruker[™] MALDI-ToF/ToF ULTRAFLEX III mass spectrometer was used for the nanotechnology-assisted laser desorption/ionization ToF and matrix-assisted laser

desorption/ionization mass spectrometry experiments. The samples were deposited as diethyl ether or H₂O/acetonitrile (1:1) dissolution (1 μ L) on the matrix-assisted laser desorption/ionization or nanotechnology-assisted laser desorption/ionization sample plate, respectively, without matrix or cationization agent, therefore working with a matrix-free laser desorption ionization procedure. The plates were dried in air at room temperature and inserted into autoflex speed ToF/ToF MS operating in positive reflection mode, with reflection voltage of 1,684 kV.

2.3 AGING OF MODEL MATERIALS

Samples of interest were submitted to natural and accelerated weathering processes with the purpose to validate the sampling method proposed in the present work. Model polymers were the primary target materials under observation, and then followed by object-based validations on a variety of non-polymeric materials (*e.g.* synthetic organic pigments). Artificial aging methods are borrowed from well-established industrial processing practices [81,86,89,128,132,265]. To test service life (performance and durability) of polymeric materials years of outdoor weathering would be necessary. Instead, being aware of the chemical nature of the base polymer, through accelerated aging one can understand the ongoing degradation patterns, detecting their early signs and aiming for advancing preventive diagnostic tools.

Factors affecting the degradation rate of materials are many: for example, moisture, light exposure and heat/cold cycles. For polymeric materials as polyolefins, when degradation initiates, their inner chemical nature is affected by auto-accelerating processes of oxidation, generally on the surface. Acceleration of the weathering mechanisms allows to follow the pristine stages of chemical degradation at a small scale, prior to visible physical cracking or color change at a large scale.

Thermal oxidative degradation tests were conducted on uncoated PI, ABS, and PVAc thin films. The ovens used were a VacuTherm by Thermo Fisher and a drying and sterilization oven *Conterm* by JP Selecta™. Further, Xenon lamps by ATLAS Suntest® models CPS+ and XLS+ were used to simulate photooxidation of PI, ABS and linseed oil. Tailored filters in compliance with ISO and ASTM standards could be added for window glass daylight simulations, however only a daylight filter mimicking outdoor solar radiation was used [132,266]. Lamps last in service 1,500 h and two of them were used to maintain optimal spectral distributions throughout the experiments. Black standard temperature sensors maintained photooxidation experiments below 50°C. Lightfastness, weatherfastness and photostability were thoroughly explored through characterization with spectral methods as FTIR spectroscopy.

In weathering studies, the validity of accelerated tests has some limitations and predictions of polymers behavior should be adapted accordingly. Mechanisms of degradation must be reproduced with the same conditions; similarly, characterization methods to evaluate the effects of degradation must focus on the observation of changes in the properties that are most likely to be affected in natural aging [86].

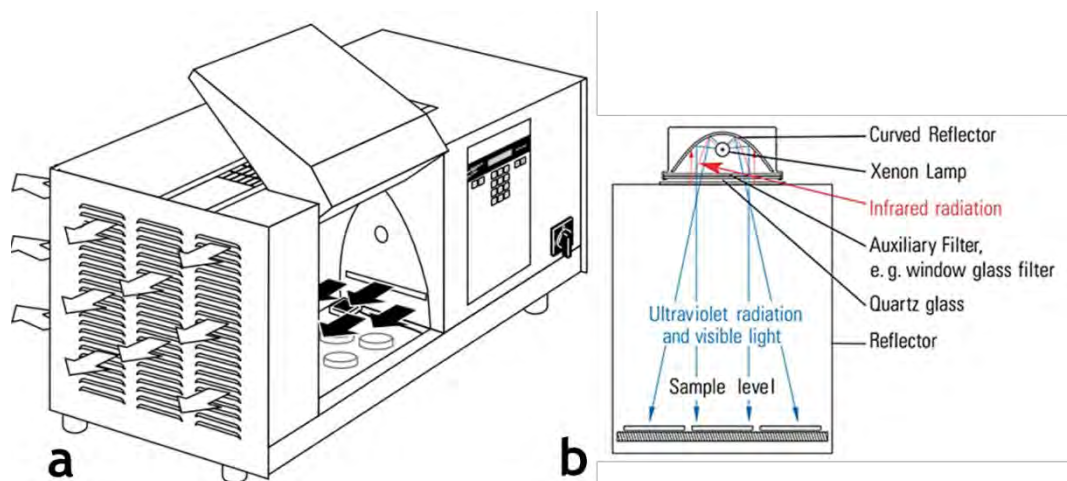


Figure 2.5: Schematic representation of Suntest® weathering chamber; a) CPS+ model scheme with arrows pointing at the air flow direction during the machine functioning; b) XLS+ model cross section of the inner configuration of the chamber. *Image® ATLAS manual from ref. [267].*

Preliminary aspects relevant to achieving a thorough selection of the experimental accelerating aging conditions are:

- accelerating factor to convert hours of artificial aging to hours of natural weathering is polymer dependent;
- if in artificial aging irradiance duration and OIT are the factors affecting the rate of degradation, it must be considered that in natural aging concurrent phenomena are contributing to the overall weathering rate of the material; therefore, the mathematical conversion of aging hours might not reflect the material behavior, but it is a good approximation;
- thickness of oxidized layers is independent of light intensity, but it increases with temperature.

Accelerating factor for linseed oil was estimated as 260 for photooxidative simulations of outdoor sunlight conditions ($1 h_{acc} = 260 h_{nat}$); therefore, 2,200 h of degradative photooxidation correspond to approximately 65 years of natural weathering. Other studies report an accelerating factor of 40 ($1 h_{acc} = 40 h_{nat}$) for thermal oxidation of linseed oil in mild conditions; therefore, for example 420 h at 80°C correspond to 2 years of natural aging. In simulations of indoor museums irradiance (*ca.* 200 lux), the accelerating factor for UP resin and PUR polyether foams is 4 ($1 h_{acc} = 91 d_{nat}$); hence 216 h correspond to 54 years of natural indoor weathering [86,138,268]. It is considered that the totality of the photoaged samples presented was at 20 cm distance from lamp, <50°C temperature and 60% relative humidity, approximately.

2.3.1 Linseed oil

The totality of the samples of linseed oil was artificially aged prior to the beginning of the current project. However, overlapping simulations for SERS validation were partially repeated and data was backed up with Py-GC/MS and SEC during the current research.

Overall, linseed oil becomes touch-dry in about 24 h, subsequently crosslinking. TITAN[®] linseed oil films were paint-brushed on glass slides (70 x 25 mm) and thickness was measured with Mitutoyo Absolute Micrometer ($50 \pm 10 \text{ } \mu\text{m}$). Films were left naturally aging and various batches were photoaged up to 2,200 h.

2.3.2 Acrylonitrile Styrene Butadiene (ABS)

Extruded films of ABS pellets from MAGNUM[®] by Dow Chemicals were shared among the NanoRestArt project partners for simultaneous accelerated testing and characterization. In the experiments here presented, uncoated ABS films were supported by magnetic bars for thermal and photooxidation up to 320 h and 410 h, respectively. Furthermore, two project partners, Commissariat à l'Energie atomique et aux Energies alternatives (CEA, France) and National Institute of Chemistry (NIC, Slovenia) proposed two new formulations for oxygen barrier passive coatings for ABS and corresponding results will be presented in Annex 3.1 to 3.4.

2.3.3 Polyisoprene (PI)

SemperGuard[®], Semperit Group[™] laboratory gloves were used as base material for the preparation of polyisoprene (PI) thin films, placed on glass slides and treated with thermal and photooxidative weathering systems. This specific brand of 1,4-*cis*-PI has smooth and coarse sides (vulcanized), both characterized at different aging times. PI is very prone to weathering under accelerated conditions forming LMW compounds [180,269], therefore it was considered ideal to understand the potentials of the sampling strategy proposed in this thesis. PI is a primary constituent of natural rubber (latex) [180], used as an art medium by contemporary artists and also present in objects from design collections [270]. In heritage science, a limited number of studies have explored the degradation pathways of PI, but many polymer science publications reported useful information [97,100,271–273]. Accelerated photooxidation of PI in Suntest lasted up to 116 h with control measures at different aging times.

2.3.4 Poly(vinyl acetate) (PVAc)

Rayt[™] S.A. white glue was used as a model material to paintbrush self-supporting films, for isothermal oxidation experiments in mild conditions (60, 80, 150 °C). Only experiments at 150 °C up to 270 h aging will be presented. The main component of the glue is poly(vinyl acetate) (PVAc) a thermoplastic polymer filled with inert calcium carbonate/sulfate and/or phthalates, actually found through FTIR spectroscopy on the aged samples. PVAc has a glass transition temperature (T_g) of about 30°C, is soluble in water, alcohols, glycols and non-polar solvents. Characterization of the films was performed at different times with FTIR and UV-VIS spectroscopies, SERS microextracts, DSC, and colorimetry.

PVAc has been selected because its degradation mechanisms, although not as a primary degradation pathway [157], lead to the formation of LMW compounds detectable with SERS. Additionally, PVAc emulsions are commonly used in artworks as adhesives, binders, and in various formulations of protective coatings. In heritage science, tackling the oxidative

behavior of PVAc is necessary to acquire information on heat applications with materials with T_g at room temperature, but most importantly the chances to detect such material on museum objects as an unwanted conservation residue.

2.3.5 Characterization methods

Traditional well-established techniques were used to determine the aging behavior of the above listed materials. SERS validations relied largely on the information achieved with other instrumental techniques. For example, SEC is traditionally known as the method to determine molecular weights in polymer science; however, its detection limits do not allow to identify LMW products forming in oxidized surfaces because of their low concentration (<1 ng approximately). Therefore, none of the techniques proposed below was able to accomplish the aims of the current research, but they all contributed to validating the SERS analytical approach proposed for the detection of early degradation markers from plastic surfaces.

2.3.5.1 Fourier transform infrared spectroscopy (FTIR) and attenuated total reflectance (ATR)

A Thermo Nicolet NT 6700 spectrometer equipped with Smart Endurance ATR device by Thermo Scientific was used. It comprised DTGS detector and sample holders for transmission measurements. Resolution of spectral acquisition was 4 cm^{-1} in the range of $4000\text{--}400\text{ cm}^{-1}$ and 32 scans, in the most measurements.

2.3.5.2 Size exclusion chromatography (SEC)

PL-GPC 50 Integrated GPC/SEC System from Agilent Technologies was used. It comprised pump, injection valve, 4-column capacity oven, and refractive index detector (RI). Calibrations have been performed with GPC/SEC Calibration Kits of PS and PEG by Agilent™ with narrow standard distribution.

SEC is based on the principle of a stationary phase made of a semi-rigid inorganic silica-based porous material, through which the liquid mobile phase passes generating a pressure gradient that allows the separation of the particles by size. Small macromolecules penetrate into the porous material, whereas the larger ones accommodate in the interstitial spaces of the column (voids). In this manner, the molecules with different sizes elute at different times and are resolved with different bands of the chromatogram. The mass detector at the end of the column generates peaks proportional to the concentration of the molecular fragments eluting. The total molecular retention volume is the sum of interstitial space and pore volumes below which value no molecules can be eluted by a given exclusion system. The difference with high performance chromatographies consists in the occurrence of separation in the given permeation range volume, instead of happening throughout a series of baseline-resolved separations. Efficiency in SEC instrumentation relies on the stationary phase packing material and the appropriate selection of the mobile phase. Instead, high performance liquid chromatography builds efficiency upon the number of theoretical plates in any given column varying according the particle size range [274].

Equilibrium conditions and rates of solute transport determine the flow pressure in the column. The mobile phase should be selected searching the least interaction with the stationary phase, since it would subtract energy to the system. Entropy controls the solute distribution, while the enthalpy value is negative. However, according to previously published models, small molecules are four times more likely to be retained than greater ones by the stationary phase [271,274]. In addition, separation in SEC would be inertly independent from temperature; however, polymer viscosity is indeed affected by temperature, as it is its refractive index. SEC chromatograph had a differential refractive index detector (DRI), highly temperature dependent. These kinds of detectors are universal detectors based on the calculation of the difference of the refractive index of a static reference of the mobile phase with a streaming mobile phase containing the sample. In the experiments here presented, temperature was set to 40 °C.

However, for LMW compounds the signal might not be proportional to the concentration of the sample. Polymer end-chains do not affect the refractive index, however they have a non-negligible weight and for molecules below 1 kDa they matter. Solubilizing the samples completely minimized the interaction with the stationary phase, potentially detrimental.

Resolution was improved for LMW oligomers by using small-pore-size gels to pack the columns. Small volumes of sample with high concentration were injected into the column with the same purpose to enhance the resolution. The separation factor depends on how flat is the slope of the calibration curve: the flatter the better. This was achieved by introducing more PS narrow distribution certified standards with close but different number molecular weights. In addition, selecting a specific separation range through appropriate columns to detect molecules of interest also improved the resolution in the lower end.

Sensitivity of the detector is crucial when the sample contains a mixture of both high and low molecular weight compounds. The refractive index of oligomers is defined as the reciprocal of the average molecular weight. Overall, spectral mismatches, meaning positive and negative changes of the chromatogram observed during measurements, might be due to a combination of effects of chemical modifications of the polymeric molecules during the analysis, changes in the molecular weight, as well as inadequate polarity of the mobile phase eluting onto the stationary one.

The difficulties in determining M_n and M_w of LMW compounds are well-known and, as described earlier in this section, molecular chain-ends have a non-negligible weight, although they might not bend the incoming light, hence they might not be detected. This limitation was overcome by introducing MALDI-ToF-MS as a complementary technique for the determination of certified standard of polar and nonpolar polymers blends of PS and PEG (0.2-1 kDa).

2.3.5.3 Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)

Thermally assisted hydrolysis and methylation-pyrolysis gas chromatography/mass spectrometry analyses were performed on microextracts either with polar or nonpolar solvents on standard certified polymers and model linseed oil samples. Pyrolysis was performed using a chromatograph CDS 500 by Thermo Scientific at 400°C for 20 s (10 °C ms⁻¹ heating rate).

For each pyrolysis, a few μ L of a 25% aqueous tetramethylammonium hydroxide solution by Sigma Aldrich™ were added through a microsyringe to the dry sample in the quartz probe. The probe was inserted in the instrument interface and pyrolyzed immediately, in order to reduce at the minimum the evaporation of the tetramethylammonium hydroxide solution. A 6890 N₂ gas chromatograph by Agilent Technologies™ was used to swipe the pyrolysis products. A flow of He at 1 ml·min⁻¹ and a HP-5MS column (length 30 m- internal diameter 0.25 mm- film thickness 0.25 μ m) were used. Temperature range was from 60°C (3 min dwell time) to 325°C (3 min dwell time), at a rate of 20°C·min⁻¹. An Agilent 5975 mass spectrometer was used (m/z 50-500, 70 eV). Compound identifications, mass data and retention times were based on the NIST05 library along with published literature.

2.3.5.4 Differential scanning calorimeter (DSC)

Q200 Differential Scanning Calorimeter (DSC) by TA Instruments™ with Al pans was used to study the thermal behavior of polymeric materials and blends with the aim to identify additives, fillers or otherwise different materials used for preparatory layers in art and as plastic constituents. Degradation mechanisms affect the molecular weight of the polymers causing in some instances loss of small molecules, in other crosslinking and increase of the molecular weight. In thermal terms, this is reflected in the shifting of the T_g which was the parameter analyzed through this method.

2.3.5.6 Color (reflectance) measurements

A KONICA-MINOLTA™ CM-700d spectrophotometer (Konica Minolta, INC., Tokyo, Japan) was used for color measurements. Color space coordinates were the CIE L*a*b* with D65 standard illuminant and 10° observer, SAV 3/6 $\varnothing$ mm illumination area were used in this study. SpectraMagic NX software was used for a comprehensive color analysis. The spectrophotometer records integrated color, product of reflectance of the different colors reflected in the same measurement and direct function of the color of samples. Reflectance is the percentage of light reflected from a surface, likely to be perceived by the human eye in the visible range (350-740 nm with 10 nm resolution). Coordinates reported may refer to the diffuse reflectance spectra (specular component excluded, SCE, or specular component included, SCI). Since a glossmeter was not available, in many analyses of shiny/transparent plastic objects, SCE was considered the most reliable group of color coordinates, mimicking values of the true color of the object irrespective of its gloss.

2.3.5.7 USB microscope

Long Working Distance (LWD) USB microscope by DinoLite™ - model AM7915MZTL with magnification range from 10-140 x and 5 megapixel sensor, automatic magnification reading and flexible LED control was used for *in situ* and laboratory visual observations with small objects and samples from extended surfaces. The extended depth of field (EDOF) feature for instant focus on different layers has helped to distinguish surface fabric and topography at microscopic level. DinoCapture© software was used to acquire the images.

2.4 OPTIMIZING MICROEXTRACTIONS

As introduced earlier, the PDMS strip sampler changed shape and ratio between prepolymer and curing agent until an optimal combination was achieved. Similarly, many other aspects of the microextraction with solvents have undergone a variety of testing and adaptations during the course of the research. Initially, even a ‘dry’ method of extraction was tested, pressing the SERS platform directly on the surface of the material under analysis, but results were not reliable for lack of reproducibility, hence they will be seldom reported.

Further testing to optimize the microextractions continued throughout the whole research involving a variety of solvents and samplers. Analytes were collected by pressing the PDMS strip samplers onto the surface of the object under analysis for about 30 s. In some instances, additionally to pressure a gentle circular movement complemented the sampling to maximize the removal of small molecules, if the area of sampling was extended enough to do so.

2.4.1 Polarity and solubility: controlling the interaction between analyte and solvent

Crucial attention was paid to the selection of solvents to transfer the small molecules from the PDMS sampler to the SERS substrates. Initially, the research focused on the detection of LMW degradation products from polymers, followed by multipurpose validation with different small molecules, as inorganic pigments, SOPs, and dyes among others. Selective removal of LMW products from the sampler with tailored solvents, combined with repeated local accumulations on plasmonic areas of insoluble species have played an essential role in the successful multipurpose application of the analytical approach hereby proposed.

Through several experiments presented in Chapter 3, it was demonstrated that transferring molecules can be tuned through solvent polarity, hence controlling the sampling of different kind of molecules physisorbed on the PDMS sampler. For example, acids and esters derived from oxidative processes on the surface of polymeric materials can be detected observing the increase of carbonyl functions in vibrational spectroscopies (C=O , $1650\text{--}1750\text{ cm}^{-1}$). Tests with polar solvents, like H_2O and EtOH , have shown that their good affinity for this kind of molecules allowing the removal of large amounts from the PDMS sampler to the substrate. On the other hand, nonpolar solvents, like hexane, cannot transfer the same molecules from the sampler to the SERS substrate, and therefore the carbonyl band is not recorded.

Tripathi *et al.* [275] expanded the interpretations on the use of solvents during the deposition of molecules on planar SERS substrates mentioning the competition of analytes in limited enhancement sites of the sensor. Several tests at different concentrations of standard analytes and with a variety of polar and nonpolar solvents confirmed that the solubility affects the binding energies of the analyte with the metallic substrate, as well as the relative intensity of the SERS signal. In their study, no PDMS sampler was used, and the research focus was on the metal/analyte interaction. According to the authors, SERS is best enhanced when the interaction of the analyte with the solvent is weak. This explanation is in line with the observed behavior of H_2O and acetone in the microextractions of Prussian blue molecules in the current study, presented in Chapter 3.

Initially, the design of the sampling included an intermediate step of deposition on a glass slide of drops of solvent pressing the sampler for wash out, subsequently collecting the mixture solvent/analyte with a glass capillary tube ($\varnothing < 1$ mm), and finally depositing the solubilized molecules onto the substrate (Figure 2.6). Eventually, the use of one-step transfer procedure with micropipette was preferred.

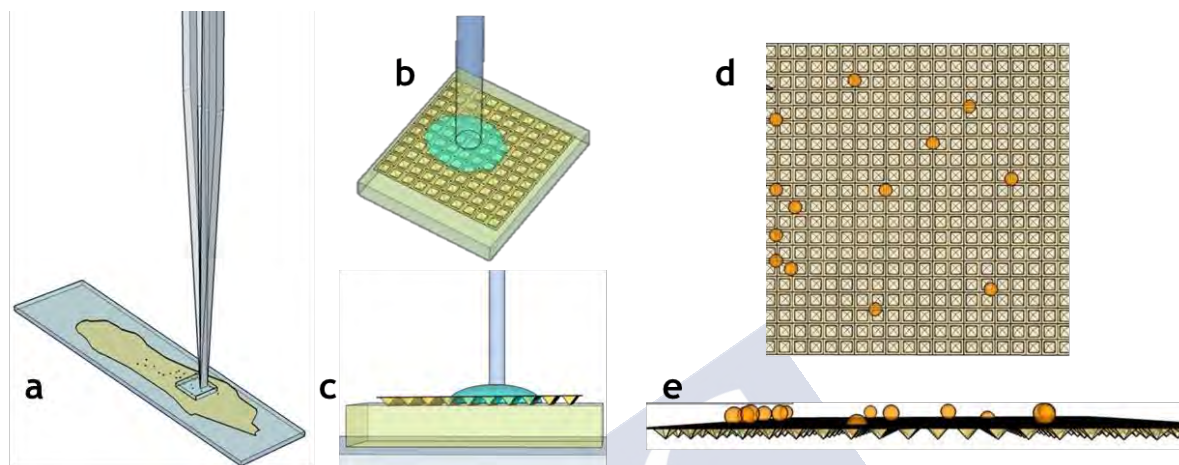


Figure 2.6: Schematic representation of the sampling strategy with intermediate step using a glass slide to wash out the PDMS strip sampler in the selected solvent (a); glass capillary tube used to drop the dissolved molecules onto the SERS platform KLARITE® type (b), in cross section (c); solvent evaporation leaving the analytes on the SERS platform (d), cross section on the inverted pyramids (e).

2.4.2 One-step transfer to SERS platforms

Minimally-invasive sampling relies on a very small amount of molecules; those physisorbed on the strip sampler in some occasions are so low in concentration that was necessary to repeat extractions and deposition on a same area of the substrate few times (drop boarder concentrated Figure 2.7). Half way in the research, in the perspective to minimize material loss, the intermediate step of washing out the sampler on a glass slide was removed and the collection of the mixture solvent/analyte was executed directly on the sampler after pressing it onto the object surface.

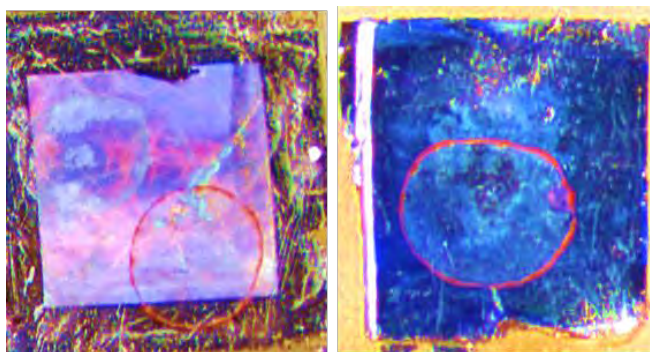


Figure 2.7: microphotographs in false colors showing on the left a KLARITE® replica with marked drops borders; on the right a SOKEN® replica with a drop in the center.

To ensure the highest concentration of sample, a micropipette was used to drop a controlled amount of 20 to 50 μ L solvent on the sampler (BrandTech Transferpette S Air Displacement, 100 μ L volume, single channel 0.1-2.5 μ L). Then for collection and dropping of the mixture onto the SERS platform a Lambda Plus Single Channel Pipettor (0.2-2 μ L volume) was employed, each of 0.75 μ L, followed by complete solvent evaporation before spectral acquisition. Figure 2.7 shows photographs in false colors of some SERS substrates with drop borders with more concentrated analyte, after solvent evaporation.

2.4.3 Materials for object-based validation

Validation of the sampling and extraction method proposed in the current project is meant as a tool for applications in cultural heritage. The complexity of composite materials and, on the other hand, the need to achieve sensitive and selective molecular data is better comprehended through validation on actual museum objects. The validation is meant to produce something similar to an *application note* of the analytical procedure, instead of for the instrument.

2.4.3.1 Plastic objects

PI loose fragments from some sculptures of Andrés Pinal were made available by the CGAC. They were dated to 1995, hence they underwent more than 20-year natural aging. ABS and PMMA objects from contemporary and historical LEGO® collections, dated from 1970 to 2015, were made available by private a collector in collaboration with the NanoRestArt project partner from the Tyndall Institute in Cork, Ireland. Those samples were analyzed with the aim to proof the ability of one-step transfer to the SERS platforms, as an alternative minimally-invasive analytical strategy to detect SOPs and CICPs in complex polymeric matrixes, when handheld Raman spectrometer set up would provide unreliable results.

2.4.3.2 Paint materials: colorants and binders in rock art

A diagnostic kit for rapid detection of small molecules was sent out to experts from the University of Vigo in a joined collaboration with the municipality of Antelas, Portugal. Paintings depicting geometrical motives were sampled to research proteinaceous binders on the one hand, and coloring media on the other hand.

2.4.3.3 Natural dyes and lakes from historical collections

Samples from a reference collection of natural dyes from the Higher Institute for Conservation and Restoration in Rome, Italy, was brought by the visiting researcher Natalia Macro in 2019. Samples comprised historical collections of grey cochineal, carmine lake and kermes, as references. Further, a leather fragment from liturgical footwear dated to the 13th century was also made available.

2.4.3.4 Inorganic pigments, synthetic organic pigments and dyes in Japanese woodblock prints

Ukiyo-e Japanese woodblock prints from the Meiji period were made available by the project partner Antonio Mirabile, paper conservator based in Paris, France. Six panels (with further felt tip pens drawings) were thoroughly characterized through SERS microextractions to address dyes and inorganic pigments. Uncertainty on the technology of production to pursue further conservation projects on similar materials motivated the research.

2.4.4 Characterization methods

During the current research, Raman spectroscopy was used in a non-destructive non-invasive manner most of the times, except when minimally-invasive sampling was indispensable to guarantee reliable molecular detection. However, Raman spectroscopy was associated to several other methods listed above to establish limitations of the sampling method and to complement the data obtained, while addressing multiple research questions on the objects/materials under investigation.

2.4.3.1 Raman Spectroscopy and 3D imaging

Raman (NR) and SERS spectra were achieved with an InVia Flex-Renishaw™ PLC, UK-benchtop spectrometer with spectral range 100-3200 cm^{-1} , spectral resolution 0.5 cm^{-1} , 1200 mm^{-1} grating lines, CCD 576×400 pix detector, and equipped with 785 and 514 nm lasers. Accumulation time was 10 s and power spanned from 1 to 5% of the nominal laser corresponding to 9-45 mW. A long working distance Leica™ objective (model 5 660 036) operated with a 65 μm slit opening. The software for data treatment was WiRE 3.2.

Alternatively, a WITec™ alpha300 R with confocal Raman imaging microscope, equipped with 785, 532, and 488 nm excitation wavelengths, was used with the additional hyperspectral chemical imaging of the samples. It allowed profiling the chemical features in the 3D images of the samples. Spectral mapping enabled to collect a spectrum for each pixel in the selected areas, while performing also single point analysis. Software for data processing were Suite FIVE 5.2 and Suite FIVE 5.2 Plus.

2.4.3.2 Macro X-Ray Fluorescence elemental imaging (MA-XRF)

Elemental imaging was used to extend the information on samples with difficult molecular identification, for example synthetic organic pigments. It was used a 2D Micro-XRF M4 Tornado by Bruker™ equipped with a polycapillary tube 20 μm Ø for Mo K radiation, detector X-Flash® with X-Ray silicon drift, single rhodium target X-Ray tube with collimator, and dual video microscope XYZ for imaging and selection of working areas. The software for data processing was ESPIR™.

3. RESULTS AND DISCUSSION

This chapter is divided into three main sections titled: *Sensing and Sampling Devices Fabrication*, *Detecting Degradation Markers in Polymeric Materials*, and *Extending the Application of SERS Devices to Small Molecules of Interest*. The first section will show the experiments conducted to optimize the fabrication of the operating devices thoroughly characterized for optimal application on heritage materials. The further sections and subsections will show how the sensing method was built upon the evidence obtained from artificially aged model materials, and then validated as a multipurpose tool for heritage science research. The degradation mechanisms of polymers will be tackled with new sensing strategies, potentially also useful for polymer science. Furthermore, new information on the technology of production of cultural objects and their preservation conditions will be provided. Upgrades of the concept of *minimally-invasive, nanodestructive*, sampling and *diagnostic tools for preventive conservation* will be discussed, providing some solutions to increase the applicability of *in situ* analysis of cultural heritage materials.

The current research led to publishing indexed journal papers referred to within this chapter [38,209,211]. The author contributed by preparing the model PS and PEG films, processing the data, writing and reviewing the manuscript partially reported in sections 3.1.3, 3.2.1 from [209]. Further, the author contributed by aging the ABS, PI and PVAc samples, fabricating the SERS platforms, following the formation of degradation markers with all instrumental methods, processing the data and editing the manuscript partially reported in sections 3.2.2, 3.2.3, 3.2.4, 3.2.5 from [38]. Finally, the author contributed by designing the research that combines data on plastic coloring media from handheld, SERS and benchtop Raman measurements for the analysis of ABS-based museum objects reported in section 3.3.1 from [211].

3.1 SENSING AND SAMPLING DEVICES FABRICATION

As an essential preliminary step of the research, the protocols for the fabrication of SERS substrates and PDMS strip samplers were optimized. Questions were posed on whether the formulation and concentration of the photoinitiators to activate the PFPEs derivative were optimal for complete polymerization and ease in demolding the replicas, or if the PDMS strip samplers would release some amounts of unpolymerized residues during sampling. In the past, PMDSs were the most used polymers for *nano* and *micro* imprints, for their ease of workability. However lately, there has been a shift from PMDSs to PFPEs [262,276,277] due to their increased chemical resistance and versatility.

3.1.1 Optimizing the polymerization experiments with UV-NIL

UV-NIL was used to polymerize different photosensitive components and to replicate patterns from nanostructures and microstructures at high precision. After UV-curing, relevant features of the films, as stickiness, thickness and transparency, were qualitatively observed to regulate possible distortions of the patterns in the replicated films. In fact, several limitations affect the replicas, including the wavelength and the intensity of the lithographic illumination source, which absence of control in most instrumental settings reflects in the loss of reproducibility of the lateral dimensions of the structures [257,278–280]. Reproducing the *nano* and *micro* patterns on extended working areas ($\sim 0.5 \text{ cm}^2$) was not straightforward.

After one year from the beginning of the experiments presented in this chapter, FLUOROLINK[®] MD700 (Figure 3.1) became the sole prepolymer employed to fabricate the replicas of the SERS substrates. Previously, the fabrication of the substrates was performed with ORMOCER[®] PFPEs derivatives and few Raman spectra presented in this chapter were collected with those substrates.

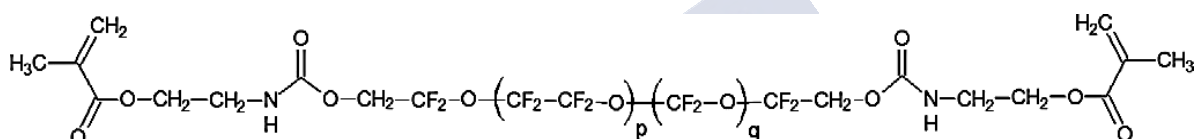


Figure 3.1: structure of FLUOROLINK[®] MD700 perfluoropolyether functionalized with urethane methacrylate groups. Adapted with permission of ref. [281]. Copyright Pergamon.

Table 3.1: photoinitiators and further experimental conditions

Abbreviation in-text	Name (IUPAC)	Structural formula
184* (powder)	1-hydroxycyclohexyl phenyl ketone	
651* (powder)	2,2-dimethoxy-2-phenylacetophenone	
MPA 2H* (liquid)	2-hydroxy-2-methylpropiophenone	
MPA* (powder)	2,2-dimethoxy-2-phenylacetophenone	

*Ormira (former IRGACURE[®]) and Sigma Aldrich are the sellers of 184/651/MPA/MPA 2H photoinitiators. Structures from ref. [282] free repository of pubchem.ncbi.nlm.nih.gov.

FLUOROLINK[®] MD700 is a surface modifier based on a perfluoropolyether functionalized with urethane methacrylate groups and usually UV-cured with the photoinitiators, such as those in Table 3.1. Throughout the preliminary experiments to reach definitive optimization of the fabrication, different ratios of prepolymer and photoinitiator were accurately mixed with 50 mL of pure acetone and stirred for 45 min with a Heidolph 2 G1 rotary evaporator at 35°C/80 rpm until complete evaporation. Prior to UV-curing, the flasks containing the mixtures were wrapped up in Al foils to avoid photo-activation and they were stored under vacuum in the oven to avoid moisture interferences during polymerization.

Sticky unpolymerized residues were observed after UV-curing, therefore the accurate reproduction of the nanopatterns in the PDMS mold was being prevented. For this reason, a couple of targeted experiments were necessary to understand the relative influence of all the experimental parameters on the film formation. Even though reproducible optical properties are extremely relevant to the SERS enhancement, these experiments evaluated only the completion of the polymerization process, disregarding the replication of the pattern *per se*. Nicolás Pajer, a visiting undergraduate intern from the University of Venice, Italy, contributed to the execution of the experiments herein presented.

Different parameters were isolated, in particular **concentration of photoinitiator, purging atmosphere and UV-irradiation dose**. The photoinitiators were mixed with the prepolymer in different amounts (1, 4, 5 wt.%). Air and N₂ constituted the purging atmospheres in pretreatment chamber where the glass slips were placed for irradiation. The purge of the lithographic chamber was set for 5 and 10 min, following available published protocols for fluorinated polymers [281,283]. Further experiments without purge pretreatment were carried out. UV-dose was set in the range from 3 to 120 s. The lamp was placed in a clean/dark room, assuming to have variations of temperature between 19 and 24° C (thermostat was not available).

After film formation, unpolymerized residues spanned from approximately 22 to 1 wt%. UV-dose was under strict control in the first series of the optimization experiments to study its influence on the rate of polymerization. The duration of the exposure spanned from 6 s to 2 min, and it was concluded that optimal irradiation dose for complete polymerization was 40 s. As for the purging atmospheres, the films polymerized with N₂ flow were found to have consistent polymerization rates [284,285], whereas those with air showed a random distribution of the polymerization.

After weighting, the glass slips were left soaking in CHCl₃ for around a week, for then determining gravimetrically the unpolymerized fraction. Curiously, the aggressive and prolonged soaking environment did not imply the solubilization of the films. Actually, the almost complete insolubility of the films provided sound evidence of the chemical resistance of FLUOROLINK[®] MD700. In the light of such data, it was decided that a simple and fast removal of the unpolymerized residue from the glass slips with a lab tissue was sufficient to obtain an estimation of the unpolymerized fraction of PFPEs.

Figure 3.2 shows the histograms for all the photoinitiator/prepolymer mixtures, including purging durations and atmospheres. Overall, the average unpolymerized fraction for the 1% photoinitiator was ~9%, for the 4% was ~3%, and for the 5% was ~3%. Furthermore, N₂

purge for 10 min resulted in 5% of unpolymerized fraction, over the 8% of the 5 min purge. Curiously, not performing any purge at all, hence conducting polymerization tests in air, has provided better average results with almost 4% only of unpolymerized fraction for all photoinitiators. This might be explained with the likely degradation of the initiator in solution. Outliers were not considered for the calculation of the average results to present statistically meaningful data.

Interestingly, among all tests, the best and worst single performances were achieved by purging 5 min with N_2 : the best result was obtained with the photoinitiator 651 at 5 wt.% yielding only 0.92% of unpolymerized fraction, and the worse performance was achieved by the photoinitiator 184 at 1wt.% yielding 22% of unpolymerized fraction. Overall, the photoinitiator 651 performed with only 4.08% of unpolymerized fraction, followed by the MPA with 4.42%, the 184 with 8% and MPA 2H at 8.6%.

The protocol considered advantageous in terms of time for fabrication and performance of the polymer comprised a ratio of 5 wt.% of 651 photoinitiator with a pretreatment of 5 min under N_2 purge and UV-irradiation of 40 s.

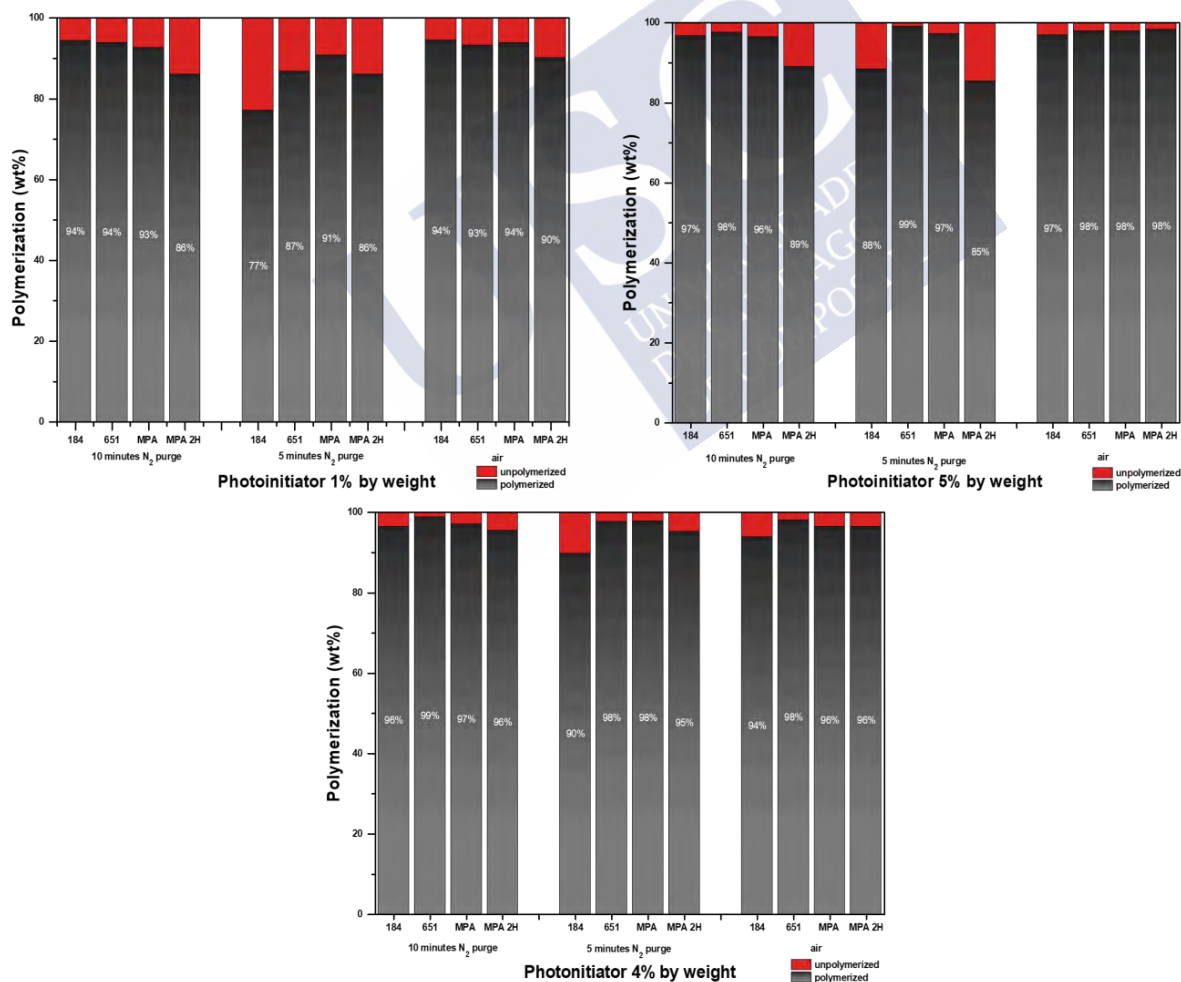


Figure 3.2: histograms comparing the polymerization tests in air and N_2 with 1 wt.% photoinitiator (top left), 5 wt.% photoinitiator (top right), 4 wt.% photoinitiator (down). Purging times of 10 and 5 min, purge-free polymerization in air are respectively presented in bars from left to right.

3.1.2 Testing PDMS samplers: physisorption and solubility

This section shows how physisorbed molecules transferred with solvents can be safely deposited on SERS Al-platforms for detection of targeted analytes. The **pressure** on the sampled area and the selection of **appropriate solvents** can be tuned in each sampling. Opposite to chemisorption, physisorption relies on van der Waals dipolar bonds with energy below 0.4 eV (weak) [286]. Activation energy is not required (Figure 3.3); hence, the interaction is fast and reversible at atomic or molecular level. Physisorption is independent of the surface morphology and temperature, although influence of moisture was reported [275,287].

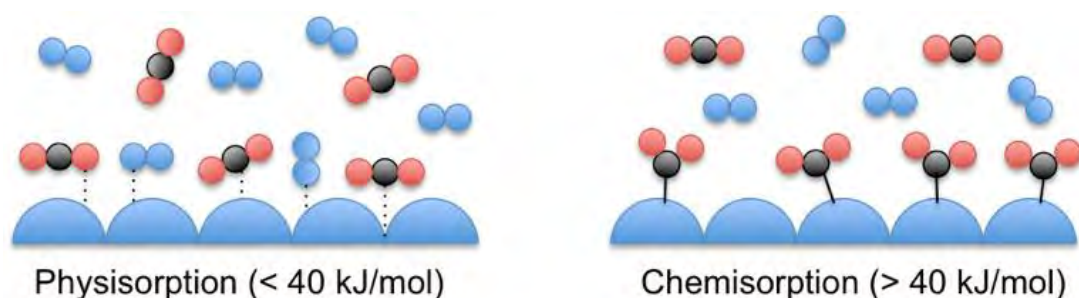


Figure 3.3: representation of physisorbed and chemisorbed molecules. Adapted with permission from ref. [288]. Copyright Wiley VCH Verlag GmbH & CO, KGAA.

PDMSs have an inorganic $-(\text{Si-O})-$ backbone associated to high surface energy and polarity, therefore they promote intermolecular interactions. However, the polar ends of the backbone are shielded by nonpolar methyl side groups. They form hydrophobic layers with good release properties having low critical surface tensions ($\sim 20\text{--}25$ mN/m). Provided the versatility of PMDS, fabricating the strip samplers with it to physically absorbing polar and nonpolar molecular fragments seemed an ideal choice.

A detailed list of SYLGARD[®] 184 components is provided in Table 3.2: Dow Corning[™] sells the elastomer as a two-part kit liquid silicone base to be mixed in 10:1 mass ratio to a curing agent. However, different ratios base/curing agent were tested to explore the tackiness of the resulting strip sampler. The ratios tested were 100:1, 50:1, 25:1, and 10:1. The liquid blends were poured onto different coarse and smooth molds of nylon webbing nets made of PS, PP, and ABS with different patterns. The resulting thickness of the films was ~ 500 μm . The samplers were meant to be transparent, flexible, and handy for the user, reason why their shape varied from elongated to circular over the years of the project.

After curing at 80°C for 2 h in the oven, the samplers with mass ratios 10:1 and 50:1 were ready for use, whereas those with ratios 100:1 and 25:1 did not film, even after 24 h in the oven. Concurrently, several solvents were being tested to secure the transfer of the analytes from the sampler to the SERS substrates. Tests with the solvents were performed only on the samplers with ratios of 10:1 and 50:1, since extreme tackiness or rigidity of the two others mass blends discouraged further investigations.

Table 3.2: reactive components in the SYLGARD® 184

Base resin component (wt.%)		
Wt.%	Name (IUPAC)	Structural formula*
$\geq 50[\text{wt.}\%] \leq 70$	Dimethyl, methylhydrogen siloxane, trimethylsiloxy-terminated	
$\geq 20[\text{wt.}\%] \leq 30$	Dimethylsiloxane, dimethylvinylsiloxy-terminated	
Curing agent (wt.%)		
$\geq 1[\text{wt.}\%] \leq 5$	Tetramethyl tetra vinyl cyclotetrasiloxane	
$\geq 0.1[\text{wt.}\%] \leq 1$	Octamethylcyclotetrasiloxane	
$\geq 0.1[\text{wt.}\%] \leq 1$	Xylene mixture of isomers	
$\geq 0[\text{wt.}\%] \leq 0.1$	Ethylbenzene	

*Chemical structures from the free repository of pubchem.ncbi.nlm.nih.gov [282].

3.1.2.1 Experiments on solubility

Droplets of different solvents at decreasing polarities, namely EtOH, CHCl_3 , and THF, were spread on clean PDMS strip samplers with a glass pipette. Each solvent had an initial volume of 1 mL and each extraction lasted around 30 min. To mimicking the actual microextraction, capillary tubes were used to collect as much solvent as possible from the samplers. At same time three different swelling behaviors and evaporation rates were observed. In addition, EtOH extracts on 10:1 ratio film were slightly yellow, whereas those with 50:1 ratio were transparent. Swelling of PDMS and fast evaporation rates of THF and CHCl_3 made more difficult to collect the solvent from the sampler before evaporation due to the motion.

It was expected that the fraction of unpolymerized siloxane/silanes that did not participate to the formation of the PDMS structure would be solubilized with the selected solvents, detected and identified with GC/MS spectrometry. The amount of unpolymerized fraction extracted could not be weighted, being below the limit of detection of the scale available. In addition, a prior calibration curve for the GC/MS spectrometry on similar samples would have

been necessary to accomplish the average amount of polysilane/siloxane detected. It is anticipated that MS counts of the molecules detected was very low, and that all fragments identified matched the polysilane/siloxane compounds family. Kala *et al.* [289] found that the limit of detection of PDMS with GC/MS is 10 pg/z L, which is in agreement with the results presented in the current work.

Furthermore, the objective of collecting such microextracts from the samplers was to determine whether the release of polysilane/siloxane during an actual sampling on heritage objects was truly negligible for subsequent ultrasensitive analyses, such as those with SERS. In this perspective, GC/MS spectrometry was the best technique available for the detection of the released molecules. Figure 3.4 shows GC chromatographs of the microextractions for ratios 10:1 and 50:1 with EtOH, CHCl₃ and THF.

For highly polar solvents, such as EtOH, the most abundant peaks detected were consistently showing the main ions (*m/z*) of oligomeric fragments of dimethylsiloxanes from all microextracts, in both samplers with 10:1 and 50:1 mass ratios. Coherently, for the less polar CHCl₃ solvent, microextracts from the 50:1 showed less polysilane-siloxanes fractions, compared to those extracted from the sampler 10:1 ratio. As expected, the most abundant unpolymerized fraction solubilized with THF and detected at retention time of around 28 min was confirmed for microextracts on samplers with mass ratio of 10:1 and 50:1; however, the amounts of extracts from the 10:1 ratio were lower than those from the more diluted 50:1.

Figure 3.4 shows that several peaks in the range of 20 to 36 min of retention time were detected. The totality of the main ions (*m/z*) identified could be ascribed to the family of polysilane-siloxanes compounds, irrespectively of the mass ratio base-curing agent used for the fabrication of the sampler. The default matching library NIST identifier proposed as the most abundant specie the tetracosamethyl-cyclododecasiloxane (CAS n° 18919-94-3) eluted at around 28 min for microextractions with all solvents. However, it is more likely that oligomeric siloxane species derived from unpolymerized fractions of PDMS were being formed or fragmented at high temperature in the chromatographic chamber. The repetitive unit of PDMS weights around 74 Da, and at a closer look of the main ions masses, they were roughly multiples of 74. This applied as well to unmatched library entries detected by the instrument.

It was demonstrated through simulations and GC/MS analysis that a very low amount of unpolymerized PDMS is extracted during the sampling. The experiments were indispensable to establishing the most suitable mass ratio base polymer/curing agent and to identifying the solubilized fragments that might contaminate SERS sensing. It is anticipated that of all SERS spectra collected from model materials and objects none has led to the detection of PDMS. Therefore, the solubilization of unpolymerized polymer/curing agent fractions from the samplers is negligible.

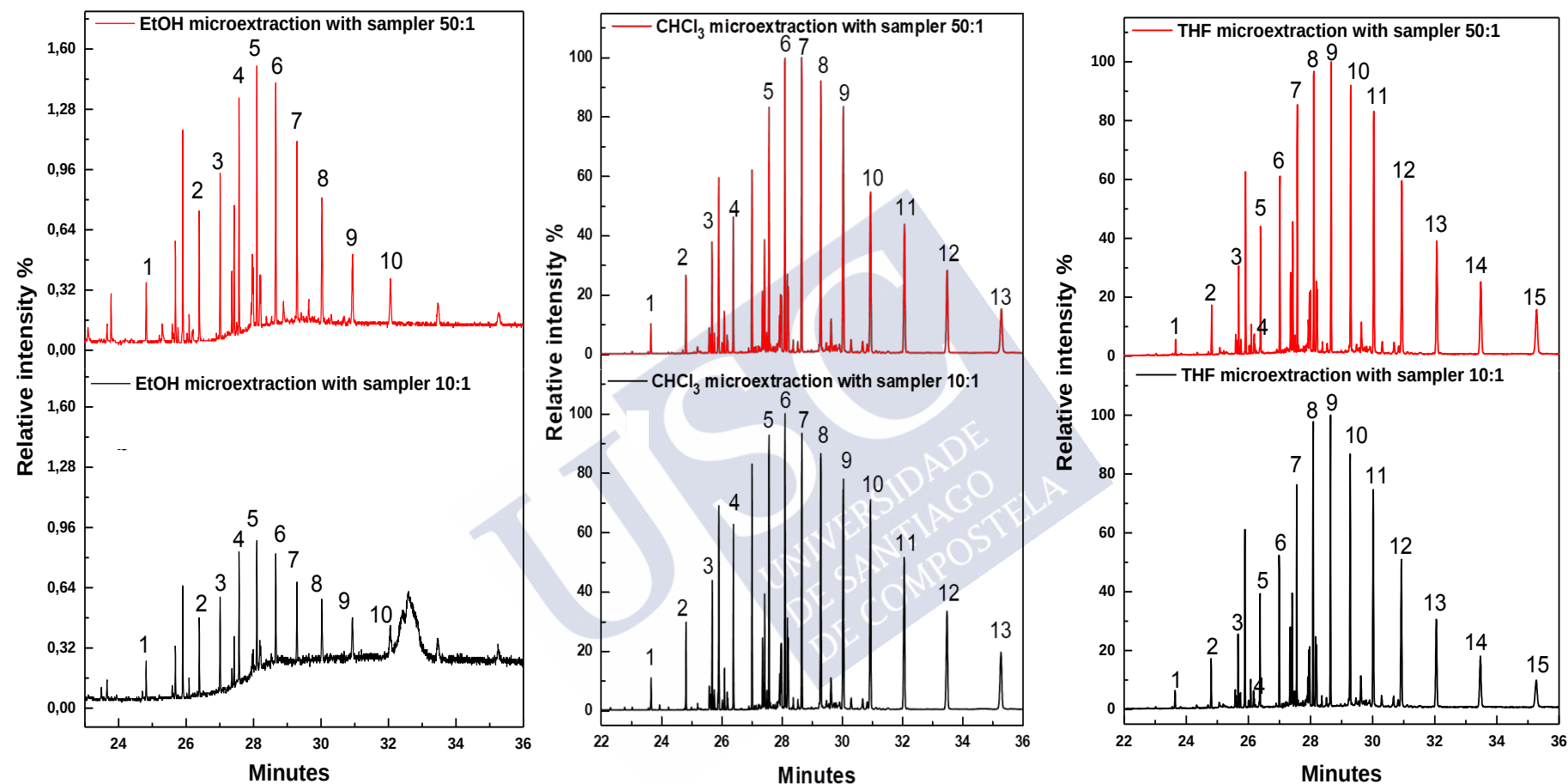


Figure 3.4: chromatograms (GC/MS) of the microextracts on samplers made with 50:1 (top) and 10:1 (down) mass ratio SYLGARD® 184: photoinitiator. On the left microextracts with EtOH, in the center microextracts with CHCl₃ and on the right microextracts with THF.

3.1.3 Assessing the thresholds of physisorption of LMW compounds

One of the objectives of the research project was to detect early degradation markers on synthetic polymeric materials used in contemporary art. Therefore, it seemed appropriate to test the ability of the PDMS strip samplers to absorb solid LMW compounds from the surface of SEC/GPC certified polymer blends for calibration. Several samplers with smooth and coarse features were tested against PS and PEG having controlled molecular weights and narrow distributions. PS and PEG were respectively considered representative of nonpolar and polar compounds. Upper molecular weight threshold were addressed with MALDI-ToF spectrometry.

The polymeric films were prepared with the help of Dr. Eduardo Bordallo. Smooth and coarse surfaces, as well as circular and elongated samplers, allowed collecting oligomeric fragments from the surface of the films. The morphology of the interface did not influence the process of physisorption (please refer to section 3.1.2).

As shown in Figure 3.5, the upper threshold for removal of oligomers was in the range of 2-2.5 kDa, either for polar and nonpolar structures. For PEG, oligomers with number average molecular weight around 0.5 and 1.5 kDa could be detected, whereas for PS oligomers up to 2 kDa average number molecular weight could be detected [38,290].

In the perspective of using the PDMS samplers to collect early degradation markers on plastic surfaces, the sampling method hereby proposed enabled to collect only nonvolatile LMW compounds compatible with molecular fragments formed during the chain scission mechanisms. Additional physisorption tests might upgrade the sampling procedure and help defining missing aspects on the influence of the pressure applied to the sampler by the operator, as well as the sampler motion during the process.

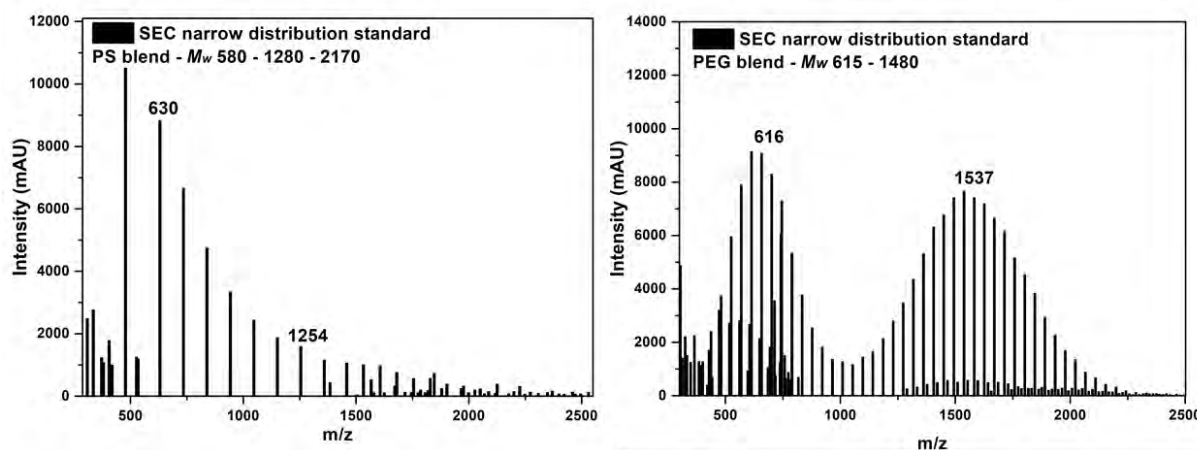


Figure 3.5: MALDI-ToF mass spectra obtained from sampling films of blends of standards of PS (left) and PEG (right). Films were prepared with diethylether mixed with LMW narrow distribution standards (0.6 - 1.48 kDa for PEG and 0.6, 1.48, 2.17 kDa for PS). Adapted with permission from ref [209]. Copyright John Wiley and Sons.

3.1.4 Summary

- PFPEs derivatives were used to fabricate high resolution replicas of microstructures from KLARITE[®] Renishaw and nanostructures SOKEN[®] FleFimo. Tests focused on determining gravimetrically the amount of unpolymerized residues to optimize the UV-NIL procedure. The experiments were based on different parameters, such as type of photoinitiator, UV-irradiation and purging atmosphere (N₂ or air), for then monitoring features of the forming films, as tackiness, transparency and swelling behavior.
- Different mass ratios of SYLGARD[®] 184 prepolymer/curing agent were tested to guarantee the optimal flexibility and solubility of the PDMS strip samplers for sampling. Physisorbed molecules were transferred from the surface of the PDMS sampler to the SERS devices with different solvents. GC/MS spectrometry was used to assess the amount of unpolymerized prepolymer/curing agent after transfer, showing negligible amounts of PMDS fractions.
- Blends of PS and PEG narrow distributions certified standards for SEC were mixed to form films. Sampling with the PDMS strip samplers was simulated using diethylether as a transferring solvent. MALDI-ToF spectrometry was used to assess to thresholds of LMW oligomer removal, up to 2.0 kDa.
- Meaningful evidence that the sensing and sampling devices fabricated suit the purpose of the research was provided. The analytical tools for microextractions and sensing were fabricated in-batch and largely characterized prior to the application of the sampling on model materials and actual objects from collections.

3.2 DETECTING DEGRADATION MARKERS IN POLYMERIC MATERIALS

Light, heat, oxygen and moisture in indoor and outdoor environmental conditions compromise service life of plastics [81,86,88]. This essential part of the research focused on the detection of degradation products from oxidized surfaces of polymers. There is extensive evidence that irradiation at long wavelengths ($\lambda \geq 300$ nm) simulating sunlight conditions initiates radical reactions leading to the formation of new chemical species. In addition, chromophoric impurities and metal complexes absorb radiation, thus accelerating the degradation processes [149,291,292].

In this section of the thesis, model polymers will be introduced in the same order as the in Chapter 1 and 2, namely linseed oil, ABS, PVAc and PI. Their aging behavior will be described discussing accelerated aging tests. Published and unpublished data on the experiments will be herein shared to expand the interpretations of the findings and to lay the foundations for sensing of LMW fragments from oxidized surfaces. In the concluding section, there will be the validation of the analytical method on PI-based museum objects.

It is worth recalling a summary of the information on the degradation mechanisms of vinyl polymers introduced in section 1.3.1. In brief, 1) hydroperoxides result from primary processes of photooxidation; 2) several types of secondary reactions lead to the formation of carbonyl and hydroxyl compounds. Rates of formation and concentrations of such compounds are traditionally associated to indexes of degradation in several types of polymeric materials [293,294]. Those indexes will be later referred as markers of degradation and evidence of their SERS detection will be provided in the following sections on a variety of model polymers and museum objects.

3.2.1 Linseed oil aging behavior: a new approach to sensing LMW oxidation products

As introduced in Chapter 1, linseed oil was selected as a model material for weathering studies, since its mechanisms of degradation are well-known [135,138,142,290,295] (Figure 3.6). Linseed oil is not a polymer; however, it behaves as such in terms of aging performance, forming a three-dimensional network. Fresh linseed oil is a liquid material, that after few hours forms a touch-dry film, crosslinking and maintaining a transparent aspect for several years. The solid film undergoes through a combination of several competing auto-accelerating reactions over time, among which eventually prevails chain scission.

Experimentally, a multi-analytical approach was fundamental to build evidence on the capability of the novel SERS method combined with PDMS strip sampler, confirming the detection of free molecules formed as a consequence of photooxidation from the complex polymeric matrix. First, traditional methods, such as FTIR and Raman spectroscopies, allowed following the evolution of the degradation process at different times. Then, Py-GC/MS allowed identifying markers of degradation previously introduced in the literature (e.g. diacid methyl ester of azelaic acid) [139]. SEC confirmed the presence of LMW compounds and further oxidation products. Finally, thermal analysis completed the information on shifting the T_g range as a result of oxidation.

Molecules without centers of symmetry can be both infrared and Raman active. Linseed oil is a compound presenting absorption in IR and scattering in Raman spectroscopy. In this respect, the most relevant difference between the two techniques is that Raman offers higher intensity of the C=C double bonds and lower intensity of carbonyl bonds than infrared. Both FTIR and Raman spectroscopies were used to follow the aging of the films, providing complementary information on the degradation mechanisms.

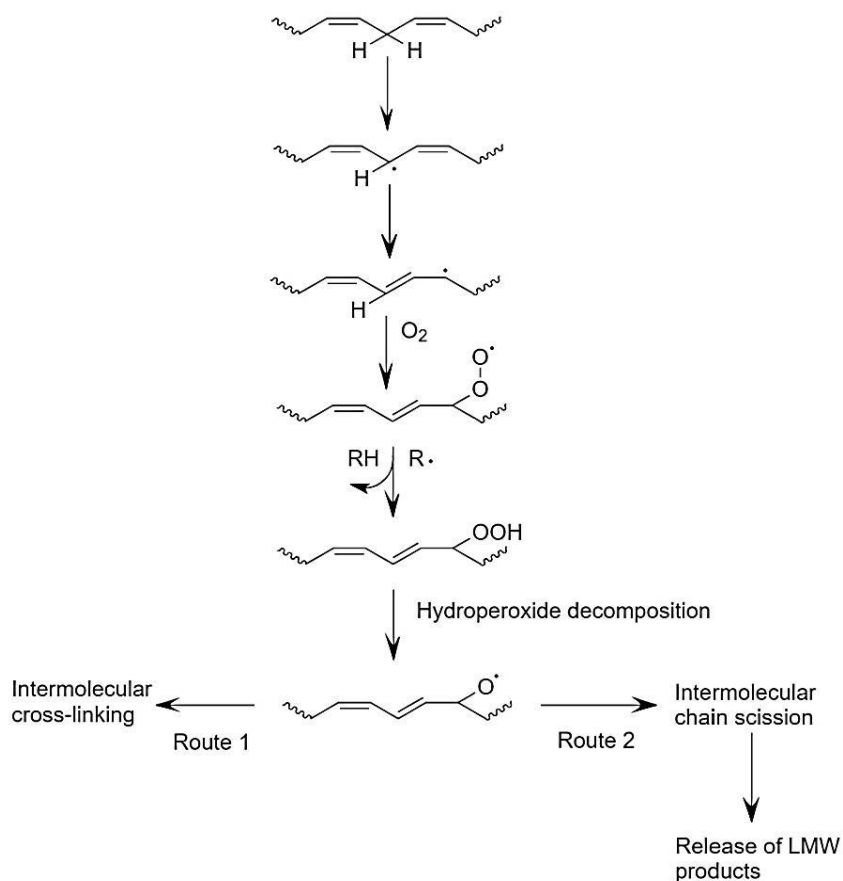


Figure 3.6: scheme of linseed oil radical reaction with formation of LMW products and cross-links from unsaturations. Both products have the same composition of the original compounds, although in the first stages of oxidation chain scission prevails. *Adapted with permission from ref [290]. Copyright John Wiley and Sons.*

3.2.2.1 ATR-FTIR spectroscopy results

The following spectra were collected on fresh, touch-dry and photo-aged films of linseed oil (50 ± 10 μ m thick) (Figure 3.7). Observations with FTIR spectroscopy of the spectral features before and after 24 h drying and 2,200 h of photoaging are reported below:

- decreasing of C=C at 3013 cm^{-1} $\nu_s(\text{=C-H})$, 1653 cm^{-1} $\nu(\text{cis C=C})$, and 726 cm^{-1} out-of-plane vibration $-(\text{CH}_2)$ and $-((\text{CH})=\text{CH})$ in the first 24 h;

- formation of a broad and intense band at 3470 cm^{-1} $\nu(\text{O-H})$ due to hydroxyl groups, with maxima at 24h, then lowered throughout photoaging;
- broadening of the carbonyl band at 1747 cm^{-1} (C=O) due to carboxylic species, showing complete loss of C=C double bonds at 1653 cm^{-1} throughout photoaging;
- yellowing of the film due to conjugated double bonds appearing after 24 h treatment.

During the first 24 h, structural changes of the liquid oil forming a 3D rubbery film mostly constituted by insoluble species have been observed (Figure 3.7 b). Further, the increase of hydroxyl group shown by the broad band centered at 3470 cm^{-1} was observed in association with the disappearance of the double bonds at 3011 , 1653 , 726 cm^{-1} . As well-known from the literature [138,139,296], the spectral changes on the film aged 2,200 h were comparable to those occurred in the first 24 h of treatment, except the complete disappearance of some peaks and the reduced intensity of some others (Figure 3.7 c).

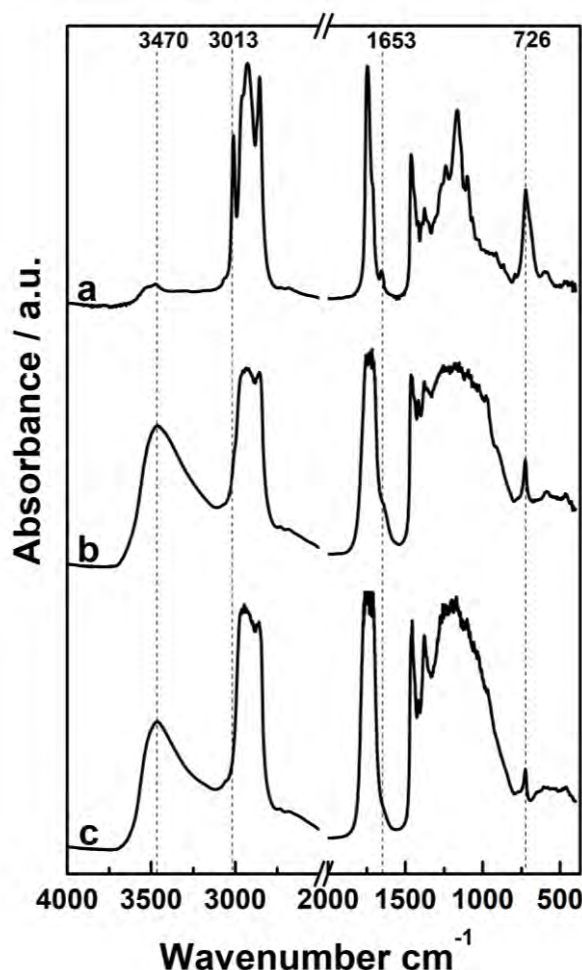


Figure 3.7: FTIR spectra from oxidized linseed oil: photooxidized (2,200 h - a), touch-dry (24 h - b) and fresh (0 h - c). Adapted with permission from ref [290]. Copyright John Wiley and Sons.

3.2.2.2 SEC results

SEC is an extremely powerful method to separate molecules by size through a porous stationary gel and an eluting mobile phase (*e.g.* THF). Intuitively, species with lower molecular weights are eluted later than heavy molecules. The intensity of the peaks refers to the average molecular weight distributions of the molecule in the eluted phase. SEC seemed the most appropriate destructive technique to build evidence on the detection of LMW compounds and contrast the results obtained with SERS. SEC allowed to discriminate small polymeric fragments ranging between 0.2 and 1 kDa against PS narrow distribution standards.

Later in this section, it will be shown that SERS reaches much lower detection limits compared to SEC, and that is an interesting novelty in the field of polymer science. However, the relevance of both methods to determine the reliability of SERS was crucial. SEC hinted the presence of chain fragments from the soluble fraction of the photooxidized film of linseed oil (2,200 h), and triglyceride components from the raw sample (Figure 3.8). The curve of the raw oil reported in black showed a triglyceride component, with a huge and narrow peak at 9.5 min, impurities and free fatty acids eluted at longer retention times.

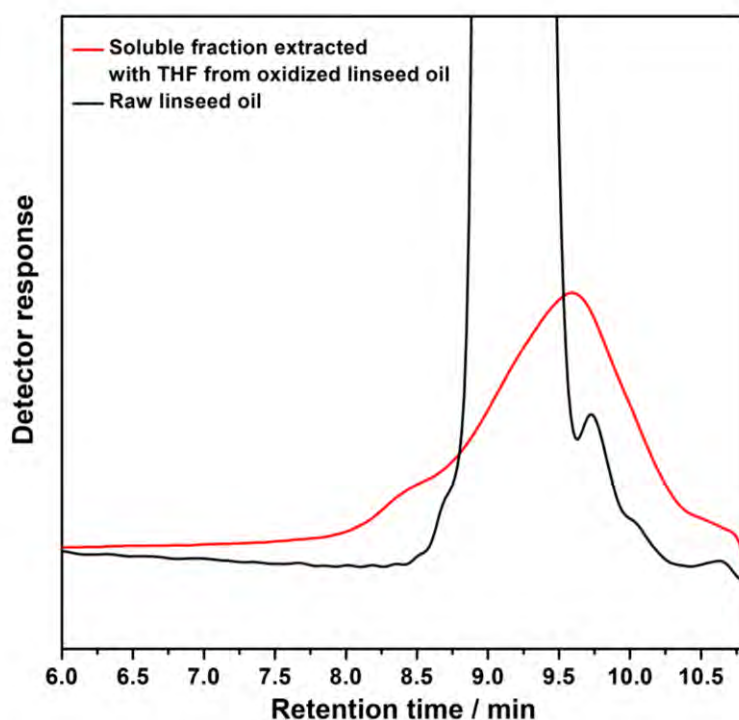


Figure 3.8: normalized SEC curves from raw linseed oil (black), and soluble fraction extracted with THF from 2200 h photoaged film (red). Adapted with permission from ref [290]. Copyright John Wiley and Sons.

On the other hand, soluble fractions extracted with THF corresponded roughly to 5 wt.% of the initial sample and comprised fractions of unpolymerized triglycerides hinted in the peak at around 8.5 min in red (Figure 3.8). Additionally, a broad and low peak eluted at about 9.6 min presented a thin and long tail. The shoulder might be due to short fragments formed by β -

scissions. Comparing raw and aged linseed oil, number average molecular weights were smaller in the oxidized oil than in the raw oil, respectively 400 against 950 Da. As expected, SEC has been a useful tool to detect the formation of LMW compounds. To notice that the amount of sample solubilized was ≤ 3 mg, requisite that makes the technique definitely invasive and destructive in heritage science applications.

3.2.1.3 Py-GC/MS results

If SEC allowed separating the molecular fragments by size, Py-GC/MS identified them after ionization and through mass spectrometry. LMW products from auto-oxidation were addressed through the thermally assisted hydrolysis and methylation pyrolysis gas-chromatography mass spectrometry version available at the USC Faculty of Biology (TAHM Py-GC/MS).

Fatty acids methyl esters (FAMES) belonging to saturated and unsaturated fatty acids were detected and can be ascribed to the triglycerides from linseed oil as follows: linoleic (FAME C18:2), linolenic (FAME C18:2), palmitic (FAME C16), stearic (FAME C18:0), oleic (FAME C18:1). Additionally to methyl esters from saturated fatty acids (palmitic and stearic), the photoaged films presented unsaturated mono and diacid methyl esters ascribed to azelaic acid (DAME C9:0). Azelaic acid (nonanedioic acid methyl ester) is considered the best marker related to the oxidation of linseed oil [139,297]. It is the most abundant product of oxidation given that most oil components have a high degree of unsaturations bearing double bonds in position C₉. At least two paths of degradation were reported [138,295], suggesting β scissions of alkoxy radicals might generate unstable vinyl radicals or alternatively, more stable allylic intermediates associated to azelaic fragments.

As the drying proceeds in the first few hours, oxidation, subsequent crosslinking and hardening of the film take place, and azelaic acid starts being detected in modest amounts (Figure 3.9). Various samples were treated using natural and accelerated photoaging methods, combined with the PDMS strip sampler method of microextractions. A naturally aged linseed oil film (1,700 h in laboratory) was gently pressed onto a sampler and the molecular fragments were transferred with THF for subsequent chromatographic analysis.

Figure 3.9 shows that azelaic acid was detected. It is worth mentioning the GC/MS is a highly convenient technique for the identification of small molecular fragments; however, it is not sensitive enough for the small amounts of sample as those extracted by physisorption with the PDMS strip sampler proposed in the current research. It was not possible to weight the extracts for lack of appropriate scales, but it was estimated in the order of ng. The electrostatic interactions of PDMS for the linseed oil fragments apparently did not affect the selectivity of the oil components, being the ratios of the peaks recorded in accordance with those published for touch-dry oil samples [138,139].

In addition to azelaic acid, linoleic, linolenic and palmitic acids were detected as further components naturally found in linseed oil naturally aged. Peaks attributable to siloxanes were also present (marked with*), and can be ascribed to a negligible solubilization of the strip sampler, easy to detect with GC/MS. This information poses the basis for the further use of ultrasensitive SERS sensors, as it has been demonstrated that well-known markers of

degradation can be transferred with the strip sampler from mildly aged samples of model polymeric films. Py-GC/MS combined with the sampling through PDMS sampler allowed the identification of those markers.

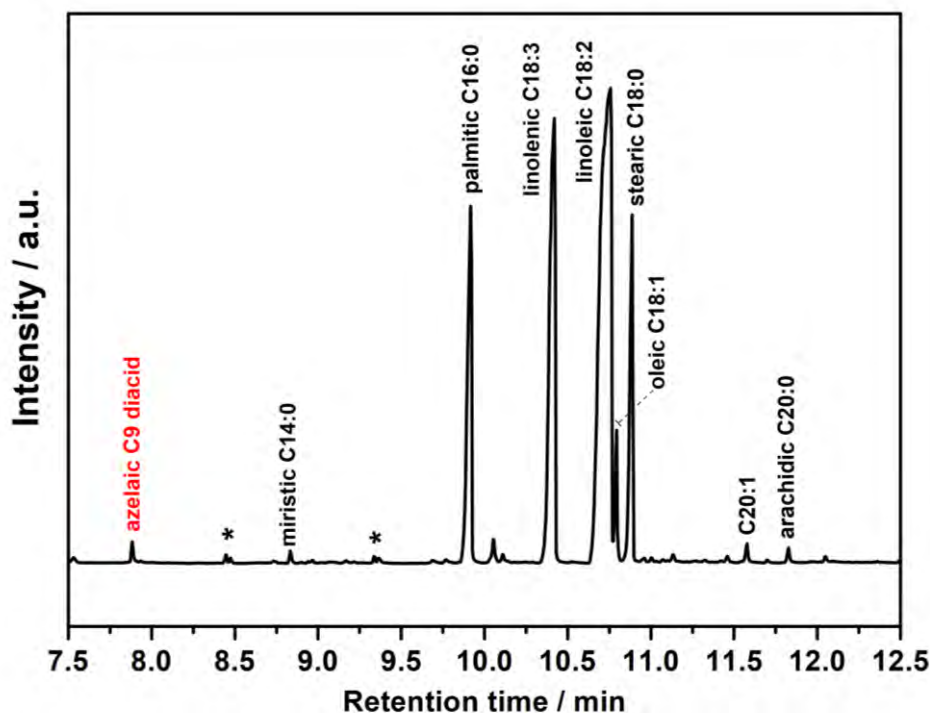


Figure 3.9: TAHM Py-GC/MS chromatogram of naturally aged linseed oil (1,700 h in natural conditions) sampled with PDMS strip sampler and THF to transfer the molecular fragments. Adapted with permission from ref [290]. Copyright John Wiley and Sons.

Furthermore, a fragment of photoaged linseed oil film (2,200 h) was solubilized in THF and the resulting soluble fraction was injected into the chromatograph. Figure 3.10 confirmed that azelaic acid is the main product of degradation of linseed oil. Published data report analysis of the oil at different aging times to study the kinetics of formation of linseed oil [138]. Similarly in the present analysis, linolenic, linoleic and oleic acids have been completely consumed with aging, whereas azelaic (DAME C9:0) and caprylic (FAME C8:0) acids show higher concentrations compared to the very initial stages of drying. Suberic acid (DAME C9:0) instead appeared at later stages. Also, intense peaks of residual palmitic and stearic fatty acids (FAME C16:0 and C18:0 respectively) have been detected.

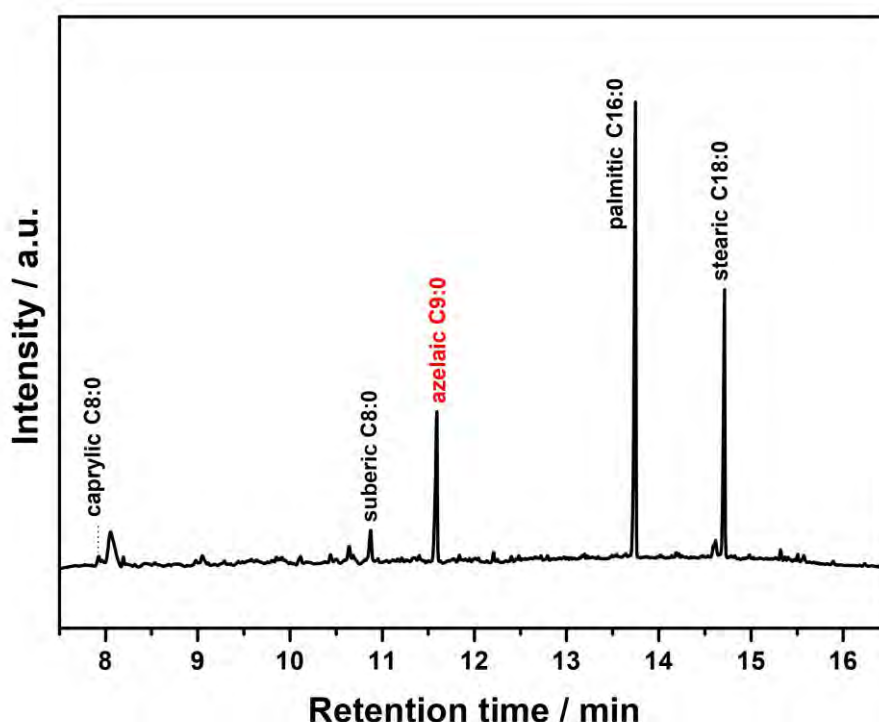


Figure 3.10: TAHM Py-GC/MS chromatogram of artificially aged linseed oil (2200 h in lab conditions) from fragment of the film solubilized with THF. Adapted with permission from ref [290]. Copyright John Wiley and Sons.

3.2.2.4 Raman spectroscopy and SERS sensing results

In general, Raman spectroscopy offers high sensitivity to double bond vibrations, while SERS lowers the limits of detection minimizing the amounts of analyte necessary to generate intense distinctive signals. In this research, SERS enabled to quench the inert fluorescence of linseed oil with both lasers utilized for the measurements ($\lambda_{exc} = 514$ and 785 nm). For this model simulation, KLARITE[®] replica substrates with inverted pyramids Al-coated were utilized. An approximate amount of 20 ng of raw linseed oil was dropped on the SERS substrate and Raman benchtop measurements were collected on the fresh and touch-dry film after 24 h, respectively Figure 3.11 a, b.

Raw oil showed a spectrum (Figure 3.11 a) featuring a band at 3013 cm^{-1} $\nu(\text{C-H})$ and quite pronounced $\text{C}=\text{C}$ unsaturations at 1656 cm^{-1} . However, observing the SERS spectrum in Figure 3.11 b, it is evident the rapid loss of intensity of the band at 1656 cm^{-1} after 24 h. Simultaneously, the band at 1264 cm^{-1} $\rho_s(\text{C}=\text{C})$ inverted the intensity with the neighbor band at 1302 cm^{-1} in-phase $\tau(\text{CH}_2)$. Although with Raman spectroscopy, the carbonyl features are less intense, the peak at 1747 cm^{-1} started to arise and broaden in association to the formation of various carboxylic species recorded.

Finally, the SERS spectrum in Figure 3.11 (c) was obtained by gently applying the PDMS sampler onto the surface of the photooxidized film (2,200 h) for 30 s, and subsequent transfer of the polymeric fragments with acetone to the SERS substrate. The bands at 3013 , 1654 , 1264 cm^{-1} disappeared due to the complete loss of $\text{C}=\text{C}$ bonds. Carbonyl features at 1747 cm^{-1} were even more pronounced than those in the touch-dry sample. Once again, the

increase and broadening of such a weak Raman signal confirmed ongoing chain scission mechanisms coherent with photooxidative processes [138,139,145,295].

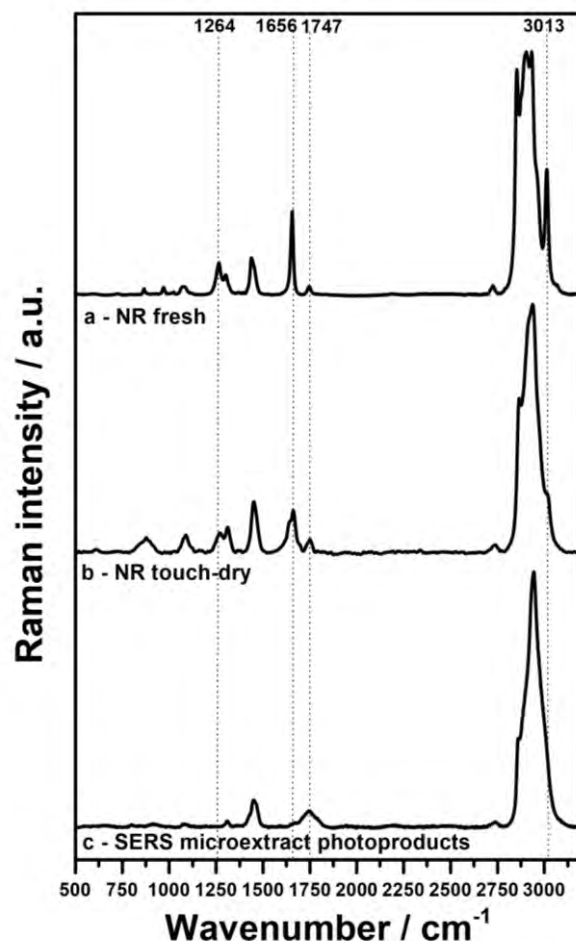


Figure 3.11: Raman and SERS spectra on linseed oil films at different aging times (λ_{exc} 785 nm). A) fresh raw oil; b) touch-dry film (24 h); c) microextract with acetone and strip sampler for the surface of a film photoaged 2220 h. Adapted with permission from ref [290]. Copyright John Wiley and Sons.

For the inherent differences among the two instrumental methods, it was not possible to establish an exact matching of LMW compounds detected by SEC with those detected with SERS. However, the SERS-based analytical procedure proposed has shown sufficient sensitivity for the detection of such fragments and to the best of the current available knowledge, no similar attempts have been yet explored. Such evidence posed the bases for further developments of the sampling method. The amount of sample necessary for a reliable SERS measurement was calculated as 10^{-10} g⁷ by using standard solutions at known concentrations of rhodamine 6 G and coumarine on KLARITE[®] replica substrates [298].

⁷ The amount of small molecules was estimated by comparing SERS intensities from extracts of standard rhodamine 6 G and coumarine at known concentrations.

3.2.2.5 Solvents polarity, oligomeric fragments and Raman sensitivity

Selective sampling of the free molecules from the aged surfaces was possible by tuning the solvent extraction to the features of the analyte. As presented in sections 2.2 and 3.1.2 on the sampling strip fabrication, either polar and nonpolar molecules stick to the surface of the PDMS. Tests with narrow distributions of standards of PS and PEG confirmed this finding (section 3.1.3). Published Raman spectra on the selectivity of the solvents show that completely nonpolar solvents, such as hexane, performed differently from highly polar water [209]. Acids and esters formed during the oxidative process and showed a greater affinity with the polar solvents, as water. Progressively with EtOH, CHCl₃ and THF, SERS spectra showed less features in the carbonyl region, disappearing with hexane. Furthermore, the aliphatic bands at 250, 400, 600, 1300, 1550, 1580 cm⁻¹ informed on the removal of nonpolar molecules with the PMDS strip samplers. Tuning the polarity of the solvents to the analyte allowed the selective removal of degradation markers at very low concentrations [298].

3.2.2.6 Summary

- Linseed oil was selected as a model material because it behaves as a polymer in terms of aging performance, forming hydroperoxides and other compounds from primary and secondary reactions of chain scissions during auto-oxidation.
- FTIR spectroscopy allowed to monitor increase and disappearance of bands related to the formation of species indicating the early stages of chain scission in polymers, (C=O and C=C), therefore considered degradation markers.
- SEC on soluble fractions of oxidized films of linseed oil compared to raw oil provided evidence of formation of LMW compounds.
- Py-GC/MS allowed detecting azelaic acid on photoaged films of linseed oil, either analyzing soluble fractions, or transferring LMW products with the PMDS strip samplers. Azelaic acid considered the best marker of degradation of linseed oil was detected at increasing aging times.
- NR signals and SERS microextracts confirmed the detection of species derived from oxidized surfaces of linseed oil films with multiple excitation wavelengths;
- SERS sensing in combination with the PDMS sampler method has been proposed as a reliable nanodestructive alternative to SEC.

3.2.2 ABS aging behavior

In this section, the rationale followed to introduce the findings on ABS aging behavior will replicate that used for linseed oil. However in the current research, ABS was the polymer characterized more in-depth compared to PI and PVAc. For example, the role of O_2 diffusion in coated films, as well as discoloration will be discussed in Annex 3.1 only since they contributed indirectly to build the evidence for SERS sensing. Traditional characterization methods, as FTIR spectroscopy and DSC, will lay the foundations to explain the full potentials of SERS sensing. In the literature, thermal and photooxidative studies on ABS and styrene polymers are numerous [149–151,292,299–302]. The most important aspect of ABS weathering described targets the mechanisms of carbonyl and hydroxyl formation, usually accompanied by weight loss data. In this research, photo and thermal aging treatments were performed on ABS films to promote the formation of degradation markers for subsequent testing with ultrasensitive SERS sensors. In the literature, the formation of ketones, aldehydes, esters, and unsaturated carbonyl compounds is reported, following the mechanism in Figure 3.12.

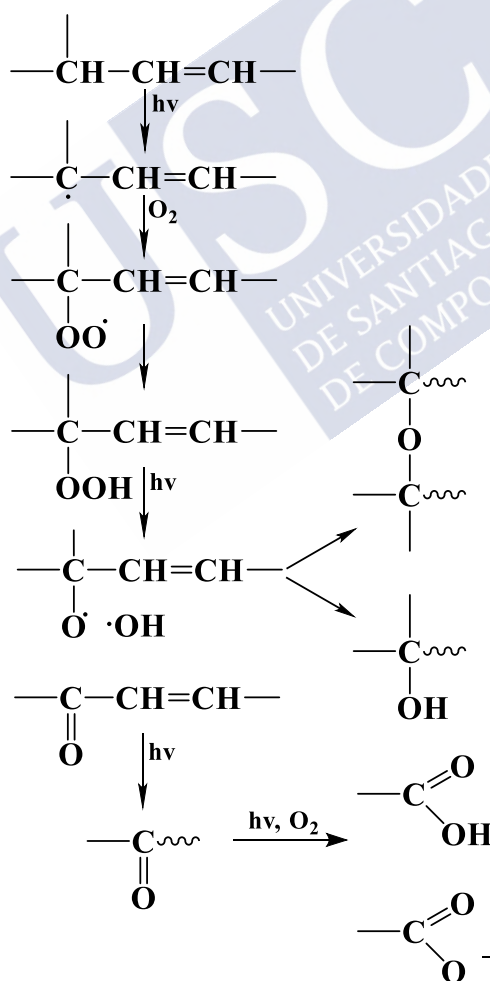


Figure 3.12: scheme of ABS photooxidation.
Adapted with permission from ref. [149].
Elsevier LTD.

Gardette *et al.* [149] reported photooxidative studies on ABS films and tackled the formation of several species reflected in the changes of FTIR spectral features. The absorbance in the carbonyl region (1718 cm^{-1}) was reported to be very fast in the first 60 h of treatment, and hydroperoxides could be determined by titrations. Primary hydroperoxides initiate forming in the α positions of PB nodules transferring to the C=C unsaturations. The $\alpha\beta$ -unsaturated ketone species manifested as a shoulder at 1695 cm^{-1} appearing after prolonged exposure. Similarly, carboxylic acids and esters showing bands at 1718 and 1736 cm^{-1} are usually determined with ammonia treatments. Possible ethers species are hinted by the increase of bands at 935 and 1060 cm^{-1} , while those at 1170 , 1265 , 1340 and 1736 cm^{-1} referred to esters $\nu(\text{C}=\text{O})$. In the OH region, increased absorption attributable to the formation of alcohols and carboxylic acids is recorded.

In general, the heterogeneity of the photooxidation products has microscopic and macroscopic explanations. The former depends on the relative size of the PB nodules, acting as centers of oxidation, in the matrix of SAN, generating a relatively high permeable copolymer. The latter depends on the layers of oxidation products forming independently of the thickness of the film. Further, the kinetics of O_2 diffusion has a role in the distribution of the oxidation products: surface C=C unsaturations are consumed earlier, whereas those in the core of the film remain unvaried for longer exposure times [86]. Finally, a macroscopic effect of degradation is discoloration and loss of transparency of the film that will be addressed in Annex 3.2 (ΔE and Δb^* values are presented comparing coated and uncoated ABS).

Coated and uncoated samples were treated to mimicking conditions as close as possible to those of naturally aged objects in museum collections. Accelerating factors derived from studies on naturally aged objects in museums were not available, therefore industrial polymer studies were considered [86,96]. Photoaging tests were conducted on 7 uncoated and 16 coated films provided by the project partners for 400 and 500 h, respectively. Figure Annex 3.3 shows photographs of the uncoated and coated ABS films before and after treatment. For coated films, ATR-FTIR spectral acquisitions in the initial stages of treatment up to 150 h were considered unnecessary, primarily because the same process was simultaneously being investigated by analysis the uncoated films. Also it was expected that the most damaging events of reactive chain scission would be lowered by the presence of the coating. Concurrently, properties such as light transmission, adhesion and compatibility with the substrate were observed, along with the gloss retaining [128,148,294].

3.2.2.1 Photooxidative aging behavior of ABS: FTIR spectroscopy results

Routine screening with diagnostic tools for rapid detection on polymer-based objects for preventive conservation purposes were envisaged by conducting the preliminary aging herein presented. In general, the oxygen diffusion rate in the matrix is controlling the kinetic of photooxidation reactions [130]. During photoaging treatment, a number of ATR-FTIR spectra were collected at approximately 10, 24, 45, 100, and 400 h ranges to confirm the aging trends reported in the literature [148,149,292]. Figure 3.13 shows comparative ATR-FTIR normalized spectra obtained from ABS films photoaged in Suntest equipment ($\lambda > 300\text{ nm}$). As expected, most dramatic changes occurred within the first 10 h treatment. $\text{C}\equiv\text{N}$ (2237

cm^{-1}) vibration is attributed to SAN which is more stable than the PB components. Since the nitrile mode did not show changes in relative intensity during aging, it was selected to normalize all spectra for meaningful data comparison. Similarly, the relative intensity of the PS bands in SAN remained constant during aging, namely bands at 700, 765, 1028, 1449, 1456, 1495, 1582, 1600 cm^{-1} showed negligible increase.

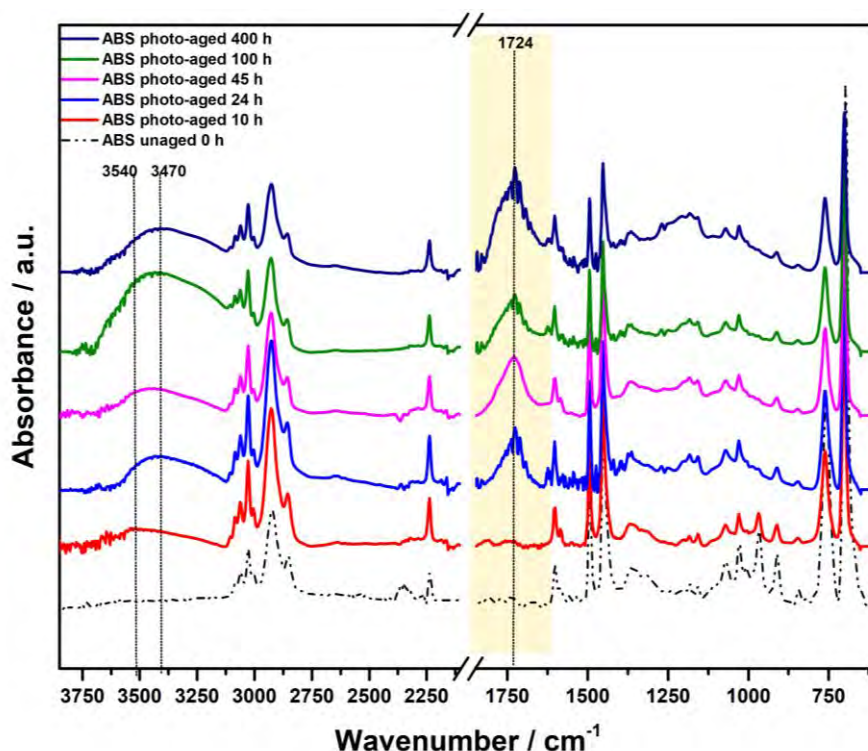


Figure 3.13: ATR-FTIR normalized spectra of ABS films exposed up to 400 h of photooxidation ($\lambda > 300\text{ nm}$). Dashed bars show rapid peaks increase (1175 , 1640 , 1697 , 1721 , 1730 , 1783 , 3470 , 3540 cm^{-1}) and progressive peak disappearance (913 , 964 , 1060 , 1600 cm^{-1}) during accelerated aging.

Carboxylic acids, hydroxyl absorptions (alcohols and hydroperoxides), aldehydes and ketones had been previously determined by reaction with acyl fluorides [302]. In the current experiments, increase of absorbance in the $\text{C}=\text{O}$ region was recorded after 10 h treatment. A broad peak with a maximum centered at 1730 cm^{-1} was observed together with shoulders at 1697 , 1721 , 1783 cm^{-1} . The intensity of the band centered at 1721 cm^{-1} increased after 10 h shifting to 1730 cm^{-1} from 24 h to the end of the treatment. Similarly, the slight shoulder at 1783 cm^{-1} appeared after 24 h treatment and maintained a constant increase rate until completion of photoaging.

Hydrogen abstraction was extensively reported to occur preferentially on the carbons from $\text{C}=\text{C}$ double bonds in α -position of BR [88,141]. Further changes could be observed in positions 913 and 966 cm^{-1} (C-H deformation vibrations), respectively symmetric stretching of 1,2 vinyl and *cis* 1,4 from BR. These two peaks decreased rapidly at 10 h treatment and disappeared completely at 400 h. In addition, the vibration at 1175 cm^{-1} was ascribed to the

lactone structures and the one at 1060 cm^{-1} to crosslinking and $\alpha\beta$ unsaturations ether bridges and $\alpha\beta$ unsaturated alcohols [149].

The C-O region ($1400\text{--}1000\text{ cm}^{-1}$) presented increased vibrational intensities associated to a slight deformation of the maxima. Further relevant changes were observed in the carbonyl C=O ($1600\text{--}1800\text{ cm}^{-1}$) region. After 24 h photooxidation, the increase of different species in the carbonyl region was confirmed by the presence of a broad peak with maximum at 1730 cm^{-1} and shoulders at 1697 , 1721 , 1783 cm^{-1} . Finally the hydroxyl O-H ($3000\text{--}3500\text{ cm}^{-1}$) region showed the extensive increase of a broad band initially centered at 3540 cm^{-1} after 10 h treatment, then shifted to 3470 cm^{-1} , and increasingly stable until 400 h aging.

As presented, several photoproducts formed during photooxidative treatment. The evolution of the FTIR spectra can be considered quite similar to that of photoaged PB [150], but quite different from PS reported in the literature [149,299]. The heterogeneity of the terpolymer structure in the film has been causing differential oxygen absorption, hence consistently higher rates of aging for the rubbery phase (FTIR spectra collected on coated samples are in Annex 3.4).

3.2.2.2 Thermoxidative aging behavior of ABS: FTIR spectroscopy results

LMW oxidation products forming during thermoxidative aging were not sufficiently concentrated to perform the sampling with the PDMS strip method. Besides not being completely certain of this outcome before the experiments, it seemed appropriate to investigate thermoxidative conditions to deepen the general understanding of ABS behavior.

Processes occurring below the T_g are representative of the long-term behavior of the polymer under thermal stress at room conditions [81,86,151]. The physical and mechanical properties of the materials remain the same during heat supply. On the contrary, thermal degradation occurs when the heat supply modifies the physical properties of the material and severe distortions at molecular level are introduced, including occurrences of phase changes(*e.g.* melting) [141]. The T_g of ABS is $105\text{--}107^\circ\text{ C}$. The experiments herein presented were conducted at 60° C up to 500 h treatment.

Figure 3.14 shows ATR-FTIR spectra collected on mildly thermoxidative aging of ABS films. In the initial hours of experiment, compared to photooxidized films, ATR-FTIR spectral features have changed less drastically. However, after 80 h appreciable and stable changes have been observed in the carbonyl region, with a maximum centered at 1731 cm^{-1} . Annex Figure 3.5 shows the photographs of thermally unaged and aged ABS films.

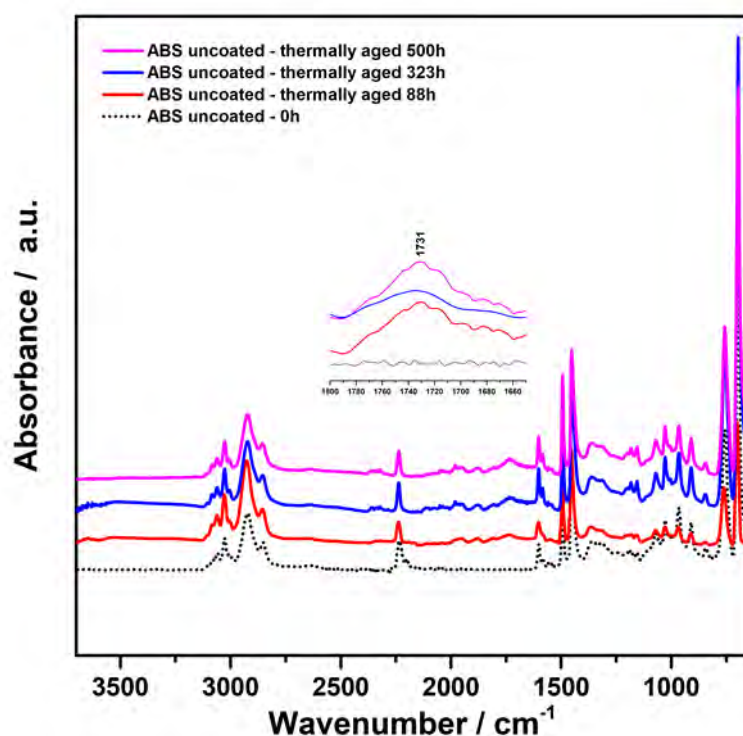


Figure 3.14: ATR-FTIR normalized spectra of ABS films exposed to 500 h of thermal oxidation at 60 °C. The insert shows the changes occurring during aging on the carbonyl region with the increase of several maxima centered at 1731 cm^{-1} .

3.2.2.3 DSC results on ABS

DSC allows comparing an unknown sample to a reference submitted to the same conditions of heat flow, duration, reaction atmosphere, and cooling rate. Experimental evidence suggests that for the majority of thermoplastics (*e.g.* ABS, PVAc) exposure to changes of temperature just below their T_g implies softening and subsequent increased flexibility of the material [81,84,86,303,304]. Instead, elastomers have a very low T_g , which enables them to show a high degree of relaxation and deformation at room temperature. Finally, thermosets present variable T_g values, hardening and crosslinking at increasing temperatures (*e.g.* epoxies). Overall, it is said that polymer molecules have a motion regime of cooperative relaxation in the temperature range around their T_g [81]. Opposite to liquids or melts, in plastics the complete flow of molecules is prevented by the crosslinks present between molecules, even in the rubbery state.

To reset the thermal history of the material [305,306] all values of T_g were derived from the second run of measurements with DSC equipment. During accelerated aging T_g showed lowering trends, although minimal changes were recorded. DSC curves were obtained at 0-141-391-419 h photoaging treatment. The presence of unknown additives and stabilizers in the analyzed films might be the reason for the increase up to $\sim 111^\circ\text{C}$ of the T_g (0 h). Consistent shifts towards lower T_g in aging experiments are reported for treatments longer than 1,000 h [307,308]. However, in these experiments the variations are not meaningful (Table 3.3).

Table 3.3: glass transition temperature (T_g) in ABS films

Aging time (h)	T_g (°C)
0	111
141	110
391	107
415	111

3.2.2.4 SEC results on ABS

SEC tests were carried out to determine if the molecular weight distributions lowered, as expected, during photo and thermal oxidative treatments. Exploring this aspect through classic chromatographic methods provides evidence to partially address the research question proposed in the current thesis: *can we detect LMW compounds from the surface of oxidized polymeric samples?*

Figure 3.15 shows normalized SEC curves obtained from fragments extracted from ABS films at different aging times (approximately 0, 24, 45, 60, 100 and 400 h). Samples were diluted according to the sensitivity of the detector and injected in 200 μ L syringes. THF was used as eluting solvent, as well as to solubilize the aged/unaged samples before filtration and injection into the column. The initial average molecular weight, *i.e.*, $M_n = 70$ kDa, decreased down to around 40 kDa after 500 h of photoageing, with an increase of the polydispersity index from 3.4 to 7.5, revealing the simultaneous development of limited crosslinking and chain scission processes. Currently, there are no other methods available to detect LMW compounds from oxidized surfaces non-destructively and non-invasively. SEC among all techniques is the only one determining, although qualitatively, M_n and M_w data directly connected to the chain scission mechanisms and LMW oxidation products. As introduced for the experiments on the linseed oil research model, a direct correspondence between SEC and SERS data is not available, but it is again safely assumed that molecules detected with the SERS sensors are actually LMW products of degradation of ABS hinted by SEC chromatograms.

Although the results presented on ABS oxidative behavior are not innovative, they were essential to have an in-depth comprehension of its degradation mechanisms allowed to expect photo-products that will be confirmed through SERS sensing in the upcoming section (SEC molecular weights for coated and uncoated samples are in Annex Table 3.6).

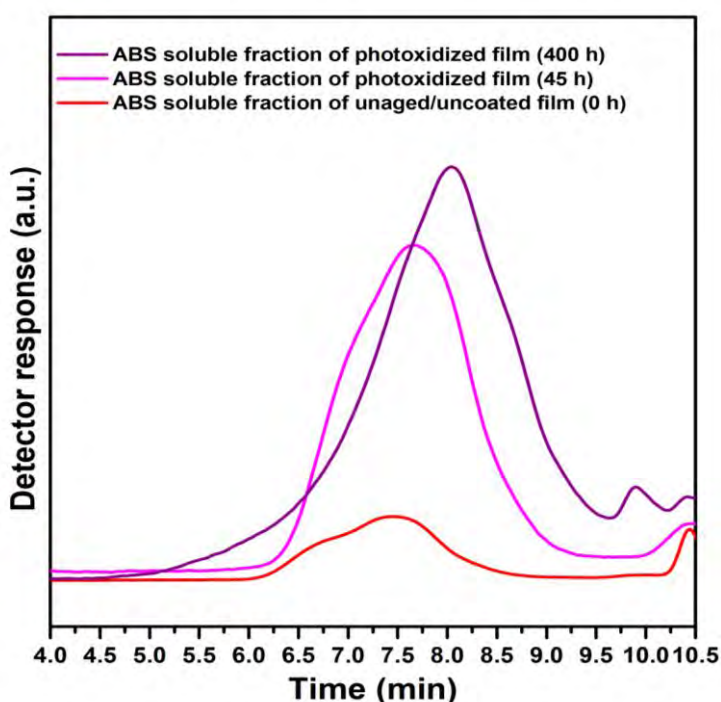


Figure 3.15: normalized SEC curves of ABS samples at 0-45-400 h photoaging treatment. THF was used as eluting solvent and to extract the soluble fraction on the photoaged film.

3.2.2.5 SERS sensing and limits of detection of LMW oxidation products in ABS

Figure 3.16 (a-f) shows stacked SERS spectra obtained from microextracts with THF and CHCl_3 on aged ABS films (150 and 400 h) compared to a NR spectrum from unaged ABS (Figure 3.16 g). KLARITE[®] replicas were fabricated with various PFPEs derivatives. An InVia Flex Raman spectrometer with 514 nm excitation wavelength, 0.09 mW power, and 1800 lines mm^{-1} grating was employed for the measurements. Nominal punctual spot diameter was 4.2 μm . Acquisition time ranged between 10 and 30 s. Dotted spectra (b, e) will be discussed at the end of the section. An overall **assignment** of the Raman bands will be discussed, deepening the features added by the **sampling method** and **solvent interaction** with the plasmonic surface. Furthermore, **mechanisms of degradation** will be additionally explored through observation of the spectra from aged samples. Finally, additional **outliers** will be included to extend the published data [38].

The typical vibrational modes of ABS components are the nitrile band of **acrylonitrile** at 2242 cm^{-1} , the aromatic ring of the **styrene** component at 1602 , 1580 and 1003 cm^{-1} , the double bond of *trans* **butadiene** at 1667 cm^{-1} (Figure 3.16 g) [51,147]. The typical band shape with maximum at 750 cm^{-1} informs on the presence of **SAN** copolymer [309]. Usually, the ratios between components vary upon processing, thus reflecting in the spectral features. Despite the concentration of photoproducts removed with PDMS was unknown but predictably very low, SERS could positively identify signals from oligomers derived from the

chain scissions of the terpolymer. The composition of the degradation markers was expected to be similar to that of unaged ABS.

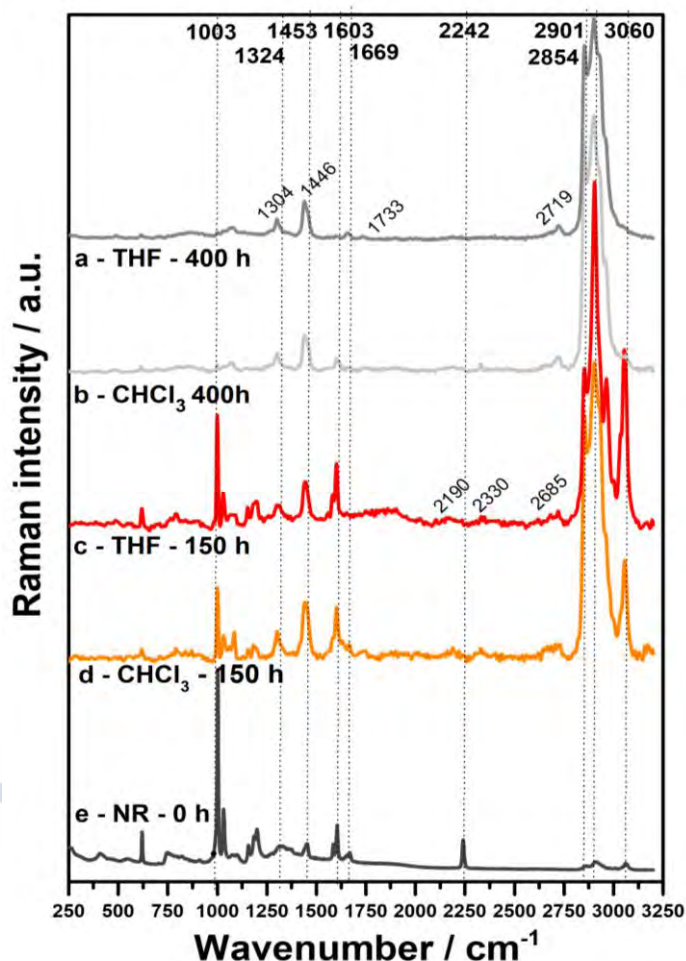


Figure 3.16: SERS microextracts on photooxidized ABS films with PDMS strip sampler: a) 400 h photoaged sample transferred with THF (replica FLUOROLINK®); b) 400 h photoaged sample transferred with CHCl_3 (replica FLUOROLINK®); c) 150 h photoaged sample transferred with THF (replica PFPE); d) 150 h photoaged sample transferred with CHCl_3 (replica PFPE); e) normal Raman spectrum on unaged ABS film (0 h).

Selective sampling of free molecules introduced in the model study on linseed oil (section 3.2.2.5) was confirmed for ABS. Polita *et al.* [310] reported evidence of the effects of solvents polarity and viscosity on the surroundings of macromolecules during extractions. Polarity and proticity of the solvent tune the selectivity of polar and nonpolar molecules. THF and CHCl_3 have relatively low polarity values, 9.1 and 9.3 respectively. Compared to CHCl_3 , THF facilitates mass transfer [311]. In addition, micro-viscosity of such molecular liquids might explain some vibrational shifts frequently reported in Raman spectra [51,147].

Table 3.4 summarizes the approximate band positions, intensities and assignments of unaged ABS analyzed with normal Raman with SERS microextracts obtained from oxidized ABS surfaces with the PDMS strip sampler (150 and 400 h treatment).

Table 3.4 Approximate band position and Raman/SERS assignments of ABS and photooxidation products

ABS 0 h (cm ⁻¹)	Intensity ^a	ABS 150 h (cm ⁻¹)	Intensity ^a	ABS 400 h (cm ⁻¹)	Intensity ^a	Assignment ^b
3060	w	3060	s	-	-	ν (=C-H) of benzene ring
-	-	3004	sh	3004	sh	ν_{as} (=C-H) of -CH=CH-R
-	-	2977	sh	-	-	ν (C-H) aliphatic
-	-	2968	sh	2968	sh	ν_s (CH)
2901	w	2901	s	2901	s	ν_{as} (CH ₂)
2854	w	2854	s	2854	s	ν_s (CH ₂)
-	-	2719	m	2719	m	-
-	-	2681	w	-	-	-
-	-	2330	w	2330	w	-
2242	s	-	-	-	-	ν (C $\equiv$ N)
-	-	2180	m	-	-	-
-	-	-	-	1733	w	ν (C=O)
1669	m	1669	sh	1669	w	ν (C=C trans)
1603	s	1605	s	1605	w	ν_s (C-C) of benzene ring
1580	m	1587	sh	1587	w	ν_{as} (C-C) of benzene ring
1453	m	1445	s	1445	s	δ_s (CH ₂)
1323	w	1304	s	1304	s	δ (CH ₂)
1200	s	1200	s	-	-	ν_s (C-C)
1179	sh	1179	sh	-	-	δ (C-H) in-plane of benzene ring
1153	sh	1153	sh	-	-	δ (C-H) out-of-plane of benzene ring
1102	w	-	-	-	-	ν (C-C) out-of-plane
1077	sh	1083	m	1083	w	ν (C-C) out-of-plane
1032	s	1032	s	-	-	δ (C-H) in-plane of benzene
1003	s	1003	s	-	-	Benzene ring breathing
904	w	-	-	-	-	ν (C-C)
750	m	-	-	-	-	CH ₂ resonance
624	s	617	m	617	w	δ (ring) of benzene

^a s: strong; m: medium; w: weak; sh: shoulder.

^b ν stretching; δ bending; s symmetric; as asymmetric.

In the first phase of treatment (150 h), spectral features were coherent with the formation of PB fragments reflected in increased absorptions at 2901, 2854, 1603, 1446, 1003 cm⁻¹ (Figure 3.16 d, f). To observe the overall inversion of the relative intensities of the bands in the aliphatic region (3080-2850 cm⁻¹) in comparison to those of the aromatic rings (1100-990 cm⁻¹), further corroborating the expected high concentration of the PB photoproducts [150,292].

In the second phase of treatment (400 h), typical ν (=C-H) of the benzene ring at 3060 cm⁻¹ disappeared, as well as the bands attributed to the aromatic ring of the styrene at 1602, 1580 and 1003 cm⁻¹. However, in addition to the δ (CH₂) modes, further residues of acrylonitrile were hinted by two medium/weak intensity bands in the ν (C $\equiv$ N) region (Figure 3.16 a, b, c) [312]. However, upon solvent transfer to the SERS substrate, spectra a, c, d, and f show the substitution of the band at 2242 cm⁻¹ with two new bands, respectively at 2330 and 2190 cm⁻¹.

Nitrile band in Raman spectra is usually reported at 2237 cm^{-1} [147,148,211]. However, the relaxation of the Raman nitrile stretching modes observed in the current research was also observed by other authors in the past [313–315]. The influence of the solvent on the dephasing of the vibration was explored through different theories, including the model and the resonant energy transfer [316]. The former explains the relaxation as the effect of a macroscopic body (liquid) embedded into a viscoelastic medium (polymer). The latter explains dephasing as a transition-dipole/transition-dipole energy transfer generating resonance. Overall, in molecular liquids dispersion forces and hydrodynamics perturb neighbors. Nitrile stretching relaxation, band broadening and new transitions can be attributed mostly to ‘environmental’ effects, among other possible contributions [315]. Nitrile-bearing species are highly polar and the affinity with the solvent must have played a crucial role in the selective removal from the PDMS strip sampler. Intermolecular hydrogen bonding with the acidic component of CHCl_3 and THF is coherent with the composition of oligomers transferred. Hydrogen bonds affect the solvent-analyte molecular system and therefore might generate vibrational relaxation of the $\nu(\text{C}\equiv\text{N})$ Raman band observed in the spectra. In the last part of the current section, possible plasmonic interactions with Al and formation of complexes will be discussed.

Degradation mechanisms are usually monitored observing the increase of carbonyl modes, clearly observed with FTIR spectroscopy [292,317]. However, with Raman spectroscopy such modes are less intense. This is confirmed observing the negligible increase of the band at 1733 cm^{-1} attributable to the $\nu(\text{C}=\text{O})$ mode, slightly more intense in the microextracts with THF (Figure 3.16 a). Solvents with higher polarity, like water, might have presented a better affinity for the carbonyl-bearing species during extraction. In addition, a broad medium intensity band at 2719 cm^{-1} , narrowing at longer exposures, was recorded in all SERS spectra. Aldehydes obtained through SERS detection are herein reported for the first time. Such carbonyl compounds show bands attributable to the $\rho(\text{CH})$ mode at around $2685\text{--}2720\text{ cm}^{-1}$ in addition to a band centered at 1733 cm^{-1} [52,312]. The finding is coherent with the formation of ABS photooxidation products reported by several authors through FTIR spectroscopy and GC/MS determinations [148,150,292]. This aspect of the research would have benefited from further experiments looking at polymer behavior in different solvent environments. However, for time reasons it was not possible to extend it.

Other notable changes due to aging were observed in the SERS microextracts from the oxidized ABS films. Unsaturation progressively decreased during aging, as observed following the band at 1669 cm^{-1} assigned to $\nu(\text{trans C}=\text{C})$ mode, shifted to 1658 cm^{-1} and broadened at long exposures (Figure 3. 16 a). THF had a slightly different effect on the removal of unsaturations showing an enhanced signal. Following the bands at 1453 and 1324 cm^{-1} attributable to the $\delta_s(\text{CH}_2)$ and $\delta(\text{CH}_2)$ modes, respectively, a definite increase with a progressive broadening and shifting to 1446 and 1304 cm^{-1} were observed. Both vibrational modes are compatible with PB and acrylonitrile residues forming during photooxidation. However, the solvent-analyte system and the plasmonic interactions affected other expected vibrational modes of styrene or SAN at 1602 , 1580 and 1003 cm^{-1} absent after 400 h. On the

other hand, apart from the $\nu(\text{C}\equiv\text{N})$ mode shifting explained above, the absence of the band at 3060 cm^{-1} confirmed higher concentrations of acrylonitrile residues at longer exposures.

3.2.2.6 Summary

- Styrene polymers and copolymers have been widely studied through photooxidative and thermoxidative accelerated aging.
- PB nodules in ABS are responsible for the initiation of formation of photooxidative products from 60 h treatment. Carbonyl and hydroxyl groups' formation was emphasized in several seminal studies, hence providing to the SERS method herein proposed solid foundations for modeling.
- Photooxidative and thermoxidative behavior of ABS films was observed, confirming previously published evidence obtained through FTIR spectroscopy, DSC, and SEC techniques.
- Microscopic and macroscopic effects of aging were widely observed through chemical identification of newly formed species, changes in molecular weight distribution and discoloration.
- SERS sensing provided evidence of chain scission in the early stages of oxidation through the formation of markers of degradation, hence lowering the limits of detection of LMW compounds on degraded polymeric films.
- Linking this new evidence to the development of *diagnostic tools for preventive conservation purposes* might be beneficial to heritage science research, and more broadly to polymer science applications.

3.2.3 PVAc behavior in mild thermal oxidative conditions

In art and conservation, PVAc spans from being a binder, an adhesive and a base material or objects [154–156,164,167,170,172,318,319]. As introduced in Chapter 1, PVAc undergoes autocatalytic reactions of degradation in photo and thermal oxidative decay [97,157–160]. The experiments herein presented focus on the solid fragments forming during thermal oxidative degradation below 150° C. New insights on the onset temperature for chain scission are provided.

Non-catalytic and catalytic deacetylation followed by deactivation are mentioned in the literature as the three steps of deacetylation (Figure 3.17) [160]. After the completion of the catalytic deacetylation and deactivation, chain scission has been proposed as an alternative route to the formation of aromatic and aliphatic residues, while degradation proceeds. Polyenes with higher molar fractions form during the non-catalytic step, reducing to LMW fractions depending on the amount of vinyl acetate neighbors available in later stages. Chain scission is reported at temperature ranges of 400-500° C in oxidative and inert conditions [160].

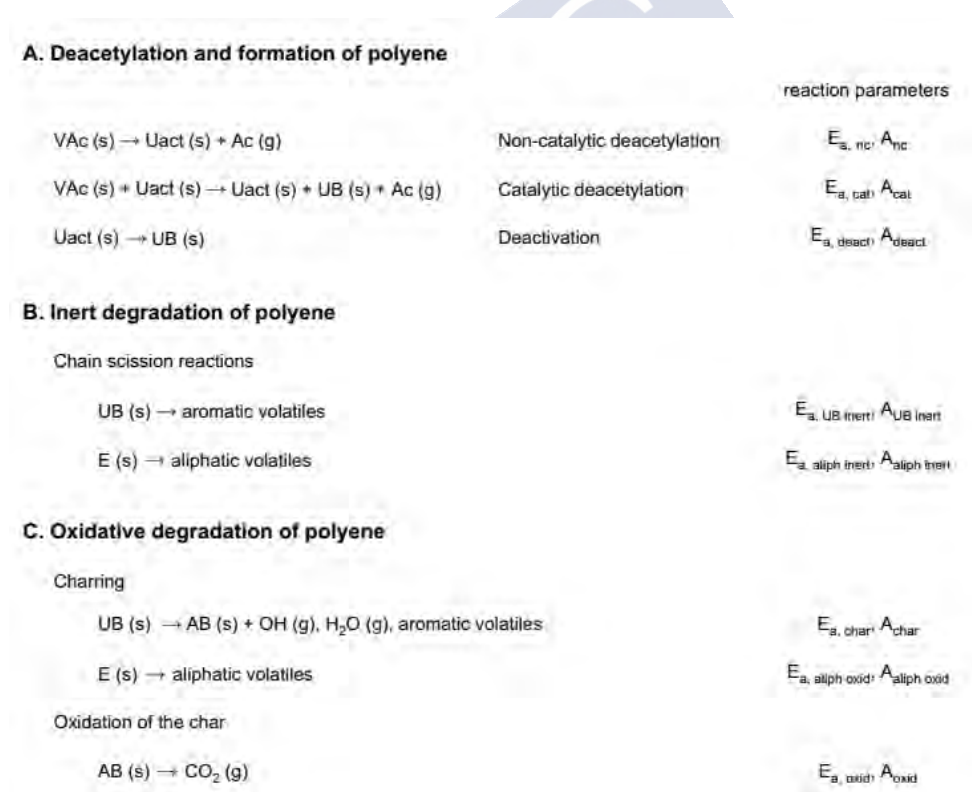


Figure 3.17: proposed mechanistic model for deacetylation (A), inert polyene degradation (B) and oxidative polyene degradation (C) of PVAc and EVA. VAc: vinyl acetate entities; Uact: double bonds catalyzing a following deacetylation reaction; UB: deacetylated vinyl acetate entities or inactive double bonds; Ac: acetic acid; E: ethylene entities; AB: aromatized solid residue or char; (s): solid; (g): gas. Note: (C) is only valid for PVAc and EVA with high weight% Vac. *Adapted with permission of ref. [160]. Copyright Elsevier LTD.*

The acetate side groups are gradually eliminated from the polymer backbone in the deacetylation step, therefore C=C unsaturations arise. Allylic chain scission reactions then occur at the completion of the degradation process [160]. After the elimination of acetic acid and the formation of new double bonds, the propagation proceeds steadily. In addition, the methylene group in α position and adjacent to the double bond is reported as a point of high reactivity. Opposite to radical chain scissions, bearing secondary and tertiary reactions with different energies involved in termination reactions. The intramolecular reaction of deacetylation continues straight to the end chain, unless being interrupted by some sort of discontinuity of the structure. Flynn [307] reported intramolecular chain reaction of elimination of acetic acid beginning at 160° C. In addition, intermediate chars formation was also reported in various publications [157,159,160]. Several publications refer to the formation of VOCs (e.g. ketene and carbon dioxide) alongside with acetic acid, which is the primary product of degradation [157,320].

The current experiments were conducted with no shielding from oxygen and light, except controlled isothermal temperature (150° C). Self-supporting films, ~60 μ m thick, prepared at room conditions with commercial Rayt™ S.A. white glue were treated for 270 h. Yellowing and hardening of the films were observed from 20 h treatment onwards (Annex Figure 3.7 photo of the samples). Annex Figure 3.8 reports normalized ATR-FTIR stacked spectra obtained at different thermal aging steps (4, 70, 100, 240, 270 h). Minimal changes of the spectral features occurred, although an overall decrease of features was recorded, as in similar studies [154,155,159,164]. As shown in Annex 3.7 from this experiment, the polymer residues darken and yellow reducing their solubility. The colored resulting substance was referred as high molecular weight polyacetylene by Grassie [157]. Alternatively, short length polyenes have been proposed by Garden [306,320].

In the current experiment, OH and water contents are progressively subtracted from the polymer backbone in the initial stages of aging. In particular, the broad band comprised between 3680 and 3100 cm^{-1} observed in the ATR-FTIR spectra of Figure Annex 3.8 disappeared after 20 h treatment, similarly to what observed by Chelazzi *et al.* [155]. Annex 3.8 summarizes as well the band assignments of the ATR-FTIR spectra.

3.2.3.1 DSC and Derivative Scanning Calorimetry (DeSC) results for qualitative considerations on the thermal behavior of PVAc

In PVAc long-term exposure leads to competing crosslinking in the unsaturated regions followed by chain scission mechanisms. SEC is usually employed to follow the associated changes in molecular weight. However, for short-term exposures the amount of oligomers might be well below the limits of detection of most instrumental settings. DSC data uncover concurrent crosslinking phenomena that will be shortly discussed in this section.

Samples between 1.2 to 5.5 mg were measured in alumina pans, setting a heat flow of 20°C/min in cycles from -70 to 200 °C. Published data on PVAc report T_g between 20 to 40 °C [293]. In the aged samples the softening slope was barely readable. A highly sensitive method to broaden the relevant signal was the derivative scanning electron calorimetry (DeSC). Figure 3.18 (a) upper curves are the first derivatives of the classic DSC signal. As

expected, the film treated up to 270 h showed an increase of the T_g onset of about 5 °C compared to the unaged film, namely from 42 to 47 °C (Figure 3.18 b). Additional transition peaks at about 1.20 and -1.90 °C were observed in the unaged and thermoxidized PVAc samples, respectively (Figure 3.18 a). Different transition temperatures indicate the presence of chemically separated domains [293]. Figure 3.18 b upper curves show a clear slope in the aged sample, meaning that the crosslinking is quite pronounced after few hundreds hours of aging. Chelazzi *et al.* [155] argued the ambiguous presence of additional peaks at low temperatures ($\sim -2^\circ\text{C}$) as result of ongoing depolymerization due to oxidation or competing crosslinking on deacetylated moieties, on both naturally and thermally aged PVAc samples. Water elimination is proposed elsewhere as an explanation of the additional peaks.

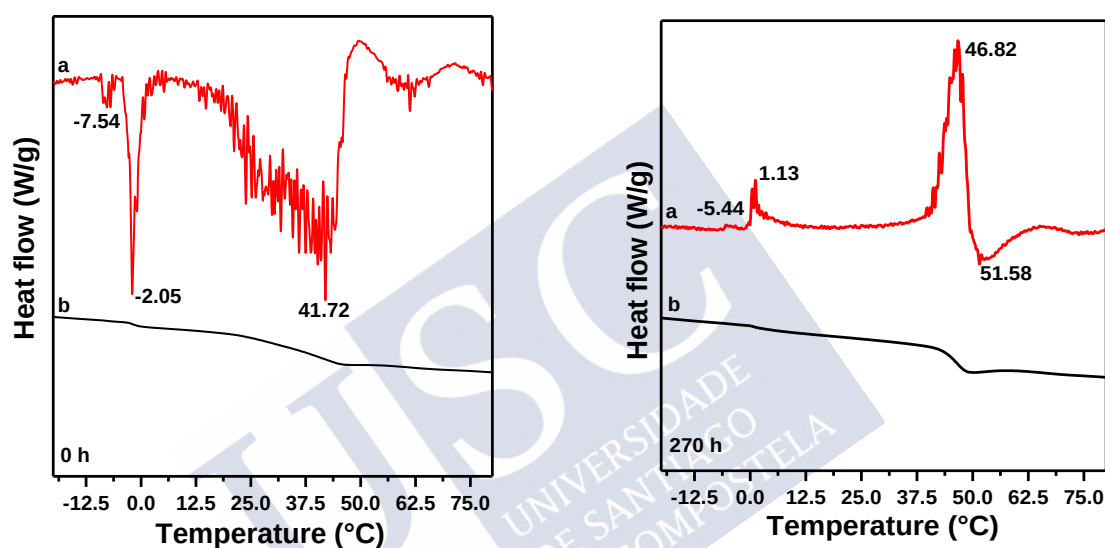


Figure 3.18: DeSC (a) and DSC (b) curves of unaged 0 h (left) and thermally aged 270 h (right) PVAc self-supporting films.

3.2.3.2 SERS: unexpected presence of oligomers

Opposite to previous evidence, solid LMW compounds PVAc from chain scission could be detected with SERS sensing after short-term exposure in thermal oxidative mild conditions. SERS spectra were collected with different substrates fabricated with ORMOCER[®]s and PFPEs derivatives as UV-curing polymers on KLARITE[®] replicas substrates. Before discussing the SERS spectra, the narrative will explore a tangential aspect of the thesis. The enhancing properties of different UV-curing polymers could seldom be explored on the same model material comparatively. The opportunity arose with PVAc films.

ORMOCER[®]s are off-the-shelf hybrid inorganic-organic polymers based on organically modified heteropolysiloxanes [321]. Strong covalent bonds between organic and inorganic moieties, contribute to the formation of the inorganic network followed by the organic crosslinking in the curing phase. In photo-lithography, they have been extensively used for their optical, electrical and mechanical adaptability [257]. Prior to the beginning of the current research, Gómez & Lazzari [263] synthesized and explored the versatility of PFPEs demonstrating their high ability of replication of *micro* and *nano* structures for electronics

devices (e.g. diffraction gratings). PFPEs received more attention in the last 10 years due to different enhanced properties discussed earlier, such as the chemical resistance [258,262,278,279,281,322].

In the current application of the PDMS sampling method, adhesion of the analytes to the *nano* and *micro* structures after solvent evaporation was questioned. Certainly, EELS measurements conducted by Gómez *et al.* [298] on the freshly formed Al_2O_3 layer provided at least the relevant evidence of a strong sealing layer between polymer and metal allowing signal enhancement, irrespective of the analytes. Spectra in Figure 3.19 (a, b) correspond to SERS signals from aged PVAc films (270 h) onto PFPE-based substrates with CHCl_3 and THF, respectively.

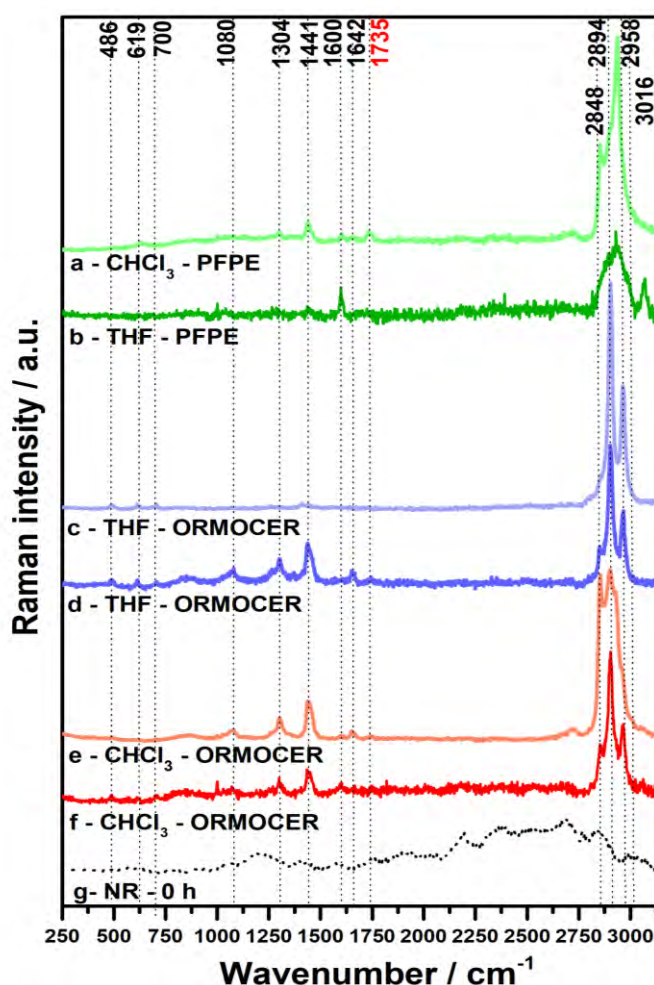


Figure 3.19: SERS microextracts (a-f) spectra collected through microextracts from surface products of thermally aged films of PVAc (270 h). Spectra (a, b) result from CHCl_3 and THF, respectively, deposited onto PFPE-based substrates. Spectra (c, d) collected with THF and deposited onto ORMOCER® substrates. Spectra (e, f) collected with CHCl_3 and deposited onto ORMOCER®. Excitation wavelength 514 nm. NR spectrum obtained directly on the aged film shows indistinguishable features.

Spectra c to f were obtained transferring PVAc fragments to ORMOCER[®]-based substrates, specifically spectra (c, d) were obtained with THF, whereas spectra (e, f) with CHCl₃. Despite several repeated measurements, the reproducibility of the spectral response from substrates fabricated with PFPEs resulted slightly lower than that of ORMOCER[®]-based substrates.

In the fabrication phase, ORMOCER[®]s showed more viscosity than PFPE's. The difference might be linked to the UV-curing performance and therefore to the replication of the lateral features. Specifically, the periodicity of platforms might be reduced. In continuous arrays of rough structures, reduced periodicity impacts greatly the signal enhancement, resulting in poorer spectral features [53].

Results from microextractions on fresh films (4 h) were inconclusive, as well as those obtained with normal Raman (on the bottom of the Figure 3.19 NR). Further systematic tests were conducted using the excitation wavelength at 785 nm, the same transferring solvents, and both KLARITE[®] and SOKEN[®] replicas fabricated with ORMOCER[®]s and PFPEs-based polymers. For the sake of brevity, inconclusive results will be omitted. Table 3.5 summarizes SERS microextracts assignments on oxidized PVAc films.

Table 3.5 Approximate band positions (cm⁻¹), relative intensity ^a, SERS assignments ^b on oxidized PVAc films.

PVAc (270 h)	Assignment ^b
3016 m shoulder	(=C-H); it appears only on the substrate cured with PFPE.
2958 s	ν_{as} (CH ₃)
2894 s	ν (=C-H) associated to CH ₂
2848 s	ν_s (CH ₃)
2716 w	-
1740 - 1735 w	ν (C=O) associated to C ₂ H ₃ O ₂ ⁻
1647 m	(C=C)
1600 w	-
1549 w	It appears only on the substrate cured with PFPE
1441 - 1438 s	δ (-C-H) associated to CH ₃ symmetrical deformation
1381 w	It appears only on the substrate cured with ORMOCER [®] THF
1304 m	ν (C-O-C)
1251 w	(-CH ₃) symmetrical deformation
1080 m	ν (C-O)
1001 w	τ (-CH ₂)
855 w	ν (C-C) + ρ (C-H) in CH ₃ (broad)
700 w	-
618 w	δ (C=O)
565 w	-
486 w	(C-C) out-of-plane bending

^a s: strong; m: medium; w: weak; sh: shoulder.

^b ν stretching; δ bending; ρ rocking; ω wagging; τ twisting; $_s$ symmetric; $_{as}$ asymmetric.

Several repeated microextractions presented in Figure 3.19 confirmed LWM compounds detection. The presence of unpolymerized residues of PVAc was ruled out by the complementary instrumental analyses presented in the previous sections (ATR-FTIR spectroscopy and DSC). The oligomers detected were compatible in composition with PVAc polyene and polyacetylene [157], although the spectra do not coincide with either of the two

available in previously published literature [222,323–325]. Solubility and relative polarity of the transferring solvents (THF and CHCl_3) were put into context (Figure 3.19). The oligomers were interpreted as short-chain fragments from the partially oxidized deacetylated moiety of PVAc. Being polar moieties, PVAc oligomers showed best affinity for CHCl_3 compared to THF (Figure 3.20 c-f). Selective removal of polar unsaturations with quite polar solvents was confirmed on PVAc, as for other model materials.

Grassie [157] proposed that in mild thermal aging of PVAc the evolution of acetic acid is not related to the reactions initiated by free radicals. Rather end-chain groups are likely to be weak points for initiation and propagation of chain reactions of degradation. It was said that PVAc degradation mechanisms do not entail the formation of products constituted by its monomeric units. Under vacuum the onset of degradation was reported from temperatures above 200°C [160]. As expected in oxidative conditions the OIT is shorter, and the onset of chain scission mechanisms was reported from 160°C [159]. The current experiments have provided evidence of a lower onset of degradative non-radical chain scission reactions in PVAc.

3.2.3.3 Summary

- PVAc mild thermal aging experiments (270 h) demonstrated that non-radical reactions can lead to the formation of chain fragments (new insight on the degradation mechanism).
- SERS spectral analysis revealed that oligomeric structures with unsaturations, possibly formed through secondary mechanisms of oxidation, are present on the surface of PVAc films.
- Performances of ORMOCER[®]s and PFPE's UV-curing polymers were discussed hinting to a slightly better performance of ORMOCER[®]s.
- The suitability of the PDMS strip sampler method was accomplished. SERS results provided new insights on LMW fractions detectable below the limits of detection of traditional methods for polymer characterization, such as SEC, DSC and ATR-FTIR spectroscopy.

3.2.4 PI aging behavior

PI model samples were submitted to photooxidative and low temperature thermal aging tests up to 250 h treatment. Before presenting the evidence, the mechanisms of PI degradation will be herein recalled through a short summary of some seminal publications. Then, although PI samples were extensively characterized, only results functional to highlight SERS sensing potentials will be presented. Complementary information is provided in Annex Figure 3.9.

As introduced in Chapter 1, studying natural and synthetic PI rubbers was necessary to enhance industrial performances [150,176,180,181,269,273,326,327]. The simplified scheme PI oxidation of is presented in Figure 3.20. Bolland and Gee [99,100,328] initiated kinetics studies on the degradative mechanisms of polyolefins. They focused on the oxidation mechanisms of mono, 1:3 and 1:4 di-olefins to explain the degradation of PI rubbers and quantify hydroperoxides, as primary products of oxidation. The importance of decomposition reactions at lower energies of activation (*e.g.* C-C, C-O) was discussed. As other authors widely confirmed later [88,97,141], the oxidation of polyolefins leads to the formation of cyclic or polymeric peroxides and hydrocarbon polymers. Overall the asymmetry of the PI molecule favors the formation of hydroperoxides, initiating preferentially on the methylene group. It is worth to remind that isolated double bonds have been repeatedly proposed as points of attack to initiate the formation of the radical species, especially on the labile hydrogen atom in α position [329,330]. Hydroperoxides form through intramolecular chain reactions, however also addition reactions contribute to the degradation mechanism [180].

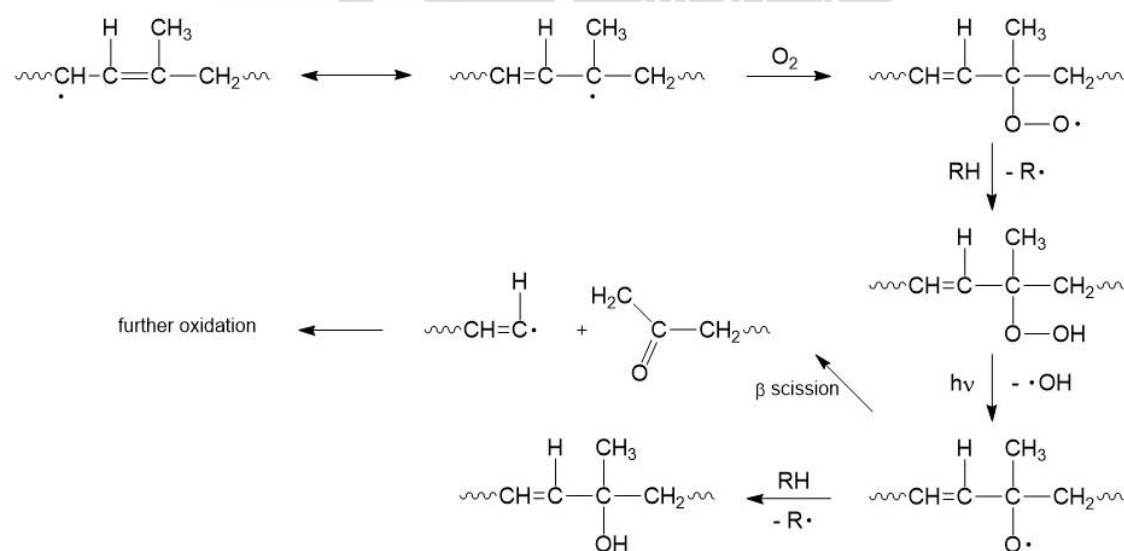


Figure 3.20: simplified mechanism of PI autooxidation showing degradation routes after initial radical formation. Although two different allyl radicals may be formed by H abstraction, the mechanism leading to tertiary radical by resonance is considered as the most probable. Adapted with permission from ref. [205]. Copyright Elsevier.

Morand [180,269] discussed the fundamental aspect of chain scission and added relevant information to understand the mechanisms of oxidation of unsaturated hydrocarbons. Alcohols, ketones and epoxides are the main secondary products of oxidation derived from

the decomposition of hydroperoxides. Various VOCs were identified in thermal aging experiments [180].

Adam *et al.* [181] reviewed the mechanisms of PI oxidation confirming the abstraction of hydrogen in the allylic position with formation of tertiary macroradicals associated to the hydroperoxides. The decrease of the average number molecular weight was reported in the first six hours of low temperature oxidative treatment through SEC coherently with β -scissions [181]. Ketones, alcohols, carboxylic acids, esters and epoxies were reported among non-volatile oxidation products derived from chain scission. Addition reactions compete with chain scission in the initial stages of degradation. In particular, peroxy radicals or macroradicals adding to the double bonds lead to the formation of tertiary hydroperoxides, alcohols, ketones, acids and esters. Several authors compared photooxidative and thermoxidative behaviors of PI to PB, both elastomers from the family of the diene polymers [150]. With SEC a lower amount of insoluble species was detected in the initial aging stages hinting to a prevalence of chain scission over crosslinking in PI, opposite to PB. Similarly, Bussiere *et al.* [150] provided further evidence that in PI the OIT leading to chain scission lasts up to 20 h in photooxidative treatment. Oxygenated species form from chain scission reactions and have a specific kinetics of accumulation competing with crosslinking, which continues even after maximum of accumulation of photoproducts is reached.

3.2.4.1 SEC: evidence of chain scission and further molecular weight changes during photooxidative experiments

SEC results on PI are presented in Figure 3.21. THF was used for the solubilization of samples of approximately 5 mg for each aging stage. Vulcanized PI is insoluble, hence a soluble fraction derived from chain scission mechanisms was observed. Chromatograms in Figure 3.21 show a progressive lowering of the molecular weight, corroborating the mechanism of degradation. In the red curve, a broad peak with the maximum at retention time of around 7 min hints to the presence of a variety of species at relatively low molecular weights up to 120 h treatment. A tail at around 8 min confirms the presence of further species. The slopes at around 9.2 and 9.8 min might belong to additives for the vulcanization. The black curve was obtained from a sample photoaged 250 h and it shows a maximum at 9.1 min confirming the trend of formation of low molecular weight fragments due to chain scission.

SEC did not allow the identification of the photoproducts and required a considerable amount of sample (~5 mg). SERS results introduced in the following section will provide evidence of specific molecular information about the photoproducts, enabling the identification of the LMW compounds physisorbed on the PDMS sampler. The sensitivity of SEC did not allow discriminating the species, even though the quantity of LMW fraction in the injected solution is much greater of the degradation markers detected with SERS.

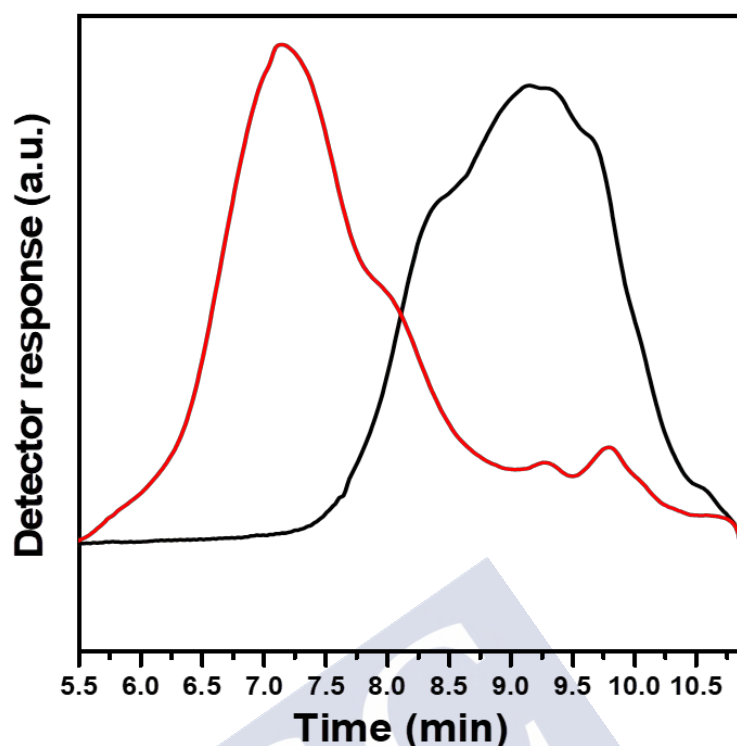


Figure 3.21: normalized SEC curves of PI photoaged up to 120 h (black curve) overlapping the unaged PI (red curve). The soluble fraction of naturally aged PI is detected at longer retention times. Slopes on the red curve refer to impurities or additives that inevitably are in the synthetic rubber and do not represent the change in molecular weight due to aging. Adapted with permission from ref. [38]. Copyright Elsevier.

3.2.4.2 SERS sensing in photooxidative experiments

The oxygenated species listed in the previous section were confirmed in SERS measurements (Figure 3.22 a-f). Simultaneously, ATR-FTIR spectra were collected at the same aging ranges (0, 20, 120 h) (Annex 3.9). For both methods, the accumulation of photooxidation products was monitored observing the formation of carbonyl and hydroxyl. In SERS microextracts, THF and CHCl_3 were used as transferring solvents. A reference NR spectrum of PI was included (Figure 3.22 f). A Renishaw inVia spectrometer was set with 514 and 785 nm excitation wavelengths for several control experiments.

Raman modes of 1,4-*cis* PI remained unvaried until 20 h treatment, as expected. Table 3.6 shows comparative band assignment of FTIR and Raman spectra with differences due to aging in bold [210,331]. Overall, the C-C modes prevail in Raman spectra, whereas methylene modes are stronger in ATR-FTIR spectra. Further, a weak band at 3038 cm^{-1} can be assigned to the =C-H stretching vibration mode. High frequencies bands in the methyl and methylene deformation region are shifted in SERS as follows: from 2960 to 2696 cm^{-1} , 2877 to 2904 cm^{-1} , and 2942 to 2966 cm^{-1} . Bands at 1373 and 1360 cm^{-1} also account for the CH_2/CH_3 deformations. Nonpolar molecules, like PI, have been reported to have intense asymmetric CH_2 stretching modes. This is more evident in the SERS spectra (a-d), showing

high intensity in that region. However, it is worth mentioning that the amplification of the CH bonds in the region can be attributed to their favorable orientation on the plasmonic surface [46,298]. Similar enhanced intensity was recorded by using FT-Raman spectrometers on different PI isomers [176].

Further, although Raman spectroscopy is not sensitive to carbonyl enrichments, microextracts (b-d) show the appearance of a new feature at 1727 cm^{-1} that can be ascribed to esters. Chain scission mechanisms explain the appearance of such carbonyl specie released preferentially, among other photoproducts⁸. As mentioned in the previous section, crosslinking occurs in the initial stages of degradation of PB, whereas in PI the process is reported at longer aging times [150].

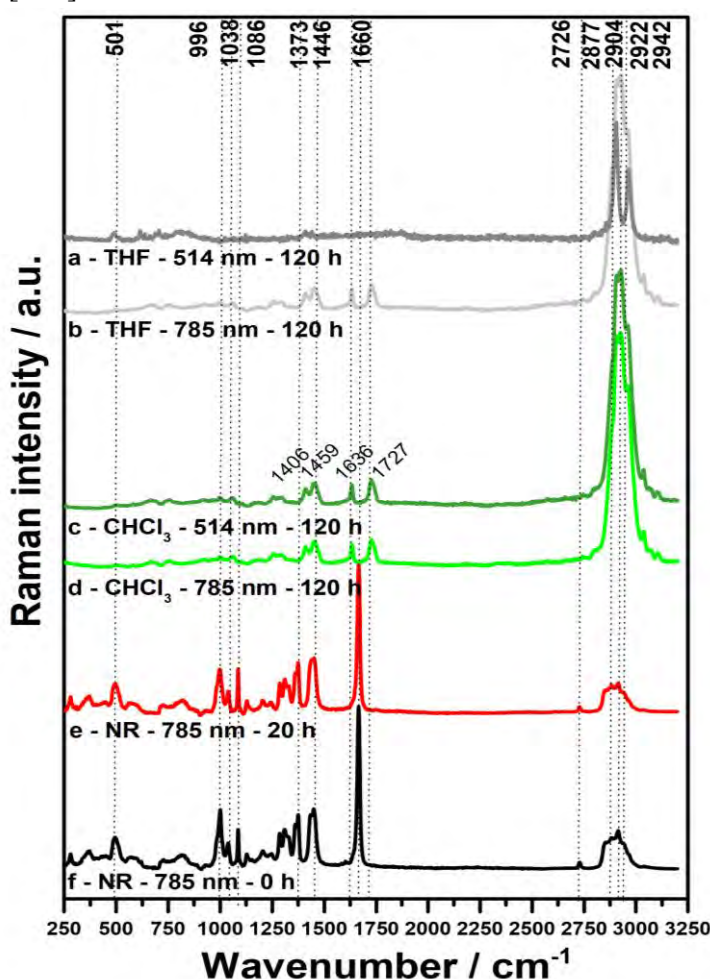


Figure 3.22 (a-f): Raman spectra from photoproducts of PI aged up to 120 h. a) SERS microextracts with $\lambda_{\text{exc}} = 514\text{ nm}$ with THF after 120 h; b) SERS microextracts with $\lambda_{\text{exc}} = 785\text{ nm}$ with THF after 120 h; c) SERS microextracts with $\lambda_{\text{exc}} = 514\text{ nm}$ with CHCl_3 after 120 h; d) SERS microextracts with $\lambda_{\text{exc}} = 785\text{ nm}$ with CHCl_3 after 120 h; e) NR spectrum with $\lambda_{\text{exc}} = 785\text{ nm}$ after 20 h; f) NR spectrum with $\lambda_{\text{exc}} = 785\text{ nm}$ at 0 h. Spectra collected with inVia™ confocal Raman microscope.

⁸ Alcohols, photo instable hydroperoxides, epoxies, aldehydes, peroxyesters, carboxylic acids, peroxides, primary alcohols and tertiary hydroperoxides are reported as oxidation products of PI.

Raman cross-section of $\nu(\text{C}=\text{C})$ modes is typically high, however some publications report the disappearance such mode in highly degraded rubbers [178]. The $\text{C}=\text{C}$ bond is electron rich and nonpolar, therefore in Raman spectroscopy shows increased polarizability proportional to increased intensity of the band. The very intense band at 1660 cm^{-1} in the Raman spectra can be ascribed to the $\text{C}=\text{C}$ stretching modes. Dramatic changes of intensity of the $\text{C}=\text{C}$ band at 1660 cm^{-1} is observed in microextracts, hinting to the severe consumption of the unsaturations in the first 120 h treatment. The wavenumber shifted to 1636 cm^{-1} and a fairly weak band is still visible at the end of the oxidation.

Bands at 1451 and 1438 cm^{-1} can be ascribed to $\text{C}=\text{C}$ vinyl vibration and $\delta_{\text{as}}(\text{CH}_2)$ deformation, respectively. Bands at 1334 , 1308 , 1282 , 1242 and 1203 cm^{-1} are ascribed to the CH_2 wagging/twisting, and to the $=\text{C}-\text{H}$ deformation/bending modes. The $\text{C}-\text{CH}_2$ stretching vibrations are assigned to various modes in the region $1100\text{-}900\text{ cm}^{-1}$.

Table 3.6 Approximate band positions (cm^{-1}), intensity^a, Raman/SERS assignments^b of PI and comparison with ATR-FTIR spectroscopy (Annex 3.9)

PI 0 h (ATR-FTIR)	PI 0 h (NR)	PI 20 h (ATR-FTIR)	PI 20 h (NR)	PI 120 h (ATR-FTIR)	PI 120 h (SERS)	Assignment ^b
-	-	3435 w	-	3436 m	-	$\nu(\text{O}-\text{H})$
-	-	-	-	-	3103 w	$\nu(=\text{C}-\text{H})$
3037 w	3037 w	3037 w	3037 w	3037 w	3037 w	$\nu(=\text{C}-\text{H})$
2958 s	2942 w sh	2958 s	2969 s sh	2969 s sh	2969 s sh	$\nu_{\text{as}}(\text{CH}_3)$
2928 s	2922 s	2917 s	2930 s	2922 s	2930 s	$\nu_{\text{as}}(\text{CH}_2)$
2917 s	2877 m	2917 s	2904 w sh	2917 s	2904 w sh	$\nu_{\text{s}}(\text{CH}_2)$
2847 s	2856 m sh	2847 s	2856 m sh	2847 s	2856 m sh	$\nu_{\text{s}}(\text{CH}_2)$
2727 w	2726 w	2727 w	2726 w	2727 w	2727 w	$\nu(\text{C}-\text{H})$ aldehyde / CH_3 def
-	-	-	-	1717 s	1727 m	$\nu(\text{C}=\text{O})$ ester / sat. methylketone
1663 w sh	1660 s	1660 m	1660 s	1663 m sh	1636 w	$\nu(\text{C}=\text{C}$ cis)
1577 s	-	1577 m	-	1577 w	-	CS_2 vulcanization
1539 m	-	1539 m	-	1539 w sh	-	CS_2 vulcanization
1435 m	1451 s	1435 m	1459 m	1439 s	1459 s	CH_2 def.
-	1446 s	-	1406 m	-	1406 m	$\text{C}=\text{C}$ vinyl
1375 m	1373 s	1375 m	1373 s	1375 s	1377 s	CH_3 def
-	1360 s	-	1360 s	-	-	CH_2 / CH_3 def.
-	1334 m	-	1334 m	-	1334 m	ω τ (CH_2)
1311 w	1308 m	1311 w	1308 m	1311 w	1308 m	$\omega(\text{CH}_2)$
-	1282 m	-	1282 m	-	1282 w	$\delta(=\text{C}-\text{H})$
-	1255 w	-	1255 w	-	1255 w	$\omega(\text{CH}_2)$
1240 w	1242 m	1240 w	1242 m	1240 m	1242 w	$\tau(\text{CH}_2)$
-	1203 w	-	1203 w	-	1203 w	$\tau(\text{CH}_2)$
1128 s	1125 m	1128 s	1125 m	1128 w	-	$\omega(\text{CH}_2)$
1093	1086 s	1093	1086 s	1093	-	$\nu(\text{C}-\text{O})$ sat. carb. acid. / ν ($\text{C}-\text{CH}_2$)
1039 w	1034 m	1039 w	1034 m	1039 m	1034 m	$\nu_{\text{as}}(\text{C}-\text{C}-\text{O})$ prim. alco. / ρ (CH_3)
931 w	995 s	931 w	995 m	-	995 w	$\nu_{\text{s}}(\text{C}-\text{C}-\text{O})$ prim. alco. / ν ($\text{C}-\text{C}$) / ν ($\text{C}-\text{CH}_3$)
874 s	891 w	874 m	891 w	874 s	891 w	CH_3
836 w	813 w	836 m	813 w	836 w	-	$\omega(=\text{C}-\text{H})$
713 m	722 w	713 m	722 w	713 m	-	$\rho(\text{CH}_2)$
741 w	-	741 w	-	741 m	-	$\rho(\text{CH}_2)$
577 w	566 w	577 w	566 w	577 w	-	$\delta(\text{C}-\text{C})$
504 w	501 s	-	504 w	-	501 w	$\delta(\text{C}-\text{C})$

^a s: strong; m: medium; w: weak; sh: shoulder.

^b ν stretching; δ bending; ρ rocking; ω wagging; τ twisting; s symmetric; as asymmetric.

On the other hand, the band at 1034 cm^{-1} can be ascribed to ¹the CH_3 rocking modes and that at 995 cm^{-1} to the C-CH_3 stretching. Typical rocking vibration of the CH_2 mode reported in the literature with bands at about 780 and 770 cm^{-1} were not identified in the current work, and this might depend on the influence of neighbor functional groups in the specific sample [176,326]. Bands at 566 and 501 cm^{-1} can be ascribed to the in-plane and out-of-plane bending modes of C-CH_2 and C-CH_3 , respectively [326].

THF and CHCl_3 have similar polarity, although the latter shows a consistent better affinity for the soluble fractions of oxidized PI in the SERS microextraction (a-d). Slight differences in the Raman spectra hint to a selective solubilization of the physisorbed fragments onto the PDMS strip sampler. Although fluorescence was better quenched with $\lambda_{\text{exc}} = 785\text{ nm}$, tests with both excitation wavelengths allowed identifying unambiguous signals from PI. Opposite to saturated ATR-FTIR spectroscopy, Raman spectra conserved clear spectral features belonging to PI throughout the entire aging.

3.2.4.3 Summary

- Among diene polymers, PI is more prone to chain scission than PB. To optimize the SERS sampling method a model polymer with unambiguous degradation mechanism of chain scission was necessary.
- Several LMW compounds bearing carbonyl and hydroxyl groups form in photooxidative experiments on PI.
- Early stages of PI degradation resulted in extensive formation of LMW oxidation products.
- Raman spectroscopy was used to deepen the data about the degradative behavior of PI, whereas ATR-FTIR spectroscopy confirmed the traditional studies of degradation of PI isomers.
- Normal and SERS spectra provided consistent data on the solubility of oxidized fragments tuned by solvent polarity with the PDMS sampler.
- Different excitation wavelengths ($514\text{-}785\text{ nm}$) proved adequate to detect PI molecular fragments.

3.2.5 Object-based validation: challenges of contemporary artworks

Collections, private galleries and museums face enormous challenges to keep up-to-date condition mapping of fast-degrading objects made of polymeric materials [117,165,206,332–335]. In the last fifteen years, collaborations among scientists and conservators have more and more often arisen for the urgent need to reduce the impact of rapid losses on plastics collections [336]. Macroscopic changes classified as superficial, deep and global reflect the degradative behavior that the polymeric materials are suffering from [205,337,338]. As widely described in the previous sections, beyond the macroscopic damages that usually alert the conservators, there are irreversible chemical changes accountable for the actual breakdown of the polymeric components. The mechanisms of degradation vary from a material to another and different new products form. Environmental monitoring and re-designing storages/display conditions are the typical measures to slowing the mechanisms and preventing loss, especially in permanent collections.

Recent research focuses on integrating artificial aging of model polymers with long-term behavior of the objects in collections, including dynamic cross-infection [118,165,167,197,198,339–344]. New diagnostic tools for preventive conservation were developed and optimized by various authors [118,344–346]. As demonstrated so far, surface monitoring with molecular sensors can indeed reduce the risk of material loss, as proved for linseed oil, ABS, PI and PVAc.

SERS sensing has received enormous attention in the cultural heritage field [16,18,37,37,347–350]. Beyond degradation studies, further aspects on the technology of production of museum objects can be accomplished through SERS (*e.g.* pigments and dyes identification). However, the achievement of using sensors that enable to reduce sample-taking to amounts as small as 10^{-10} g is new and incredibly promising [210]. To be reminded the uniqueness of artistic objects and the aesthetic features they bring that make them ‘untouchable’ even for research purposes [3,110,351].

The next section presents the validation of the novel SERS-based analytical method on a loose fragment from *Traxe de Home* by Andrés Pinal. The artwork is stored in the permanent collection of the CGAG. In 2008, after cleaning and repairs⁹, a display case was designed for isothermal storage and to limit human contact with the material. However, during the short gap between 2001 and 2008, irreversible breakdown of the artwork occurred. Figure 3.23 shows the photographs with various insets on the most degraded areas, rapidly worsted, after a second condition survey was conducted [205]. The collaboration with the CGAC gave the opportunity to reiterate a number of analyses (*e.g.* FTIR spectroscopy) and estimating the rate of degradation, monitoring the natural aging behavior of the rubber [333].

Furthermore, the very artist, Andrés Pinal, contributed to expand the information available on the fabrication of the objects, which is an ideal scenario to foster participative conservation practices. This way conservators and scientists could build the case of interventive and preventive conservation treatments for the transmission of meaning and materials to the future generations, without altering the artists’ will and perspectives.

⁹ Fragments were exposed to ammoniac vapors, lacunae were substituted with newly fabricated latex of PI, cotton swabs were replaced and talc was applied on surface.

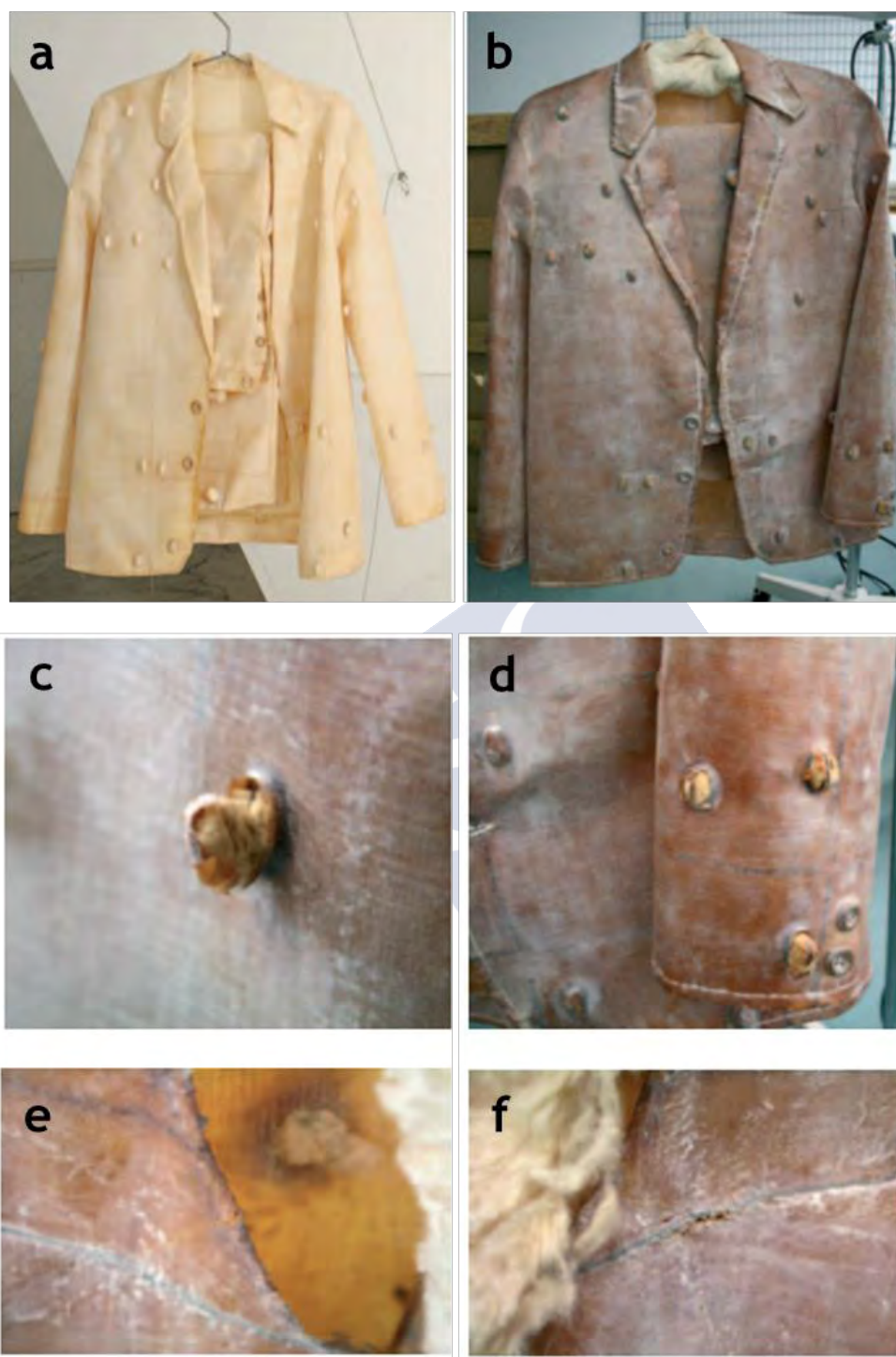


Figure 3.23: photographs of the artwork *Traxe de Home* by Andrés Pinal currently in the permanent collection of the Centro Galego de Arte Contemporanea (GCAC). Comparison of the same object in 1996 (a) and 2008 (b). Details from the most degraded areas, The analytical results reported in this section were collected in 2018, after 22 years of natural aging. Adapted with permission of the authors from ref. [205].

3.2.5.1 ATR-FTIR and SEC on naturally aged PI from a contemporary artwork by Adrés Pinal *‘Traxede home’*

In a previous methodological paper by Lazzari *et al.* [333], a Py-GC/MS chromatogram showed that the latex utilized by A. Pinal for *Traxe de Home* was a vulcanized natural rubber of PI, presenting some impurities and low contents of fatty acids. Also, spectral data showed that the material was treated with talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) as an additive, as often in rubbers. As in the previous investigations, ATR-FTIR spectrum in Figure 3.24 detected talc bands at 3667 cm^{-1} , 1003 cm^{-1} and 666 cm^{-1} that can be ascribed to the $\nu(\text{O-H})$, $\nu(\text{Si-O})$ and $\delta(\text{OH})$, respectively [352]. Unfortunately, the relative intensity of the silicate compared to the signals from the 22-year old highly weathered rubber allowed only an ambiguous identification of PI. For a comprehensive assignment of the ATR-FTIR bands of PI please refer to Table 3.6.

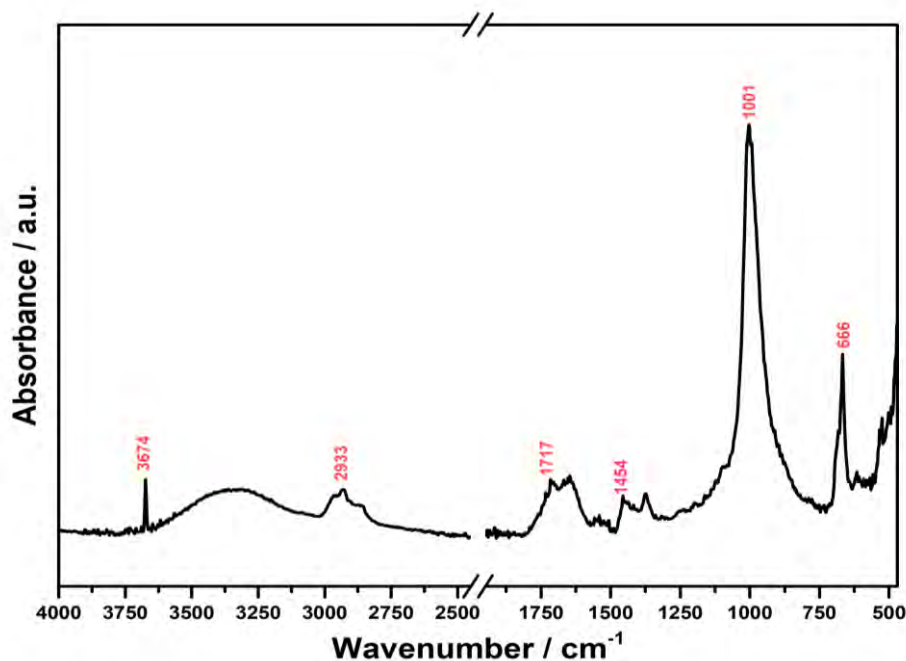


Figure 3.24: ATR-FTIR spectrum from a fragment of natural rubber from *Traxe de Home* by A. Pinal in the permanent collection of the GCAC.

SEC curve in Figure 3.25 expanded the information in Figure 3.25 on the photooxidation of PI. The initially insoluble polymer underwent extensive breakdown demonstrated by the increase of the soluble fractions from 20% by weight ($M_n = 135\text{ kDa}$) in the model PI (120 h photoaging) to the 50% by weight ($M_n = 27\text{ kDa}$) in the naturally aged PI (22-year). As for the model polymers, SEC data backup SERS evidence on the detection of isoprene LMW compounds from the naturally aged surface of the artwork.

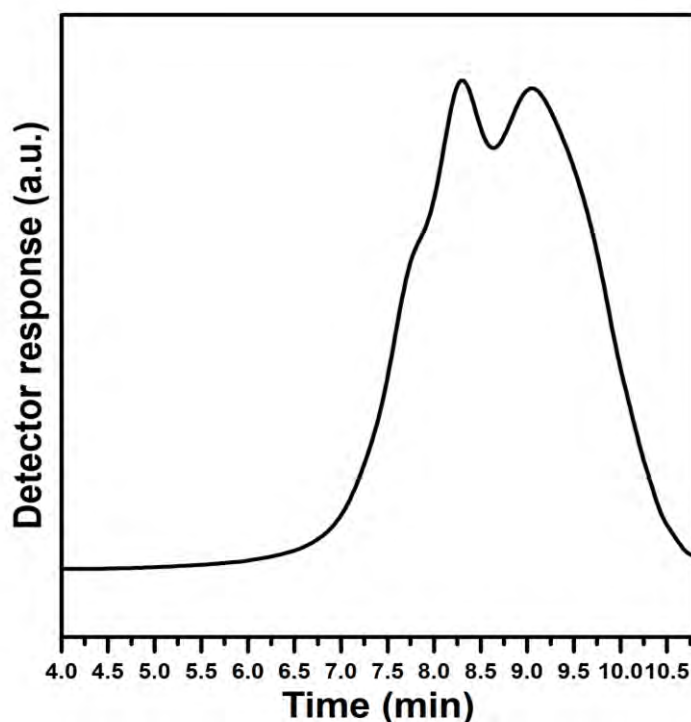


Figure 3.25: normalized SEC curve on natural rubber (PI) naturally aged in indoor conditions for 22 years. The fragment belongs to *Traxe de Home* by A. Pinal in the permanent collection of the CGAC. Adapted with permission from ref. [38]. Copyright Elsevier.

3.2.5.2 SERS sensing on naturally aged PI from a contemporary artwork by Adrés Pinal ‘Traxe de home’

The detection of oligomers of isoprene was confirmed by several repeated SERS microextractions presented in the spectra (a-d) of Figure 3.26 obtained with $\lambda_{\text{exc}} = 514$ nm. NR spectrum was collected with $\lambda_{\text{exc}} = 785$ nm (Figure 3.26 e). Both KLARITE[®] and SOKEN[®] replicas gave excellent enhancing results. In particular, spectrum (a) was obtained on a KLARITE[®] replica and spectrum (b) on SOKEN[®] replica Al-coated platforms. PDMS extracts were transferred to the substrates with CHCl_3 . Following, spectrum (c) was obtained on a KLARITE[®] replica with THF. Finally, spectrum (d) was obtained from dry sampling with a SOKEN[®] replica, directly onto the polymeric surface¹⁰. Overall, CHCl_3 provided spectra with more features than those with THF. Oligomers of degraded PI are highly polar (e.g. carboxylic species) and the slightly higher polarity of CHCl_3 compared to THF might favor the solubilization of the oligomers from the PDMS.

In several examples presented earlier, the methyl and methylene bands are rather increased by the SERS plasmonic effect, as confirmed by comparing the spectra with the NR spectrum in Figure 3.26 (e). To be observed the band at 3065 cm^{-1} , assigned to $\nu(\text{=C-H})$, has been enhanced on the SOKEN[®] replicas (b and d), either with CHCl_3 or through direct dry sampling. The bond angle and subsequent molecular cross-section might have been

¹⁰ The spectrum is reported for the sake of completeness, although it has to be pointed out that the measurement would not be reliable, if one had no other spectra for comparison.

influenced in contact with the pillar-like nanostructures. Further, the carbonyl region vibrations (1700-1800) are not as pronounced in Raman as in ATR-FTIR spectroscopy (please refer to Figure 3.26), although a band at 1720 cm^{-1} is hinted in spectrum (a) of Figure 3.26. The vibrations at 1447 cm^{-1} , attributable to the methylene deformation, are intense and well-detected in all SERS spectra, as well as in NR. The band at 1304 cm^{-1} is assigned to the $\omega(\text{CH}_2)$. The C=C unsaturations at 1665 cm^{-1} undergo to a considerable decrease in the microextracts of the oxidized oligomers comparing SERS to normal Raman spectra. To point out that in CHCl_3 microextracts (spectra a-b in Figure 3.26) the most intense C=C band shifts to 1591 cm^{-1} . Further, intense bands at approximately 1034 and 1010 cm^{-1} can be attributed respectively to $\nu_{\text{as}}(\text{C-C-O})$ and to $\nu_{\text{as}}(\text{C-C-O})$ of primary alcohols.

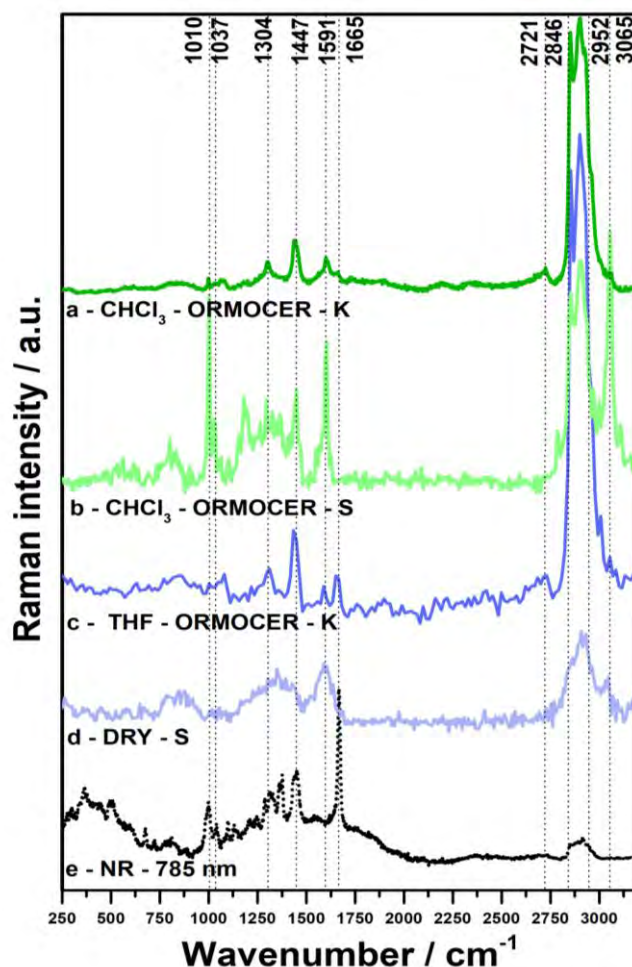


Figure 3.26: SERS microextracts (a - d) and NR (e) from *Traxe de home* by A. Pinal. SERS microextract (a) on KLARITE® replica with CHCl_3 . SERS microextract (b) obtained on SOKEN® cured with ORMOCER® polymer and transferred with CHCl_3 . SERS microextract (c) obtained on KLARITE® replica with THF. SERS microextract (d) obtained on SOKEN® replica through dry/direct sampling.

As anticipated in previous studies, Py-GC/MS helped to clarify the composition of the natural rubber used by Pinal. Degradation products were identified and the durability of the

material was assessed [333]. However, the amount of sample removed for analysis was of about 5 mg. SERS sensing could have anticipated the detection of oligomers before visible clues appeared. Unfortunately, before 2008 the assemblage of such an analytical tool kit designed specifically to perform fast screening of the surface of plastic artworks was not available. Hopefully, the current research provided sound integrated and multi-analytical evidence that indeed low amounts of material can provide reliable insights on ongoing degradation mechanisms in polymer-based objects.

3.2.5.3 Reflections on the nanodestructive sampling and its potentials

The initial aim of the present thesis was to demonstrate whether SERS sensing combined with the PDMS strip sampling method were suitable for the identification of LMW degradation products on polymer-based contemporary artworks. A thorough analysis of the evidence from model polymers and the objects confirmed that the novel method enables to detect LMW compounds reliably. In addition, for the first time small amounts of molecular fragments derived from oxidation could be detected with SERS, whereas SEC, Py-GC/MS and FTIR spectroscopy failed due to their reduced sensitivity. A new tool to monitor polymer aging behavior with direct identification of oligomeric degradation markers was made available. But **why** is this achievement so crucial to the future of applications on cultural heritage objects?

As introduced, *‘sampling is invasive and invariably causes damage, however small’* [2,11,353]. Is the removal of $\sim 10^{-10}$ g causing really any damage? Can multi-spectral imaging/portable instrumentation substitute the specificity and reliability of molecular information provided by SERS sensing? Prior to the beginning of the current study, a procedure with a total amount of extracted sample in the order 10^{-10} g, to the best of the author’s knowledge, was not available [209,210,298]. However, a relevant knowledge-gap is yet to be filled. Future research should be conducted to upgrade the definitions of non-destructive and non-invasive sampling in cultural heritage aiming for standardization. Furthermore, based on the current evidence condition reporting should be conducted encouraging periodical molecular screenings on the surface of polymer-based objects. Screening time ranges should be tailored, as in precision medicine, to the object’s need to implement preventive measures [10].

3.2.5.4 Summary

- Challenges faced by the conservators with the rapid decay of polymeric materials in contemporary artworks collections are unprecedented.
- Andrés Pinal’s artworks made with natural rubber of PI were extensively studied in several collaborations with the CGAC, providing insights on naturally aged materials monitored in short and mid-terms with several instrumental methods.
- SERS sensing associated with the novel sampling method was validated on *Traxe de home* to assess selectivity and sensitivity on naturally degraded objects, solvent tunability, solvent-free detection, and enchantment of the signal of nanostructures versus microstructures.

3.3 EXTENDING THE APPLICATION OF SERS DEVICES TO SMALL MOLECULES OF INTEREST

Once the validation of the analytical method was accomplished on polymer-based model materials and objects, further application endeavors were pursued. Could the SERS substrates with the PDMS strip samplers be reliable sensing devices on *a variety of small molecules*? The need of multipurpose analytical toolkits in heritage science research has been introduced in Chapter 1 and highlighted in several publications [3,5,351,354–357]. Multi-analytical approaches are often necessary to validate data [154,164]. On the other hand, exploiting the sensing system at its best potentials should be considered the analyst priority. In this perspective, addressing further research questions on small molecules, not only to inform managers and conservators on the conservation conditions of the objects, but also to understand manufacturing technologies of the objects seemed a further exciting challenge. Direct and indirect data on the objects help to achieve informed and comprehensive preservation strategies.

The following and final section of *Results and Discussion* is devoted to a series of experiments conducted on historical and actual objects to further validate the analytical method, but with the aim to address research questions on coloring media that are usually obtained through destructive analytical methods or with very expensive imaging instruments [153,358–360]. Mixing components is in not uncommon in coloring technology and SERS can help uncovering some unclear aspects beyond the complexity of the matrices under investigation.

A group of ABS-based LEGO[®] toys from two contemporary and historical collections was analyzed. Handheld and portable instrumentation, often preferred in museums, needs first to be validated against reference materials and with benchtop instrumentation. In the pilot study herein presented, the potentials of detecting synthetic organic pigments in complex polymeric matrices with Raman spectroscopy and SERS were explored for the first time. SERS on sub-micrometric samples solubilized with CHCl₃ was tested.

Further, rock art paintings from the prehistoric Portuguese dolmen of Antelas were analyzed. The analytical toolkit was sent out to fellow researchers for sampling for the first time from the beginning of the research. Coloring agents, binders and conservation products were searched and the results will be later summarized. Further, natural dyes from a collection of standard references was analyzed and compared with extracts from a loose fragment of leather derived from footwear dated to the 14th century. These two case studies will be presented, showing on the one hand the thresholds of failure of the sampling method, and on the other the relevance of working with historical reference materials to draw appropriate conclusions on natural dyes and capabilities of SERS enhancement on dyes.

Finally, six panels of *Ukyo-e* Japanese woodblock prints were analyzed with Raman and SERS settings to explore the technology of production of pigments and dyes during the Meiji industrial revolution. MA-XRF and 3D confocal Raman imaging provided useful insights on the multicomponent coloring media detected in several hues.

3.3.1 LEGO®: characterizing complex polymeric matrices with handheld, benchtop and SERS Raman

Table 3.7 shows the list of twenty-three analyzed LEGO® objects, including sixteen contemporary and seven historical objects. For all objects an identification name, description, size and L*a*b coordinates are presented. The numbers in bracket in the ‘Type’ column represent the numerical classification based on number of studs (short side X long side). Figure 3.27 shows a photographic image of all analyzed objects.

Table 3.7: list of analyzed LEGO® bricks including name, dating, size and color coordinates. *Adapted with permission from ref. [211]. Copyright Elsevier.*

Object Name	Dating	Type	Length X width X thickness (mm)	Color coordinates (CIE)		
				L*	a*	b*
Black1	2015	Brick (1 X 1)	15.5 X 7.5 X 11	13.28	-0.45	-2.37
White3	2015	Brick (1 X 1)	15.5 X 7.5 X 11	83.10	0.24	5.65
Pink1	2015	Brick (2 X 4)	32 X 16 X 12	75.57	26.31	-12.45
Grey2	2015	Brick (2 X 3)	23 X 15 X 10	57.48	1.18	1.25
Brown1	2015	Brick (2 X 3)	23 X 15 X 10	45.46	9.61	8.23
Wine1	2015	Brick (2 X 2)	17.5 X 17.5 X 12	44.96	18.92	9.55
Blue1	2015	Plate (2 X 6)	33 X 16 X 5.5	39.89	-9.52	-41.32
Blue5	2015	Wedge (2 X 2)	17.5 X 17.5 X 12	67.94	-34.17	-19.87
Green1	2015	Brick (2 X 2)	17.5 X 17.5 X 12	42.73	-62.30	30.12
Green3	2015	Wedge(1 X 1)	15.5 X 7.5 X 11	69.18	-19.23	69.48
Colorless1	2015	Wedge (1 X 1)	15.5 X 7.5 X 11	-	-	-
Black4	2015	Plate with wheels (2 X 2)	17.5 X 18 X 12	13.31	-0.20	-0.76
Yellow	2015	Cylinder (2 X 2)	16,5 X 12	79.87	7,44	84.12
Red	2015	Brick (2 X 4)	23 X 15 X 10	51.69	26.62	1.81
Purple	2015	Brick (1 X 1)	15.5 X 7.5 X 11	31.11	25.48	-41.36
Grey5	2015	Brick with propeller (2 X 4)	23 X 15 X 5.5	57.48	-1.18	-1.25
Green7	1972-1979	Brick (2 X 6)	69 X 34 X 22	51.57	-42.22	18.54
Blue6	1972-1979	Brick (2 X 4)	33.5 X 16 X 12	49.62	-20.14	-17.11
Grey3	1972-1979	Plate (2 X 8)	65 X 16 X 5.5	64.16	-2.13	2.68
White1	1972-1979	Brick (2 X 4)	33.5 X 16 X 12	87.48	2.45	18.65
Colorless 2	1972-1979	Brick (2 X 2)	16.5 X 16.5 X 12	-	-	-
Yellow	1972-1979	Brick (2 X 2)	17.5 X 17.5 X 12	79.04	10.07	69.17
Red	1972-1979	Brick (1 X 1)	15.5 X 7.5 X 11	44.71	47.19	27.82

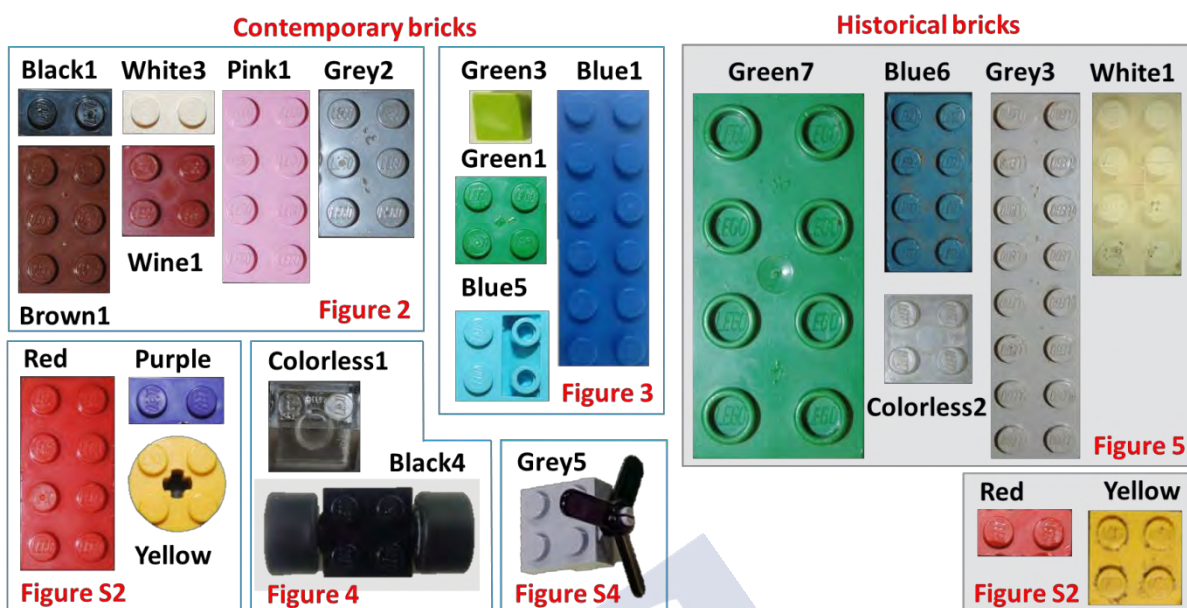


Figure 3.27: photograph of analyzed contemporary and historical LEGO® objects. Adapted with permission from ref. [211]. Copyright Elsevier.

All ABS Raman spectra were characterized by a main band at 1003 cm^{-1} , attributable to the benzene ring breathing vibration from the styrene acrylonitrile (SAN) part of ABS. Additional bands attributable to vibrations of the aromatic ring were found at 1003 and 1035 cm^{-1} . The complete list of bands and assignments of the spectrum [92] recorded with Raman benchtop instrumentation was shown in Annex Table 3.10.1.

3.3.1.1 Pigments detection comparing three analytical strategies

As the use of Raman handheld instrumentation allows a rapid non-invasive screening of objects, a low cost and light-weight handheld spectrometer was firstly employed to take Raman spectra of colored ABS brick and to assess its diagnostic capabilities. Figure 3.29a shows Raman spectra recorded with handheld instrumentation. The majority of spectra displayed good resolution. ABS bands centered at 1003 and 1035 cm^{-1} were visible in all objects, except for Black1 which showed a noisy spectrum with unidentifiable features. In addition, other bands attributable to either CICPs or SOPs used to achieve the desired coloration were observed in most spectra. Such features were marked with an asterisk in the spectra to distinguish them from the ABS bands. Specifically, bands attributable to the presence of TiO_2 were visible in White3, Pink1 and Grey2 spectra at ca. 412 and 620 cm^{-1} , overlapping with ABS bands but showing more intense features. Brown1 and Wine1 displayed non-ABS features at 409 and 505 cm^{-1} , attributable to Pigment Brown 29 (PBr29-C.I. 77500), an inorganic pigment of black mixed iron (III) oxide and chrome (III) ($(\text{Cr,Fe})_2\text{O}_3$) within an hematite structure [92]. In order to better assess merits and limitations of handheld instrumentation, an equivalent analysis was performed with benchtop instrumentation and recorded spectra are shown in Figure 3.28 b. All analyzed objects displayed strong bands at 620 , 1003 , 1032 , 1185 , 1200 , 1451 and 1603 cm^{-1} attributable to

ABS. For these spectra also additional bands associated either to CICPs or SOPs were observed for all objects. As in Figure 3.28 a, such additional bands were marked with black asterisks to distinguish them from the ABS bands. Specifically, Black1 and Grey2 objects showed bands attributable to the presence of carbon black (CB) with a typical vibration centered at 1302 cm^{-1} and a broadened band at 1599 cm^{-1} overlapping with the symmetric stretching vibration of the benzene ring from ABS. White3, Pink1 and Grey2 objects showed a shoulder at 610 cm^{-1} and an additional band at 445 cm^{-1} associated to the presence of TiO_2 . For Pink1 the broad band at 445 cm^{-1} showed a higher relative intensity compared to the other spectra where TiO_2 was also detected. Bands centered at 222, 292 and 411 cm^{-1} in Brown1 and Wine1 were identified as the dark brown and the reddish shades of Pigment Brown 29 (PBr29-C.I. 77500), an inorganic pigment of black mixed iron (III) oxide and chrome (III) ($(\text{Cr,Fe})_2\text{O}_3$), within an hematite structure [93,361]. Direct comparison of spectra taken by handheld and benchtop instrumentation showed that in spite of the lower spectral resolution and smaller spectral window, handheld instrumentation performed satisfactory characterization of ABS materials.

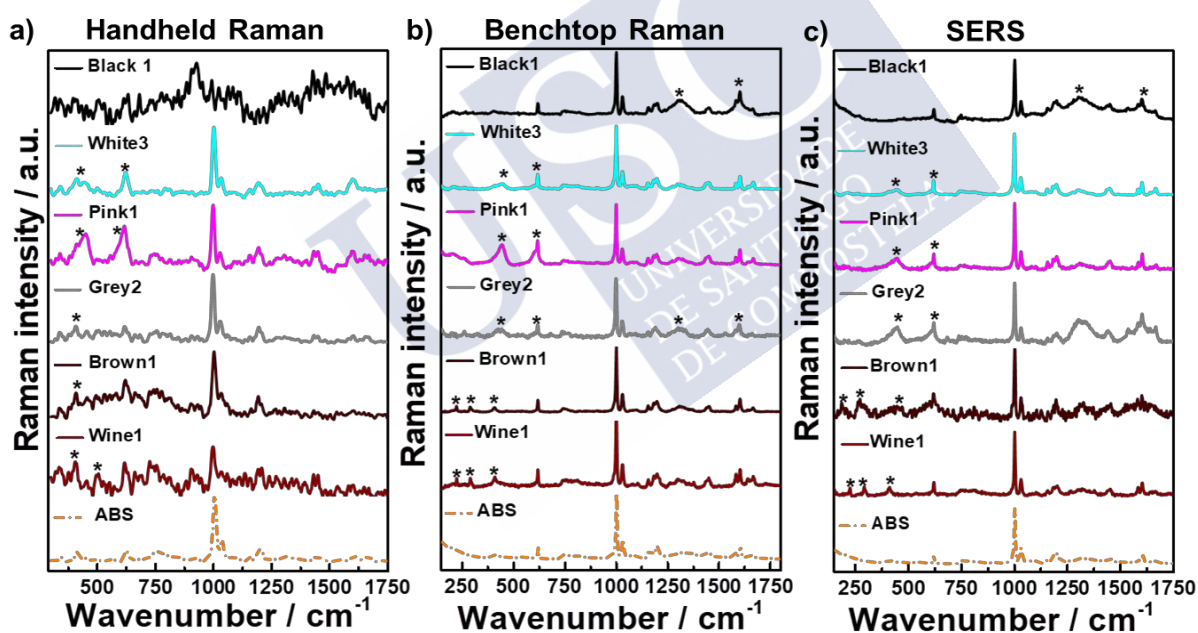


Figure 3.28: spectral analysis of contemporary colored ABS objects and reference ABS. a) handheld Raman spectra; b) benchtop Raman spectra; c) SERS spectra recorded with benchtop Raman instrumentation. All spectra were recorded with 785 nm wavelength illumination. Black asterisks indicate colorant component bands. Adapted with permission from ref. [211]. Copyright Elsevier.

As an alternative method, also SERS measurements were performed to test its suitability for the identification of coloring media in complex polymeric matrices, namely plastics used for contemporary artworks and design objects. As shown in Figure 3.29 c, clear spectral signals were obtained for all objects analyzed. The position and intensity of bands obtained was ca. equivalent to those obtained by Raman benchtop analysis, thus further confirming previous assignments.

Bands associated to the presence of TiO_2 at 443 cm^{-1} and CB at 1301 and 1603 cm^{-1} in Grey2 presented enhanced features compared to features obtained by Raman benchtop. These data confirm the capability of SERS to generate high intensity spectral features from sub-micrometric sampling through a simple one-step procedure. Hence the method is suitable for museum collections analysis, whereby instrumentation for *in situ* analysis might not always be available and sampling must be kept minimal to preserve the integrity of the analyzed object. The ability to obtain high quality spectra from minimally-invasive sampling is an important aspect. In fact, although the high sensitivity of SERS for the characterization of colorant and colorant mixtures in objects has been widely reported, its practical application is still limited by the need for extraction procedures, usually performed by complex three/four steps procedures with hazardous chemicals [348,362].

3.3.1.2 Raman sensitivity in discriminating copper phthalocyanines

Interestingly, Raman and SERS spectroscopies also proved effective in chemical differentiation of pigments used to achieve similar color hues such as those used in dark and light blue- and green-colored objects. Figure 3.29 a shows handheld Raman spectra of such objects. The spectrum of Blue1 showed strong bands associated to the presence of Copper Phthalocyanine (CuPc) pigments centered at 489 , 680 , 746 , 1141 , 1337 , 1524 cm^{-1} , likely Pigment Blue 15 (PB15, C.I. 74160). Such pigment belongs to the family of green and blue copper phthalocyanine SOPs, commonly used in paint formulations due to their high performance in stability, resistance to migration and good transparency [251,363]. The Raman spectrum of Blue5 showed bands at 685 , 745 , 1144 , 1195 , 1340 and 1529 cm^{-1} , also associated to the presence of CuPc SOPs, likely PB15. The spectrum of Green1 showed bands attributed to Pigment Green 7 (PG7, C.I. 74260), a chlorinated CuPc commonly used in plastics for its excellent light fastness and dispersion properties at 682 , 739 , 779 , 818 , 1082 , 1212 , 1340 and 1538 cm^{-1} . Green3 also showed bands characteristics of the presence of PG7 at 1533 , and 742 cm^{-1} [364,365]. Analogously to the analytical procedure showed in Figure 3.28, benchtop Raman and SERS analyses were performed on these objects to assess limitations of handheld instrumentation. The Raman benchtop spectrum of Blue1 (Figure 3.29 b) showed spectral features attributable to ABS at 1003 and 1032 cm^{-1} . In contrast to spectra of other colored objects shown in Figure 2b, whereby ABS bands constituted the predominant features, ABS bands in Blue1 showed relatively small intensity. In fact, the Raman spectrum of Blue1 was dominated by strong additional bands centered at 481 , 677 , 744 , 777 , 950 , 1104 , 1142 , 1340 and 1529 cm^{-1} , confirming the presence of a blue copper phthalocyanine dye (CuPc), likely Pigment Blue 15 (PB15, C.I. 74160) [251,363–365]. The Raman spectrum of Blue5 showed strong similarities with the spectrum of Blue1. Specifically, in addition to more pronounced ABS features, the following bands were observed, centered at 680 , 747 , 1142 , 1340 and 1529 cm^{-1} , also suggesting the presence of CuPc dyes. Initially the polymorph β -CuPc (PB15:3) was identified in Blue5 from comparison with spectral databases and diagnostic spectral shifts [251,363]. However, CuPc polymorphs present similar spectral features and in complex matrices where contributions from other components are present, spectral shifts are not sufficient to support a reliable discrimination. Band intensities also vary

between CuPc polymorphs and therefore intensity ratios are used as more reliable polymorphic markers [363]. Specifically, the presence of PB:15(0) and PB:15:3 in Blue1 and Blue5 might be confirmed by the calculation of intensity ratio of bands at 749 and 679 cm^{-1} which was equal to 1.5 and 1.1 for Blue1 and Blue 5, respectively. These values are in agreement with values reported by Defeyt *et al.* [363]. for Raman identification studies of CuPc used in modern artists' paints [363]. For clarity, bands attributed to CuPc pigments were marked with black asterisks in the spectra. Similar analysis was also carried out for two shades of green, also shown in Figure 3.29 b. The spectrum of Green1 showed bands at 264, 288, 346, 644, 686, 738, 778 818, 1081, 1212, 1276, 1340, 1537 and cm^{-1} which were attributed to Pigment Green 7 (PG7, C.I. 74260) [364,365]. On the other hand, the light green Green3 brick presented intense ABS features and also showed bands characteristics of CuPc compounds at 660, 747, 1378, and 1537 cm^{-1} , which were attributed to presence of Pigment Green 36 (PG36, C.I. 74265) [364,365].

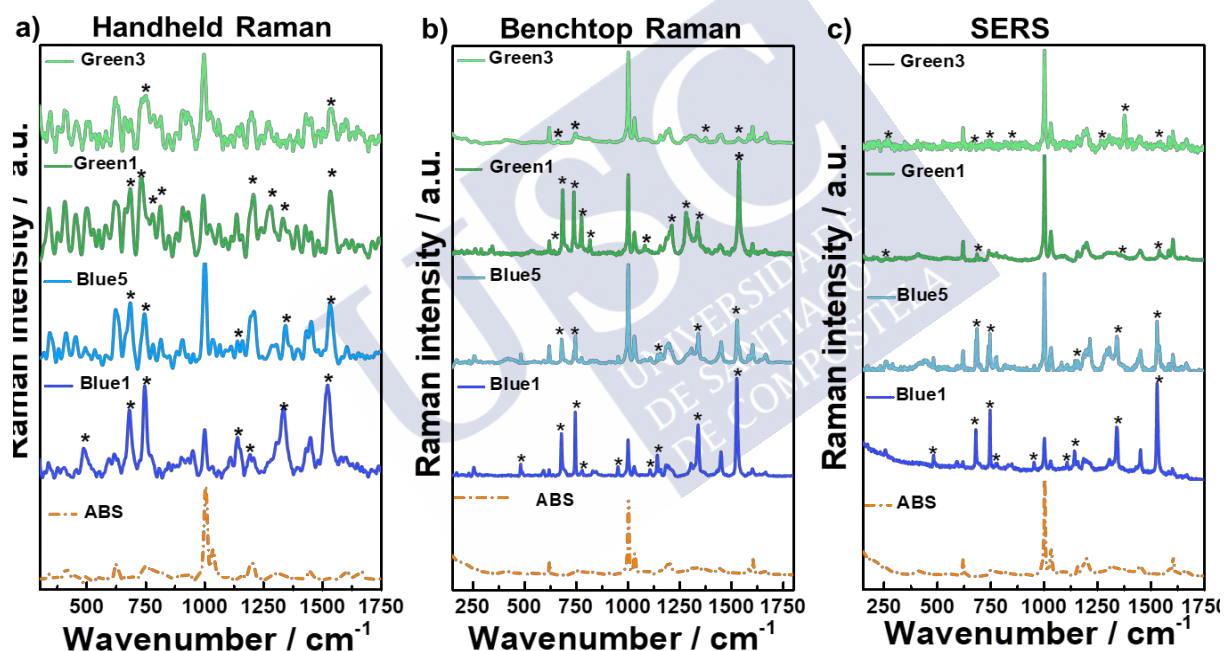


Figure 3.29: spectral analysis of contemporary green and blue colored ABS objects and reference ABS. a) Handheld Raman spectra; b) Benchtop Raman spectra; c) SERS spectra recorded with benchtop Raman instrumentation. All spectra were recorded with 785 nm wavelength illumination. Black asterisks indicate colorant components bands. Adapted with permission from ref. [211]. Copyright Elsevier.

The identification of CuPc polymorphs was obtained also by direct comparison of corresponding reference spectra from Raman spectral libraries [364,365]. Blue and green objects SERS spectra are shown in Figure 3.30 c. SERS spectra of good intensity were obtained for all colors, clearly showing presence of CuPc pigments in the objects formulations. Compared to Raman spectra, the ratio between the intensity of ABS bands and the intensity of colorant bands increased, showing that the ABS component was more easily extracted in CHCl_3 than the CuPc component, due to the latter poor solubility in organic solvents. However, clear presence of the CuPc SOPs was still observed, as shown by the

number of bands marked with black asterisks in the spectra. It should also be mentioned that additional Raman (handheld and benchtop) and SERS measurements were also carried out on red, purple and yellow colored objects (Annex Figure 3.10 a-f). For all samples ABS spectral contribution was evident, but no conclusive identification of SOPs was obtained.

3.3.1.3 PMMA vs ABS: technological choices

Although it is known that ABS is the main polymer used in LEGO® objects formulations, the use of Raman instrumentation allowed the identification of some cases in which alternative polymers or polymer blends were used to enhance mechanical properties and color of the objects [366]. Figure 3.30 shows Raman and SERS spectra of Colorless1 and Black4 objects, in which different polymer formulations have been found.

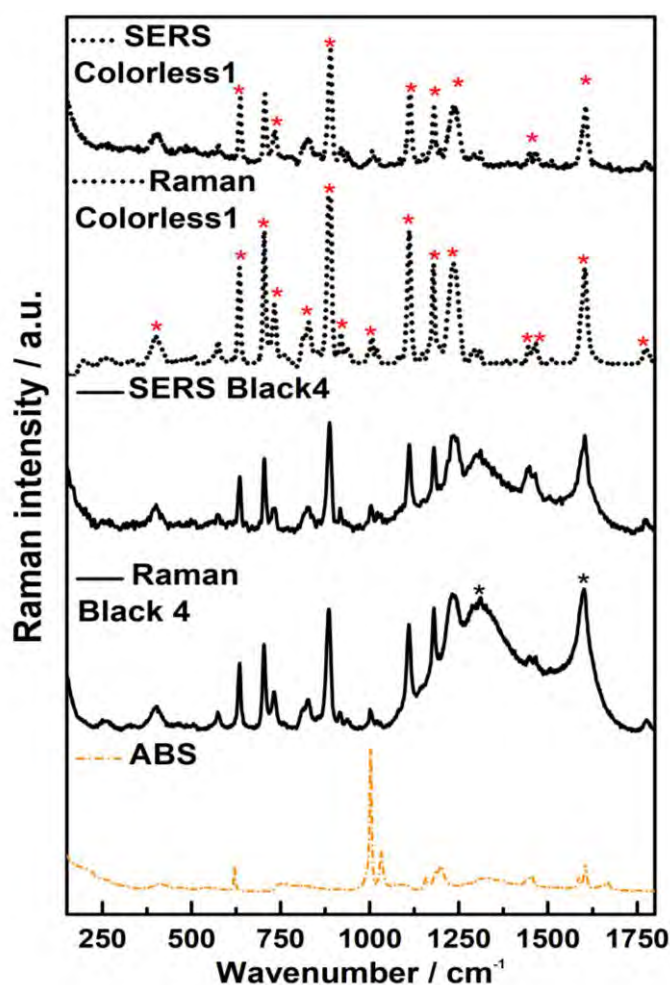


Figure 3.30: Raman and SERS spectra of Colorless1 and Black4 containing additional polymers to ABS. Both spectra were taken with benchtop instrumentation at excitation wavelength 750 nm. Adapted with permission from ref. [211]. Copyright Elsevier.

Specifically, in Colorless1 the strongest contribution was given by the presence of polycarbonate (PC) which characteristic bands were observed at 404, 636, 705, 734, 823, 887,

919, 1111, 1178, 1184, 1237, 1448, 1463, 1603 and 1778 cm^{-1} in both Raman and SERS spectra [367]. For clarity, PC bands were marked by red asterisks in the Colorless1 Raman spectrum. PC achieves superior transparency and presents lower yellowing with ageing [149]. In another example, the Raman and SERS spectra of Black4 also showed Raman bands attributable to PC at 404, 634, 708, 732, 832, 890, 922, 1008, 1109, 1179, 1237, 1448, 1465, 1603 and 1773 cm^{-1} . Black4 also showed broadened bands at 1603 and 1303 cm^{-1} attributable to CB (marked by black asterisks). In this case it has been hypothesized that the use of PC was intended to impart additional mechanical features to the brick (*e.g.* tensile and flexural strength, elasticity, hardness), as the piece was built to support the wheel attachment. This hypothesis was confirmed by the fact that the Raman spectrum of plain brick Black1 shown in Figure 3.30 a did not show any additional polymer to ABS. ATR-FTIR data for Black1 and Black4 shown in Annex Figure 3.10.2 confirmed the Raman attributions. The hypothesis related to enhance mechanical properties was also supported by the analysis of another grey brick, Grey5, built to allow optional propeller attachment which Raman spectrum also showed presence of PC (Annex Figure 3.10). As already observed for the previously analyzed colored ABS objects, spectra obtained by Raman and SERS showed comparable band intensity and resolution.

3.3.1.4 Historical LEGO® collection

Finally, LEGO® objects from the 1970's were also analyzed to test the reliability of Raman handheld and benchtop instrumentation for polymer and colorants identification on naturally weathered samples. Five historical objects were selected with colors corresponding to previously analyzed contemporary objects (refer to Annex Figure 3.10 for spectra of red and yellow of the historical objects). From an initial visual inspection of the photographs shown in Figure 3.28, superficial scratches and dirt residues were observed in all historical objects. Direct comparison with contemporary objects suggested photooxidation induced color alterations, particularly evident in the yellowed White1 and Colorless2 objects. Handheld Raman spectra of historical objects are shown in Figure 3.31. Green7 showed CuPc PG7 bands already found in contemporary Green1 with diagnostic bands at 637, 820, 1212, 1397 and 1534 cm^{-1} . Also CuPc was identified in Blue6 from bands at 684, 1124, 1337, and 1528 cm^{-1} . Presence of TiO_2 , already found in contemporary White3 and Grey5, was confirmed for White1 and Grey3 from the bands at 442 and 617 cm^{-1} . Colorless2 brick showed the following bands attributable to poly(methylmethacrylate) (PMMA), marked with red asterisks in Figure 3.31 b: 484, 593, 707, 745, 815, 964, 992, 1186, 1274, 1303, 1448, and 1734 cm^{-1} [368].

Benchtop Raman spectra of historical objects are shown in Figure 3.31 b. Historical Green7 and Blue6 showed presence of CuPc PG7 and PB15, as previously found in contemporary objects. To the best of the available knowledge, there is no published evidence that explains the technological choice to substitute the blend of ABS and PMMA (historical brick, Figure 3.31) with plain PC (contemporary brick, Figure 3.31) for the fabrication of transparent LEGO® objects during the last forty years. However, in both cases gloss and transparency were the main features to achieve.

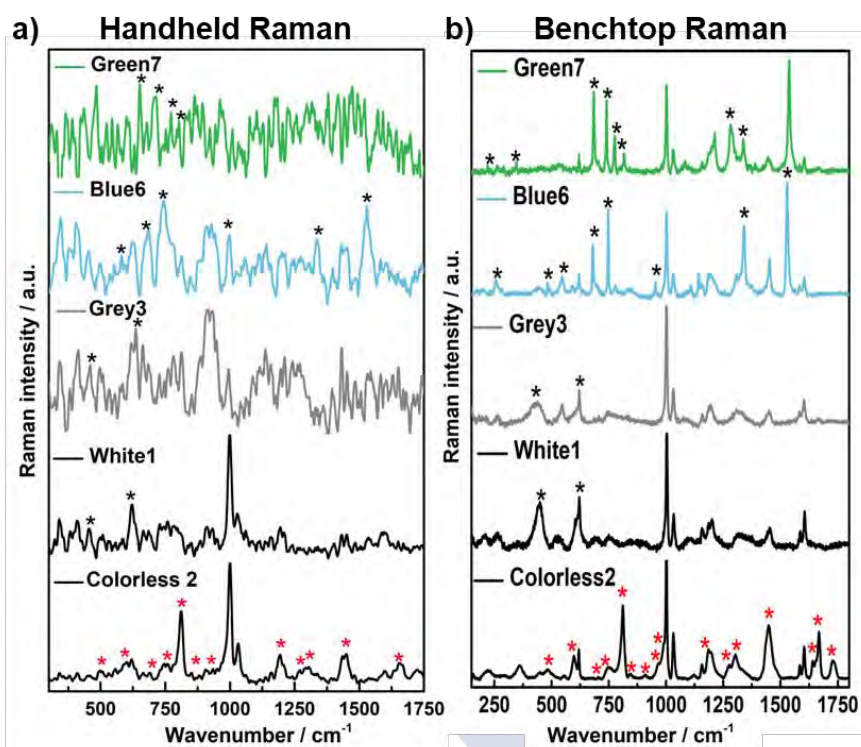


Figure 3.31: spectral analysis of historical colored ABS objects and reference ABS. a) Handheld Raman spectra; b) Benchtop Raman spectra. All spectra were recorded with 785 nm wavelength illumination. Black asterisks indicate colorant components bands. Red asterisks denote PMMA bands. Adapted with permission from ref. [211]. Copyright Elsevier.

Conclusive evidence on the oxidation of Colorless2 could not be determined because of the overlap of PMMA bands with ABS diagnostic bands for potential identification of oxidation [149,369]. As no evidence of degradation can be discussed, the macroscopic change in color/yellowing observed in the historical objects compared to the contemporary objects was ascribed to the well-known poor yellowing performance of ABS reported in several publications [149,152,210]. Further color identification in historical objects is provided by spectra collected with handheld Raman instrumentation and comparison with spectral databases (Annex Figure 3.10).

3.3.1.5 Summary

A summary of polymer and colorants identified in analyzed contemporary and historical objects is reported in Table 3.8. This section of the thesis, published in 2020 [211], represents the first example of systematic chemical characterization of contemporary and historical LEGO® toys performed by Raman spectroscopy, combining Raman handheld and benchtop instrumentation, as well as SERS optimized for minimal-invasive analysis. The aim was to provide the foundations for the spectroscopic interpretation of complex colored polymeric matrices, assessing merits and limits of each technique and their potential for fast and reliable analysis of museum objects. Benchtop Raman instrumentation was effective for

the non-invasive and non-destructive identification of the main polymer and pigments, proving enough sensitivity even to identify subtle chemical compositional differences between similar color hues (green and blue phthalocyanines).

Table 3.8: list of analyzed contemporary and historical objects and identified polymer/colorant components. Reproduced with permission from ref. [211]. Copyright Elsevier.

Object Name	Identified polymer/color component
Contemporary	
Black1	ABS, CB
White3	ABS, TiO ₂
Pink1	ABS, TiO ₂
Grey2	ABS, CB, TiO ₂
Brown1	ABS, PBr29, (Cr,Fe) ₂ O ₃
Wine1	ABS, PBr29, (Cr,Fe) ₂ O ₃
Blue1	ABS, CuPc (PB15)
Blue5	ABS, CuPc (PB15:3)
Green1	ABS, CuPc (PG7)
Green3	ABS, CuPc (PG36)
Colorless1	ABS, PC
Historical	
Black4	PC, CB
Green7	ABS, CuPc
Blue6	ABS, CuPc
Grey3	ABS, TiO ₂
White1	ABS, TiO ₂
Colorless2	ABS, PMMA

At a first glance SERS analysis showed sensitivity comparable to benchtop Raman analysis. However, the great advantage of SERS relied on the use of a novel minimally-invasive sub-micrometric sampling. This alternative approach is extremely desirable in museum settings and could well replace conventional Raman spectroscopy, when portable instrumentation is not available and/or does not provide reliable data. These results can be extended to historical plastic objects, not sampled in this pilot study to preserve the integrity of the material. Experimental results and methodological approach presented are recommended in real museum decision-making scenario: the initial screening of the object examined should be performed by non-invasive handheld instrumentation; if the chemical identification of pigments and dyes dispersed in the polymeric matrix is inconclusive, then minimally-invasive SERS should be performed.

3.3.2 Pushing to failure the diagnostic rapid kit: case study of the Dolmen of Antelas, Portugal

In the Iberian Peninsula, megalithic rock art is rather spread, although limited examples of well-conserved paints survived [370–374]. Antelas is a national Portuguese monument since 1990, known as the **best preserved painted burial dolmen** in Europe [375]. The Neolithic site is located in the municipality of Oliveira de Frades in Viseu district, northwestern Portugal. A completely sealed gallery at the entrance of the tomb leads to the crypt with mural depictions (circular plant with 2 x 2.5 m area). Before the excavation of 1902s, more than half of the painted surfaces were buried, therefore well-preserved, whereas those exposed to light, freeze and moisture cycles weathered over the millennia [371].

Considered the *Sistine Chapel* of megalithic prehistory [375], the chamber is constituted by **eight granite blocks** (Figure 3.32) displaying cosmological motives painted in dichromatic tones of black (carbon black) and red (limonite and hematite) [376]. The myth of eternal return was represented through moon and sun with spirals and zigzags symbolizing the labyrinthian walks that should have prevented dead ones from returning to earth [372,377]. Style, degree of detail and preparatory materials found on some blocks led to hypothesize that at least six different painters took part to the decorative endeavor [371]. In particular, the headstone of the chamber and the neighbor block were accurately prepared with a kaolin layer, overlapped by finely powdered mineral pigments, reported as viscous, possibly due to the use of vegetal and animal binders (Figure 3.32a) [371,378–382].

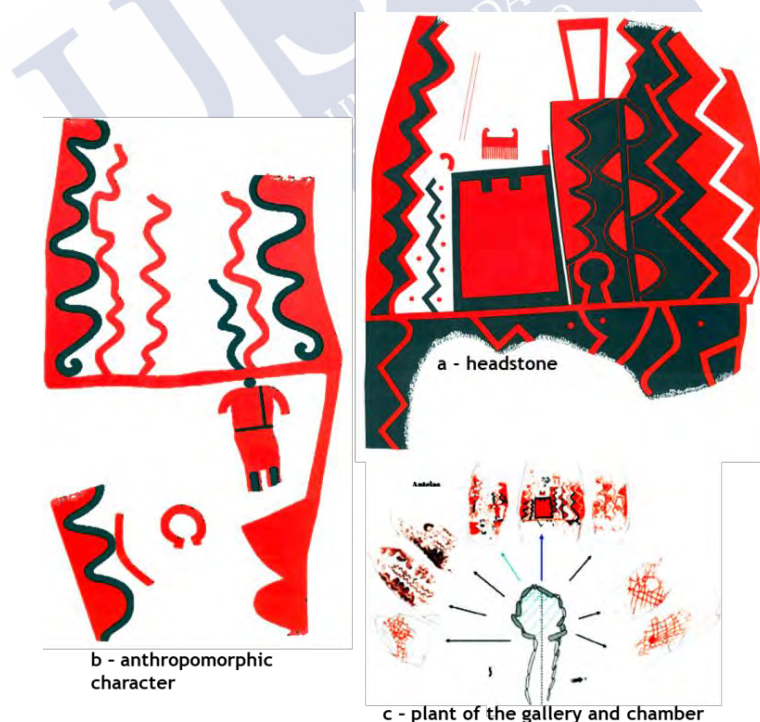


Figure 3.32: representations of the motives on the headstone (a) and neighbour granite block (b) from the funerary chamber of the megalithic monument of Antelas, Portugal, in the plant (c). Adapted with permission from ref. [371,372]. Copyright Direção-Geral de Energia e Geologia (DGEG) and Universidade do Porto.

A feminine figure was depicted next to the headstone, as a rare anthropomorphic example in rock art (Figure 3.32 b) [375]. The author of this thesis considers the conservation project held in 1957 an excellent example of interdisciplinary collaboration [371]. Back then, the national geological service was involved with archeologists, conservators, architects and mine engineers to decide whether the uncovered painted surfaces had to be transferred to a monitored indoor environment. However, the exfoliating behavior of the gneiss-based stone around the chamber would have provoked stability issues, increasing the probability of damaging the paints. Therefore, ahead of times, *in situ* preservation strategies were implemented together with instrumental analytical work.

De Albuquerque e Castro and co-workers [371] reported that an extremely low quantity of sample - *infima* - from detachments was used to prepare a thin section and a qualitative elemental analysis was performed. The latter revealed the presence of Fe, Mg, Mn, Si, Cu, Na, Ti, Al and C; and the former confirmed the presence of iron oxide minerals. Unfortunately, the claims about the use of animal and vegetal binders, as well as the use of blood from sacrificial victims in the red paints were not supported by analytical data [371]. Instead, black was, correctly, described as a soluble coloring medium possibly used without a binder from burnt organic materials.

In 2019, the collaboration held with the Department of Mining Engineering of the University of Vigo, Spain, gave the opportunity to explore whether organic binders in low concentrations could be SERS-detected through the PDMS strip sampler method. A survey of the materials from a geological standpoint was conducted by the fellow researchers. A rapid diagnostic kit with the PDMS strip samplers was sent to the site. An internal report of the most recent field mission mentioned a yellowish substance on the non-painted areas of the geometrical patterns on the headstone and elsewhere. Two ‘*service*’ *research questions* were posed: 1) **what is the yellowish substance**, 2) **was there any residue of animal/vegetal binder in the paints?** However, a third ‘*methodological*’ *research question* arose during the tests of the rapid diagnostic kit: 3) **what are the solubility and concentration thresholds of the PDMS strip sampler method?**

The amount of material physisorbed on the PDMS strip samplers was considerably low, below the limits of detection of the scale available in our laboratory. Some minuscule fragments of mineral/rock were visible on the strips and were documented with optical microscope (Annex Figures 3.11). Searching for compounds like oils and not having the opportunity, at least in the short-term, to repeat the sampling, the decision to proceed with a slightly more aggressive extractive protocol was taken. Soaking the strip in a dish for ~1 min with 250 mL of CHCl₃ would have maximized the chances of extracting any type of compound physisorbed on it. The solution was transferred into a vial left opened evaporating overnight. Following, the vial was rinsed with 20 μ L of clean CHCl₃ (Corning[®] Lambda[™] Plus single channel pipettor). Finally, 1.5 μ L were dropped onto the SERS-substrate and few accumulations on the same area of the plasmonic surface helped increasing the concentration

of the analyte. Solid residues could be observed in all vials from the six¹¹ sampling strips under analysis.

Figure 3.33 (a-d) shows SERS spectra with $\lambda_{\text{exc}} = 532$ and Raman mapping of the detected compounds and the sampling area. After the microextracts were transferred to the substrates, subsequent experiments with SOKEN[®] and KLARITE[®] replica substrates were conducted. The WITec instrument was used repeating the analysis $\lambda_{\text{exc}} = 488, 785$ and 532 nm. Further, the residual analytes in the vials were re-solubilized with water and ethanol to test solubility and polarity of different solvents, following the analytical approach introduced in the section about polymer degradation (3.2). (Additional SERS spectra of hematite and further findings are in Annex Figures 3.11).

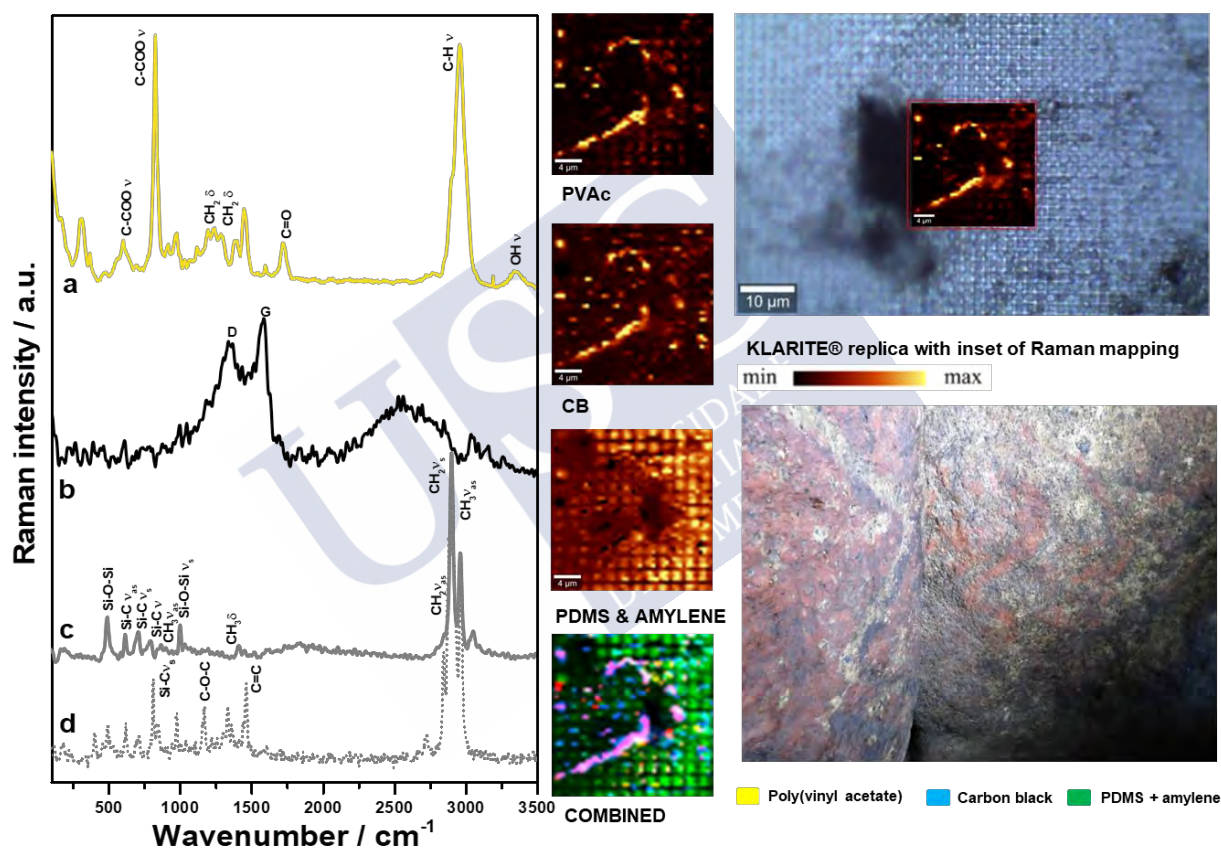


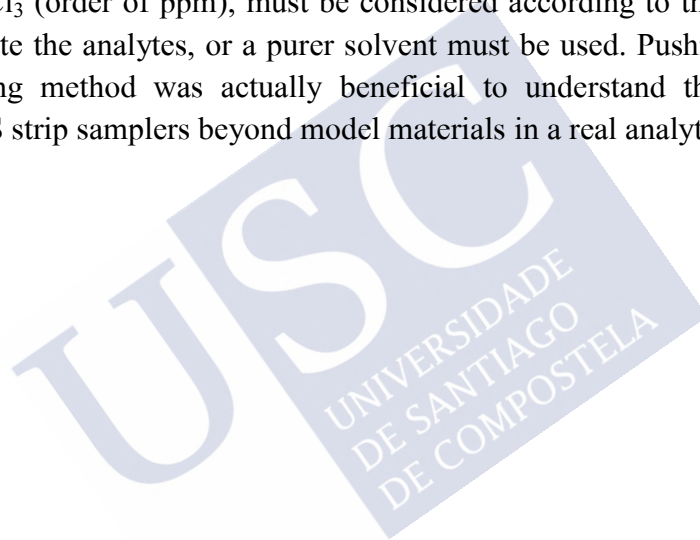
Figure 3.33: SERS microextracts (a - d) obtained with $\lambda_{\text{exc}} 532$ nm with the WITec instrument, microextracts with CHCl_3 . Spectrum (a) PVAc from the surface of sample RNC6+; spectrum (b) CB organic pigment; spectrum (c) PDMS from sampler and (d) in combination with amylen from CHCl_3 as contaminants.

In most instances, four different components were identified during the extractive procedure: a coloring medium (CB or hematite), an unwanted conservation material, two unwanted sampling contaminants. In particular, spectrum (a) in Figure 3.33 shows the

¹¹ PDMS samplers were named after the six sampled areas: PC4, NC5, RNC2, RIC2, RNC6+ and AC5. Fellows from the University of Vigo selected the granite blocks to address coloring media red and black, preparatory layers, as well as odds like the yellow substance on non-painted areas.

presence of PVAc (bands assigned in-text), which constitute the yellowish substance questioned earlier. The adhesive is nowadays often considered an unwanted material in conservation practice [167,319,383]. However, to the best of the author's knowledge, the use of PVAc was not documented in internal condition reports. Difficult to assess when PVAc was applied on the surface, however its removal was considered necessary for a proper conservation of the monument. The finding is very useful to build the history of the object / site for future treatments. Spectrum b in Figure 3.33 shows D and G bands of CB amorphous organic pigment from the black area sampled in the photograph down on the right.

PDMS and amylene (spectra c-d in Figure 3.33) were detected as a result of solubilization and over-concentration of the analyte, respectively. Although this is a negative result, it is a valid result in the attempt to validate the sampling method. It is definitely not a strategy to pursue in the future that of soaking for ~1 min the PDMS, because this would lead all the unpolymerized PDMS fractions of the sampler to contaminate the analyte. Then, amylene, a stabilizer used in CHCl_3 (order of ppm), must be considered according to the accumulations necessary to concentrate the analytes, or a purer solvent must be used. Pushing involuntarily to failure the sampling method was actually beneficial to understand the thresholds of solubility of the PDMS strip samplers beyond model materials in a real analytical scenario.



3.3.3 Natural dyes and leather components from historical objects identified through novel SERS extractive approaches

Until about ten years ago, high-performance liquid chromatography (HPLC) was the most successful analytical method to identify red lakes components in heritage objects [384–393]. Instead, single-molecule detection coupled with other chromatographic methods (*i.e.* thin layer chromatography) have not reached the expected applicability envisaged by various scholars on actual museum objects [12,394,395]. SERS became the predominant method for dyestuff research in museum settings, being highly selective and sensitive [13–16,348,350,396–402]. The success can be explained by observing few favorable aspects of the technique. The amount of sample taken for measurements is of few *ng* for ultrasensitive SERS, whereas few *mg* are necessary for HPLC [12,347]. Further, the high fluorescence of dyestuff is well-known in the literature [390,396,401–403]. For example, anthraquinone compounds have an average absorbance cross-section of $\sim 10^{-15} \text{ cm}^2$, whereas a typical Raman scattering cross-section is $\sim 10^{-30} \text{ cm}^2$ [395,402]. The ability of SERS to quench the fluorescence was demonstrated by various authors [13,396,398]. Chromophores in mixtures of dyes from actual historical fabrics and paintings have been identified with various extractive methods (e.g. degrading acids) [18,348]. Recently, novel SERS-sampling strategies allowed small molecules detection on heritage objects, focusing on lowered removal of material from their surface [210].

In 2019, a collaboration with the Higher Institute for Conservation and Restoration of Rome, Italy, allowed to analyze **natural dyes references** from a historical collection together with a loose fragment of **historical leather** ($\sim 2 \text{ mg}$) belonging to the lining of a pair of **papal sandals** [404]. The suitability of *nano* and *micro* Al-coated SERS platforms combined with a PDMS strip sampler for nanodestructive removal of free molecules was tested on the leather fragment to obtain information on the coloring materials and manufacturing technology [405]. Comparisons with the reference dyes extracted from dried microorganisms brought new information on leather-making, while serving to optimize novel analytical procedures. Further, to date SERS-based identification of chromophores used in historical leather has not been published. The experiments herein presented show the advantages and drawbacks of a progressive extractive approach with water, ethanol and further mixtures, combined with the silicone sampler strategy optimized in previous works [209–211].

Leather is a natural material, underexplored in heritage science, used as a fabric and derived from the skin of animals [406]. Like other skin-based products, leather is a flexible material consisting of interweaving fibers with high tensile strength, good heat insulation and vapor transmittance properties [406]. For millennia men specialized in the fabrication of a variety of leather types for different purposes by impregnating raw hides with fatty acids [407]. The space between the fibers is filled with oils that prevent biodegradation, allowing the durability of the skin. Salts, acids and water baths allow raw hides to become soft and relatively durable materials through slow drying (*e.g.* parchment). However, what distinguishes leather from pseudo-leathers is a chemical-physical transformation called **tanning**. Tanning is indeed the most relevant step of leather-making and its success depends

on the interaction between the collagen¹², main leather component, and tanning agents (*e.g.*, mineral salts/plants and oxidizing unsaturated fatty acids). The most relevant properties provided to raw skin by tanning are the increase of shrinkage temperature and the resistance to biodeterioration [406]. Also, increased hydrophilic properties are conferred to the new structure, with water uptakes up to 600% [406]. The key process consists of few strong covalent bonds and many weak hydrogen bonds holding together collagen molecules. Added fatty acids provide new crosslinks that strengthen the structure.

The leather sample made available for this part of the research belongs to a liturgical clothing collection preserved in the Museum of San Elia (Viterbo in central Italy). In 2010, Jervis and co-workers [404] initiated investigations on a pair of papal sandals of most interest in the collection. Although diagnostic tests were conducted then, the identification of dyes in the shoe lining was still unclear. Historical and technological researches placed these high-status pontifical sandals among the few available preserved examples of gilded shoes dating to the 13th century manufactured in Sicily [404]. Gilded leather was reported in Europe only from the 15th century onward when Spain was under the Arab rulers. Therefore, the sandals analyzed might have constituted a rare example of Islamic advanced manufacture, a testimony of the slow spreading of leather-making from the Middle East to Europe [404]. The lining was reported to be in poor conditions (*i.e.* shrinkage temperature 42° C) for obvious aging reasons, but also because it was made of pseudo-leather (alum-tawed). As for the tanning, the tawing procedure includes a weak interaction of potash alum with collagen mixed with water, salt, flour, and egg yolk that produces a soft material. Aluminum salts, however, can be washed out if wet (not a risk in lining materials).

Leather is constituted by collagen, which is the most abundant biomolecule forming extracellular tissue in animals [408,409]. It is formed by several amino acids acting as building blocks connected through so-called peptide bonds. Amino groups (NH₂) from one amino acid link to the carboxyl group (COOH) of another forming an amide (O=C–NH peptide bond). Amino acids as glycine, proline and hydroxyproline bond in long chains with residual C=O groups that might bond together with NH side groups. As a consequence, an α -helix might form. Length, diameter and quantity of the fibers determine the type of collagen (*e.g.* 26 types have been identified). Non-collagenous and collagenous domains within the connective tissues form according to the packing degree of the fibers, the position of end groups and the intramolecular connectivity with the helical chains.

Preliminary analyses on the coloring media used to dye the lining were pursued through a historical natural dye reference collection with grey cochineal, kermes and carmine. Cochineal is a scale insect (*Dactylopius coccus*) from which several red dyestuffs are produced, after drying and pulverization [410,411]. In Mexico, Chile and Peru cochineal cultivation on cactus plants was extensively practiced for centuries [387,412–417]. In modern times, cochineal has been widely traded. Cochineal was broadly classified as **grey** and **black**:

¹² Collagen is a protein constituted by amino acid units, containing amino and carboxylic groups linked by covalent peptide bond of the carboxylic group and the adjacent amino group. Side chains change the properties of the protein. Twenty amino acids constitute collagen (300 nm chain with about 1000 units), among which the main are glycine (30%), imino acid proline (10%) and hydroxyproline (10%).

the procedure of heating the insects in the oven, opposite to boiling them, respectively, is the main difference between the two types of cochineal [418]. Grey cochineal was sold for higher prices due to the better performing tinctorial strength of its extracts. When treated with mordants (*e.g.* $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ - alum), the chromophore precipitates forming a lake (**carmine**¹³), a less soluble form of the same dye [387,403,419]. Identifying the chromophore of cochineal, **carminic acid**¹⁴, has fascinated artisans, artists and chemists well before the existence of spectroscopy. And it still does. In Raman spectroscopy, the spectral signature of lakes results in slight shifts of the majority of the bands compared to the corresponding chromophores [14,395,403].

Celis *et al.* [413] reported a didactic SERS study on cochineal dyes and relative spectral differences (Figure 3.34), noticing that more intense spectral features derive from bottom residues of the extracts opposite to the supernatant fraction for a variable concentration of the chromophores. Separation of the components during manufacturing of the dyestuff, followed by the dyeing process and complexation might account for several compositional changes reflected in the spectra [396,397,413]. Similarly, in modern paintings analysis ultrasensitive and selective SERS identification of mixed anthraquinone dyes in cross-sections with frequent bands shifts and changes in relative intensities was reported [14,24,420]. Approximate Raman bands of carminic acid are the following: 1635, 1579, 1448, 1324, 1222, 1069 and 449 cm^{-1} [396].

Insightful *ab initio* calculations conducted by Osticioli and co-workers [403] on expected spectral signatures of red lakes allowed to discriminate between anthraquinone Al-complexes and dyes. Paint samples in cross-section from masterpieces of the Italian Renaissance (*e.g.* Leonardo's *Last Supper*), enabled the identification of chromophores, including carminic and **kermesic**¹⁵ acids.

Kermes is another scale insect (*Kermes ilicis*) from which dyestuff was extracted for millennia [421]. It has been traded by Egyptians and Romans throughout the Middle Ages, although the tint obtained from it is less intense than the red from cochineal. Kermes is harvested from oak trees (*Quercus coccifera*), native of the Mediterranean region, and spread throughout the Maghreb and Atlantic Europe. In the 13th century, kermes was even accepted in exchange for rent payments by landlords [418]. Overall, it is considered the oldest known red dyestuff. SERS bands of kermesic acid are the following: 1703, 1590, 1457, 1371, 1330, 1091, 1029, 953, 842, 794, 729, 646, 615, 564, 240 cm^{-1} [14,403].

¹³ Carmine is a metal coordination complex of aluminum and carminic acid, less soluble than its chromophore. It is produced boiling the powdered insects of cochineal in an alkaline medium, filtering the insoluble residue and adding the metal salt, *i.e.* alum, to precipitate the pigment.

¹⁴ Carminic acid is an anthraquinone linked to a glucose sugar unit (<https://pubchem.ncbi.nlm.nih.gov/compound/10255083#section=2D-Structure>).

¹⁵ Kermesic acid is a tetrahydroxyanthraquinone substituted by methyl and carboxy groups (<https://pubchem.ncbi.nlm.nih.gov/compound/11727234#section=2D-Structure>).

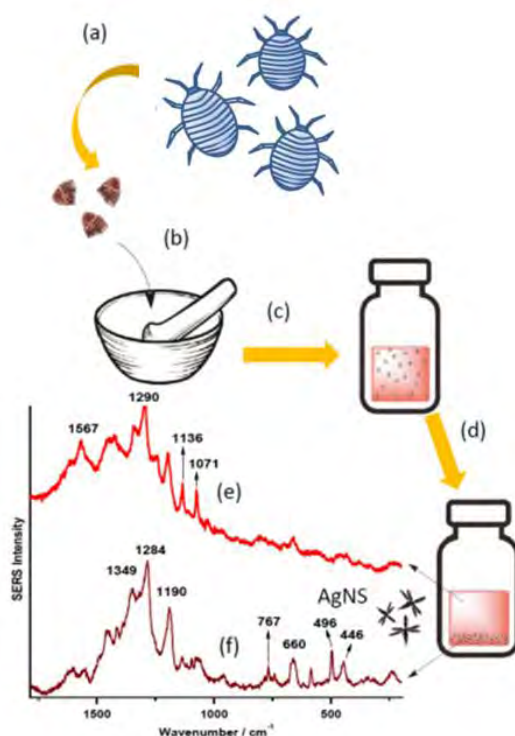


Figure 3.34. Representation of the extraction process to obtain the cochineal dye involving the following processes: drying (a), grinding (b), water suspension (c) and separation of supernatant and bottom residue (d). SERS spectrum obtained by using Ag nanostars and a sample obtained from the supernatant (e) and the bottom residue (f). Adapted with permission from ref. [413]. Copyright Springer Nature.

SERS spectra of anthraquinones might undergo band shifts due to chemisorption of the dye on the metal substrate [14]. Interestingly, the best signal enhancement reported in the literature when the excitation wavelengths matched the localized plasmonic resonance of the metal, rather than the absorption of the dyestuff on it [395,402]. Quality assurance for the reproducibility of the SERS substrates and their enhancement capabilities for dyes detection was questioned by Farling *et al.* [37]. A flowchart approach to ensure safe and minimally-invasive detection of dyestuff with SERS was proposed. Although alizarin is generally used to test the substrate fidelity (before direct analysis on historical samples), carminic acid was considered the best anthraquinone structure for this end. Batch-to-batch variability in the silver colloids was pointed out, proposing to research further on alternative nanostructures. This part of the thesis presents for the first time the application of Al-coated platforms on actual historical leather for simultaneous sensing of the coloring media and leather components.

3.3.3.1 SERS microextracts

As a preliminary *calibration* of the system, chromophores were extracted from the reference materials using EtOH and a mixture of EtOH:H₂O for exploratory SERS analysis. Then, 30 s dry-contact between the PDMS sampler and the leather fragment was performed. Physisorbed free molecules were collected washing the sampler out with EtOH. Further, a series of gentle peelings by scalpel on the outer layer of the fragment was performed under an optical stereomicroscope. Submicrometric grains were removed from all sides of the leather, mimicking a homogenous surface sampling to compare the SERS microextracts. Peeled grains were placed in a glass vial and collected with a Corning® Lambda™ Plus single-channel pipettor in about 2 μ L of solvent (H₂O, acetone, NH₄OH 28% in H₂O and CHCl₃) or mixture (acetone:H₂O, EtOH:H₂O). An average volume of $0.35 \pm 0.10 \mu$ L was dropped on the four corners of each Al-coated platform. After solvent evaporation, dropping was repeated 2-3 times to increase the concentration of the analytes (up to an average of $0.75 \pm 0.10 \mu$ L per sample). Figure 3.35 summarizes the extracts.

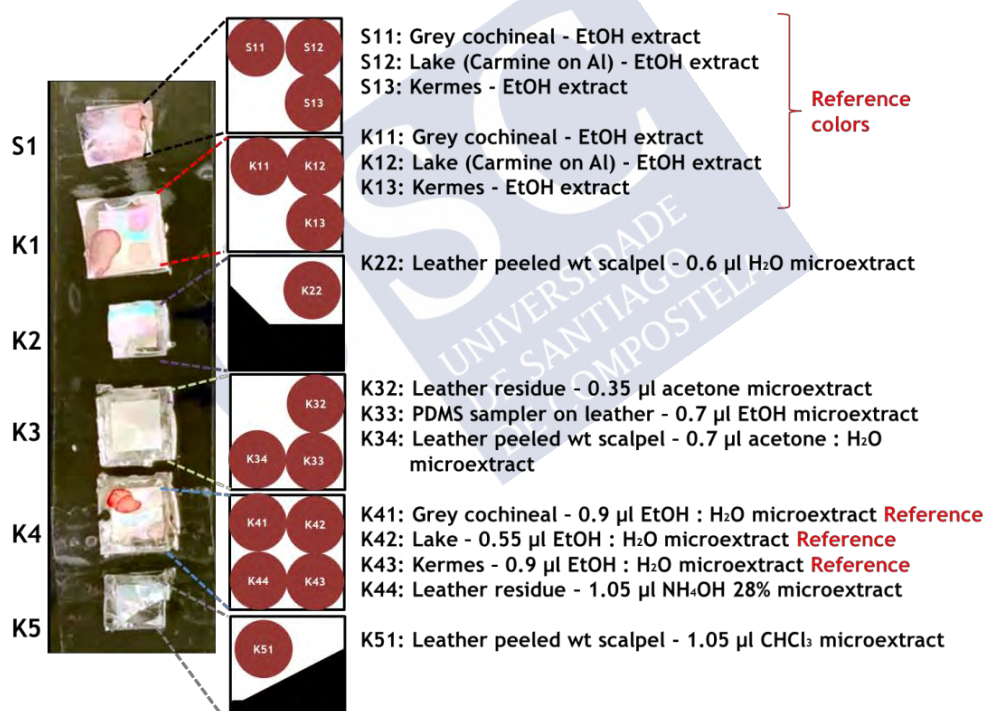


Figure 3.35: summary of the sampling and SERS extracting procedure with natural dyes standard reference materials and historical leather fragment. Samples were obtained by the collaboration with the Higher Institute for Conservation and Restoration of Rome, Italy.

3.3.3.2 Reference natural dyes and collagen components

Textile fibers from archaeological and historical fabrics carry the complexity of several uncontrolled occurrences with additional chemical-physical changes due to aging [388,413,422–425]. Therefore, it is not surprising that the SERS results about to be presented are not straightforward to interpret. Further no studies on historical leather have been carried out with SERS. Figure 3.36 summarizes the SERS spectra obtained from microextracts on reference historical materials of grey cochineal, kermes and carmine. Microextracts were

progressive, first with EtOH, and then with a mixture EtOH:H₂O. Further comprehensive results obtained on SOKEN[®] and KLARITE[®] replica substrates at different wavelengths are plotted in Annex Figure 3.12.

Overall, bands recorded on the microextracts with EtOH reflect typical anthraquinone modes [16,396,398,403,411]. In the region around 1640 cm⁻¹ bands are assigned to $\nu(\text{C}=\text{O})$ of the rings, whereas at around 1450 cm⁻¹ strong modes are attributed to the CC and $\delta(\text{C}-\text{OH})$ ring modes; further strong modes at about 1320 cm⁻¹ are assigned to $\delta(\text{C}-\text{H})$ in-plane modes, and finally weak modes at around 400 and 1000 cm⁻¹ are attributed to the ring vibrations. Specifically, the kermes spectrum in Figure 3.36a shows a broad band centered at 1642 cm⁻¹ attributable to the ring stretching, $\delta(\text{C}-\text{OH})$ and $\delta(\text{C}-\text{H})$ modes. Similarly, the band centered at 1591 cm⁻¹ is assigned to the ring stretching and $\delta(\text{C}-\text{OH})$. Following, the medium band at 1470 cm⁻¹ is assigned to the $\delta(\text{C}-\text{H})$ mode, as those at 1445, 1340, 1311 and 1200 cm⁻¹ that also additionally account for the $\delta(\text{C}-\text{OH})$ vibrations. Finally, the band at 1071 cm⁻¹ is ascribed to the CH deformation mode. Carmine and grey cochineal SERS spectra in Figure 3.36-b.c show close similarities to that of kermes microextracts, with some differences in the band at around 1645 cm⁻¹ being assigned to the $\nu(\text{C}=\text{O})$ and those at 1626 and 456 cm⁻¹ to the stretching vibration of the ring [14,398].

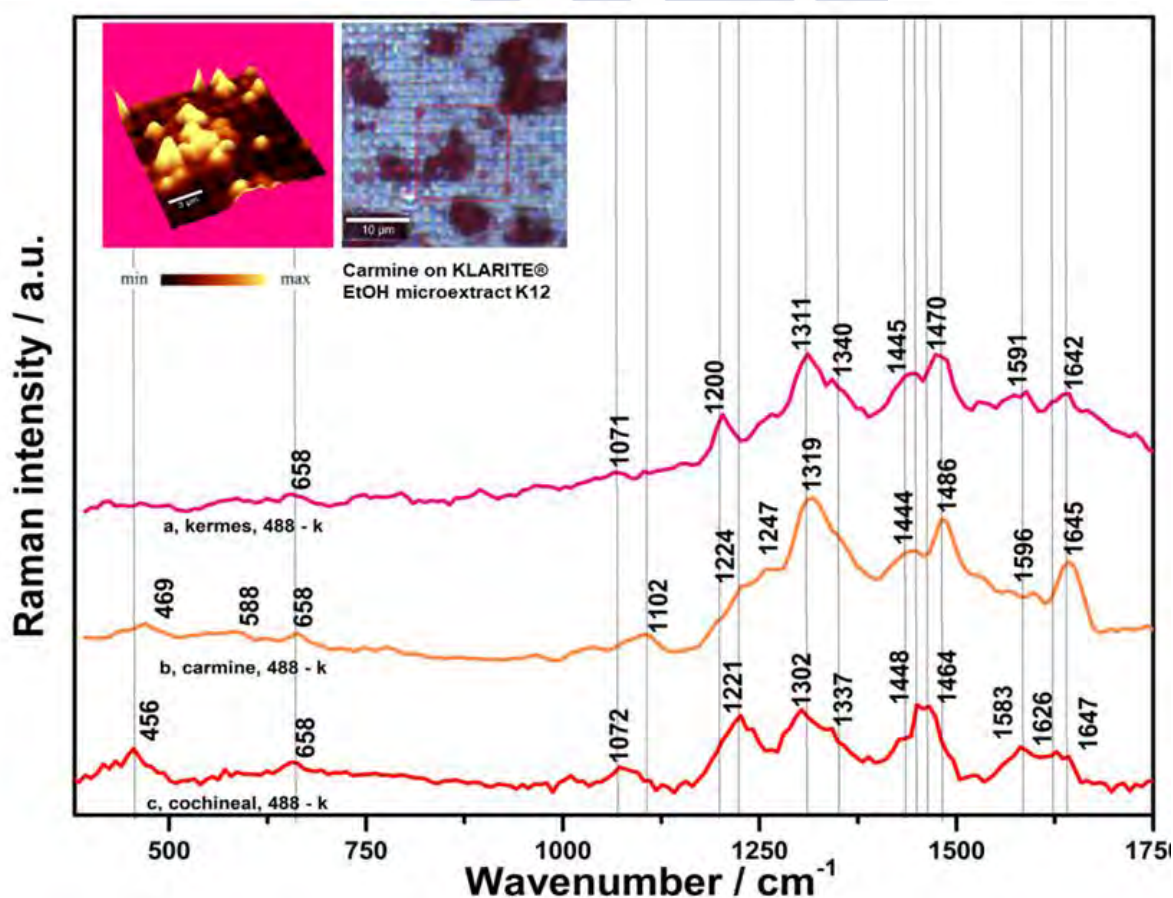


Figure 3.36: summary of SERS microextracts on natural dyes from historical reference materials of kermes (a), carmine lake (b) and grey cochineal (c). All microextracts were with EtOH transferred to KLARITE[®] replica substrates illuminated with 488 nm.

The main Raman bands of anthraquinone were detected in the majority of extracts from the leather fragment. Nonetheless, frequent band shifts and changes in relative intensities can be explained as a result of metal ion complexation of lake manufacturing coupled with the plasmonic interaction [14,402]. SERS analyses of the extracts from cochineal, compared to the extracts from dyed archaeological textiles and paintings, have been consistently reported as multi-components [387,389,391,413]. Biomolecules purification through alkaline media can yield *per se* in a significant variability of the dyestuff. In addition, regional differences in composition of the harvested insects reflect in the composition. Berbers and co-workers [387] pointed out consistent regional the compositional clustering of cochineal and kermes lakes from Europe and South America, providing HPLC evidence of minor and major components for the different groups.

A progressive sampling of the alum-tawed leather fragment provided new information on the dyes used in the lining of the sandals, but also more broadly on Sicilian-Islamic footwear manufacturing technology. Figure 3.37 shows SERS spectra obtained with the PDMS sampler method from free molecules on the leather surface ($\lambda_{\text{exc}} = 488 \text{ nm}$, EtOH microextracts). Then gentle mechanical peelings and subsequent transfer to the Al-coated platforms were performed with the above listed solvents. SERS allowed selective discrimination of various leather components. For example, *phenylalanine* was identifiable with the bands marked in red of both spectra in Figure 3.37. Further, the regions belonging to **lipids**, **amides**, **proline** and **hydroxyproline** have been highlighted with background colors from high to low frequencies, respectively.

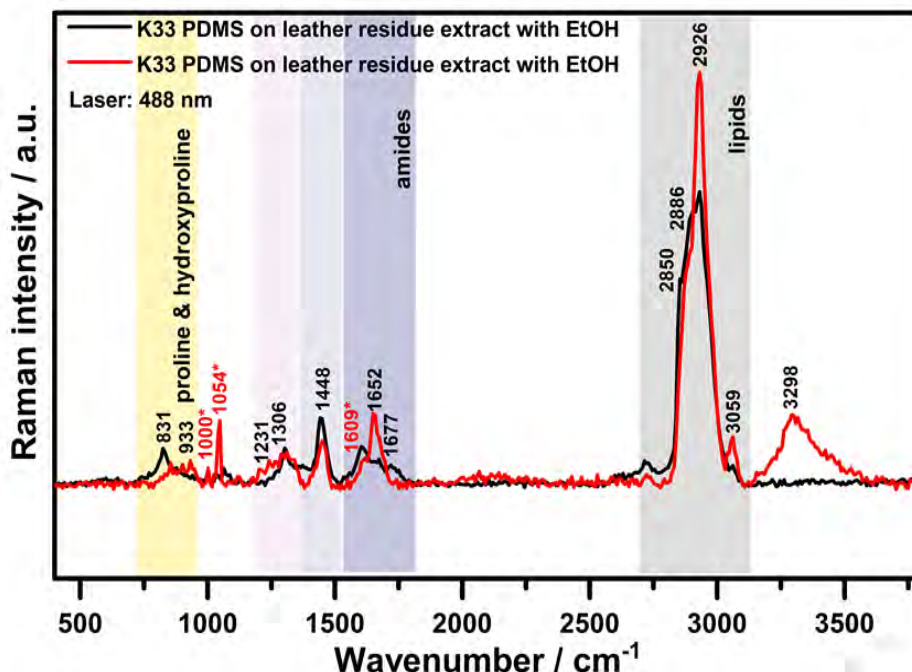


Figure 3.37: SERS microextracts with EtOH transferred from the PDMS sampler to KLARITE® replica substrates. This sampling on the leather fragment occurred before peeling procedures and lead to the detection of different collagen components.

SERS allowed detecting different collagen components with a simple one-step transfer procedure to the Al-coated platforms. Opposite to dye detection, no spectral manipulation was necessary to reduce the fluorescence of the signal. Raman spectroscopy is sensitive to two secondary structures within collagen: α -helix and β -sheet, being the former more abundant in collagen type I and III, the latter in type IV and VII [409]. Frequencies of Amide I and III show differences in the secondary structures. General assignment of Raman bands from leather follows. The band at 3298 cm^{-1} is attributable to the $\nu(\text{NH})$ mode. Deformation modes of CH_3 and CH_2 are respectively assigned to the bands at 2926 and 1448 cm^{-1} . Bands at 1677 and 1652 cm^{-1} account for the Amide I mode (α -helix in the red spectrum and β -sheet for the black spectrum) [409]. Amide III is reflected by the presence of the band at 1231 cm^{-1} . Residues of the helical structure of collagen are reflected in the bands at about 1000 and 1609 cm^{-1} attributable to phenylalanine, specifically, bands at 1000 and 1054 cm^{-1} are attributable to the phenyl ring vibrations.

Figure 3.38 shows the discrimination of dyestuff and leather obtained through a solvent mixture (acetone: H_2O). Intense phenylalanine signals can be explained by a greater abundance of collagen type IV instead of type I in the area sampled [408,409,426]. Changes in relative intensity of the bands of phenylalanine might be due to a favorable extraction with water, being both polar compounds. Bands ascribable to an anthraquinone structure (namely, 1635 , 1481 , 1322 , 1028 cm^{-1}) were also detected from different areas of the same microextract. The spectra resemble more closely that of carmine, rather than kermes, that one would expect to be used in Mediterranean Europe in the 13th century [403,421]¹⁶.

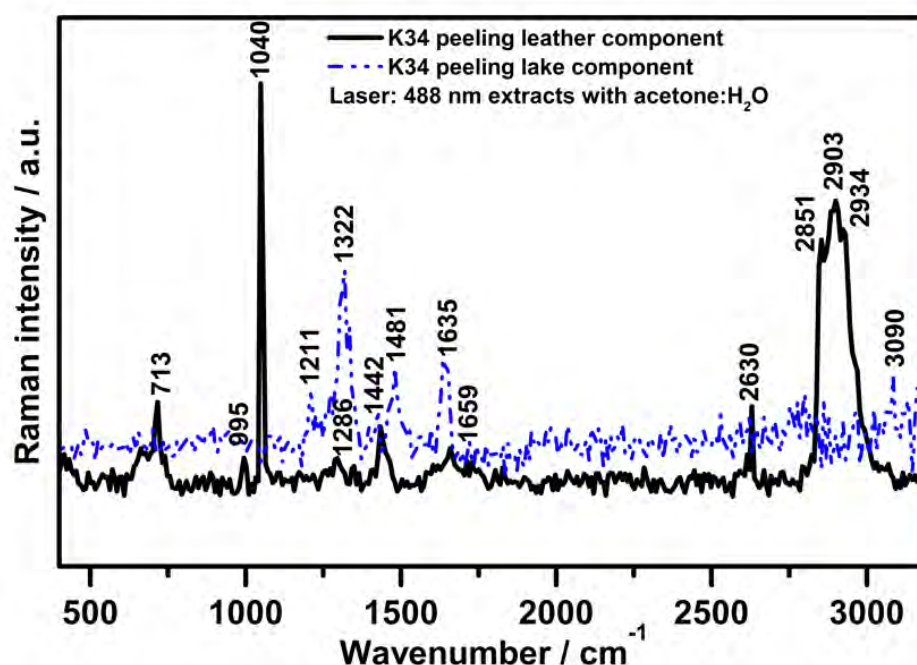


Figure 3.38: SERS microextracts with acetone: H_2O transferred to KLARITE® replica from peeled leather (extract K34) with detection of leather and lake components.

¹⁶ The importation of cochineal from Latin America to Europe was from 1523 onward [410].

The dating of the lining should be revised, either hypothesizing historical maintenance of the sandals or posterior manufacture. Importation of cochineal from Latin America to Europe initiated from 1523 onward [403,415,421]. However, the anthraquinone Raman fingerprint might be shifted for lake formation, or degraded due to aging. 3D Raman mapping allowed multicomponent discrimination of physically mixed molecules, unbounded chemically but closely placed one another. Figure 3.39 on the right shows SERS mapping and spectral results of microextracts from the leather fragment. Microphotographs obtained with the WITec confocal microscope (Figure 3.39a) show different magnified areas of a KLARITE© replica substrate with H₂O microextracts from sample K22. The corresponding 3D Raman maps highlight the main anthraquinone spectral features at 1645, 1480 and 1319 cm⁻¹ (Figure 3.39b). Below the maps, SERS spectra from microextracts with solvents and mixtures (acetone:H₂O, H₂O, NH₄OH 28% in H₂O) are displayed (Figure 3.39 c-e). For ease of identification, the SERS spectrum of carmine from the reference library obtained with EtOH is placed in Figure 3.39e (for band assignments refer to the previous comments on Figure 3.36). Apparently, the richest spectral features are provided by the mixture with acetone:H₂O of the microextracts from peeled leather grains in sample K34. Subsequent, H₂O microextracts from sample K22 showed a very similar spectrum, whereas the spectral response with CHCl₃ in sample K51 was too weak to be reported. After the peeling procedure, the leather sample was soaked in NH₄OH 28%, heated at 40 °C and sonicated for 1h. Some degraded spectral features do not prevent, however, from an unambiguous identification of carmine from sample K44.

Although the anthraquinone signal was barely distinguishable in CHCl₃ microextracts, interesting information on leather components was confirmed through the mild extractive approach experimented. Figure 3.39 (g-j) shows SERS mapping and spectral results from microextracts on peeled grains of leather. 3D Raman maps (Figure 3.39 g-h) highlight bands of the helical residues of phenylalanine and collagen, respectively. 3D maps help to assess the consistent distribution of collagen bands on the scanned area on the left, more abundant, compared to more scattered spectral hints of phenylalanine helical residues. SERS spectra in Figure 3.39 i-j show identical features of both leather components, although some vibrational modes are more intense in one spectrum compared to the other. Specifically, bands at about 3070, 1608 and 1007 cm⁻¹ with dotted background lines in spectrum i of Figure 3.39 are relatively more intense than those displayed for phenylalanine microextracts with the mixture acetone:H₂O in Figure 3.38.

Overall, in microextracts from the leather fragment the interplay of affinity and polarity of the molecules interacting is not straightforward to interpret. If one aims to assess the effect of the solvent polarity, direct comparison of SERS microextracts from peeled fractions should be made with caution. Like many heritage materials, leather (or alum-tawed pseudo-leather) resulted in a complex composite with nonpolar amino acidic components mixed with polar red lakes. Peeling of submicrometric grains from a small surface was inertly arbitrary, although it provided consistent SERS evidence. Further, reduced amounts of analytes, inertly carrying inhomogeneous concentrations and compositions, were handled dropping an average amount of 0.75 μ L for each extract on the Al-coated platforms, which might account for

further overlooked variability. Interestingly, despite the reduced sampling surface, the PDMS method allowed the transfer with EtOH of collagen residues. Polar red lakes were promptly extracted with increasingly polar solvents as acetone, EtOH, H₂O, mixtures, and NH₄OH conversely hand, nonpolar collagen and phenylalanine helical residues were detected in CHCl₃ extracts that provided only weak anthraquinone signals. Intermediate selective SERS-detection capability was achieved with the mixture acetone:H₂O showing lake and collagen components from the different mapped areas belonging to the same extract.

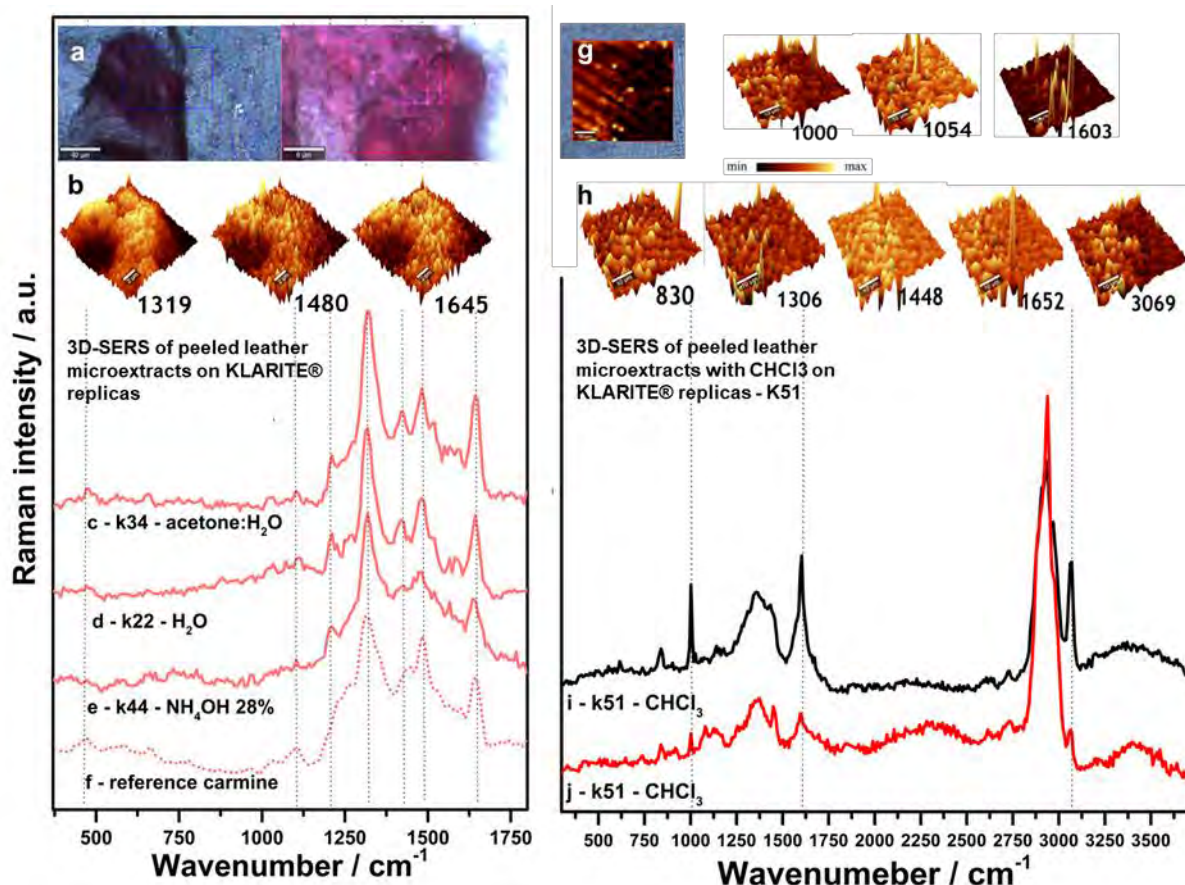


Figure 3.39: SERS microextracts and 3D mapping obtained from the leather fragment with different solvents. A) microphotograph at various magnifications of KLARITE® replica substrate, with blue and red areas corresponding to the map below; b) 3D Raman map with main bands of anthraquinone from; c) SERS microextract with mixture of acetone:H₂O -K34; d) SERS microextract with H₂O - K22; e) SERS microextract with NH₄OH 28% in H₂O - K44; f) reference carmine from the historical collection; Raman mapping from K51 microextract with CHCl₃; corresponding 3D mapping with highlights on phenylalanine and collagen bands. On the right, g) overall Raman map of microextracts with CHCl₃ - K51. Top row 3D map of phenylalanine main bands; h) collagen 3D map; i-j) SERS microextracts with CHCl₃.

3.3.3.3 Summary

The current research demonstrated that Al-coated SERS platforms enable sensitive and selective detection of red lakes and leather components from historical objects. The properties of the enhancing substrates were tested in previous experiments [210,290,298], and further optimizations have been implemented by using historical dyes reference materials. Analytical procedures for the extraction of multi-components followed a progressive strategy

ranging from a minimally-invasive physisorption of free molecules with a PDMS strip sampler to gentle surface peeling with a scalpel and finally soaking the leather in NH_4OH 28%. Polar and nonpolar solvents and mixtures (*i.e.* water, EtOH, acetone, and CHCl_3) were tested to explore their suitability for mild extractions, before soaking the fragment into the strong base. Further, the limiting analytical condition of working on a unique leather sample (~ 2 mg) was summed to the difficulties in assessing which grains were being removed from its surface through the sampler and the scalpel. However, the anthraquinone structure was consistently detected in microextracts on references and a leather fragment. Three main bands at around 1640 cm^{-1} , 1450 cm^{-1} , 1320 cm^{-1} , are assigned respectively to $\nu(\text{C}=\text{O})$, the CC and $\delta(\text{C}-\text{OH})$ ring modes and $\delta(\text{C}-\text{H})$ in-plane modes, were detected in the majority of SERS microextracts. Changes in band position and intensity have been recorded in cochineal, kermes and carmine spectral signatures; however, the current experiments suggest that carmine was used to dye the lining of the sandals under investigation. New information on Sicilian-Islamic footwear technology was achieved, although dating of the sandals might be reconsidered. The alum-tawed pseudo-leather showed diagnostic bands of collagen at 1677 and 1652 cm^{-1} accounting for the Amide I mode. Amide III was reflected by the band at 1231 cm^{-1} . Further, residues of the helical structure of collagen were reflected in the bands at about 1609 , 1054 and 1000 cm^{-1} attributable to the phenyl ring vibrations. Overall, the three progressively stronger extractive steps led to consistent conclusions on the composition and distribution of collagen and dyestuffs components with great impact provided by 3D Raman imaging scans. Future improvements to broaden the application of the extractive approach proposed to historical leather would need the preparation of mock-ups following historical recipes for tanning and dyeing, as well as for the precipitation of anthraquinone chromophores through metal salt complexations.

3.3.4 Japanese Ukiyo-e woodblock prints: detecting pigments and dyes

In East Asia woodblock printing techniques have been in use since the 7th century AD [252]. *Ukiyo-e* printing was imported from China to Japan, flourishing there throughout four centuries (16th-20th centuries) [427]. This kind of prints has been extensively exploited in the 19th century as a consequence of lowered fabrication costs and increasing demands for commercial supplies. In the Western world iconic prints, as the Great Wave by Hokusai (1830), have contributed to further commercialize the *Ukiyo-e* woodblock prints. In a short time, several technological adaptations of the production methods occurred [428,429].

In brief, the steps of fabrication of woodblock prints include: 1) carving the drawing lines in the woodblocks; 2) sealing the block with a slightly adhesive medium; 3) brushing the color on the corresponding block; 4) pressing the rice paper onto the block to print the reverse drawing; and 5) repeating the reverse printing for each color [430]. In general, the coloring media were thickened with starch and other inorganic fillers. Several recipes with traditional Japanese names of dyes and pigments have been reported in handbooks and publications on compositional identification [191,256,428–440]. Section 1.6.2 reported further details on the technology of production of woodblock prints.

In this section of the thesis, an attempt to detect and systematically identify the coloring media used in a series of six panels of woodblock prints made available through collaborations is presented (Figure 3.41). In one of them the signature, the year of fabrication of the woodblock¹⁷ and the address of the printing shop were indicated. The panels were selected as an example of cheap printed material, witnessing the industrial revolution ongoing in the late Edo-early Meiji periods in Japan [441]. (Annex 3.13 reports the remaining photographic images of the panels under study).



Figure 3.40: selection of photographs of the panels under investigation (n° 1 - 3). The remaining panels (4-6) are in Annex 3.13.

¹⁷ The date of the woodblock is 11th of January 1897, which is the 29th year of the Meiji period (1868 - 1912).

During the Meiji era, Japan was growing industrially and technologically, and the use of cheaper inks and the gradual dismissal of traditional woodblock printing techniques had started [434,436,442]. The overall aim of the research was to achieve a greater understanding of the fabrication technique and conservation conditions of the prints. Raman mapping with SERS sensors was combined with elemental imaging (MA-XRF spectrometry). As throughout the whole thesis, the investigation was targeted to test SERS substrates with the PDMS strip samplers to demonstrate their effective sensing potentials on small molecules.

3.3.4.1 Preliminary optimization to the one-step SERS sensing method on Japanese woodblock prints

The current section introduces ATR-FTIR spectroscopy and spectrophotocolorimetry results, as preliminary information for the general assessment of the prints. Color grouping will help to present the findings as follows: reds, purples, blue, yellow, greens, orange, pink, brown and black. Table 3.9 summarizes the corresponding CIE $L^*a^*b^*$ coordinates for the colors grouped. To be mentioned that the range of molecular weights for all colorants identified was between 0.2 and 0.8 kDa. Small molecules are ideal for the validation of the one-step SERS method proposed in the thesis. Small molecules were physisorbed through PDMS strip samplers with various solvents and solvent mixtures. The transfer to the SERS substrate with solvent was a direct dropping just after the collection on the print with no further sample preparation.

Table 3.9: color coordinates obtained with the spectrophotometer Konica Minolta™ CM700 (specular component excluded) on the six panels of Japanese woodblock prints

Color	CIE Lab coordinates (D65)		
	L^*	a^*	b^*
Red	41.11	51.78	29.19
Light purple	67.83	7.35	-9.21
Dark purple	33.51	24.83	-33.61
Blue	48.04	-11.57	-24.79
Yellow	75.42	0.64	31.77
Olive green	47.39	-5.02	6.42
Bright green	60.17	-25.73	15.04
Orange	56.81	35.89	31.63
Pink	81.03	7.34	18.23
Brown	60.71	2.91	11.1
Black	28.23	0.53	2.38
White	85.67	-0.12	13.88
Paper	88.11	0.85	14.46

In traditional Japanese printing, pure cellulose was pressed onto woodblocks previously prepared with a rice starch, heated before the application to favor gelatinization between coloring media and paper. Furthermore, mica powder was added to the colorants to provide a

metallic glitter to some hues (*e.g.* grey silver), concurrently functioning as a thickener of the gel (Kirazuri technique) [254]. When the print dried, the excess of powder was brushed off the print and the grains would enhance light reflection. The presence of uneven patterns, preferentially in white and black areas, observed in clothing of high-status characters can also be ascribed to the Kirazuri technique [254,429,430] (Figure 3.42). ATR-FTIR spectra in Figure 3.43 show bands belonging to polysaccharides in all panels analyzed.



Figure 3.41: inset of panel n°3 (a) with false color photograph to highlight the patterns on the clothing of the high status character according to the Kirazuri technique.

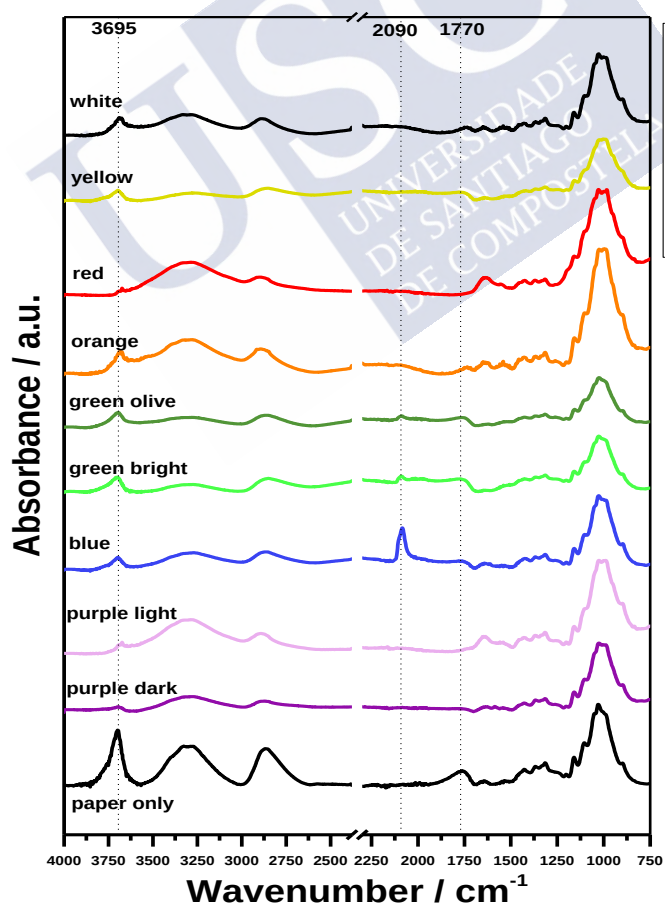


Figure 3.42: ATR-FTIR spectra of the different colored areas on the six Japanese woodblock prints (color indicated on the top left).

Rice starch and cellulose are based on polysaccharide macromolecules and have very similar spectra; therefore a distinction between the two could not be accomplished with FTIR spectroscopy. Starch is mainly constituted by linear and branched glucose-based chains, respectively amylose and amylopectin, plus additional fractions of impurities below 2% wt. [443]. They might include proteins and minerals, though not detected in this study. The region $1100\text{--}1200\text{ cm}^{-1}$ was assigned to the $\nu(\text{C-O-C})$ of the glycosidic components of cellulose and starch. Similarly, bands between $1200\text{--}1450\text{ cm}^{-1}$ were ascribed to $\delta(-\text{CH})$, whereas the band at 2870 cm^{-1} corresponded to $\nu(-\text{CH})$. Finally, a broad band in the region $3000\text{--}3550\text{ cm}^{-1}$ was assigned to the $\nu(\text{O-H})$. As a well-known consequence of photo-degradation of carbohydrate-based macromolecules, aldehydes and ketones arise, as reflected in the formation of a broad band in the carbonyl region (1770 cm^{-1} assigned to the C=O stretching mode), while the intensity of the bands corresponding to the O-H and C-O-C bonds decreases [443,444]. The carbonyl band was recorded in the majority of the prints, except those containing Prussian blue, where a strong distinctive band at 2090 cm^{-1} was assigned to the $\nu(\text{C}\equiv\text{N})$ of the cyanide bridges. Such band was recorded in the areas colored either with blue, or with bright and olive green, although in the latter was less intense (Figure 3.43).

As anticipated, mica powder was brushed onto the woodblocks to provide a glitter effect to solid colors. This claim was confirmed by the presence of an additional band with the maximum at 3695 cm^{-1} consistently detected in all prints and that could be ascribed to the $\nu(\text{O-H})$ vibration from the inner-surface of hydroxyl groups belonging to mica phyllosilicates [445]. Unfortunately, the most intense band of muscovite, the most compatible mica, at 1027 cm^{-1} (in-plane Si-O stretching mode) overlaps with the $\nu(\text{C-O-C})$ mode of carbohydrates; therefore, ATR-FTIR spectroscopy did not allow a conclusive identification of the mica.

Further, complete MA-XRF spectrometry data in Annex Figure 3.14 shows that elements such as Ca, K (X), Al, Mn, Zn (Y) and Si (Z) were consistently detected throughout the entire surface of the prints (XYZ crystal configuration). Figure 3.44 shows MA-XRF spectrometry for panel n°6.

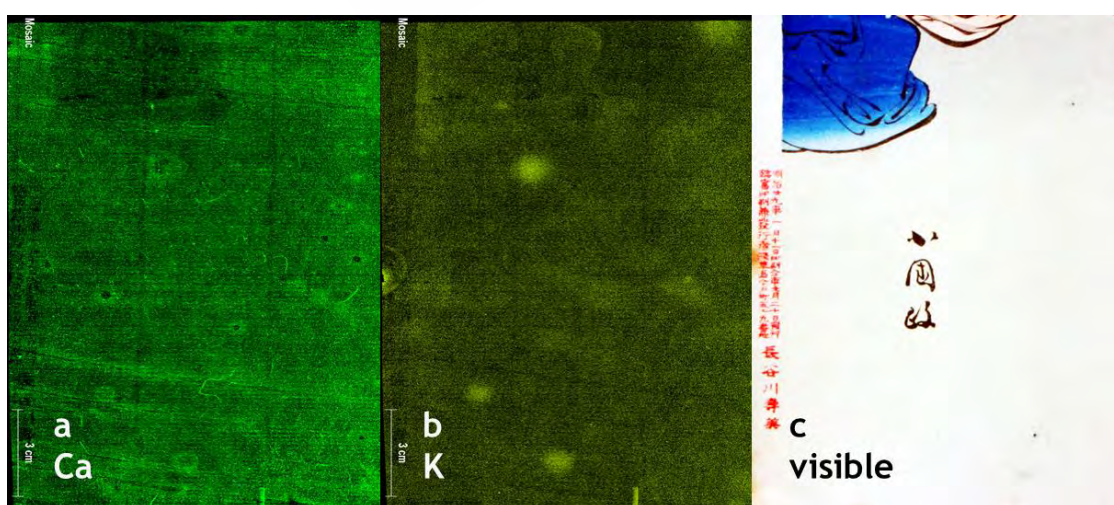


Figure 3.43: MA-XRF elemental mapping of panel n°6 of the woodblock prints (a) calcium, (b) potassium and (c) visible photograph of the panel. Circular spots with high concentrations of Ca and K might be self-assemblages mica formed during paper sizing.

Those elements are typically present in a variety of micas in association with $10\cdot\text{O}_2$. Interestingly, Ca and K signals were stronger in specific circular areas (in print n°6, Figure 3.44), and this might result from a tendency to self-assembly of fine grains of the mica with starch during gelatinization. The following section will be focused on the validation of the analytical method on water-soluble dyes and pigments, as well as on their contextualization within the Japanese woodblock printing techniques in the Meiji era.

3.3.4.2 Reds

Figure 3.44 shows three spectra (a, b, c) acquired illuminating the prints directly in the red areas through the benchtop Raman spectrometer. Spectrum (a) in Figure 3.44 was collected on the red columns from panel n°2 with the WITec instrument ($\lambda_{\text{exc}} = 488 \text{ nm}$ power $\leq 0.1 \text{ mW}$ - integration time 2 s and 30 accumulations). Further tests were conducted with $\lambda_{\text{exc}} = 532$ and 514 nm , although the excessive fluorescence did not allow molecular identification. During acquisition, the spectral features have changed leading to complete disappearance in some repetitions, meaning that the power of the laser, although kept intentionally very low, was sufficient to promote photo-degradation of the red coloring media. Regardless the poor ratio signal to noise, the spectral fingerprint of azo β -naphthol dyes could be identified in the region $1100\text{--}1700 \text{ cm}^{-1}$. Figure 3.44 (a) shows a spectrum acquired with the WITec instrument ($\lambda_{\text{exc}} = 785 \text{ nm}$) presenting the characteristic bands of **acid red 73** with relative intensities in line with published data [348,446–448]. In the literature the dye presents the following bands: a very strong broad band at 1145 cm^{-1} $\nu_s(\text{C-N})$, a strong broad band at 1248 cm^{-1} with shoulders at 1240 and 1222 cm^{-1} (overlapping of phenyl-OH modes and C-C skeletal stretching of acid red 26), a weak band at 1306 cm^{-1} , a medium band at 1372 cm^{-1} (aromatic ring vibrations/*N*-phenyl stretching), a very strong band at 1431 cm^{-1} overlapping $\nu(\text{N=N})$, a weak band at 1464 cm^{-1} (azo-benzene ring vibration), a medium band at 1505 cm^{-1} (azo-benzene ring vibration), a very strong broad band at 1598 cm^{-1} (aromatic quadrant vibration) with shoulders at 1575 cm^{-1} (overlapping with aromatic ring vibration in acid red 26) and a band at 1623 cm^{-1} (azo-benzene ring vibration in acid red 73).

In this research the bands detected assigned to the β -naphthol dye acid red 73 were the following: a weak band at 1147 cm^{-1} $\nu_s(\text{C-N})$, usually among the strongest bands for this compound, a very strong band at 1235 cm^{-1} with a shoulder at 1204 cm^{-1} assigned to the phenyl (OH), two strong bands at 1418 and 1437 cm^{-1} $\nu(\text{N=N})$, slightly shifted possibly due to the effects of bands combination and/or photo-degradation, two medium intensity bands at 1497 and 1513 cm^{-1} (azo benzene ring and aromatic quadrant stretching vibrations), a very strong broad band at 1588 cm^{-1} (aromatic quadrant stretching). Bands assignment is in good agreement with published data, however the relative intensity of the strongest bands of acid red 73 is not corresponding to that of spectrum (a), and additional bands are present [446]. Reasonable assignments for other two similar azo β -naphthol dyes are hypothesized, namely, **acid red 27** and **acid red 26**. They present a medium intensity band at 1287 cm^{-1} (aromatic ring vibration), absent in the acid red 73 and visible in Figure 3.44 (a), a strong broad band at 1360 cm^{-1} (aromatic ring vibration and *N*/phenyl modes) with a shoulder at 1334 cm^{-1} that might result from the combination of the acid red 73 band shoulder at 1330 cm^{-1} and acid red

27 and/or 26 bands at 1326 and 1346 cm^{-1} . Finally, the very strong band at around 1590 cm^{-1} is characteristic for acid red 73, but it presents a shoulder at 1575 cm^{-1} (aromatic ring vibration) that can be ascribed either to acid red 27 or 26¹⁸ [20,348,365,450–458].

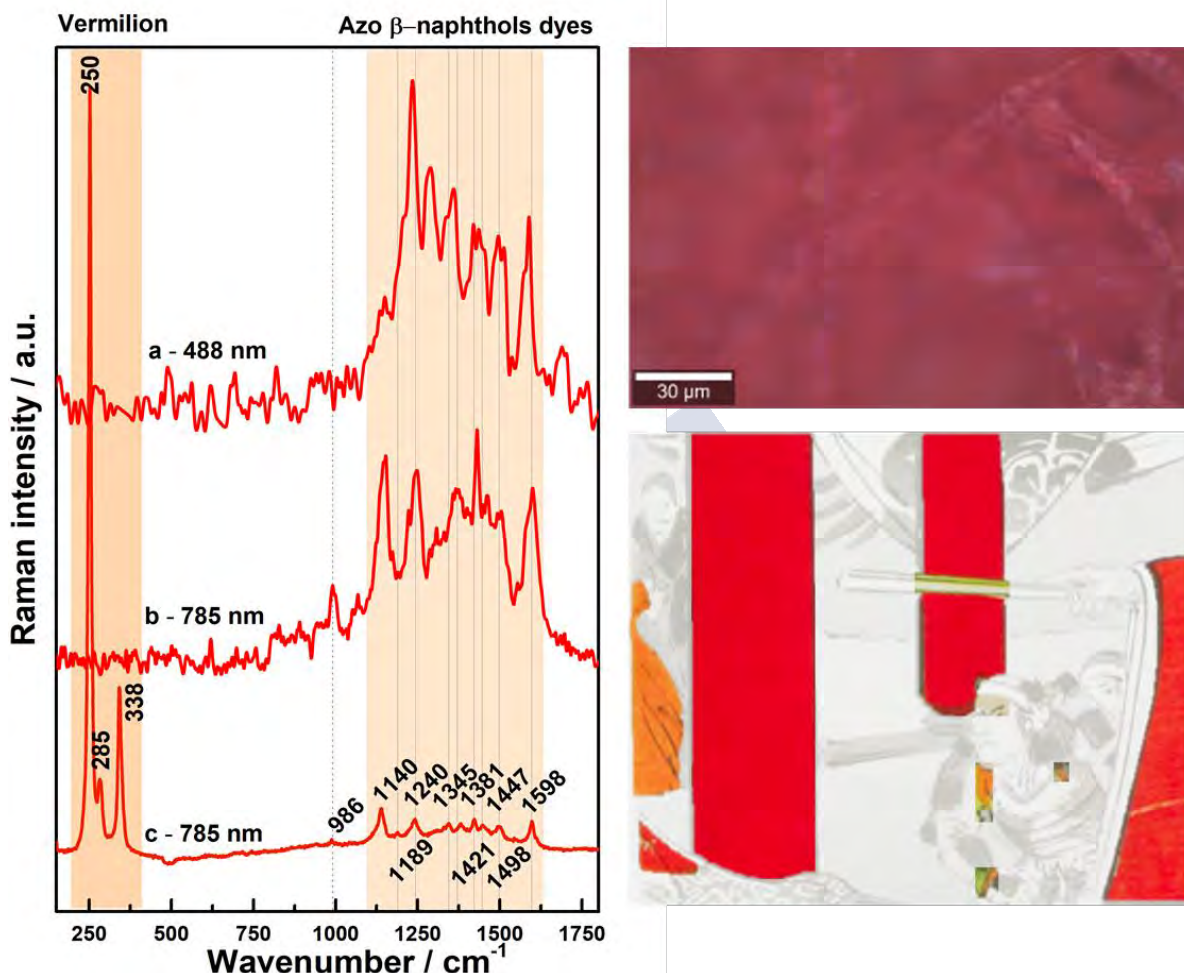


Figure 3.44: stack offset normal Raman spectra acquired with different excitation wavelengths and instruments (laser spot ≤ 1 mm $\varnothing$): (a) 488 nm WITec multiplied by 1×10^5 , (b) 785 nm WITec multiplied by 1×10^3 , (c) 785 nm InVia. On the right in the top row optical microphotograph of red area; in the lower row inset from panel n° 2 with highlights of red and orange patterns.

Spectrum (c) in Figure 3.44 was acquired with the InVia instrument ($\lambda_{\text{exc}} = 785$ nm) on the red sleeve of the character holding a child (on the right of Figure 3.44). Very intense bands at 250, 285 and 338 cm^{-1} correspond to the trigonal crystallographic phases of red vermilion (HgS) [459–465]. In addition, all most intense bands of azo β -naphthol dye (acid red 73) are in the same spectrum. This confirms that mixtures of inorganic well-established

¹⁸ Acid red 73 was patented in 1882 and is commercially known as cotton red. Acid red 27 was patented in 1878 and is commercially known as amaranth. Acid red 26 (1878) is commercially known as Ponceau 2R. The anionic mono and diazo dyes contain self-forming sulfonic groups in the form of a sodium salt. Traditionally, the precipitation on inorganic substrates was carried out to reduce the dye solubility and customize the color hues. In fact, by only substituting Na^+ ions with higher valence ions (Ca^{++} , Sr^{++} , Ba^{++} , Mn^{++}) in solution lesser soluble pigments form [91,449,450].

vermilion and new synthetic organic azo β -naphthol dyes were being employed during the Meiji period by introducing several, perhaps unstable, dyes in the traditional *ukiyo-e* printing palette. Furthermore, mercury sulfide has highly scattering Raman cross-section, which explains its high relative intensity compared to the organic band region [446,447,466]. (Figure 3.45 recalls the molecular structures of the β -naphthols).

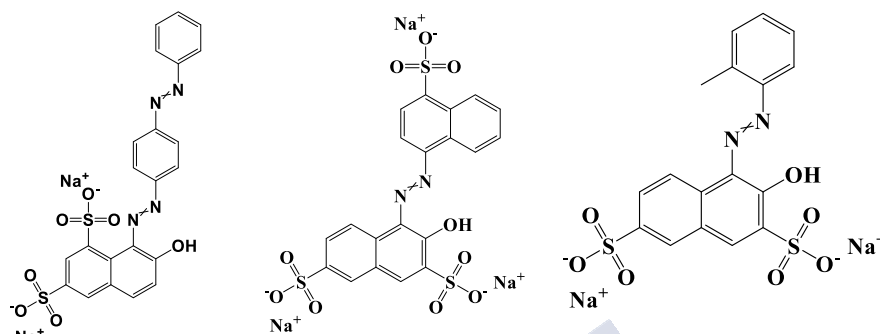


Figure 3.45: molecular structures of acid red 73 (left), acid red 27 (center), acid red 26 (right). Chemical structures from the free repository of pubchem.ncbi.nlm.nih.gov [282].

It is highly relevant to mention the weak band at 986 cm^{-1} in Figure 3.44 c can be ascribed to barite (barium sulfide) reported as a cheap extender in printing inks [449,467]. In addition, MA-XRF mapping in Figure 3.46 a and b led to conclude that water-soluble azo β -naphthols were the only source of color in the red brilliant columns, demonstrated by high concentration of barium, whereas on the clothing the barium signal was weak and abundant mercury was detected, being the visible hue slightly more orange/opaque. Additional demonstration of the exclusive use of water-soluble dyes in larger areas is confirmed by the back of the prints, showing wet-like paper marks resulting from a deeper penetration of the dye, undetected in the back of other red areas (Figure 3.46 c) [348,446].



Figure 3.46: MA-XRF elemental mapping of vermilion (Hg) (a), and lake-baring organometallic mixture of azo β -naphthols precipitated on barium sulfide (Ba) (b); back of panel n°2 (c).

Barium sulfide is commonly used as a white pigment that when dispersed in an organic soluble mixture becomes transparent and enhances the brilliance of the color [448]. Therefore, in this case a naphthalene sulfonic acid lake might be forming [91]. At this stage of the Meiji era, though, the use of barium lakes might have been to some extent an unintentional result of the optimization of old printing techniques, while using new and cheap materials as woodblock print inks. The absence of the symmetric stretching band at 1160 cm^{-1} (in spectra a, b, c in Figure 3.44) corresponding to the sulfonic group vibration and the presence of the band at 986 cm^{-1} inform us that barite was partially unreacted underneath the azo naphthol acid dye layer and the organometallic bond of the lake is unstable [91,449].

Further evidence on barium-lake pigment use was collected during the tests conducted to validate the SERS sampling method on the printing materials. PDMS strip samplers were used in combination with pure polar solvents, as water and acetone with polarity of 10 and 5, respectively. Replicas of SOKEN[®] and KLARITE[®] were used to collect the small molecules removed from the surface of the prints. In Figure 3.47 spectra obtained with different excitation wavelengths are presented: a) $\lambda_{\text{exc}} = 514\text{ nm}$ water-extracted on pyramidal substrate; b, c) $\lambda_{\text{exc}} = 785\text{ nm}$ respectively on pyramidal and cylindrical substrates water-extracted; d, e) $\lambda_{\text{exc}} = 488\text{ nm}$ respectively water and acetone microextracts on cylindrical substrates. A mixture of acetone and water was tested leading to intermediate results. The latter were not introduced in the graph since they do not add meaningful evidence. Figure 3.47 right summarizes Raman imaging on different types of substrates.

For clarity, spectra obtained with the same laser were overlapped, and straight lines were drawn against the reference spectrum of PR 60:1, a naphthalene sulfonic acid, downloaded from the Soprano Spectral Raman Library [365]¹⁹. It is relevant to stress that high fluorescence and low intensity signals, due to the reduced concentration of compounds, affected greatly the quality of the SERS spectra. Not to mention the fact that analyzing composite materials that underwent photo-fading, such as actual prints, might not necessarily provide readable results. Therefore, baseline corrections and other spectral manipulation seemed the least processing necessary for the identification of the compounds.

Spectra in Figure 3.47 are resulting from the same red areas mentioned in Figure 3.44 (column and clothing areas in the MA-XRF spectrometry image 3.46). Overall, the SERS methodology confirmed and extended the colorants identification obtained by normal Raman analysis. In all instances one-step solid-liquid microextraction with polar solvents (water and acetone) was conducted to transfer the small molecules from the strip samplers to the SERS substrate.

Spectra (a, b, c) in Figure 3.47 result from microextractions with water: mixtures of acid reds β -naphthols dyes (acid red 73, 27 and/or 26) were detected. Both $\lambda_{\text{exc}} 514$ and 785 nm lasers provided bands previously discussed for normal Raman spectra in Figure 3.44, although $\lambda_{\text{exc}} 514\text{ nm}$ spectral features are weaker (tests with the $\lambda_{\text{exc}} 532$ high fluorescence and no useful signal). Briefly, the most characteristic bands for acid red 73 at 1144 cm^{-1} $\nu_s(\text{C-N})$, 1239 cm^{-1} phenyl (OH) and 1377 cm^{-1} (aromatic ring vibrations/*N*-phenyl stretching) were present in the

¹⁹ Overlapped spectra were multiplied respectively by the same factors to provide comparable intensities, whereas the reference PR 60:1, obtained from pure standard SOP, was divided by 100.

spectra (a, b, c) of Figure 3.47. Further, a broad band at 1364 cm^{-1} present in spectra (b, c) could be ascribed to the aromatic ring vibrations/N-phenyl stretching of acid red 27. Bands at 1446 , 1461 , and 1599 cm^{-1} , respectively $\nu(\text{N}=\text{N})$, azo-benzene ring vibrations and aromatic quadrant stretching are weaker than those of reference acid red 73 and/or combined with those of acid red 27, namely 1516 and 1574 cm^{-1} $\nu(\text{C}-\text{N})$ and aromatic ring vibrations. In addition, spectrum (a) shows a strong broad band at 1503 cm^{-1} (azo-benzene ring vibrations) referable to acid red 73.

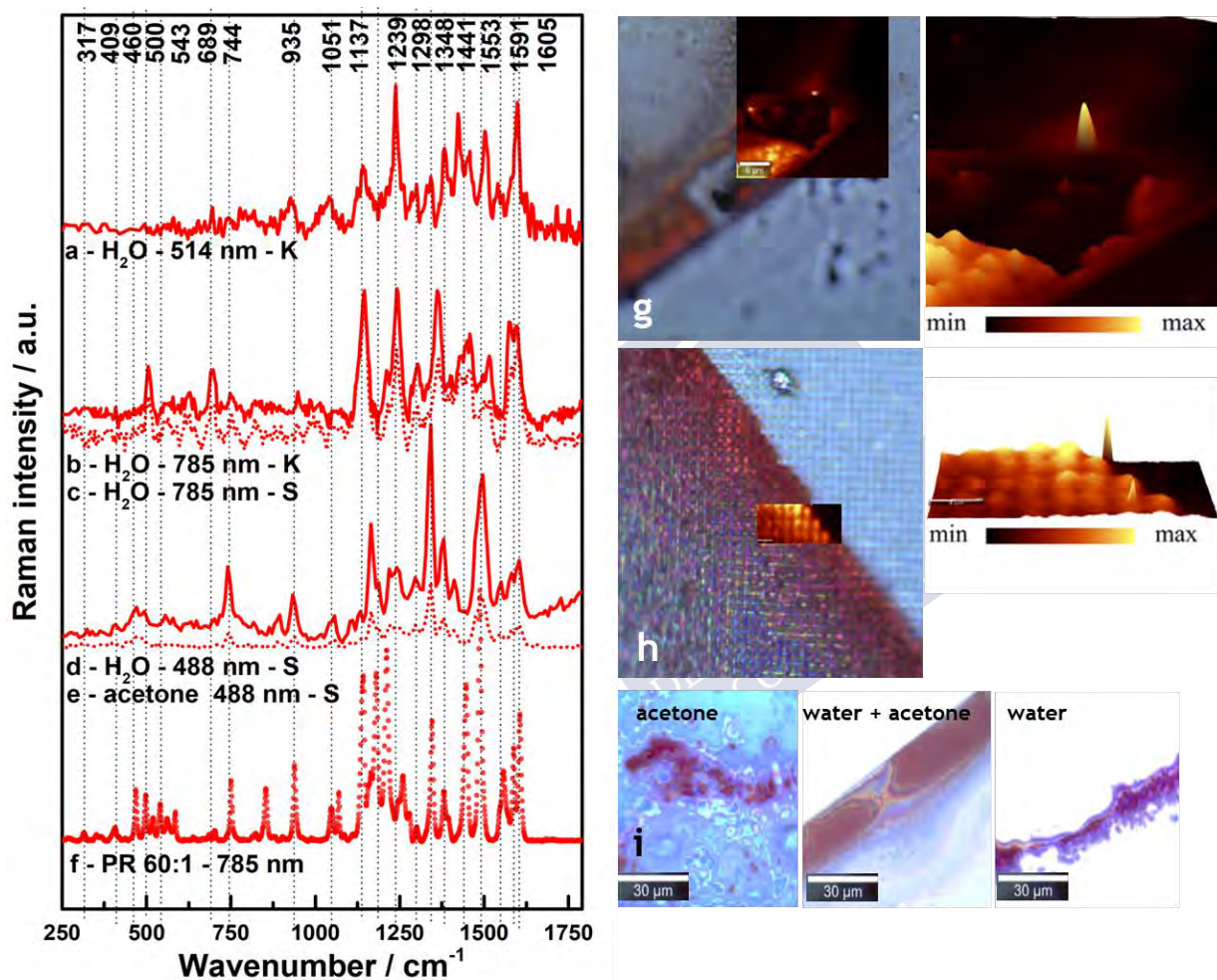


Figure 3.47: stack offset SERS microextracts: (a) λ_{exc} 514 nm with InVia on KLARITE[®] replica with H₂O; (b, c) λ_{exc} 785 nm with InVia extracted with H₂O multiplied by 5, b) straight line KLARITE[®] replica, c) dotted line SOKEN[®] replica; (d, e) λ_{exc} 488 nm with WITec on SOKEN[®] replica multiplied by 10, d) straight line microextracts with H₂O, e) dotted line microextracts with acetone; f) λ_{exc} 785 nm reference spectrum from Soprano Spectral library, PR 60:1, Sunbrite Red, C.I. 16105, naphthalene sulfonic acid (Ba-salt) [468]. On the right visible micrographs on substrates and 3D mapping: (g) SERS microextract with H₂O on SOKEN[®] replica corresponding to spectrum-type b in figure 3.48 (a); (h) SERS microextract on KLARITE[®] replica corresponding to spectrum-type b in Figure 3.48 b; (i) microphotographs of solvents mixtures on SOKEN[®] replicas to observe the behavior of small molecules in connection to surface tension.

Spectra (d, e) in Figure 3.47 resulted from sampling with water and acetone, respectively, and were collected with λ_{exc} 488. Although in the same order of magnitude, the intensity of spectrum (d) is considerably higher than that of spectrum (e), likely as a result of solvent

polarity. Water solubilizes higher quantities of the azo β -naphthols dyes than acetone, which is reflected by the intensity of the bands.

Interestingly, spectra (b) and (c) show evidence that the geometry of the SERS substrates used for signal amplification, in this case, had no influence on the band position and intensity. The molecular identification was instead affected by the laser excitation wavelength, solvent and sample concentration. Another factor taken into account was the depth of sampling layer combined to the solubility of the components: a progressive removal of different colorants from the mixture through the silicone strip sampler might explain the differential results. Chronologically, the initial samplings (a, b, c) would be consistent with water-soluble red disazo and monoazo acid dyes. On the same areas of the prints, namely on the columns, the sampling was reiterated to optimize the SERS strategy and a metal azo salt pigment (insoluble lake) was detected (d, e) in Figure 3.47.

Historically, metal salt azo pigments were produced initially as lithographic inks derived from water-soluble dyes precipitated onto inorganic substrates [450]. The first reported is Lithol Red (PR 49) in 1899. Subsequently, a lake-pigment, Lake Red C (PR 53), was introduced in 1902, and its corresponding barium salt (PR 53:1) is still one of the dominant products used in lithography and printing toner owing to its successful bright red hues [449]. Unfortunately, a conclusive identification of the spectra recorded with $\lambda_{\text{exc}} = 488$ (d, e) was not possible, although several comparisons with the Synthetic Organic Pigments database (Soprano), even after comparing to further scholarly publications on azo acid dyes. The date on the print referring to the woodblock production is 1897. Then none of the metal salt azo pigments had been patented yet [469]²⁰. To bear in mind, laser power and natural weathering might have caused alterations of the spectral features, for photoaging of the compounds, therefore weakening and deforming the bands further complicating the interpretation of the data. As hypothesized earlier, the used of Ba-lakes might result from an unintentional, but successful combination of coloring media and methods being experimented during the several Meiji industrial transitions.

3.3.4.3 Purples

Purple is considered the color of the Meiji revolution [448]. From 1860 onwards, a number of triarylmethane dyes were progressively being commercialized and imported from Germany [255,448,470–474]. Four aniline homologs were hypothesized as the most probable in use on the panels investigated, in particular: 1) non-methylated pararosaniline (basic fuchsine), 2) mono-methylated rosaniline (magenta), 3) di-methylated pararosaniline (magenta II), 4) trimethylated pararosaniline (new fuchsine) (Figure 3.48). In similar studies on Japanese woodblock prints, they were found mixed with methyl and crystal violet, respectively *N*-hexamethyl and derivatives of *N*-methyl pararosaniline (tetra, penta and hexa) [448].

Aniline dyes were attractive for printers because of their especially small particle size facilitated the penetration into the cellulose fibers [474,475]. Unfortunately, though, despite

²⁰Pigment Red 60:1 is commercially known as Sunbrite Red (C.I. 16105:1) and it was patented in 1902 by BASF

of the bright and intense purple hues, the detection of such small molecules was more complicated than for other coloring media. As naphthalene sulfonic acid dyes, aniline dyes were not considered an artistic improvement compared to natural dyes used in the Edo era; however, they made life easier for printers and they displayed limited signs of photo-fading [476].

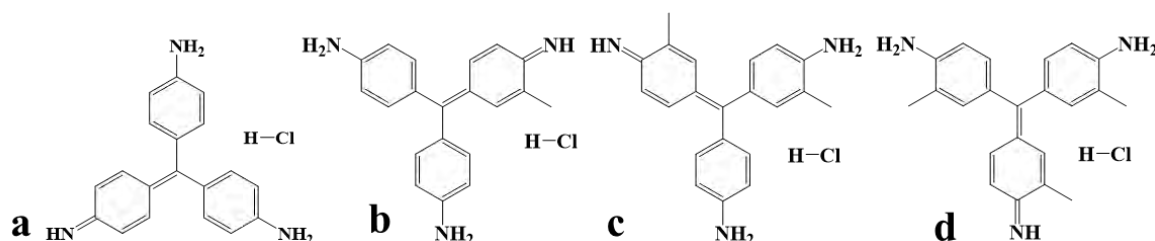


Figure 3.48: molecular structures of non-methylated pararosaniline or basic fuchsine (a), mono-methylated rosaniline or magenta (b), di-methylated pararosaniline or magenta II (c), trimethylated pararosaniline or new fuchsine (d). *Chemical structures from the free repository of pubchem.ncbi.nlm.nih.gov* [282].

In 1856, Perkin patented mauve, an impure aniline compound obtained with disulfide and potassium dichromate [255]. This achievement was a milestone of modern synthetic chemistry. Soon after Hofmann patented magenta (rosaniline hydrochloride), an impure aniline compound obtained with stannic chloride [255,476]. Perkin and Hofmann worked throughout several routes to synthesize aniline-based dyes and the initial attempts included mixtures of aromatic compounds and strong acids, dangerous for safety reasons and with uncertain yields. However, compared to natural dyes textile factories had finally found cheaper and brighter coloring media to be used on a variety of fibers [255,477]. The addition of elemental sulfur in the crystalline phase is mentioned in various seminal publications as mean to accelerate the reaction of coupling [475,478–480]. Overall, the resulting compounds were unstable due to the limited characterization methods and knowledge on the synthesis processes. Prior to the Meiji period, the purple was produced by mixing red safflower and/or hematite with Prussian blue [256,437,439]. At a fast pace throughout the end of the 19th century, natural dyes were being substituted by synthetic compounds [481–485].

Cesaratto *et al.* [434,448] conducted extensive mock-up experiments through artificial photoaging of standard aniline dyes to accomplish insights on the transition from the Edo to the Meiji era and to investigate the fading of the prints in the collection of the Metropolitan Museum of Art in New York, US. Raman spectroscopy enabled deepening the information on the production of aniline dyes. Only higher methylated grades show different Raman features, otherwise Raman spectra of most of the compounds pararosaniline/aniline are identical ²¹. Additionally, Persaud *et al.* [486] and Freeman [487] seminal papers, respectively on Raman and SERS bands assignment and solvent-plasmon interactions of triphenylmethyl dyes helped interpreting the spectra, navigating through the limited fluorescence quenching below 200 cm⁻¹ and above 1750 cm⁻¹. The reduced particle size of the dyes (approximate range 50-500 nm)

²¹ The assigned bands of methyl / crystal violet and pararosaniline are 245, 336, 414, 439, 517, 565, 640, 732, 824, 910, 1174, 1288, 1343, 1352, 1366, 1429, 1519, 1589, 1617, 3202, 3216, and 3356 cm⁻¹.

might have complicated the detection. It was reported that Japanese printers learned to reduce the size of the aniline dyes to improve the penetration into the paper fibers [448]. Curiously, the hue of the prints is still vivid and opaque, opposite to what reported for earlier Edo prints made of pigments with larger grains [359,428] (Figure 3.49).



Figure 3.49: photograph of panel n°5 (left) with the dark purple curtain showing no sign of fading; photograph of panel n°3 (right) showing curtains light and dark purple with lilac background.

Raman spectra were collected with normal and SERS settings with $\lambda_{\text{exc}} = 514, 532$ and 488 . Overall assignments of the phenyl carbenium bonds fall into the low frequency region up to 450 cm^{-1} and the three-phenyl rings vibrations above 400 cm^{-1} , including in-plane and out-plane modes, C-H deformation modes, and aromatic-carbon bonds stretching modes. Bands at $234, 416$ and 441 cm^{-1} can be assigned to a combination of in-plane and out-of-plane and breathing modes. The two bands at $416\text{--}441 \text{ cm}^{-1}$ can be assigned to the out-of-plane carbenium and phenyl-ring deformations (Figure 3.50). NR analysis of dark purple with $\lambda_{\text{exc}} = 514 \text{ nm}$ in Figure 3.50 (f) shows a spectrum with rich features that can be ascribed to the aniline family compounds, possibly affected by photo-fading²². On the other hand, illumination of the same areas with $\lambda_{\text{exc}} = 785 \text{ nm}$ in NR settings was inconclusive. Band shifts might be due to the strengthening of the carbenium-phenyl bonds [448].

Broad weak bands at $515, 563$ and 914 cm^{-1} can be ascribed to the phenyl-ring skeletal vibrations, whereas those at $728, 760, 805 \text{ cm}^{-1}$ to the out-of-plane δ (C-H) bond deformation. The latter band is generally assigned to crystal violet instead of pararosanine; however, possible shifts, as in spectrum b of Figure 3.50 might be occurring. Published data on SERS detection of pararosanine mention a characteristic band at 1177 cm^{-1} [448], consistently detected in the current investigation. Further pararosanine signature bands are the phenyl-ring at 1367 cm^{-1} assigned to stretching mode. Following, bands at $1296, 1437$, and 1534

²² Raman bands reported for aniline are at $419, 441, 531, 567, 731, 761, 808, 911, 1178, 1295, 1368, 1437, 1485, 1532, 1585, 1619, 2798, 3562$ [448].

(with a shoulder at 1522 cm^{-1}), 1586 , 1621 cm^{-1} can be assigned to a combination of modes of C-C ring stretching modes reported for pararosaniline and crystal violet [448].

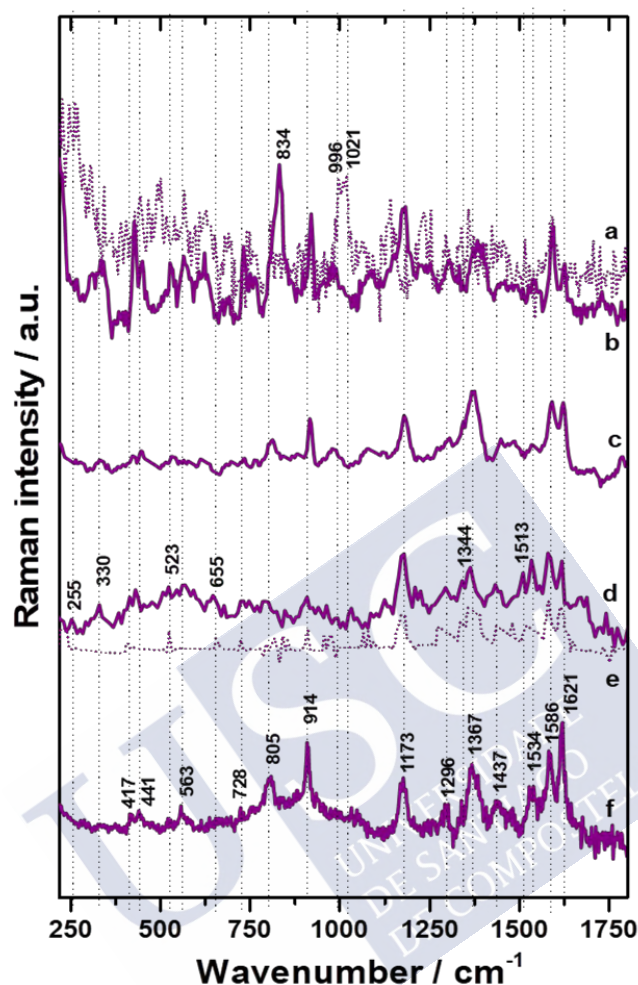


Figure 3.50: dark purple stack offset baseline SERS/NR spectra. (A) SERS microextract with H_2O , λ_{exc} 785 nm with InVia on KLARITE® replica; (b) SERS microextracts with acetone, λ_{exc} 785 nm with InVia on SOKEN® replica; (c) SERS microextract with H_2 , λ_{exc} 532 nm with WITec straight line on KLARITE® replica; (d, e) SERS microextracts, λ_{exc} 488 nm with WITec straight line on SOKEN® replica; (f) normal Raman λ_{exc} 514 nm with InVia.

In the literature [448,488], photo-fading due to progressive demethylation reflects on the following band shifts. The band at 725 cm^{-1} shifts to 732 cm^{-1} , whereas the bands at 743 and 786 cm^{-1} disappears; shoulders at 1186 and 1337 cm^{-1} decrease in intensity, and the band at 1390 cm^{-1} passes from being a shoulder to disappearing. Further evidence of protonation should reflect in the formation of bands at 3200 and 3350 cm^{-1} (N-H stretching modes), however not detected in the current study due to high fluorescence.

SERS signals from microextracts with water ($\lambda_{\text{exc}} = 514\text{ nm}$) were highly fluorescent and no useful bands were identified. Fluorescence quenching was favored through a combination of strategies, including reiterative repetitions of the measurements at low laser power. Finally,

SERS with $\lambda_{\text{exc}} = 532$ and 488 nm wavelengths pointed to the identification of multicomponent organic compounds in the purple areas (Figure 3.51 c, d, e), including a carotene-bearing compound and aniline derivatives (Figure 3.52).

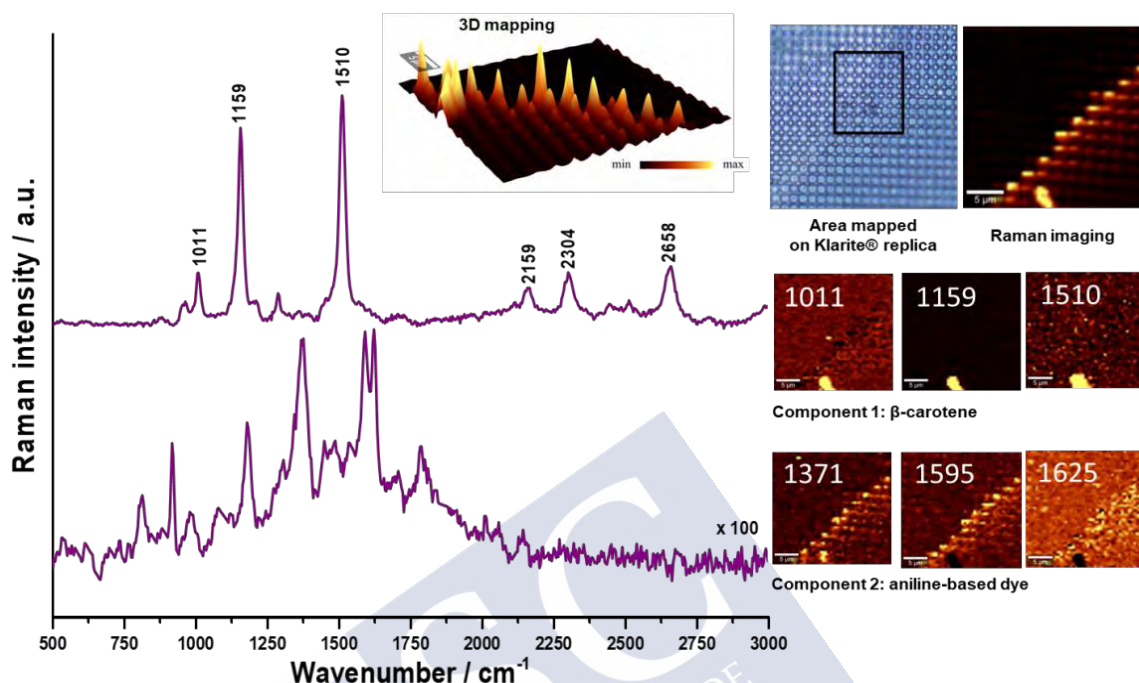


Figure 3.51: multicomponent Raman imaging. On the left, SERS microextracts collected with H₂O on KLARITE® replica, $\lambda_{\text{exc}} = 532$ with WITec. Top spectrum (component 1) associated to the mapping on the right with three main maxima corresponds to β -carotene. Down spectrum (component 2) with three main maxima corresponding to an aniline-based dye.

SERS spectra collected from microextracts obtained with water disclosed the multicomponent nature of the dark purple hue, either from synthesis or from mixing of different types of dyes and pigments. Several publications mentioned Raman spectroscopy as an excellent tool to detect carotenoids in biological organisms, such as plants and bacteria [482,485]. In fact, the upper spectrum in Figure 3.52 confirms the skeletal features of a carotenoid: $\nu(\text{C}=\text{C})$ at 1510 cm^{-1} , $\nu(\text{C}-\text{C})$ at 1159 cm^{-1} and $\delta(\text{C}-\text{CH}_3)$ at 1011 cm^{-1} (component 1) [483–485]. Raman imaging helped to visualize and contrast the presence of the aniline dye (component 2) mentioned above (Figure 3.51 right). The bands match closely those of β -carotene and possibly those extracted from carrots or purple onion [482]. Selective Raman mapping was presented including only the values of the most intense bands of the two components to integrate the visualization of the chemical information. This feature of the WITec confocal microscope increased enormously the comprehension of the molecular dying system.

The presence of carotenoids (*e.g.* β -carotene) was not mentioned before among the coloring media of the Edo or Meiji eras. However, being the early Meiji a period of experimentation, it cannot be ruled out that instead of the usual saffron added to Prussian blue to yield purple, β -carotene from purple anions was added to intensify the hue. The first patent filed for the synthesis of β -carotene was in 1960 [489]. Therefore, considering the use of all

other pigments and mixtures, it can be safely assumed the extract used for this prints is a natural. Another possible, but unlikely, explanation for the presence of β -carotene could be related to bacteria or fungi formed through time on the surface of the paper. Foxing marks (typical brown stains) [490] common in degraded paper were found on various prints (Annex Figure 3.13). The degradative phenomenon is caused by fungi which might synthesize carotenoids in their metabolic processes [482]. However, the spectral features of carotenoids were not detected in other areas where the stains were.

No published data mentions the presence of crystalline sulfur in the purple areas of the prints, whereas the current research presents novel evidence of sulfur use in aniline dyes during the Meiji period, consistent with experimentations in the synthesis procedures of Perkin and Hofman [474,491] (Figure 3.52). In light purple areas, crystalline sulfur (S_8) was consistently detected from direct Raman analysis, hinting to an intentional addition of sulfur to the aniline synthesis. Hofmann, Hodgson and further authors involved in early synthesis experiments of anilines mentioned the addition of sulfur to amines to accelerate the coupling reactions and to control the amount of methylated groups of the yielding homologs in presence of hydrochloric acid (*e.g.* diphenylamine, dithioaniline, Merz's thioaniline, and a new thioaniline) [474,475,491]. Spectra in Figure 3.53 show the characteristic bands of elemental sulfur in the crystalline phase (S_8). Bands at 153, 182, 217, 250, 440 and 472 cm^{-1} can be ascribed to the fundamental Raman modes (symmetries A_1 E_1 , E_2) of orthorhombic sulfur [478–480]. The most intense bands of the spectrum at 153, 217 cm^{-1} and 470 cm^{-1} correspond respectively to the $\delta(\text{S-S})$ and $\nu(\text{S-S})$ modes. The interpretation is consistent with the reference spectrum of sulfur collected with λ_{exc} 785 nm laser and downloaded from the RRUFF Spectral database [480,492].

The presence of crystalline sulfur in the purple areas was confirmed by the MA-XRF spectrometry (Figure 3.52). For orange and green hues presented later, yellow was added to the main coloring medium (*e.g.* Prussian blue or vermilion) to enhance the intensity of hues. Yellow was obtained with glassy arsenic sulfide, showing the S signal in the MA-XRF mapping in Figure 3.53b. However, the absence of As in the purple areas Figure 3.53a, in addition to the high concentration of S detected in the upper curtain, rules out the addition of arsenic sulfide to achieve a light tone of purple. This indirect evidence confirms that aniline-based compounds containing crystalline sulfur were definitely and intentionally being used for the fabrication of the Meiji prints.

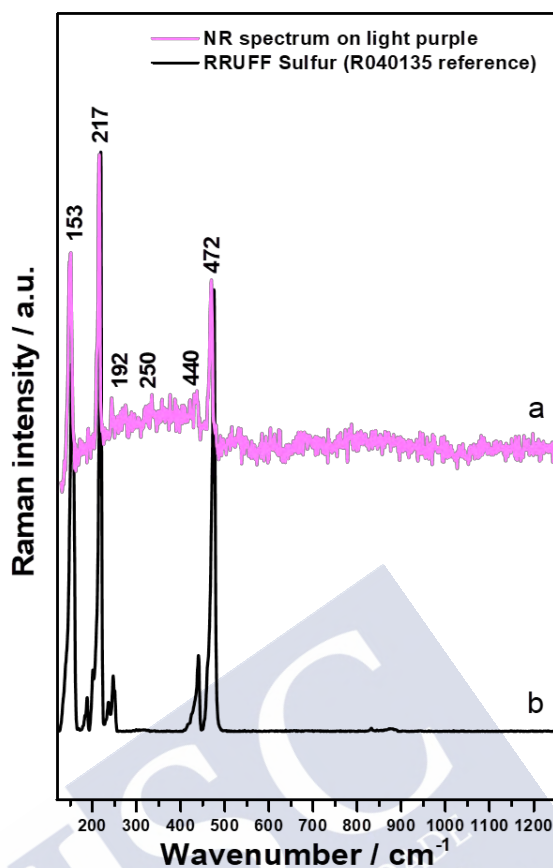


Figure 3.52: stack offset normal Raman spectra of light purple area (a) λ_{exc} 785 nm with inVia; (b) λ_{exc} 785 nm reference spectrum RRUFF sulfur (R040135).

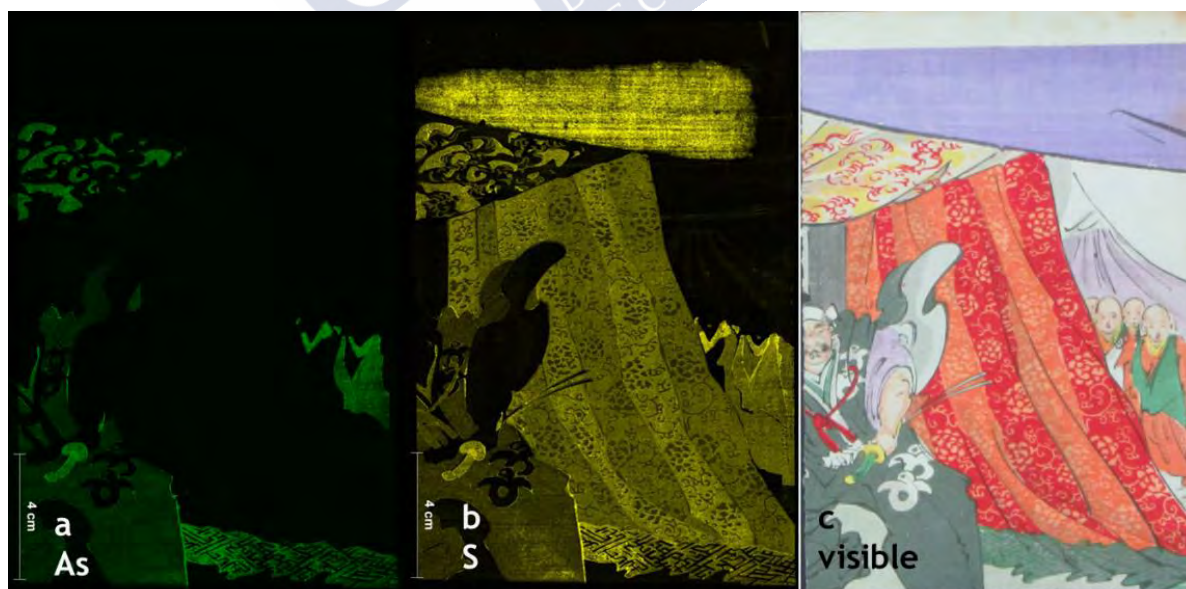


Figure 3.53: MA-XRF spectrometry imaging mapping of As (a) and S (b) found in panel n° 1 (c), including light purple and lilac (aniline-based dyes), yellow (arsenic sulfide), orange (vermillion mixed with arsenic sulfide), and red (8-naphthol-based dyes).

In conclusion, photo-fading is the key explanation of the bands shifts in the Raman spectra introduced in this section [448,488,493]. Therefore, a conclusive assignment to either of the compounds listed at the beginning (namely, non-methylated pararosaniline, mono-methylated rosaniline, di-methylated pararosaniline and trimethylated pararosaniline) could not be achieved. The mechanism of de-methylation, previously demonstrated through the preparation of mock-ups in studies on similar prints, can be extended to the current results [448]. In addition, it was observed that pararosaniline compounds fade under the laser during analysis, as occurred with all excitation wavelengths. Opposite to the majority of the colors, purple was extremely difficult to detect, also considering that no standard compounds were available to contrast the identification. As mentioned above, the especially small particle size did not make the PDMS strip sampling method optimal for such a class of small molecules. Further analyses should be pursued for exact molecular identification (*e.g.* Py-GC/MS). However, all Raman spectra collected belong to aniline-based compounds. In addition, the presence of crystalline sulfur strengthens this evidence. Finally, the detection of carotenoids adds novel information to the history of purple, color of the Meiji revolution.

3.3.4.4 Blue

Prussian blue (PB27, ferric ferrocyanide) was detected as a dark blue, or mixed with hematite in brown and with arsenic sulfide in bright and olive greens. This organometallic compound was introduced in the *Ukiyo-e* woodblock printing in 1831, in the late Edo period throughout the Meiji period [256,434,438]. It appeared in the famous landscapes of Hokusai and it is considered ‘revolutionary’ ever since [428,476]. From there on, printing inks shifted to brilliant and vivid hues never used before. Prussian blue was the first synthetic pigment difficult to solubilize, invented in 1704 by Diesbach in Germany [255,494]. It arrived to Japan through unknown commercial routes, after having established in Europe as an art pigment, appreciated for its chemical stability, fine texture, and overall light-fastness [476]. It was also produced in China at low-costs and still showing very high quality features that convinced the Edo printers to use it [476]. Analytical evidence from normal Raman, SERS, ATR-FTIR spectroscopy and MA-XRF spectrometry will be discussed to clarify the use of such a relatively old organometallic compound in the panels under investigation. Opposite to the current study, Caggiani *et al.* [465] found out that the Raman excitation wavelength at 785 nm yielded a less intense spectrum, whereas the 532 nm laser showed clearly all the bands of the organometallic compound.

Overall, SERS microextracts allowed the identification of the Prussian blue pigment, further expanding the capability of the analytical protocol proposed. Acetone, water and mixture of the two were used to remove small molecules physisorbed on the PDMS strip sampler. Microscope images of replica-substrates of SOKEN[®] in Figure 3.54 a and KLARITE[®] replica in Figure 3.54 b were collected to compare the sensitivity with different excitation wavelengths (488 and 785 nm) and solvent behaviors. The richest spectral features were obtained with the laser excitation at 785 nm in spectra (a) and (d), respectively showing water microextracts on KLARITE[®] replica substrates. The mixture of acetone and water yielded in a spectrum with intermediate characteristics (Figure 3.54 b). Following, spectrum

(c) is a microextract with acetone on a replica of SOKEN[®] and it shows very fine spectral features. Finally, spectrum (e) results from normal Raman with the 488 nm excitation wavelength. Other measurements were collected systematically in all experimental settings available, but the results were not conclusive, hence they were omitted.

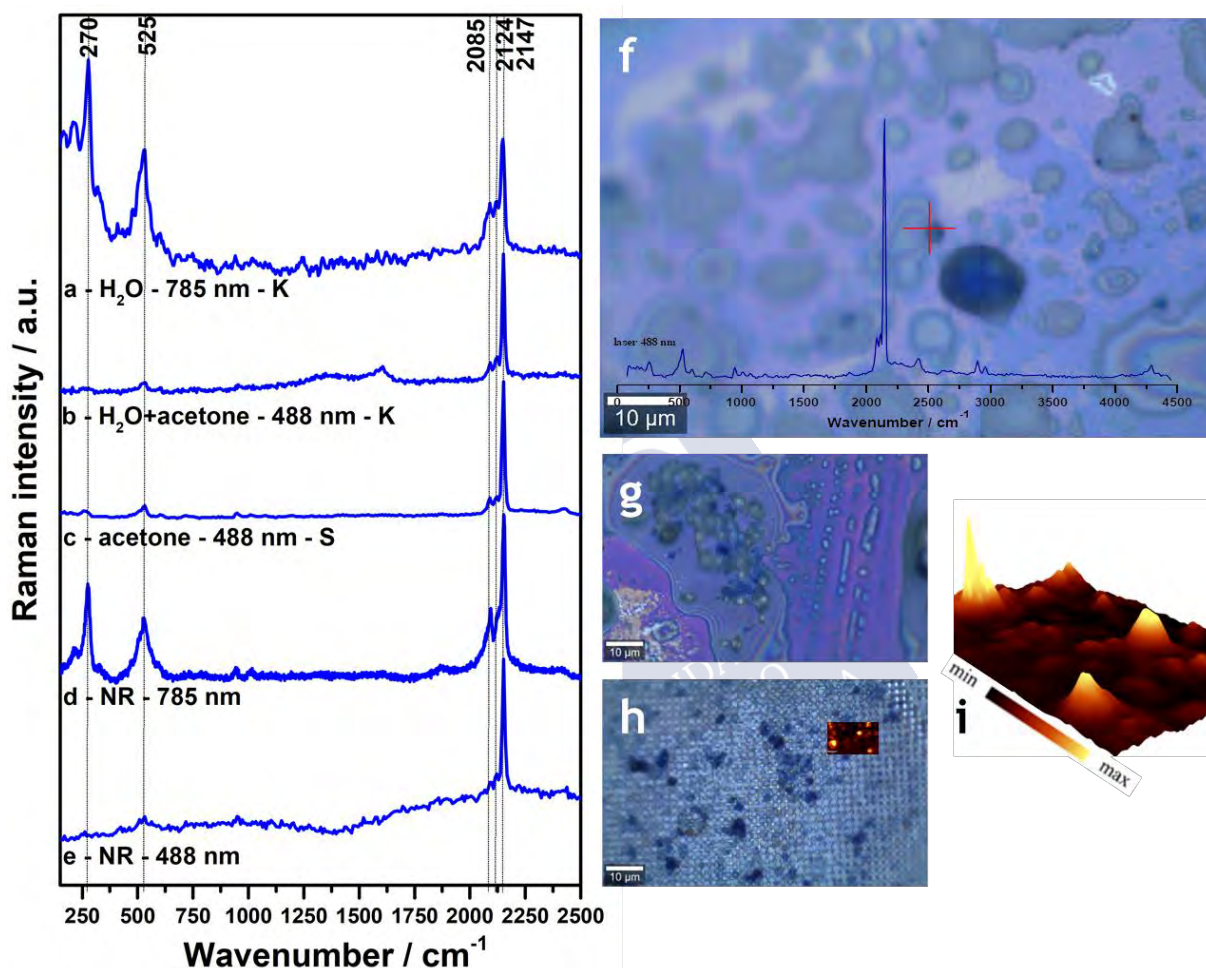


Figure 3.54: normal Raman and SERS microextracts obtained on blue areas of the panels. Spectrum (a) is a water microextract on KLARITE[®] replica ($\lambda_{\text{exc}} = 785 \text{ nm}$); (b) SERS microextract with H_2O and acetone, $\lambda_{\text{exc}} = 488 \text{ nm}$; (c) SERS microextract with acetone on a SOKEN[®] replica, $\lambda_{\text{exc}} = 488 \text{ nm}$; (d) normal Raman, $\lambda_{\text{exc}} = 785 \text{ nm}$; (e) normal Raman, $\lambda_{\text{exc}} = 488 \text{ nm}$.

Preliminary data collected with ATR-FTIR spectroscopy in Figure 3.42 showed a strong distinctive band at 2090 cm^{-1} in panel n°6, assigned to the $\nu(\text{C}\equiv\text{N})$ of the cyanide bridges. Such a band was also recorded in the areas colored either with blue, bright and olive greens. Characteristic Raman vibrations of Prussian blue are at 255, 270, 525, 945, 1019, 1196, 1864, 2085, 2124 and 2147 cm^{-1} [495]. The band at 255 cm^{-1} was assigned to the C-Fe-C deformation mode; similarly, the band at 270 cm^{-1} corresponds to the Fe-CN-Fe deformation mode. Further, bands at 2093, 2131, 2153 cm^{-1} belong to the $\nu(\text{C}\equiv\text{N})$. In particular, the band at 2085 cm^{-1} can be ascribed to the $\text{Fe}^{2+}\text{-CN-Fe}^{3+}$, the band at 2124 cm^{-1} to CN^- vibration, and the band at 2147 cm^{-1} to the $\text{Fe}^{2+}\text{-CN-Fe}^{3+}$ vibration.

In the literature, it is widely reported that Prussian blue is insoluble in water and less in acetone [495–498]. However, in microextracts with acetone distinctive and unequivocal spectral features of the pigment were visible. Reflecting on the polarity of the solvents and solubility of the pigment, signal enhancement with acetone might depend on the lower surface tension of acetone, hence more spread distribution of the droplets on the substrate (Figure 3.54 a with spectrum inset). This behavior might favor the formation of colloid-like agglomerates that accumulate on the plasmonic areas, then enhancing the Raman scattering. Signals detected on the microextractions with acetone on SOKEN[®] replicas were more intense than those extracted with water; however, when KLARITE[®] replica was used, the signal of the extract with water was equally good (respectively Figure 3.54 a and c). Hence, it is demonstrated the ability of the analytical method to combine the potentiality of SERS with the affinity of the compounds with the metallic substrate and the solvent after transfer. In this case, an important role was played by the shape and dimension of the plasmonic structure generating the resonant Raman signals. Clearly for Prussian blue, smaller acetone colloid-like drops adhered better to the cylindrical nanostructure, whereas bigger water colloid-like drops fitted better the micro-pyramidal cavities. Further, demonstration of the selective SERS sensitivity was given by the weak C≡N signal recorded with $\lambda_{\text{exc}} = 488 \text{ nm}$ with the water extract on the cylindrical nanostructure, and medium intensity of the same spectral mode with the H₂O:acetone mixture in the same experimental conditions.

The interaction analyte-solvent on SERS substrates has not been extensively explored in the literature. However, Gómez *et al.* [209] demonstrated the importance of the affinity of the analytes with the metallic substrates, the solvent polarity, and the subsequent influence on the relative intensity of SERS signals. Earlier, Tripathi *et al.* [275] interpreted the use of solvents during the deposition of molecules on planar substrates mentioning the competition of the analytes for the limited number of enhancement sites on the surface. Several tests at different concentrations of analytes and with a variety of polar and nonpolar solvents confirmed that the solubility affects the binding energies of the analytes with the metallic substrate, as well as the relative intensity of the SERS signals. According to Tripathi *et al.* [275] signal is best enhanced when the interaction of the analyte with the solvent is weaker. This explanation might help clarifying the differential and intermediate behaviors observed comparing H₂O and acetone interactions with the Prussian blue molecules on the substrates. The most intense bands ascribed to the CN stretching mode decreased relatively to the other spectral features when water was utilized, as shown in spectrum (a) of Figure 3.54.

Further molecular identification and data on pigments mixing was achieved through Raman imaging (Figure 3.56 a–b–c). H₂O microextracts were placed on a replica of KLARITE[®] illuminated with the laser at 785 nm (WITec). The PDMS strip sampler was swiped onto the blue area in Figure 3.55 b and it is likely that the black lines were touched during sampling. In fact, both Prussian blue and carbon black were detected in the spectrum below Figure 3.55. Furthermore, Raman imaging enabled the identification of the two components and their relative characteristic spectral features. Mapping in Figure 3.55 c shows the D and G bands of carbon black respectively at 1348 and 1593 cm⁻¹, adding to the previously discussed bands of Prussian blue at 277, 524, 2089 and 2155 cm⁻¹. Raman

spectroscopy was indeed sensitive to even the smallest concentrations of coloring media detected on such prints.

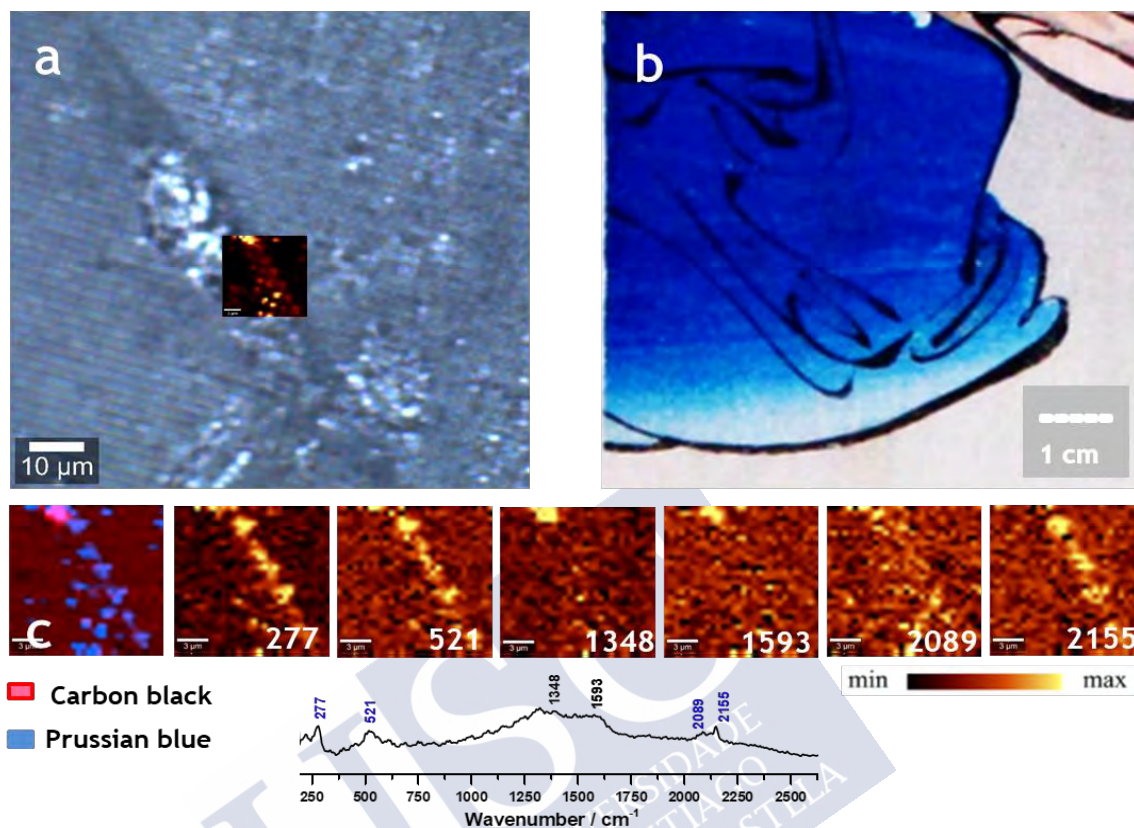


Figure 3.55: combination of Raman mapping inset and visible mapping on KLARITE® replica (a) of water microextract on blue areas in panel n°6 (b). Raman mapping with relevant bands of carbon black and Prussian blue (c). WITec instrument, $\lambda_{exc} = 785$ nm.

Mixing of pigments and dyes was confirmed by MA-XRF spectrometry. The images in Figure 3.57 show the presence of Prussian blue, identified through iron in the maps (a-c).

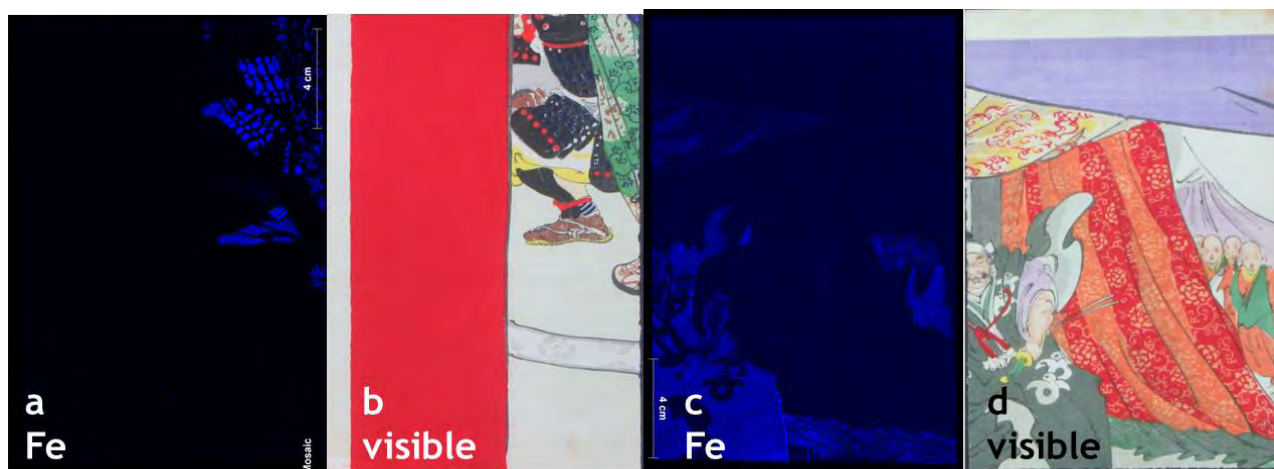


Figure 3.56: (a - c) MA-XRF spectrometry imaging combined with visible photographs of panels n°4 (b) and n°1 (d). Mixing of Prussian blue with arsenic sulfide (yellow) yielded various green hues (d) (olive and bright).

The blue patterns of the armor in panel n°4 (b) and in the green clothing of various characters in panel n°1 (d) revealed high content of iron. To a closer observation, brown details in both panels show the presence of iron as well, namely in the skin of the foot in panel n°4 and in the darker shadows of the skin on the faces of all characters in panel n°1. In the Meiji era, as later will be widely explained, mixing of Prussian blue with arsenic sulfide was common to obtain various hues of green (olive and bright in 3.56 c - d).

Summarizing, Prussian blue (PB27) was very appreciated by *Ukiyo-e* printers, since its appearance at the end of the Edo era (1831). This research confirmed that Prussian blue was extensively used during the Meiji era, having ideal mixing behavior and durability to photo-fading. SERS allowed to map possible accidental mixtures with carbon black, however confirming high sensitivity of the technique. In addition, normal and SERS measurements confirmed that all blue areas contained Prussian blue. Acetone on a SOKEN[®] replica enabled the best signal enhancement ($\lambda_{exc} = 785$ nm). The formation of colloid-like agglomerates with H₂O and a possible reduced signal enhancement compared acetone and (or mixed solvents) was discussed. Finally, MA-XRF spectrometry allowed to identify mixtures of blue with arsenic sulfide to obtain various green hues.

3.3.4.5 Yellow

Overall, in the panels analyzed plain yellow areas are few and they are displayed a very bright hue, despite the time passed (Figure 3.57). Yellow was utilized as the main color only in the clothing of the warrior in panel n°2, otherwise it appears mostly as finishing tone to brighten some details. Similarly, to aniline-based dyes, yellow well represents the transition to the Meiji era in woodblock printing [256,436]. Various authors discussed whether arsenic sulfides, synthetic and natural, can help defining dates and techniques of pigment production in the rapidly growing Meiji printing industry. This study confirms that indeed synthetic arsenic sulfide represents the definitive transition from the Edo to the Meiji era [256,436].



Figure 3.57: photographs of insets of panels n° 1, 2 and 4 (left to right) where yellow areas are present.

Sources for the production of arsenic sulfide are various. Natural **orpiment** is a monoclinic arsenic sulfide (As_2S_3) forming by sublimation in volcanic bedrocks or by decay of **realgar**, another similar mineral, both classified as non-metallic sulfides [440,459,499]. **Pararealgar** instead is the photo-degradation product of realgar and **alacranite**, slightly more orange-brown and found as well in similar ores, but less common than the first two mentioned. Alacranite, also mentioned as a source for the production of synthetic arsenic sulfide, displays a series of solid solutions (*e.g.* $\text{As}_8\text{S}_8 - \text{As}_8\text{S}_9$) [440,500–502]. Finally, **arsenolite** (As_2O_3) is the oxidized form found in natural crops and massively smelted in Central Europe and East Asia to produce glass arsenic sulfides [503,504]. The five minerals have been alternatively used throughout art history as mineral sources for the production of yellow and red glassy pigments. As far natural orpiment was concerned, roasting and recrystallization by sublimation were reported as the most common methods of preparation of the pigment [501,503]. Natural sources, however, did not suffice for the demands of supply of golden and red pigments. In addition, grinding and powdering the mineral sources was rather time consuming [256,436]. Yet, since the antiquity in Egypt, Asia and Rome trades of orpiment-like powders have been reported, accounting as expensive pigments also known for being prone to light-induced degradation [504].

Various literary treatises mentioned artificial orpiment, being the most notable Cennino Cennini's the 'Libro dell'arte, o Trattato della pittura' (1437) [505]. The protocol for the preparation of synthetic arsenic sulfide is not completely clarified [501]. The documentation of the technology of production of synthetic arsenic sulfides is relatively new [256,462,500,504]. Four dry-process and two wet-process routes have been reported and experimentally reproduced through mock-ups [501]. As reference materials, their composition has been characterized with various instrumental settings (*e.g.* optical microscopy and Raman spectroscopy) to match the evidence obtained investigating paintings, sculptures and prints from all over the world [501]. On the other hand, natural orpiment, realgar and pararealgar were widely characterized with X-Ray diffraction and other mineralogical methods for studies not related to conservation, art history and archaeology. Spectral database on classic minerals are widely available but were not of use in gathering information on synthetic glasses [364,365].

The general formula suggested for glassy arsenic sulfides is ($\text{g-As}_x\text{S}_x$). In one experimental set-up, the four dry-process mock-ups prepared followed the ratios $\text{g-As}_{40}\text{S}_{60}$, $\text{g-As}_{34}\text{S}_{66}$, $\text{g-As}_{30}\text{S}_{70}$ shading from orange to bright yellow. The pure As and S with chalcogenide additives are heated at 800 °C for 48h under vacuum and cooled in cold water (melting/quenching) collecting the sublimation products. The analysis on the respective resulting amorphous pigments helped defining past methods of production of arsenic sulfides [501,503]. On the other hand, the wet-process yields to the precipitation of a fine powder derived from heating a hydrochloric solution of arsenic oxide in a stream of hydrogen sulfide (from pyrite). Alternatively, thioacetamide can be used to produce hydrogen sulfide. In both instances, the wet-process requires purification to eliminate the excess of arsenic oxide [501]. Particle size of the precipitates makes them not ideal for use as pigments being too small [256].

Grundmann & Richter [504] made a significant effort to clarify the importance of non-stoichiometric glass arsenic sulfides. Curiously, cakes of glass realgar-based arsenic sulfide are still collected in the Universalmuseum Joanneum in Graz, Austria [504]. However, these objects were misinterpreted and neglected for a long time, until recent scientific investigations connected them to trades of base materials for As-based pigment production in Europe [504]. Polarized light microscopy allowed to distinguish the method of preparation of the pigment through observation of the particles shape and size. In particular, the wet-process yields a fine golden precipitate (0.2 – 2 μm), whereas the dry-process roasting and/or sublimation mixed with crystalline sulfur and arsenolite yields variously colored smooth particles (1 – 30 μm), or octahedral and irregular shapes, or colorless particles [504]. The As-S system includes stable and congruent melting phases in ratios of 4:3, 4:4 and 2:3. No phase transformations occur at heating, up to the melting point (380 °C), and during sublimation the chemical composition stays the same. The high viscosity of the melt inhibits the nucleation of new orpiment crystals during the cooling phase, also called quenching [501]. As anticipated, archeological excavations in proximity of the workshops of the smelters of arsenolite uncovered that in Central Europe tons of red and yellow arsenic sulfides glasses were produced in the 17th century, due to the high demands of bright pigments and scarcity of mineral ores [501]. Glassy arsenic sulfides were stabilized forms of natural orpiment that would not undergo further light-induced changes [500,501]. Figure 3.58 shows a microphotograph with inhomogeneous particles distribution derived from the yellow areas of the prints, after H₂O microextract on PDMS strip sampler and transfer to a KLARITE[®] replica. The rounded shape can be observed in most particles with a diameter ranging from 1 to 10 μm . The color is dark yellow, however on the printed panel resulted much brighter.

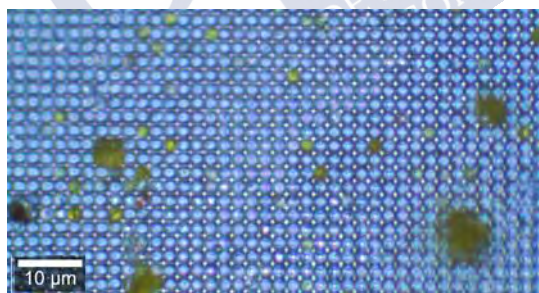


Figure 3.58: micrograph of yellow particles removed with water and PDMS sampler, transferred to a KLARITE[®] replica substrate. The objective of the WITec Raman microscope was magnified 50x.

Vermeuleun *et al.* [500] reported that pararealgar was seldom used as a source for pigment production, as demonstrated by analytical investigations on some European paintings. Luo *et al.* [436] and Zaleski *et al.* [256] in subsequent studies on Japanese prints collected at the Metropolitan Museum of Art in New York, US, outlined the transition from the Edo to the Meiji era focusing on synthetic arsenic sulfides used in yellow and green in various series of prints. The comparative study conducted by Zaleski *et al.* [256] on

subsequent reprints of the famous series by Katsushika Hokusai ‘A Tour of the Waterfalls in Various Provinces’ helped highlighting the transition to the early Meiji period (1834). The older series revealed the use of natural orpiment in the yellow areas mixed with indigo and Prussian blue in the green areas. The later series presented synthetic arsenic sulfides in the yellow and green areas mixed exclusively with Prussian blue. Orpiment, a very expensive pigment, was seldom used for commercial prints, although it was found in the ‘Pink Fuji’ series by Hokusai dated prior to 1849 [256,428,448]. To give an idea of the number of times ‘Fifty-three stations of the Tōkaidō’ by Hiroshige was reprinted (between 12,000 and 15,000) one can understand the relevance of selecting durable and cost-effective coloring media [428]. In early Meiji prints, the addition of turmeric in the yellow areas to intensify the color is reported; however, no definitive evidence could be collected in this respect in the current investigation [430].

Although multi-analytical approaches were necessary to accomplish unambiguous information on the use of glassy arsenic sulfides, Raman spectroscopy provided indeed the most useful insights on the crystallography and chemistry of the pigment in various studies on historical and mock-ups samples [501,503]. The broad band at 341 cm^{-1} , assigned to the symmetrical stretching vibration of the AsS system, is an unequivocal signature of amorphous arsenic sulfide, and further satellite bands can be employed to uncover the technology of production of the pigment. The relative intensities of the additional features can be analyzed to expand the information. Figure 3.59 shows Raman spectra collected in normal settings directly on the yellow areas of the prints with three different excitation wavelengths, (785, 514 and 488 nm, a, b and c respectively). The best scattering was provided by the laser at 785 nm; however, the main feature was identifiable with all lasers. As anticipated, the broad band centered at around 340 cm^{-1} attributable to $\nu_s(\text{As-S})$ was recorded. Satellite bands that indicate the use of crystalline sulfur were detected at 150, 219, 470 and 494 cm^{-1} (assigned to S-S bonds).

The band at 494 cm^{-1} was reported only in sulfur-rich arsenic glasses brightly colored, as those analyzed in the current research. The band at 235 cm^{-1} was attributed to the $\delta(\text{As-As})$ presence of a *nano* realgar-like phase dispersed in the glassy arsenic sulfide matrix [501]. Luo and co-workers [436] attributed the band at 235 cm^{-1} to alacranite derived from arsenolite smelting. Overall, the current findings are coherent with arsenic sulfide glass produced through dry-process. Unfortunately, bands of arsenic oxide are overlapped by the main and satellites bands described earlier. However, the presence of oxidized degradation products cannot be ruled out, or could be below the limit of detection.

Provenancing the mineral source of arsenic sulfide would have been out of the scope of the current research. However, in the literature it is reported that mines of arsenic sulfides occurred in northern Japan (Gunma) and China, and massive arsenic glass production findings were discovered in the Aizu region in central Japan [436,500,504]. Takamatsu [429] reported the introduction of arsenic sulfide glasses in printing in 1846, possibly due to its competitive price of less than a third compared to gamboge, an imported yellow pigment traditionally used in woodblock printing³¹².

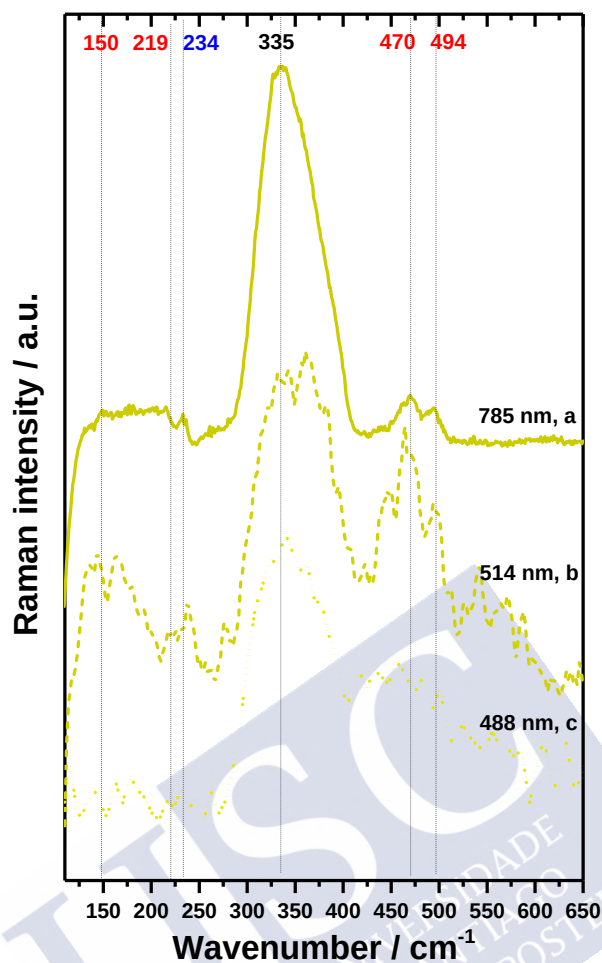


Figure 3.59: normal Raman spectra baselined collected with lasers at $\lambda_{\text{exc}} = 785$ (a) and $\lambda_{\text{exc}} = 514$ (b) with InVia and $\lambda_{\text{exc}} = 488$ with WITec.

SERS analytical protocol allowed the identification of multiple coloring components (Figure 3.60). H_2O and acetone microextracts transferred onto SOKEN[®] and KLARITE[®] replica substrates illuminated with various excitation wavelengths (488 and 785 nm) confirmed the presence of amorphous arsenic sulfide (Figure 3.60 a-b), crystalline sulfur and an organic component close to a naphthol structure (Figure 3.60 c-d). The main modes of the coloring components were indicated on the Raman mapping on the top of Figure 3.60 (341 and 471 cm^{-1} for glass arsenic sulfide; 1147, 1234, 1461, 1598 cm^{-1} for the naphthol-like molecule).

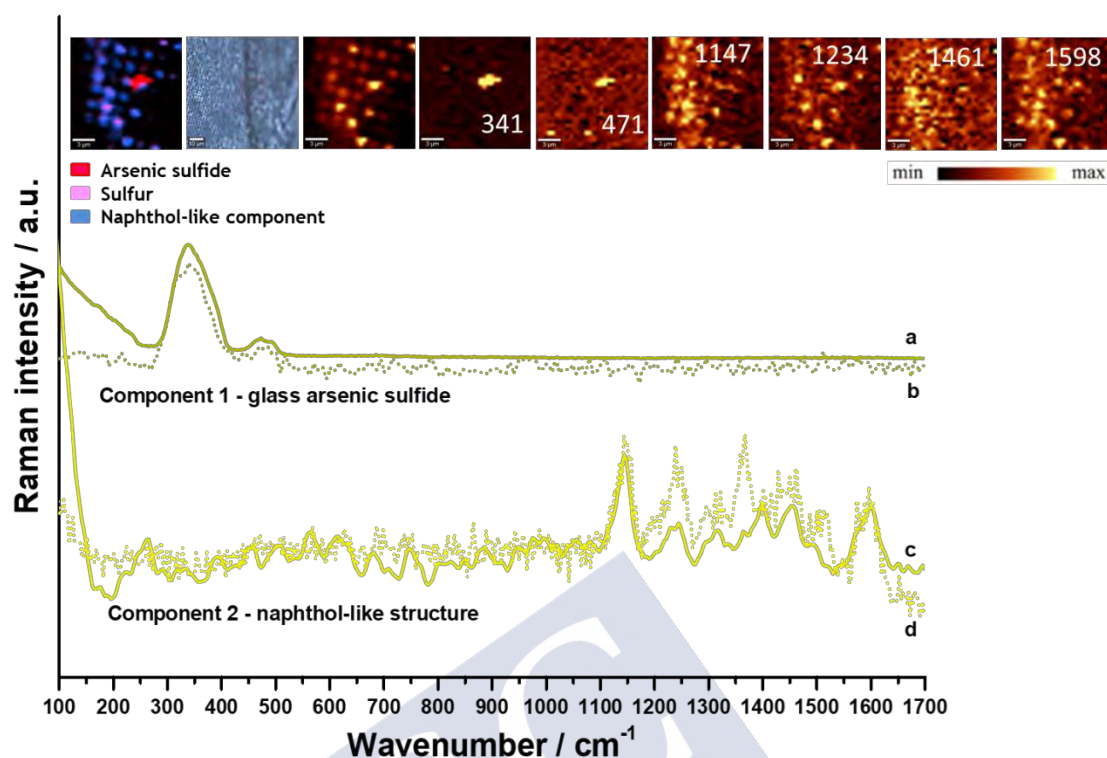


Figure 3.60: SERS microextracts (a-d) and Raman mapping on the top row. (A) SERS microextracts with H₂O on KLARITE® replica, $\lambda_{\text{exc}} = 785$; (b) SERS microextract with acetone on SOKEN® replica, $\lambda_{\text{exc}} = 488$; (c) SERS microextracts with water on KLARITE® replica, $\lambda_{\text{exc}} = 785$; (d) SERS microextract with H₂O on SOKEN® replica, $\lambda_{\text{exc}} = 785$.

Red disazo naphthols were patented in 1902 by the German chemists Schraube and Voigtlaender-tetzner (US713507A) [506], and yellow naphthol was not mentioned 1950's, although it exists nowadays. The presence of any red dye into the ink mixture, however, would have changed the hue radically. Turmeric spectral features have been accurately compared to those in spectra c-d of Figure 3.60, ruling out its use in this instance. Although various studies mentioned the use of phyto-polyphenols to intensify the color with cheap extenders, further analyses would be necessary to clarify the chemical nature of the component 2 in yellow in the Meiji prints here analyzed [256,396,448].

Overall, the analytical work conducted on the yellow areas of the panels confirmed the presence of glass arsenic sulfides, as a further technological evolution occurred in Japanese woodblock printing during the Meiji era. The shape and size of the particles demonstrated that the dry-process method of production was being used, and further evidence in this respect was provided by the satellites Raman bands identified in normal and SERS setting of crystalline sulfur. Raman mapping allowed to visualize multi-component coloring. Raman mapping revealed to be an advanced tool to achieve complete information on the peculiar inorganic pigment, widely studied in heritage science literature [152,216,507–509].

3.3.4.6 Greens

Among all colors, ATR-FTIR spectroscopy enabled to differentiate greens and blue due to the presence of the cyanide band belonging to Prussian blue (Figure 3.42). In addition, reflectance measurements reported in Table 3.9 enabled to determine the color coordinates for olive and bright green hues found in several areas of the prints. MA-XRF atomic mapping, presented later, allowed inferring qualitative information on the amounts of yellow added to the bright green. Again Raman spectroscopy allowed the comprehensive identification of arsenic sulfide mixed with Prussian blue in the green areas of the prints analyzed (Figure 3.62). The different concentrations in the mixture of yellow and blue yielded different tones of green, as expected.

Band filtering mode with the software Project 5 allowed to further improve the Raman mapping and to visualize the molecular information in a very straightforward way (Figure 3.61 b). Bands at 341 and 478 cm^{-1} were assigned to the ν (As-S-As) and to the crystalline sulfur, respectively. On the other hand, bands at 268 , 526 and 2152 cm^{-1} were assigned to the Fe-CN-Fe deformation mode and to the ν (C $\equiv$ N) [495,498,501].

Meiji confirmed to be the period of embracing experimental challenges. As introduced before, although Prussian blue was already in use in Europe since the 18th century, its presence in Japan was relatively new (1831) [256,476,510]. Synthetic arsenic sulfides were also resulting from the consolidation of recent technological advances (Figure 3.61 c), and the evidence on green coloring media confirms both findings.

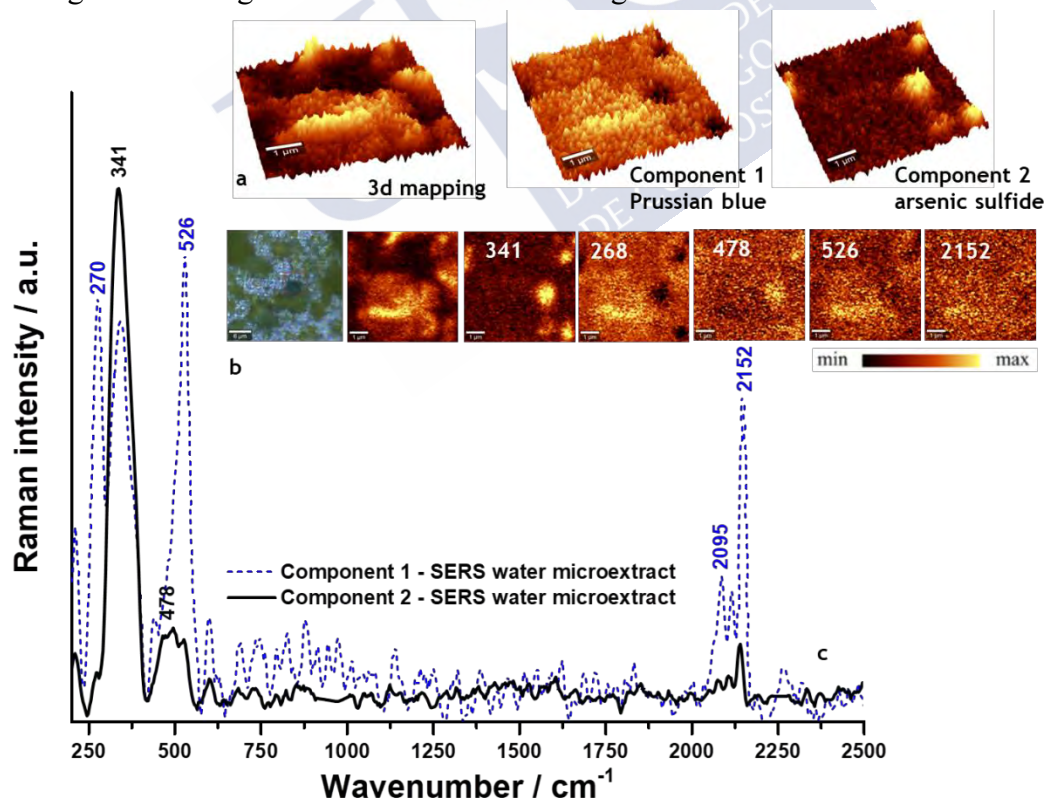


Figure 3.61: olive green images and SERS microextracts with $\lambda_{\text{exc}} = 785\text{ nm}$. 3D Raman mapping of the overall components, component 1 and component 2 (a); visible, overall mapping and band mapping of the components (b); SERS spectra (c).

MA-XRF atomic imaging focusing on As (Figure 3.62) allowed to visualize the higher concentration of yellow in brighter greens areas, as one would expect. The yellow collar of the monk-like figure on the background in Figure 3.62 b, with a bright green scarf appear high in As in Figure Figure 3.62 a, similarly to the handle of the sword in the same panel (n°1). On the other hand, the clothing of the warrior figure in green olive corresponds to a less intense As signal, to counterpart the high signal of Fe in Figure 3.62. Following, the yellow and green areas in panel n°4 responded with intense As signal in the MA-XRF mapping (Figure 3.62 c). The green areas confirmed the ongoing practice of mixing pigments in the Meiji woodblock printing. The exclusive use only of Prussian blue with glass arsenic sulfide can be considered as a result of the mature transition to a new industrial era.

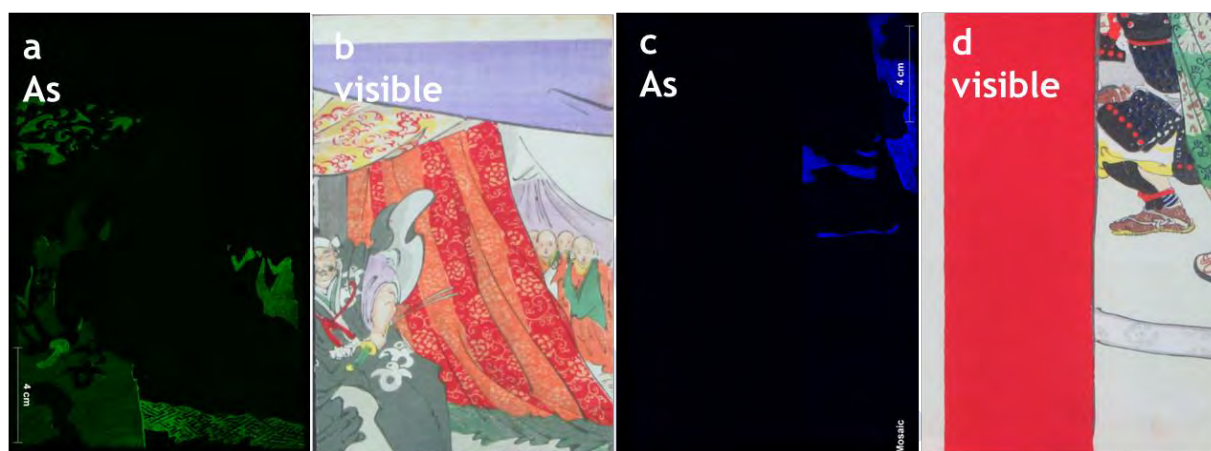


Figure 3.62: MA-XRF elemental mapping of showing As in the yellow and green areas at different concentrations from panels n°1 and 4.

3.3.4.7 Orange, pinks, brown and black

The colors presented in this larger and final section are grouped together because the components detected have been previously introduced. The section provides little news on the Meiji printing techniques, but it completes the evidence. However, new insights will be provided on the use of **hematite** in Meiji printing. A further reason to put less emphasis on these findings lies in the limitations in exploiting the SERS method proposed due to reduced sampling areas. PDMS strip samplers could not work at their best potential since orange, pink, brown and black areas of the prints were below the size of the PMDS strip sampler ($\sim 4 \text{ cm}^2$).

Orange

Orange was obtained with the pigment vermilion (HgS), above introduced in the mixture with β -naphthol dyes. It was detected on its own, or in some red hues. Raman spectroscopy and MA-XRF spectrometry confirmed the finding. Orange was used on the clothing of the monks in the background and on the curtains of panel n° 1 and n° 2. Since the antiquity, vermilion was chemically produced through dry-process (heating/grinding) of the natural occurring minerals cinnabar or meta-cinnabar [459,463]. It is generally described to have a trimolecular hexagonal unit comprising S-Hg-S chains running along the C-axis [499]. In the 18th century, the wet-process of production was introduced [466]. The spectral signatures of

cinnabar and vermilion are identical in Raman spectroscopy. Similarly to arsenic sulfide, mercury sulfide has intense vibrations at frequencies below 500 cm^{-1} .

In the current research, vermilion was detected a number of times with normal Raman and SERS settings, however with the latter reproducibility was fair. On the other hand, MA-XRF imaging unequivocally identified the elemental signature of Hg in the orange areas of the clothing and curtains. Figure 3.63 shows the MA-XRF (a) imaging insets introduced earlier section 3.3.4.2 that helped mapping Hg as an exclusive indicator of the pigment under analysis.

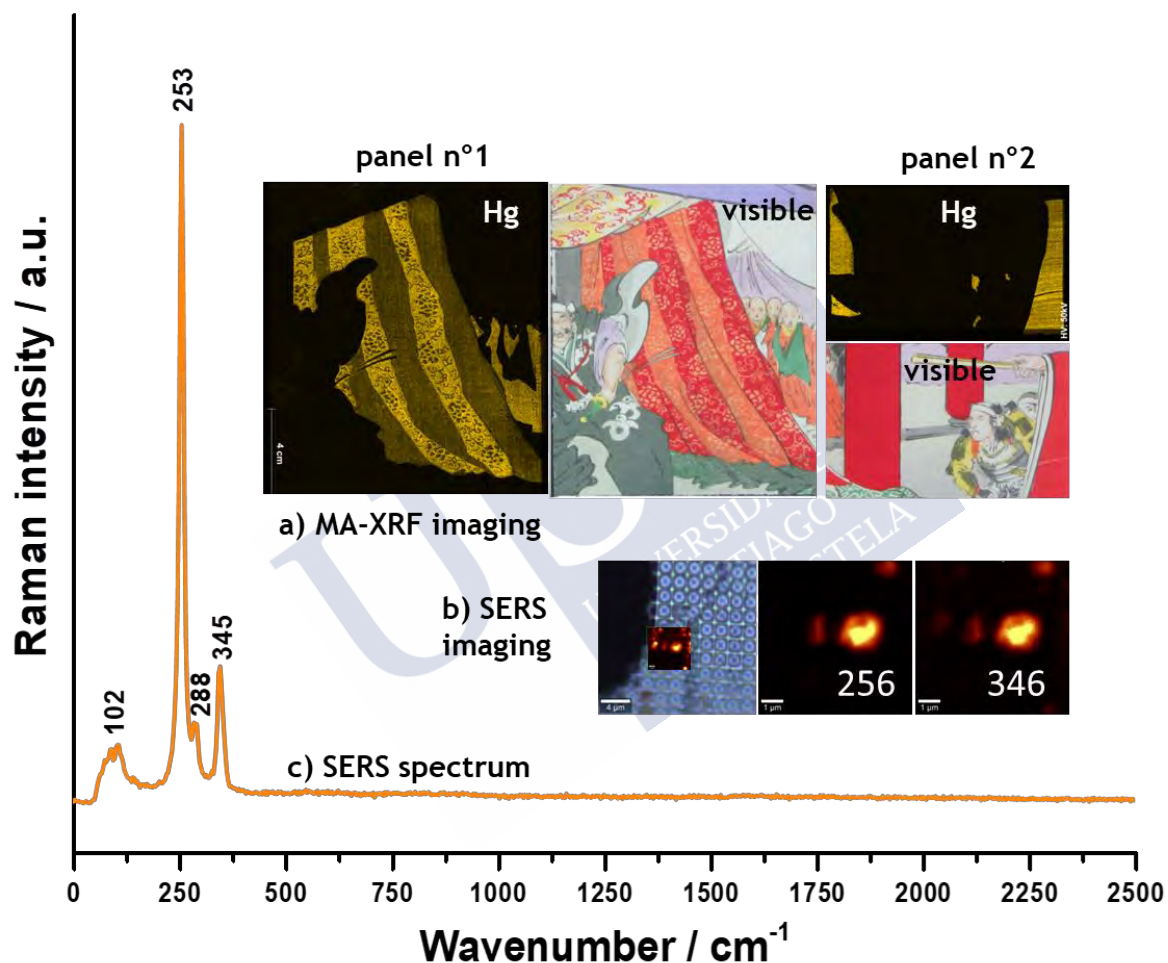


Figure 3.63: overall results of MA-XRF elemental imaging highlighting Hg (a), SERS imaging with band filtering mode (b) associated to SERS microextract with H_2O on KLARITE[®] replica with $\lambda_{\text{exc}} = 785\text{ nm}$ (c) obtained on orange areas of panels n° 1 and n° 2.

Further, SERS mapping and spectrum (Figure 3.63 b-c) confirmed the presence of the inorganic pigment vermilion transferred onto KLARITE[®] replica substrate with water and illuminated with $\lambda_{\text{exc}} = 785\text{ nm}$ laser. Opposite to the spectra where vermilion is mixed with β -naphthol dyes (Figure 3.63), the region between 1000 and 1700 cm^{-1} did not present spectral features, as expected. Bands assigned to vermilion are marked in Figure 3.63 c with the

following vibrations: 102 cm^{-1} lattice modes, 253 cm^{-1} δ (S-Hg-S); 228 and 345 cm^{-1} ν (S-Hg-S).

As mentioned earlier, vermilion was a well-established pigment and its use in the Japanese woodblock printing is not surprising. However, in these prints it seems to respond to the need of limiting color spreading all over the clothing and the complex patterns of the curtains. For more extended areas of the drawing, naphthol red dyes were preferred, although they were more prone to wetting the paper (as shown in the back of panel n°2 in Figure 3.46).

Pinks

Pink was used in two skin tones, dark and light. A further different light-salmon pink was used on the clothing detail in panel n° 6. Figure 3.64 shows the highlights of where pink was used on the various panels. Surprisingly, for pink hues coloring components detected were numerous [448]. Skin areas were lighter in the inner surface of the shapes and slightly reddish in the outer borders. The composition of the inks changed accordingly. A microscope photograph at was inserted to show various colored powder grains distributed on the paper fibers. The surface for sampling was quite reduced compared to other colors and this made SERS detection less reproducible than in other instances. The sampling protocol could not allow a deliberate selective removal from the dark and light areas. Attempts with different excitation wavelengths, substrate structures and solvents were made.



Figure 3.64: photographs in gray-scale with highlights of the panels with pink areas on the skin (light and dark) and on the clothing (light salmon). On the right down, microscope photograph of the paper fiber with dispersed colored grains.

Raman spectroscopy demonstrated that only in the light-salmon area vermilion could be unequivocally identified (Figure 3.65 a). In the same spectrum, additional bands hinting to the presence of azo β -naphthol dyes were detected in the region $1000\text{--}1600\text{ cm}^{-1}$, but the high molecular cross-section of vermilion biased the relative intensities of the coloring components (for complete naphthol band assignment please refer to section 3.3.4.2). Following, spectrum

b in Figure 3.65 has demonstrated the use of hematite reported for the first time in the literature related to the fabrication of Meiji woodblock prints.

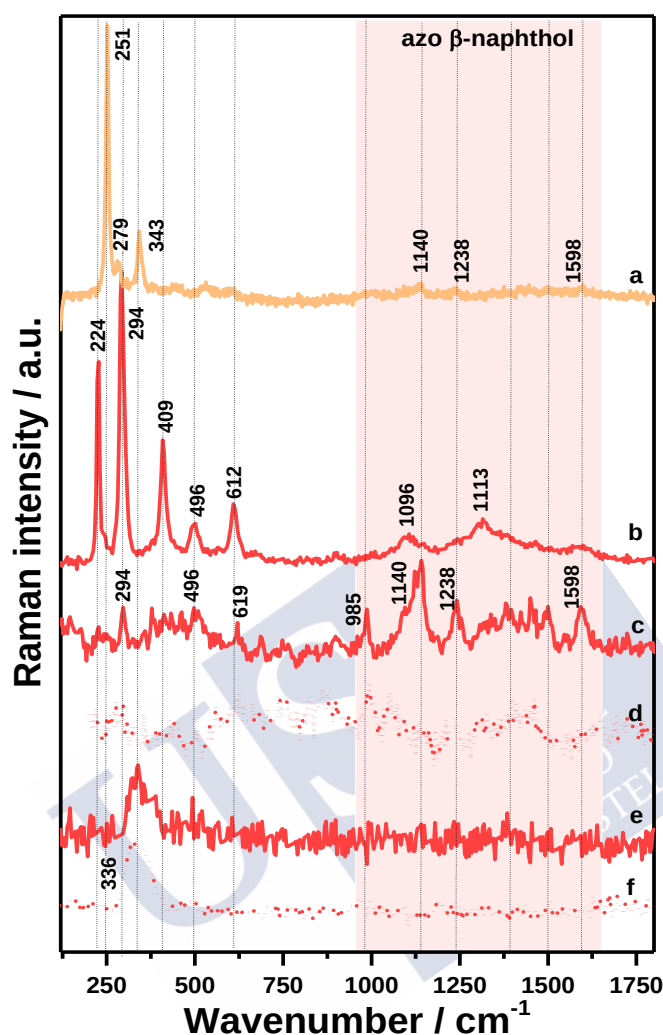


Figure 3.65: Raman spectra obtained on the pink areas of the prints. (A) NR spectrum of vermilion and naphthol dye detected on the light salmon area of the clothing in panel n° 6, $\lambda_{\text{exc}} = 785$ nm; (b) NR spectrum of hematite in the skin with $\lambda_{\text{exc}} = 785$ nm; (c) NR spectrum of naphthol with $\lambda_{\text{exc}} = 785$ nm; (d) SERS microextracts with H₂O on KLARITE® replica, $\lambda_{\text{exc}} = 785$ nm; (e) NR spectrum of glass arsenic sulfide with $\lambda_{\text{exc}} = 785$ nm; (f) SERS microextract with acetone on SOKEN® replica substrate with $\lambda_{\text{exc}} = 488$ nm.

If certainly hematite is a coloring medium used since prehistory, the fact that for such a specific detail of the skin tone kept serving the tastes of experienced printers is curiously reassuring. Instead substantial innovations echoed in color mixing observed in other pink areas. Again azo β -naphthol dyes were detected through normal Raman settings and SERS in microextracts with H₂O with $\lambda_{\text{exc}} = 785$ nm (Figure 3.65 c-d). Finally, glass arsenic sulfide was also detected. It is difficult to say, if it was sampled from the inner or outer areas of the skin;

however, it could be hypothesized that yellow might be used to brighten the slightly reddish tones of naphthols and hematite in the clearer area of the skin (Figure 3.65 e-f.)

MA-XRF imaging confirmed the presence of a Hg-based pigment in the light-salmon clothing in panel n° 6 (Figure 3.65). However, being Hg a very heavy metal possibly covered the expected signal of S (Annex 3.14). An alternative interpretation for the absence of S might relate to the low concentration of pigment used to yield the very light tone visible in the photo (top left Figure 3.66). S was below the limits of detection and further quantitative comparisons should be pursued through atomic % calculations, however discarded for the time being. Instead, the presence of hematite was hinted by the intense signal on the outer areas of skin (Figure 3.67 right). The borders of the faces showed a higher concentration of Fe and no Hg was detected.

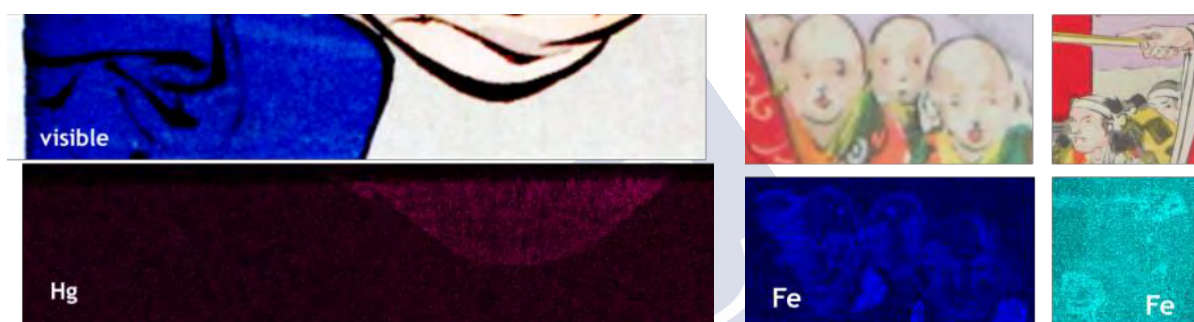


Figure 3.66: MA-XRF elemental mapping. On the left, Hg-based pigment in the light-salmon area. On the right insets of the Fe-based pigment on the outer boards of the skin.

In conclusion, pink varies surprisingly despite the limited areas of the prints on which it was used. Four components (vermilion, hematite, azo β -naphthol dye, arsenic sulfide) were detected unequivocally with Raman spectroscopy and MA-XRF spectrometry, being for the first time presented spectral evidence of hematite in Meiji woodblock prints.

Brown

The footwear in panel n°4 and the decorations of the curtain in panel n°5 were colored in brown. As for other small areas and fine details of the prints, mineral pigments were preferred to azo β -naphthols and Ba-lakes, possibly due to their reduced wettability (refer to section 3.3.4.2).

Figure 3.67 shows the results obtained with Raman spectroscopy and Raman imaging. SERS spectra (a – b) were obtained respectively with acetone on SOKEN[®] ($\lambda_{exc} = 488$ nm) and H₂O on KLARITE[®] ($\lambda_{exc} = 785$ nm) replica substrates. Attempts with the opposite structures and solvents were not successful. The presence of glass arsenic sulfide, identified with the main band centered at about 335 cm^{-1} (spectrum a in Figure 3.67) is suspected to be a contamination derived from the yellow thin footwear sole of panel n° 4. Following, SERS spectrum b in Figure 3.67 is a H₂O microextract that enabled the identification of hematite and carbon black. The low frequency region is populated with bands assigned to the iron oxide (Fe₂O₃): 226, 294, 409, 498, and 604 cm^{-1} . Several authors divide characteristic hematite Raman bands in two broad classes, A_{1g} and E_g. Bands at 221 cm^{-1} and 491 cm^{-1} are

assigned to the A_{1g} mode and the most intense bands 290, 409, and 605 cm^{-1} at the E_g modes [463,511,512]. Bands in the region 200 - 300 cm^{-1} were assigned to the Fe atom vibrations. The band at 226 cm^{-1} was ascribed to the movement of iron cations along the C-axis. Bands at 409 cm^{-1} and 605 cm^{-1} were assigned to symmetric mode of O atoms relative to other cations in a plane perpendicular to crystallographic C-axis and Fe-O stretching vibrations, respectively [495].

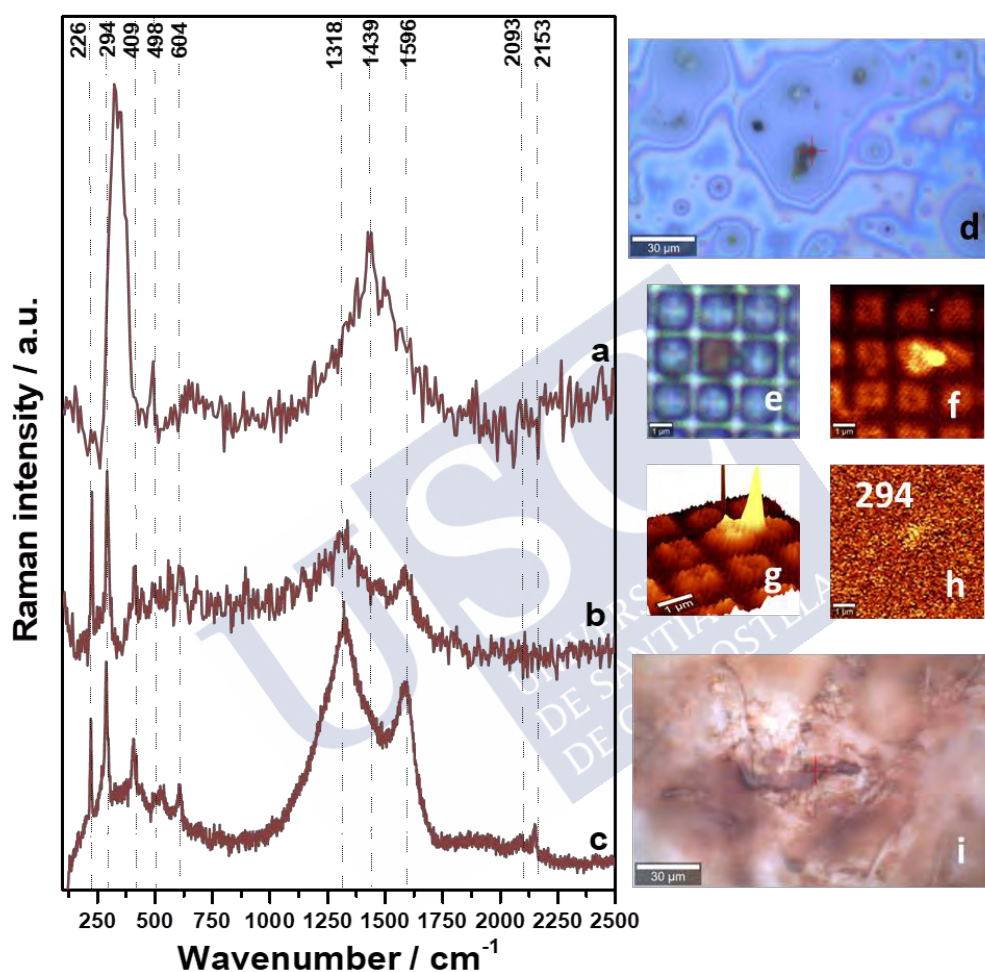


Figure 3.67: Raman spectra collected on the brown areas of panels n° 4 and 5. (A) SERS microextract with acetone on SOKEN® replica of glass arsenic sulfide, $\lambda_{\text{exc}} = 488 \text{ nm}$; (b) SERS microextract with H_2O on KLARITE® replica from hematite and carbon black, $\lambda_{\text{exc}} = 785 \text{ nm}$; (c) NR spectrum of hematite and carbon black detected on the footwear in panel n° 4, $\lambda_{\text{exc}} = 785 \text{ nm}$; (d) microphotograph of SOKEN® replica with acetone; (e) microphotograph of KLARITE® replica with corresponding (f) Raman mapping overall; (g) 3D mapping and filtering on band 294 cm^{-1} (h); (i) microphotograph with red cross corresponding to NR spectrum (c).

Carbon black contributions to the spectral features were identified by the presence of the D and G bands respectively at 1318 and 1596 cm^{-1} . As shown in sections 3.3.4.4 and 3.3.4.6, carbon black was often mixed with other coloring components to darken the hues. Finally, Prussian blue most intense bands at 2093 and 2153 cm^{-1} were detected in spectrum c in Figure 3.68 and might be resulting from a contamination with the neighbor colors.

MA-XRF spectrometry could not distinguish between Prussian blue and hematite, since both contain Fe. S and As were not detected in the brown areas, that is why glass arsenic sulfide detected with SERS (Figure 3.68 a) is likely to be a contamination. However, it cannot be ruled out that the pigment is below the limits of detection.

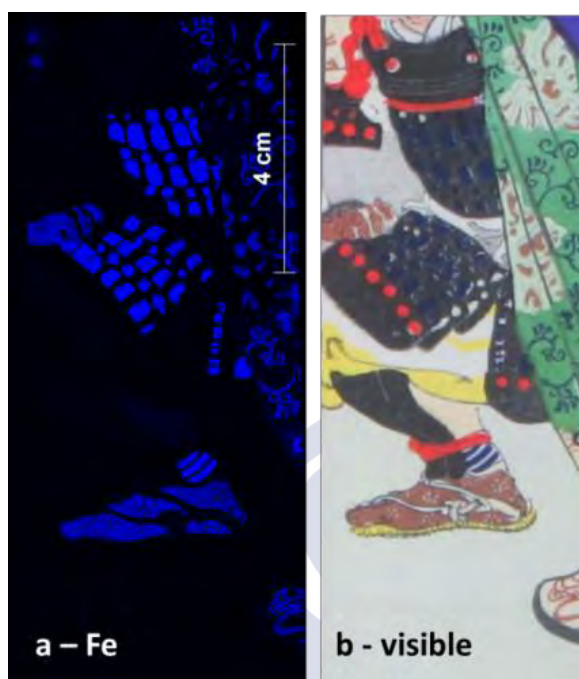


Figure 3.68: MA-XRF elemental imaging of panel n°4 with highlight on Fe (a) corresponding to brown and blue areas (b).

Black

Amorphous organic carbon black was utilized as a coloring medium in the Meiji prints. As demonstrated experimentally, carbon black was mixed with blue, brown and olive green to darken the hues. Raman normal settings allowed to detect consistently the pigment with the excitation wavelengths at 785 and 488 nm. The surface of the black sampled areas was too limited to achieve consistent analytical results with the PDMS strip sampler method. Figure 3.69 shows integrated spectral information and imaging. The main D and G carbon bands were detected at 1322 and 1590 cm^{-1} , respectively (in Figure 3.69 a–b–c). A good SERS signal was obtained from water microextracts transferred onto KLARITE[®] replica substrates (Figure 3.69 a). Normal Raman spectra were collected with excitation wavelengths at 488 and 785 nm (b-c). Raman filtering mode allowed mapping the areas on substrate with best signal (Figure 3.69 c -g), especially the G-band at 1590 cm^{-1} . Microphotographs were collected to understand the pigment particle distribution within the fibers of the paper (Figure 3.69 d).

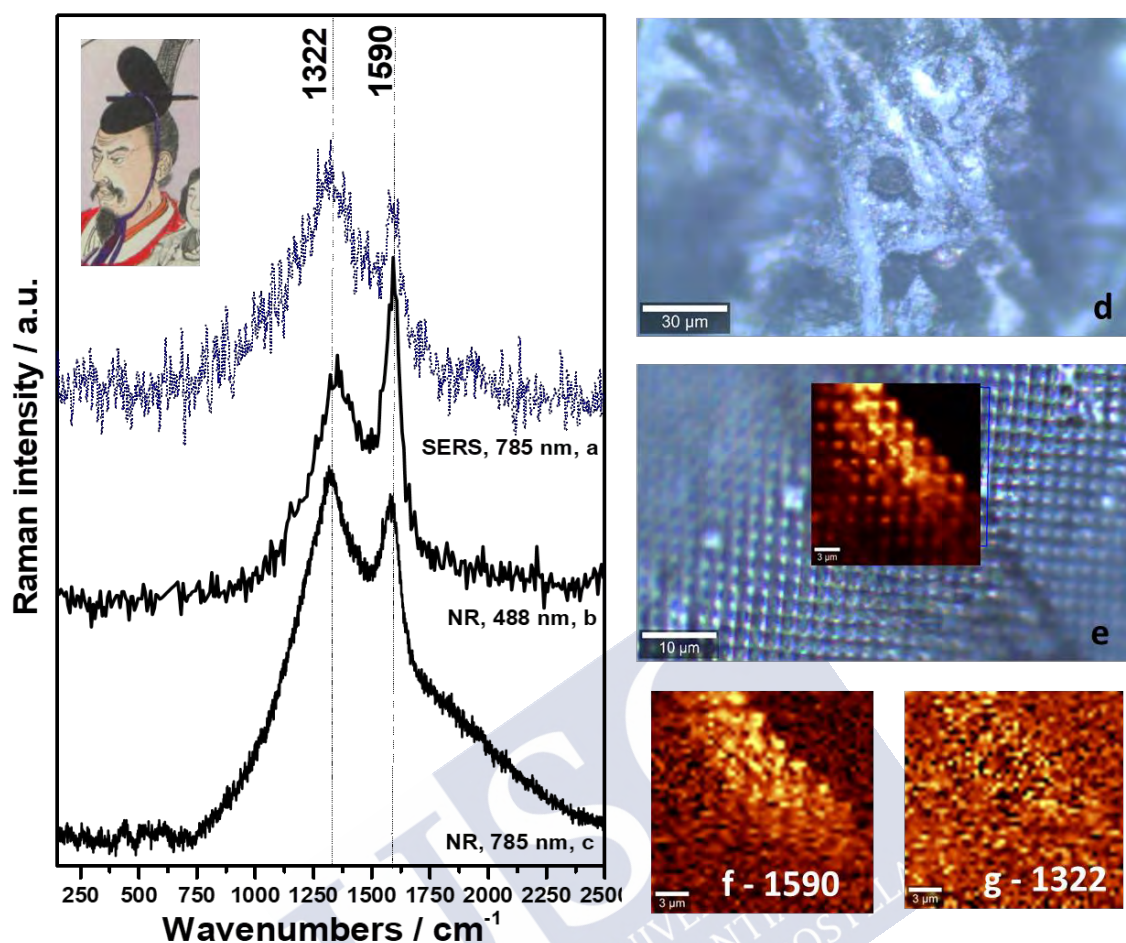


Figure 3.69: Raman and SERS spectra (a - c), micrograph on black area (d) and SERS mapping on KLARITE® replica substrate

Overall, orange, pinks, brown and black were constituted by traditional coloring components mentioned in several publications [509,513]. With the exception of hematite, not previously mentioned in Meiji printing literature, other pigments identified were vermilion and carbon black. The presence of Prussian blue and glass arsenic sulfide, typical of the Meiji palette, is rather due to sampling contaminations instead that intentional mixing, with the current evidence. Finally, the addition of β -naphthol dyes in the skin-pink and orange colors was confirmed by repeated collection of Raman spectra. MA-XRF imaging provided complementary information for most colorants.

3.3.4.8 Outlook and summary

New insights were provided on Japanese woodblock printing from the Meiji era. The novel analytical sampling method proposed in this research was further validated on a new class of small molecules of dyes and pigments, ranging from 0.2-0.8 kDa molecular weight. For the first time, the tools of Raman and MA-XRF imaging were consistently combined to provide new specific evidence on objects previously studied only with micro-destructive

analytical methods [359,430–432,439]. Table 3.10 summarizes the findings achieved with Raman spectroscopy. (Annex Table 3.15 shows molecular structures and molecular weights).

Table 3.10: Small molecules detected with SERS and NR settings on Japanese woodblock prints from private collection.

Color	Solvent for SERS microextractions	Laser (nm)	Molecular identification of multi-components
Red	water	488	• Azo β -naphthol (organic dye)
		514	• Ba-naphthalene sulfonic acid (lake)
		785	• Vermilion (mineral pigment)
Purple	water, acetone	488	• Methylated and non-methylated homologues of pararosaniline (organic dye)
		785	• Crystalline sulfur • Carotene
Blue	water, acetone, mix	488 785	• Prussian blue (organometallic pigment)
Yellow	water, acetone	488	• Azo β -naphthol (organic dye)
		514 785	• Crystalline sulfur • Glass arsenic sulfide (mineral pigment)
Green	water	785	• Glass arsenic sulfide (mineral pigment) • Prussian blue (organometallic pigment)
Orange	water	785	• Vermilion (mineral pigment)
Pink	water, acetone	488	• Azo β -naphthol (organic dye)
		785	• Glass arsenic sulfide (mineral pigment) • Hematite (mineral pigment) • Vermilion (mineral pigment)
Brown	water, acetone	488	• Hematite (mineral pigment)
		785	• Carbon black (organic pigment) • Prussian blue (organometallic pigment) (?)
Black	water	488 785	• Carbon black (organic pigment)

The mere fact that red azo β -naphthols²³ and purple aniline homologues²⁴ could be spectrally determined with minimally-invasive SERS microextracts is a novelty in the field of Meiji printing studies. Further, findings could be correlated to photo-fading mechanisms thanks to previous experiments on mock-ups samples [448]. MA-XRF spectrometry could not provide useful information on these two classes of new synthetic organic compounds (reds and purples), nor could FTIR spectroscopy. Therefore, nanodestructive SERS sampling allowed to reach limits of detection and specific information that other techniques failed to obtain. Evidence on the Ba-lakes has led to controversial conclusions, previously observed by other authors [446,447]. Large red areas have shown the presence of Ba signal with MA-XRF imaging and unreacted barite was detected with Raman spectroscopy. Spectral data was consistent with the composition of the lake Sunbrite Red (PR 60:1), patented in the early 20th century. The unintentional making of a Ba-lake would be coherent with the intense experimental transition held during the Meiji era.

²³Acid red 73, 26 and 27 and Ba-salt naphthalene sulfonic acid lake.

²⁴Non-methylated pararosaniline, mono-methylated rosaniline, di-methylated pararosaniline, trimethylated pararosaniline.

Prussian blue, considered revolutionary in the Edo printing period, was consistently used throughout the Meiji era, as Raman spectroscopy and MA-XRF imaging demonstrated. The colloid-like aggregates forming in the interaction with the solvent of the organometallic pigment gave the opportunity to reflect on the SERS scattering and weak plasmonic interactions, as well as on the formation of new metal complexes that might shift the Raman bands. Prussian blue was mixed in several occasions with arsenic sulfides, carbon black and hematite to form new colors. Glass arsenic sulfides were produced through dry-process (sublimation / quenching) and satellite Raman bands detected on the various prints could not only confirm that synthetic yellow arsenic sulfide was used, but also that crystalline sulfur was added to brighten the hue. Greens (olive and bright) resulted from a combination of arsenic sulfides and Prussian blue. ATR-FTIR spectroscopy could distinguish blue and greens for the cyanide band, together with Raman spectroscopy and mapping that separated very well the mixed coloring components. A secondary group of colorants (orange, pinks, brown and black) revealed the consistent use of traditional organic and inorganic pigments, such as vermilion and carbon black in combination with coloring media introduced in the Meiji period. Hematite was detected for the first time in a research on Meiji woodblock prints.

Swiping the PDMS samplers on the surface of the prints was sufficient to physisorb polar and nonpolar molecules to the Al-platforms with H₂O, acetone and mixed as transferring solvent. H₂O revealed to be the best solvent, except for Prussian blue that provided slightly better results with acetone.



4. CONCLUDING REMARKS

This thesis aimed to explore novel sampling strategies for the detection of small molecules from the surface of different materials. SERS Al-coated platforms were devised and tested on model samples and actual objects to validate their potentials for application in the cultural heritage field. The methodological trajectory of the thesis aimed to optimize the fabrication of the sampling and sensing devices, comprising the PDMS strip samplers for the removal of the free molecules from the surfaces and the *micro* and *nano* structured SERS platforms. Furthermore, data collected with handheld and benchtop spectrometers and compared to SERS spectra provided reliable molecular sensing for *in situ* applications. The sampling strategies optimized experimentally were adapted to the peculiarities of the analytes under study, however aiming for a multipurpose applicability of the SERS platforms.

Besides the successful results in the detection of LMW degradation products from plastic surfaces, the most relevant scientific novelty has been providing a highly sensitive alternative to SEC for the identification of oligomers from oxidized polymers. The thesis addressed the **research question** on SERS sensors for plastic artworks providing insightful information with minimal amounts of materials and enabling to confirm the presence of solid fragments derived from different degradative processes. Furthermore, other types of small molecules relevant to heritage science research were detected (*e.g.* dyes and pigments).

In the last fifteen years, Raman spectroscopy applications have had a considerable success in the fields of cultural heritage, biological chemistry, safety and environmental applications. SERS has indeed pushed the limit of detection beyond traditional Raman and allowed reducing the quantity of material sampled. In general, the issue of sampling is crucial to determine the success of the analytical methodologies proposed to study heritage materials, and in this thesis an upgraded conceptualization of minimally-invasive sampling was argued. The damage caused by sampling the surface of polymer-based contemporary artworks with the PDMS strip samplers is arguably destructive, having estimated an amount of sample removed of $\sim 10^{-10}$ g. The thesis provided evidence of consistent molecular identification of LMW oxidation products on well-studied model polymers, underexplored in heritage science (*e.g.* ABS and PI). Further background information was achieved by testing the sampling steps on model materials, as linseed oil and PVAc, commonly used for the manufacturing and conservation of heritage objects. Various classes of organic synthetic/natural dyes and inorganic synthetic/mineral pigments were consistently detected on paper, leather, stone and plastic supports.

The **research question** on the suitability of SERS sensors to detect small molecules in low concentration was addressed through a slight change in perspective. SERS literature tends to focus on the relevance of signal enhancement by comparing SERS to normal Raman

spectroscopy data. Instead, this thesis focused on the ability of SERS to achieve reliable spectral information from complex matrices, even if with relatively low signal/sample concentration. The goal was not only to quench the intrinsic Raman fluorescence, but also to obtain spectral data from barely visible samples not analyzable in normal Raman settings. The chances of positive compound identification were further complicated by several factors as the wavelength dependence, the variability of the localized plasmonic enhancement, the periodicity of the *micro* and *nano* structures, the motion of the analytes through the transferring solvent and the different molecular cross-sections of the analytes. The complexity of the differential influences was assessed through several experiments designed to observe the specific contribution of each variable on the spectral response. In some instances correlating the variable to improved spectral data was not straightforward; however, the successful attempts were highlighted in the discussion of thesis.

Critical evaluations on the extent of selectiveness of the PDMS sampling method were accomplished. The ability to physisorb polar and nonpolar molecules combining the polarity of the transferring solvent and its affinity with the analyte played an essential role to ensure the molecular sensing. For example, polar solvents, more suitable for the removal of polar components like carboxylic acids, allowed enhancing the signal of photooxidative products on polymeric surfaces. Further, CHCl_3 revealed more suitable to discriminate synthetic organic pigments in ABS matrices (e.g. LEGO[®] bricks) and so on. Overall, testing selective sampling and extractive protocols by tuning solvents polarity and analyte solubility revealed useful to achieve unknown molecules, often encountered in actual heritage objects.

The **research question** on the impact of SERS-based diagnostic tools for early detection of degradation markers on the surface of polymeric artworks was accomplished. The findings of accelerated aging tests on model materials were validated on actual PI-based objects by Andrés Pinal preserved in the permanent collections of the CGAC in Santiago de Compostela. The possibility to access artworks allowed facing the challenges posed by composite naturally weathered materials and to explore the applicability of the analytical method thoroughly. Tailoring an existing technology with new analytical protocols to the field of preventive conservation provides tools to address pressing issues among cultural heritage managers. The rate of decay of plastics is unprecedented compared to traditional heritage materials, and this thesis provided new strategies to overcome the issue of fast diagnosis *in situ*.

Technological **research questions** on how heritage objects were produced in the past have been addressed in this thesis, as well as the identification of unwanted conservation treatments. SERS platforms provided insights on coloring media used in contemporary and historical collections of LEGO[®] bricks, providing evidence on the use of PC and ABS in different periods of production. Further, the sampling kit was sent as a toolbox to non-experts analysts to achieve coloring media and binders on the prehistoric rock art site of Antelas in Portugal. The reduced concentration of samples removed from various colored areas of the wall paintings combined with exceeding solvent use during the extractive procedures led to detect solvent stabilizers and PDMS residues from the sampler. However, this partial contamination of the analytical data did not prevent from detecting undocumented conservation treatments with PVAc adhesives that yellowed the surface over time. Further,

natural dyes references of grey cochineal, kermes and carmine lake were tested on the SERS platforms to exploit their potentials in quenching the well-known fluorescence of anthraquinones molecules. Water-soluble synthetic organic colorants (e.g. β -naphthols) were detected in prints helping to define the transition from the Edo to the Meiji period in Japan through material witness. Traditional woodblock printing methods relied on natural dyes that were progressively being mixed to synthetic pigments resulting from a global interest in chemistry of dyes for industrial applications.

An overview of the three chapters of the thesis is provided as follows:

- In Chapter 1, *Introduction*, the framework of the research was provided, describing the limiting conditions of sampling in the field of cultural heritage and identifying a knowledge-gap on the definition of minimum amount reachable through SERS sensors. Further, the decision to keep using aluminum as a plasmonic metal to coat the platforms was based on prior experiments conducted by fellows from the same research group. The satisfactory evidence obtained on the enhancement factor of the Al-coated platforms used was confirmed in the current research. Further, the combination of the optical properties and Bragg's diffraction effects were strengthened by using several KLARITE[®] replicas for the majority of the experiments. On the other hand, SOKEN[®] nanopillar replicas provided novel information on the ability of solvents with low surface tension (e.g. acetone) to provide the necessary motion to aggregates of colloid-like particles of insoluble compounds (e.g. Prussian blue) allowing their detection. Materials analyzed (linseed oil, ABS, PI and PVAc) were introduced upon their chemistry, degradative behaviors and use in artworks/heritage objects. Similarly, museum-based validations were introduced in the wider framework of experts' collaborations aiming to enhance heritage science tools and services. The shift of focus to detecting coloring media was explained outlining the technology of production of ABS-based toys, Japanese woodblock prints and further complex materials.
- In Chapter 2, *Experimental methodology and materials*, the fabrication on the sensing devices, the accelerating aging tests parameters, the tangential experimental constraints were contextualized. Most relevant was the section on the optimization of the SERS microextractions that described the analytical protocols followed experimentally. The fabrication of elastomeric lithographic stamps and coating procedures was presented in detail to navigate the reader through the process of preparation of the SERS sensors. Each section was accompanied by a brief list of the characterization methods utilized to monitor the relevant parameters, while collecting data on the sampling devices (e.g. SEM for the replication of the nanostructures).
 - Chapter 3 was divided in three subsections following the main themes embraced in the thesis: *Sensing and Sampling Devices Fabrication*, *Detecting Degradation Markers in Polymeric Materials*, and *Extending the Application of SERS Devices to Small Molecules of Interest*. In the first section, an overview of the polymerization rates of FLUOROLINK[®] MD700 helped reaching an optimal operating protocol for the fabrication of substrates through UV-NIL. The 2,2-dimethoxy-2-phenylacetophenone (651) photoinitiator at wt. 5% with 5 min N₂ purge and 40 s UV exposure were observed as the best options to fabricate

suitable SERS substrates. Further, the PDMS strip samplers were thermally polymerized following the 10:1 ratio of SYLGARD[®] 184 and curing agent. The safe application of the strips was assessed experimentally prior to the application on actual objects. Simulations with various solvents were performed and a negligible amount of unpolymerized SYLGARD[®] 184 was released and detected with GC/MS. Except for the samples from Antelas wall paintings, PDMS residues did not contaminate the SERS measurements. Further, PS and PEG blends of SEC standards with narrow distributions were prepared as films to simulate the PDMS sampling by physisorption. The upper molecular weight thresholds were 1.2 and 1.5 kDa for nonpolar and nonpolar polymers, respectively. Overall, the sampling devices were tested and optimized in several controlled conditions allowing a thorough understanding of their advantages and drawbacks.

The evidence on degradation markers was built upon accelerating aging tests on linseed oil, ABS, PVAc and PI. As expected, the photo-degradative behavior lead to competing mechanisms of crosslinking and chain scission reflecting in the formation of carbonyl and hydroxyl species. Further loss of mechanical properties and yellowing were observed in the photoaged samples. The formation of LMW photoproducts was backed up by Py-GC/MS, FTIR spectroscopy and SEC for artificially and naturally aged linseed oil as a first model material, and extended to the other polymers with similar degradative behavior. In addition, ABS was thoroughly investigated by conducting parallel thermal oxidative experiments. SERS microextracts on photoaged ABS films (400 h) confirmed the accumulation of hydroperoxides followed by the chain scission in the SAN and PB components. Further, for the first time evidence of chain scission was observed in mild isothermal oxidation experiments (150°C) of PVAc through SERS microextracts. SEC reduced sensitivity would have prevented from achieving such information due to the limited concentration of the solid fragments. Following, PI (1,4-*cis* polyisoprene) films and PI-based objects were tested to strengthen the evidence on the suitability of the SERS sampling method to detect LMW degradation markers. The successful validation of the SERS extractive method on naturally aged complex materials was invaluable. In collaboration with the conservation department at the CGAC, *Traxe de home* by Andrés Pinal was monitored, allowing an in-depth understanding of the natural aging behavior of the object throughout several years. This thesis allowed to test the applicability of the SERS sampling method proposed validating promising preventive conservation tools for contemporary artworks.

The thesis strengthened its underlying contribution to develop multipurpose tools for heritage science research by collecting new evidence on small molecules of coloring media and unwanted conservation products. Industrial synthetic pigments, as carbon black, hematite and copper phthalocyanines, were identified in complex matrices of design objects (*e.g.* LEGO[®] toys). The analytical protocol comprised the benchtop Raman spectrometer to collect background evidence on industrial pigments, followed by the handheld instrumentation to extend the information for *in situ* analysis. SERS sampling was an alternative analytical tool for routine screening of plastic objects when handheld data was not satisfactory. The poor resolution of the handheld instrument was a major drawback in color detection.

Submicrometric fragments from contemporary LEGO® bricks were solubilized with CHCl_3 and dropped on the Al-coated fragments.

A different type of validation of the method was conceived to initiate disseminating the method with non-experts. The sampling kit was shared with research fellows and several PDMS strip samplers were sent to Antelas. Wall paintings of the famous dolmen were analyzed. Several extractions to improve the chances to detect the materials were pursued. This led to unintentional solubilization of the PDMS sampler and to detect amylene from the solvent stabilizer. However, the detection of carbon black and hematite, in addition to PVAc as a residue of previous undocumented conservation treatments, was not prevented despite the analytical contaminations.

Grey cochineal, kermes and carmine reference historical materials were used to test the response of the SERS Al-coated platforms to anthraquinone chromophores. For the first time, SERS dyes microextracts from historical leather allowed discriminating collagen and coloring media. A progressive mild extractive protocol, including the PDMS strip sampler method, allowed the identification of few components of the aluminum-tawed leather used in the lining of high-status liturgical footwear. A gentle peeling of the leather fragment, followed by H_2O or EtOH extractions on the submicrometric grains removed was performed. Subsequently slightly more aggressive agents, as NH_4OH 28%, confirmed the results on the presence of the chromophore carminic acid. CHCl_3 showed better affinity with phenylalanine from collagen.

Japanese woodblock prints from the Meiji period were thoroughly characterized with SERS Al-coated platforms and MA-XRF spectrometry. Synthetic organic pigments, as disazo naphthols and anilines, were identified with the SERS sampling strategy using H_2O and acetone as a transferring solvents with various *nano* and *micro* structures and excitation wavelengths. Reds and purples confirmed the definitive transition from the Edo to the Meiji era showing revolutionary features in terms of hues and fabrication technology. Barium lakes, still well-established among printing inks, were used in large areas of the prints (*e.g.* columns) as a result of the artisans to experiment cheap materials yet highly lightfast. Prussian blue was a late introduction in Japanese woodblock printing methods (1830), although being around for over hundred years already in Europe. SERS sensing showed comprehensive information on the organometallic pigment, speculating on the colloid-like behavior of insoluble particles transferred to Al-coated platforms with various solvents. Further, glass arsenic sulfide (yellow) was detected on its own and mixed in green hues. In the late 19th century, traditional mineral pigments, like orpiment and natural dyes as gamboge, were progressively being substituted with cheaper alternatives as glassy arsenic sulfides that served the purpose of providing brilliance to the colors. Hematite and vermilion were detected in red, orange, brown and pink hues confirming the use of traditional mineral pigments in the Meiji period, and the extensive mixing.

4.1 FUTURE OUTLOOK

The thesis left many open areas for further exploration to achieve more comprehensive scientific, methodological and applicative approaches. Few relevant aspects will be following mentioned for possible future work.

From a methodological standpoint, commonly used SERS substrates rely on pastes and colloids with nanoparticles, whereas this research was based on SERS platforms. Tests could be run to compare the response of colloids and platforms with standard analytes at known concentration. This would provide more insights on batch-to-batch variability in the fabrication of SERS sensors, providing general data and quality assurance of SERS sensor response.

The issue of physisorption is prominent to further upgrading this research. A devoted effort should be made to expand the experimental/theoretical evidence on the influence of all parameters determining the removal of free molecules from the PDMS surface (*e.g.* pressure, polarity, temperature). Solid-solid interfaces should be modeled to observe the interaction with LMW compounds. Similarly the solid-liquid interface behavior should be analyzed to assess the interaction with the solvent during the molecule transfer.

The sampling protocols presented in the current thesis could be used for other relevant applications expanding their research impact on societal concerns. For example, environmental pollution due to microlitter could be explored with SERS sensors for discrimination of plastic materials in waste management plants. Further, security applications, like passengers control in airports, could be improved for the fast detection of narcotics in reduced concentrations.

Heritage sciences should build experimental evidence on mock-ups prepared with traditional artists/artisans recipes beyond accelerating aging tests with model materials. The behavior of composite materials is rather different from that of pure/standards analytes and therefore the object weathering rate are affected. This thesis based various interpretations of the data on previously published materials by scholars that had spent a considerable amount of energy on the preparation and characterization of mock-ups. This approach is not new in heritage science, but yet sometimes validations of analytical methods lack in taking advantage of the information provided by this approach. The collaboration with the conservators could enormously improve the understanding of the materials behavior during mock-ups preparation.

In the EU and worldwide, policy makers take advantage of the recommendations formulated by experts comprising various research achievements that could be transferred to society through regulations and standardization of protocols to improve human lives (*e.g.* medicine, education). Research on cultural heritage materials is not of less importance and few standardized regulations on sampling were mentioned at the beginning of the thesis. Scientists have the responsibility to communicate and disseminate why their technique is reliable and how it could improve the management of cultural heritage in general. Experts can be specific on the amount of sample to be removed from cultural objects, and new standards with reference to specific analytical methods should be formulated to help translating the experimental advancements to field applications.

Integrating the current research with spatially offset Raman spectroscopy (SORS) would be an ideal completion of the information provided by SERS for cultural heritage. Recent accomplishments of SORS in mobile laboratory settings focused on non-destructive analysis of cultural heritage. The combination of subsurface and surface information seems quite promising as a tool for heritage science research. Diffusion processes can be studied with SORS and this enables providing sound information on conservation treatments and preparation methods reducing even further the need for sampling the objects. The combination of the information could be beneficial to expand the applicability of Raman spectroscopy to cultural heritage materials.



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6. ANNEXES TO THE INTRODUCTION

ANNEX 1.1: CORE-LOSS EELS OF Al_2O_3

Core-loss EELS tests were conducted to evaluate the influence of Al_2O_3 forming after coating the SERS platforms with pure Al [42].

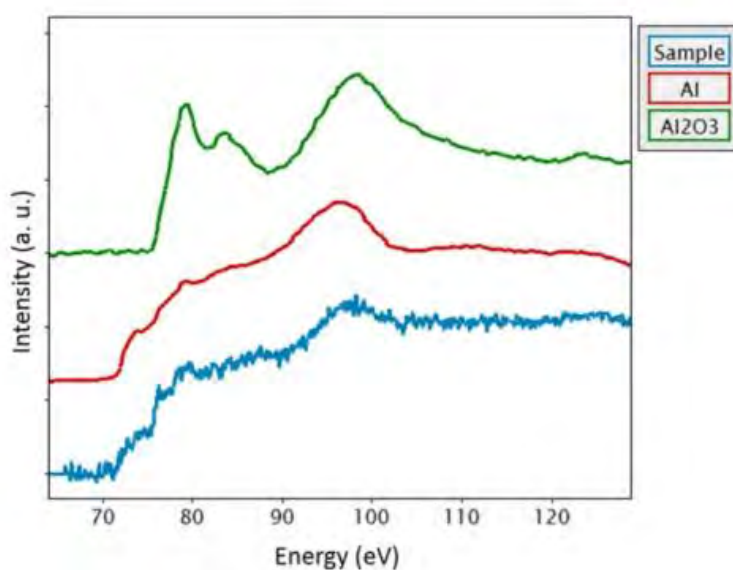


Figure Annex 1.1: core-loss EELS signal of the Al $L_{2,3}$ edge acquired with EELS from the sample compared with $L_{2,3}$ edges of standard metallic Al and Al_2O_3 . The fine structure of the signal acquired from the sample is clearly different from that of Al_2O_3 but closely matches that of Al, indicating that the oxide layer thickness in the sample is negligible. *Reproduced from ref [42] with permission from the Royal Society of Chemistry.*

ANNEX 1.2: FDTD SIMULATED ELECTRIC FIELD INTENSITY DISTRIBUTION

A solution 1×10^{-6} M of standard rhodamine was used on KLARITE© replica SERS substrates to simulate the electric field distribution and to explore the dependence on the wavelengths of excitation. Confocal Raman mapping is shown with the electric field simulation with 514 and 785 nm lasers [42].

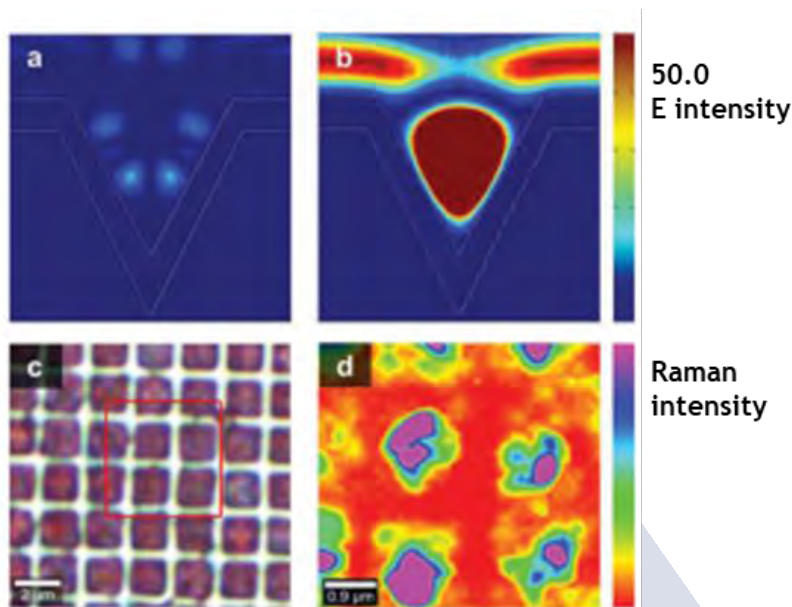


Figure Annex 1.2: FDTD simulated electric field intensity distribution in the ideal Al-coated inverted pyramid arrays excited with a plane wave at 514 nm (a) and 785 nm (b), and confocal Raman imaging map of R6G from 1×10^{-6} M solution at 514 nm excitation wavelength on an inverted pyramid SERS device (d) obtained from the red square area of the photograph (c). *Reproduced from ref [42] with permission from the Royal Society of Chemistry.*

ANNEX 1.3: FTIR & RAMAN SPECTROSCOPY ASSIGNMENTS OF PI

IR cis	IR α -trans	Raman cis	Raman α -trans	Assignment
3036 w	3053 vw	3033	3052 w/sh	=C-H str
	3015 w		3019 m	=C-H str
	2975 vs		2972 m	CH ₃ str _{asym}
2962 vs	2965 sh	2957		CH ₃ str _{asym}
2928 vs	2936 sh	2929	2934 s/sh	CH ₂ str _{asym}
2915 sh	2915 vs	2910	2910 vs	CH ₂ str _{sym}
	2890 wsh			
	2880 wsh	2878	2881 vs	CH ₃ str _{sym}
2855 vs	2852 vs	2853	2857 s/sh	CH ₂ str _{sym}
	2830 sh		2828 m/sh	CH ₃ str _{sym}
		2724	2728 w/br	
1665 w	1668 m	1662	1670 s/1666 s/sh	C=C str
1645 w	1447 s	1445	1643 w/sh	C=C vinyl
1450 s			1452 m	CH ₂ def _{asym}
	1433 sh	1431	1432 ms	CH ₂ def _{sym}
	1382 s		1384 m	CH ₃ def/C-C str
1377 s		1369	1371 mw	CH ₃ def
1359 sh	1358 sh	1359	1361 vw	CH ₃ /CH ₂ def
	1330 vw		1329 m/1319 vw	CH ₂ wag/twist
		1321		=C-H def (1,2)
1311 w		1308		CH ₂ wag/=C-H def (3,4)
1286 vw		1286	1288 m	=C-H bend _{ip}
	1280 vw		1279 m	CH ₂ wag/twist
1242 w	1254 vw	1238	1252 mw	CH ₂ wag/twist
	1207 m	1201		=C-H bend _{ip}
1166 m	1150 m		1158 w/br	C-O str/CH ₃ wag
1130 w		1130		CH ₂
1100 w	1096 m		1100 w/br	C-CH ₂ str
1089 w	1089 w	1070		C-CH ₂ str
	1051 w		1053 m	CH ₃ rock
1038 w	1030 w	1038	1035 m/br	CH ₃ rock
929 vw	990 w	996	1010 m/998 m	C-C str/C-CH ₃ str
975* w				C-C str
889 mw		889		CH ₃
	883 m		881 mw	=C-H bend _{oop} /
	862 m			CH ₃ wag
837 m	844 w			=C-H wag
	800 m	816	802 m	=C-H wag
764 w	751 w		785 m/758 mw/br	CH ₂ rock
740 w		728		CH ₂ rock
			600 w/br	C-C-C def
565		565		C-C bend (cis)
496		493		C-C bend (cis)

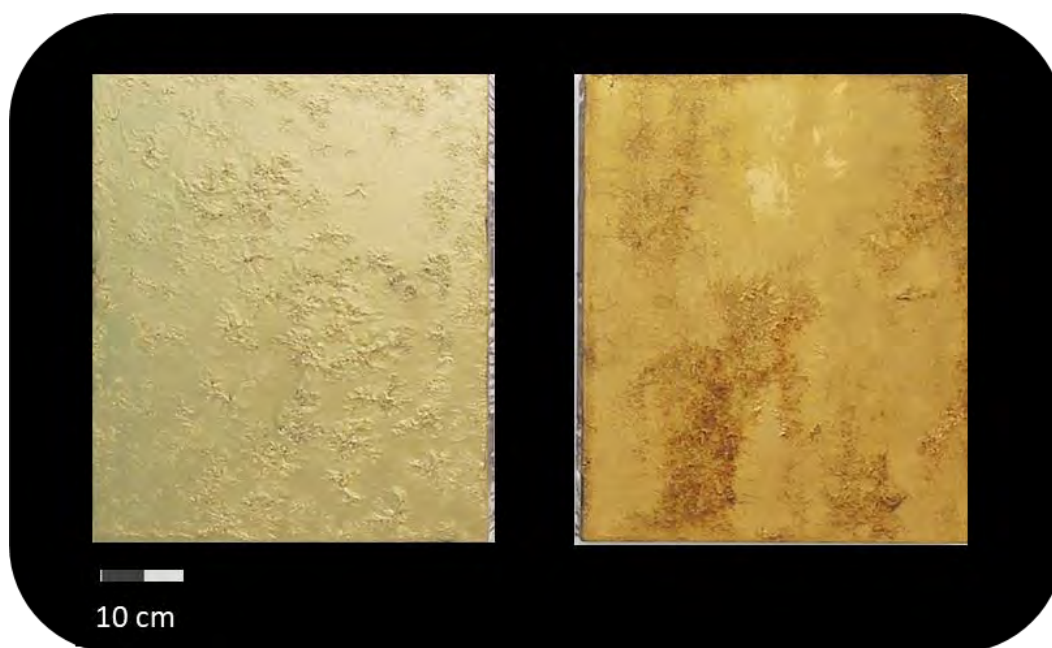
Annex Table 1.3: band assignments with FTIR and Raman spectroscopy of *cis* and *trans* polyisoprene isomers: 1,4-*cis* and 1,4-*trans* [179], Raman spectra of 1,4-*cis* [514] and of α -1,4-*trans* polyisoprene [176]. Asterisks indicate modes observed in degraded material. *Reproduced from ref. [178]. The author of the thesis could not be reached.*

ANNEX 1.4: COLLABORATION WITH THE CGAC – ARTIST INTERVIEW

(Collaboration with the *Centro Galego de Arte Contemporánea* - CGAC). During the initial phase of the thesis, an interesting parallel project on the fabrication and degradative behavior of contemporary paints was conducted in collaboration with the undergrad Carlota Garcia Pardo. Different supporting materials were used to reproduce paint/binder/oils layers to mimicking the technique used by the painter Manuel Eiris. Two twins golden canvases (Figure Annex 1.4) collected in the CGAG were found decaying rapidly and surprisingly differentially, although the materials declared during the interview were the same. The artist reported a horizontal multilayer-painting method. From the inner to the outer layer materials were: gouache, saltwater solution, lanoline oil with grapefruit acid, and tea constituted the

preparatory layer. Then, PVAc adhesives, surfactants and drying teak and mineral oils were employed. Finally, a commercial alkyd resin (golden spray) coated the objects.

The research approach was comprehensive: scientists, conservators and the artist gathered together to define the problem of differential weathering and clarify the intents of the artist, as well the need of the collection managers to prolong the durability of the acrylic and alkyd paints identified by FTIR spectroscopy, DSC and py-GC/MS. The project was connected to the overall aim of the thesis (extending the knowledge on heritage materials), but not to its specific aims on optimizing SERS sensing. Therefore, the results will only be only mentioned in the annexes in Chapter 3.



Annex Figure 1.5: *Aún te vas a morir de saturnismo* (2013, 2015) (60 x 50 x 5) cm. Photographs of the replica paintings by Manuel Eiris. Paints and preparatory layers were applied horizontally by brush and spray. The artwork on the left was fabricated in 2013 in Belgium, that on the right in 2015 in Spain.

(Survey of materials and interview to Manuel Eiris on the fabrication processes - in Spanish)

Obras: *Aún te vas a morir de Saturnismo*.

Artista: Manuel Eiris.

Fecha de la entrevista: 12/12/2016

Entrevistadores: personal del CiQUS y del CGAG que están a realizar un proyecto de estabilidad de plásticos en obras contemporáneas. Carlota García Pardo, Daniela Reggio, Massimo Lazzari, Thaïs López Morán

Año de realización de las obras de interés: 2013, 2015.

Proceso de creación y Concepto del trabajo:

- ¿Técnica utilizada en la realización de la obra?
- ¿Número de capas de materiales en la obra?

- Descripción de materiales.
- ¿La mezcla de tantos materiales fue en proporción o aleatoria? ¿Cuáles fueron las mezclas?
- ¿Alguna razón en concreto por la elección de los materiales? ¿Buscaba alguna característica en concreto de algún material?
- Tipo de herramientas utilizadas para desempeñar la obra: ¿Pinceles, espátulas?
- ¿Se basó en algunas propiedades de ciertos materiales utilizados para adquirir algún aspecto visual de la obra?
- ¿Sabría decirme los componentes exactos de la superficie? ¿Materiales "más abundantes en la superficie?
- Proceso de creación.
- ¿Pretendía conseguir ciertas propiedades ópticas en la obra? ¿Trabajó con alguna luz en concreto para hacer juegos de colores, brillos?
- ¿Tipos de pinturas y tintes utilizadas?
- ¿Requisitos para la conservación?
- ¿Gama de colores monocromática?
- ¿Buscaba degradación de materiales, para dar algún aspecto de interés a la obra?
- Opinión respecto al envejecimiento material y la restauración.
- Deseos concretos para la conservación de su obra.

Transcripción entrevista de Manuel Eiris.

Minutos de 0:00 a 00:11. (Primer video)

Thaïs: ¿Es mezclado con primal y agua? ¿Nada más?

Eiris: Nada más y agua, agua del grifo, no agua destilada.

Minutos de 00:00 a 08:49. (Segundo vídeo).

Massimo: ¿son los más comunes?

Eiris: Sí, los que tengo son todos B60, pero ahora hay otros me parece.

Thaïs: Hay varios primal, porque yo trabajo con varios, está el A33...

Eiris: Ese

Massimo: A algunos le cambiaron la composición con los años, no es siempre el mismo producto, es decir que el producto siempre lo venden con el mismo nombre, pero cambian la composición.

Thaïs: Me imagino que lo harán por abaratar o por...

Massimo: si, si, no sé, no tengo ni idea de cuantos años dura uno.

Thaïs: y, ¿lo compras directamente a la casa o donde lo compras?

Eiris: Lo compré en Agar Agar, en Vigo, pero a mí me dijeron en Kremer, que bueno, que no me pueden garantizar cuando tiempo tal pero...

Thaïs: La verdad es que nunca entré en el almacén a oscuras para verlo.

Eiris: Tienes que ponerlo primero a la luz

Massimo: Sí, sí, primero a la luz para que cargue

Thaïs: Claro, primero a la luz para que cargue

- Eiris: Y me dijeron en Kremer, que eso también se va gastando, si chupa mucha luz durará menos, pero, vamos que en principio...
- Thaïs: jo pues con las horas que estuvo en la exposición madre mía!
- Massimo: Sí, bueno, pero luego lo tienes allí en el almacén a oscuras.
- Thaïs.: Si, después está a oscuras, si.
- Eiris: Efectivamente además no es lo mismo una luz así muy intensa, pero dijeron que vamos que 70 años por lo menos puede durar en teoría, pero bueno hay obras de los 60 que todavía lo conservan.
- Massimo: si, además hace muchísimos años que se empezó a usarlos, bueno 60 años o así, pero no 100 o así. Curioso, si, es algo que podríamos hacer, porque a nosotros siempre nos explican el mecanismo de luz y tal... pero no tengo ni idea del tiempo que aguenta.
- Eiris: claro, es que...y además eso es complejo, porque es que no sabes realmente...
- Thaïs: claro ni cuanto tiempo estuvo expuesto a la luz, ni a que cantidad de luz, además en galerías o ferias es imposible controlar.
- Massimo: claro, mucho más expuesto, vale.
- Eiris: también a veces le meto este espesante.
- Thaïs: espesante, ¿que espesante es?
- Eiris: espesante para acrílicos, me gustaría encontrar un espesante para óleo pero bueno...
- Thaïs: y ¿nunca has probado con un carboximetil?
- Eiris: ah no sé ¿sí?
- Thaïs: si, un carboximetil, además de utilizarlo nosotros como un adhesivo de muy baja densidad, se utiliza mucho como carga tanto en acrílico como en óleo es un polvo blanquecino que tú lo mezclas y queda transparente no te afecta para nada al color y lo que te da es carga.
- Eiris: pero entonces ¿no da fluidez?
- Thaïs: No es líquido pero le puedes meter agua, y en el óleo puedes meter aceites.
- Eiris: aah vale, vale, vale.
- Thaïs: dependiendo de la fluidez que quieras le metes más aceite o menos.
- Eiris: y ¿puede quedar así como un aspecto de miel?
- Thaïs: si,
- Eiris: que guay!
- Thaïs: pues el carboximetil en Agar Agar lo tienes.
- Massimo: que es una tienda que hay en Vigo ¿no?
- Eiris: Si, está en Vigo y es genial.
- Thaïs: si, es una tienda que hay en Vigo de productos de arte y de restauración, que está en camelias,
- Massimo: ah si, me suena, si.
- Thaïs: son proveedores, nosotros le compramos mucho, o lo compro ahí o en Madrid en CTS tiene mucho pero también hay cosas que no las tienen sobre todo en tema de productos, tiene mucho de maquinaria y de cargas porque trabaja mucho con la restauración arquitectónica. Pero por ejemplo para pintura se queda un poco cortito, eso lo consigo mejor en Agar Agar.
- Eiris: depende de para que , por que no es lo mismo comprar en una tienda de arte un barniz que no comprar un Gamma, al final te compensa realmente, quiero decir igual cuesta la mitad de esté.
- Thaïs: es que esos botes son de lo más caro que hay.

Eiris: por eso pero en una tienda de arte no te dan la oportunidad de comprar eso, en Agar Agar los hay de 3L.

Massimo: ¿La calidad es la misma?

Eiris: Bueno incluso mejor, a veces. Quiero decir en ese caso era un barniz, pero este es medio.

Thaïs: Está claro que el tamaño grande siempre compensa mucho más.

Eiris: y ese es titán y este creme.

Massimo: el primal podrás comprarlo en un bote de medio litro, de uno, de 5,¿

Thaïs: sí, sí.

Minutos de 0:00 a 23:28.

Daniela: Si no te molesta te hacemos también unas preguntas.

Eiris: sí, claro.

Massimo : si no son demasiado serias. Había el listado del escrito de la obra por un lado

Thaïs: Sí, eso es lo que me mandó el.

Eiris: el primer material es este, el gouache.

Massimo: si, pero tenemos preguntas, de cómo los echaste

Carlota: si, del proceso.

Eiris: claro, en la lista aparecería del final al principio.

Thaïs: el Gouache marca Talens, que era de Rebecca.

Eiris: Si, esos son los materiales de Rebecca que quedaron en el estudio.

Massimo: si,si,si, no sé ¿ ¿podemos coger una pequeña cantidad de muestra?

Thaïs: claro es que era lo marrón que veíamos

Massimo: si, si claro, ¿esto es un gouache de verdad? ¿Goma arábica de verdad?

Thaïs: sí, sí, claro yo creo que si, estas marcas son las que utilizo yo normalmente.

Massimo: de toda la vida¿ no ?

Thaïs: sí.

Eiris: si, lo es porque se deshace.

Thaïs: si, si que se deshace.

Eiris: además compre hoy una cosa¿

Thaïs: que compraste cuéntame.

Massimo: oxirrom, pintura metálica.

Eiris: es acero y claro no viene absolutamente nada.

Massimo: no pueden ponerlo porque claro si no el competidor le quitaría la idea.

Daniela: ¿como lo aplicaste en la obra?

Carlota: ¿con pincel?

Eiris: Con brocha , encima de la superficie, sobre esta tela.

Massimo: aaah ahora te coincide¿

Carlota: valsee, si, porque hemos hechos unas medidas

Daniela: y nos sale fibra, celulosa,¿

Eiris: si, y esto montado sobre una tabla.

Daniela: esto sería como primera capa, y luego Bio True.

Massimo: ah pero se lo echaste así encima o ¿como?, porque eso es tan líquido que al final.... empapa algo pero es que eso al final es como si echases agua.

Thaïs: si, porque tiene un tensioactivo.

Eiris: pero bueno no hizo mucho porque es agua.

Daniela: ¿Lo hiciste porque te lo enseñaron o es algo tuyo?

Eiris: no, porque era parte de los materiales que se dejó la artista en el estudio.
 Daniela: vale, el concentrado de lanolina de aceite de pomelo
 Carlota: lanolina, es como un jabón, una detergente, o algo así por lo que leí yo.
 Eiris: si, si es como un gel, como un jabón, pero tiene... lanolina es como una especie de cera, esto es como una de las claves para que hubiese el plegamiento ese.
 Massimo: si, entonces, algo sí que quedo de eso, porque echaste bastante además ¿no? Con brocha también ¿no? Eso sí que queda, bueno quedó eso seco y formo como las grietas pero si, y ¿eso también es un producto comercial para la casa?
 Thaïs: yo creo que sí, no sé si se le echa a los suelos
 Eiris: y con aceite
 Thaïs: para suelos de madera se utiliza ¿no?
 Carlota: si, bueno yo estuve buscando la marca comercial, y bueno ponía que se utilizaba para fregar los suelos.
 Thaïs: si, la lanolina se utiliza normalmente por lo que yo conozco para cuando friegas el suelo darle brillo y el agua no penetre tanto, que limpie la superficie y a la vez como si fuese una pequeña cera que le das para que cierre el poro y tal.
 Daniela: y ¿no se utiliza nunca como aglutinante para la pintura?
 Massimo y Thaïs: no, no.
 Massimo: ¿tu encontraste o encontramos la marca no?
 Carlota: si, bueno nosotros no habíamos encontrado la marca, pero este fin de semana me puse a buscar y si, tengo la foto del producto jaja.
 Massimo: ah bueno descubrimos que tuvimos que buscar todo en holandés, estuviste en Belgica ¿no? Jajajaja
 Eiris: si, sii, además había alguna que eran como marcas blancas de un supermercado.
 Massimo: si, lo vimos jajaja
 Carlota: si, las colas blancas
 Eiris: si porque la chica en lo que trabajaba era con madera y con muebles.
 Thaïs: claro y por eso utilizo lanolina, de ahí viene su sentido.
 Eiris: le preocupaba así la restauración y tal así que esa es la razón.
 Daniela: ¿Kombucha?
 Eiris: kombucha es como una especie de té fermentado.
 Carlota: sí, es un té fermentado
 Massimo: si, si pero bueno eso es un líquido lo echas ahí y no pasa nada, empapa quizás ¿no?
 Eiris: empapa si, yo creo que es como si fuese cerveza.
 Daniela: ¿se secó y luego echaste el resto o lo hiciste todo al mismo tiempo?
 Eiris: se secaba, lo echaba y lo dejaba secar, solo que había cosas que aunque las dejases secar como por ejemplo el gouache
 Thaïs: el gouache se activaba en cuanto le echases cualquier cosa
 Eiris: claro, en ese caso lo que hacía era
 Thaïs: y, ¿y esto al secar queda totalmente seco o queda pegajoso?
 Eiris: esto queda totalmente seco, las cosas que quedan más pegajosas sería la lanolina, entonces el tema era que yo lo que hacía en esos caso era darle mucha cantidad de lo otro, para no arrastrar con el pincel.
 Thaïs. ¿Hacías todo con pincel? O ¿algo en plan baño?
 Eiris: en plan baño un poco.
 Thaïs: aunque lo aplicaras en pincel lo hacías muy superficial
 Eiris: si y luego con la brochaba era como que le ayudaba pero intentando no arrastrar.
 Daniela: cola de madera.

Thaïs: cola, ¿qué es? ¿Cola blanca?

Eiris: sí

Thaïs: ósea PVA.

Daniela: sí.

Eiris: esto va encima de la lanolina, puede ser y otra cola de madera

Daniela: si dos distintas entonces, pero parece que encontramos solo una composición de cola, el PVA.

Eiris: ¿Cuál?

Carlota y Daniela: bueno no sabemos cual, es PVA.

Massimo: ah las colas blancas

Thaïs: pero, ¿eran distintas las colas?

Carlota: sí, eran dos marcas distintas.

Thaïs: bueno aunque sea distinta marca si es PVA es PVA.

Daniela: sí, pero no sé porque usaste dos marcas distintas, si tenían distintas propiedades o algo

Massimo: ah pero tenía ahí dos botes y lo echo.

Daniela: ¿para ti tenían la misma función?

Eiris: sí.

Daniela: y ¿el champú?

Eiris: el champú, volvió otra vez a humedecer cuando lo echaba y costo que se secase

Daniela: como lo dejaste días?

Eiris: si, el siguiente

Daniela: color teca sobre óleo natural, primer aceite que utilizas, casi al final, ¿ así como ultima capa?

Eiris: si, en este caso era pues eso como la chica esta tenía un vínculo con la restauración de madera lo tendría por esos motivos y lo eche.

Eiris: mira este xyladecor, lo utilice para el otro dorado.

Daniela: para el más homogéneo digamos, ¿el segundo?

Eiris: creo que puede depender de la cola, de la capa de cola que le metí

Massimo: si

Eiris: y esto es lo que le eche por encima y lo que lo plegó todo.

Massimo: ah

Carlota: ¿pero esto que es?

Eiris: aceite alcohol avellana.

Daniela: esto no está en la lista

Carlota: no

Carlota: pero, ¿esto lo echaste solo al segundo?

Eiris: no, no, esto lo eche en los dos, huele fuerte, es lo que provoco que se plegará es lo que reacciono con la cola, una vez se echase esto, se plegaba.

Massimo: ah sí disolvió un poco la cola, que ya se había secado supongo.

Eiris: ah sí.

Massimo: si supongo porque huele entre alcohol y éter.

Thaïs: si, espera, huele alcohol y ahora no me doy cuenta de lo que es

Massimo: ¿podemos coger unas gotitas?

Thaïs: ¿tú tienes más de esto?

Eiris: si, llevároslo.

Thaïs: me quedo con la intriga.

Eiris: pero yo creo que esto no es bueno, porque seca las mucosas.

Thaïs: ah pues si seca las mucosas tiene algo de cloroformo además de tener alcohol puede tener tricloroetileno.

Massimo: bueno te lo decimos

Thaïs: si además de secar las mucosas tienes que utilizarlo con mascarilla porque además de quedarte dormido porque es cloroformo te seca mucho las mocosas, es lo que decía él, el eter es muy parecido.

Eiris: pues si, Macía a mi me cuenta que él para utilizar el spray utiliza siempre mascarilla, y además se llevo un susto porque fue acumulando y ahora rechaza a la trementina.

Massimo: bueno esto si nos lo prestas utilizamos una pequeña cantidad y te lo devolvemos

Eiris: si

Daniela: entonces la proporción de materiales que utilizaste no fue casual, fue para evitar que se evaporase demasiado.

Massimo: para que no se mezclase más bien, para cubrir la capa anterior.

Eirisi: sí.

Daniela: ósea ¿nada lo mezclaste anteriormente?

Eiris: no.

Daniela: todo como capas pero en proporciones útiles, ¿no fue aleatorio?

Eiris: exacto.

Daniela: ¿buscaste alguna característica concreta de los material? ¿Alguna elección en concreto?

Carlota: claro, por ejemplo este que hace que se te plieguen las capas ¿Pensasté que iba a pasar?

Eiris: no.

Daniela: entonces, fue porque quedaban esos materiales allí y los utilizaste, ¿no eran materiales que tu buscaste para provocar esa aspecto?

Eiris: si

Daniela: ¿tipo de herramientas utilizadas? ¿Espátulas?

Eiris: no, no, brochas.

Daniela: ¿querías dar unas propiedades ópticas utilizando esos colores? por ejemplo

Minutos 0:00 a 23:42 (cuarto vídeo).

Eirirs: no, las propiedades ópticas en este caso sería dejar que se escurra, utilizar la cantidad necesaria para llegar a ese punto

Daniela: ¿trabajaste con alguna luz en concreto?

Eiris: no, luz natural, y con la pintura en horizontal.

Daniela: ¿te interesa algún requisito para tus obras?

Thaïs: si, yo corroboró que sí.

Daniela: ¿te interesa que los materiales se queden como son que no se degraden?

Thaïs: a ver por lo que yo lo conozco no le importaría que se formase una patina, pero si le importaría que se craquele, pero no le importa que se note el paso del tiempo.

Daniela: dejar las condiciones actuales para un tiempo largo, si Thaïs hace el trabajo de dejar todo como está, ahora tu estas contento.

Thaïs: hombre el preferiría que no se meta nada en la obra.

Eiris: claro.

Thaïs: pero el ya es una persona que se preocupa por el material que utiliza, ¿si uso esto se craquela? j.

Daniela: ¿cuáles son tus criterios entonces para la conservación de la obra?

Eiris: digamos que no le hagáis a la tela y que se craquele.

Thaïs: A ver él lo que no quiere es quedarse sin obra

Eiris: claro que se caiga o esas cosas

Daniela: ¿A la parte mecánica te interesa, digamos el efecto de la luz...?

Thaïs: ¿te importaría que variara el color en la obra?

Eiris: no

Massimo: es como un envejecimiento natural que se forma la pátina y todo eso

Eiris si incluso que se pliegue o tal pero si hay esa fractura o tal no.

Daniela: la parte mecánica te duele más, digamos ¿el daño mecánico no te gustaría?

Eiris: sí, digamos en el caso de esa fractura o que se despegue ¿

Daniela: y ¿las obras tendrían que ser réplicas, gemelas?, están envejeciendo de forma distinta ¿qué piensas de eso?

Eiris: eso es por dos motivos porque son distintas marcas y porque lo utilicé en distintas proporciones.

Daniela: entonces, ¿que sean distintas ahora es natural para ti?

Eiris: digamos que yo la copia no la hice con la intención de que fuesen réplicas si no de repetir los mismo materiales y el mismo proceso.

Daniela: entonces no es una identidad de estética.

Eiris: no claro.

Thaïs: la historia que tiene detrás tela, es más el concepto que la obra en sí.

Eiris: si, claro yo que sé es por ejemplo como si decimos que hay dos personas diferentes y corremos un km los dos hacen lo mismo pero en distinto tiempo.

Eiris: el cuadro azul por ejemplo tiene el título que habla de una pintura que se, yo que estaba dando capas y cuando iba en la capa 38 se desprendió todo, utilice una pintura de interiores.

Thaïs: ¿esto en composición es acrílico?

Eiris: no, es aerosol con disolvente .

Thaïs: ya, pero es esmalte.

Eiris: no,no, es en base a agua.

Eiris: esto es la pintura plástica que hizo que se desprendiese todo después de aplicar esta.

Thaïs: después de aplicar ¿esta?

Eiris: si, porque esta es una pintura que compré porque era la más barata que había

Thaïs: ósea ¿pintura de interiores? ¿Una pintura plástica?

Eiris: si, es una pintura plástica

Thaïs: un acrílico será y te profundizo tanto que te arranco todo

Eiris: es una pintura muy mala de paredes, la mas barata que había por lo que tiene mucho pigmento

Thaïs: y poco aglutinante, le diño mucho peso seguramente, no te agarro y te tiró de todo para abajo

Eiris: bueno, si, si tenía un exceso de pigmento.

Thaïs: al tener un exceso de pigmento, creo ¿no?

Thaïs: claro al tener falta de aglutinante y exceso de pigmento eso pesa demasiado no tiene adhesividad y cae.

Eiris: entonces que paso, yo seguí dando capas y capas¿

Thaïs: pero esto se lo pusiste de preparación

Eiris: no, eso lo metí en una de las capas

Thaïs: ¿así puro?

Eiris: no con agua, y entonces lo que paso después que empezó a hinchar después de darle no se cuantas más capas por encima hizo una burbuja y abrías la burbuja y se pelaba todo, y cuando pelabas se veía por detrás que se veía blanco, un pigmento que era eso, por eso sabía que era... y por debajo tenía una pintura marrón, después de la cual le había dado esta blanca.

Massimo: vale, vale entonces ¿justo ahí se pelo esa capa?

Eiris: justo ahí.

Thaïs: y ese es el título de la pieza azul

Eiris: entonces la pieza azul lo que hice fue yo lo que tenía pensado era acabar la pieza azul con esa pintura, lo que hice fue tirar la tela esa, por eso el tema de que si se fractura o no se conserva tal lo rechazo.

Thaïs: y decidiste montar una tela nueva

Eiris: entonces lo que hice fue tirar la tela esa que se había desprendido y solo aplicar esa y en el titulo contar la historia.

Massimo: bueno eso está muy bien ahora.

Thaïs: y entonces, ¿sabemos lo que es eso?

Daniela: No está escrito que es, se puede buscar en internet, dice cómo aplicarlo pero no dice

Massimo: en cualquier casa anotarlo

Eiris: ahora tengo unos sprays, estos son geniales, son de base agua, y es como pulverizar acrílico.

Daniela: con pigmento y agua

Eiris: aun así es tóxico la resina se pulveriza y tal

Thaïs: pero siempre lleva algo de disolvente, para que se evapore más rápido y seque rápido

Eiris: queda mucho más mate

Thaïs: te cuenta de que el alcohol y el agua se pueden mezclar perfectamente, entonces en vez de echar una base solo acuosa echas los dos y seca más rápido, nosotros por ejemplo utilizamos muchas veces mezclas de agua alcohol, al 50 % para cuando tienes que aplicar un producto y la superficie está muy impermeable y para hacerlo más permeable le echas agua alcohol, el alcohol rompa la tensión activa del agua y penetre

Massimo: además pone genobables y si fuera solo agua no...

Daniela: el pigmento; no tendría por qué ser toxico?

Thaïs: no, el pigmento no tiene porque ser tóxico, los tóxicos son lo que tú le añades, entonces le echan disolventes para que evaporen antes y sequen antes, acetonas, alcohol.

Massimo: si, bueno no se como es la normativa ahora, pero que ponga agua no significa que haya solo agua, el agua puede ser el 10 %

Thaïs: es en base agua de tal manera que pueda ser soluble en agua, pero que tengaa mas componentes seguro.

Eiris: si pero hay una, cosa, que no es lo mismo.

Thaïs: no porque la tempera es lo mismo que el gouache, goma arabica con pigmento

Daniela: pero, ¿también con agua?

Thaïs: pero es soluble en agua siempre, además la tempera es soluble en agua siempre, porque la goma arabica siempre se activa en agua, cosa que los acrílicos no.

Eiris: no, es lo mismo este

Massimo: este sí que no lleva agua.

Eiris: claro, que este pone en acrílico, pero este es muy tóxico

Massimo: si no sé que llevará eso, ¿huele mucho?

Eiris: si, si, será tolueno.

Eiris: pues bueno, de todas maneras utilizar pigmentes tóxicos en un spray sería algo..., lo peor de lo peor.

Thaïs: en cuanto utilizas un aerosol, utiliza mascarilla.

Eiris: y nada, ese queda como este, este de acrílico queda como más mate.

Thaïs: pues este, ya es mate.

Eiris: bueno P ero este sigue siendo como esmalte sintético.

Thaïs: si, este es más mate.

Eiris: si es diferente, es como un acrílico.

Massimo: será una acrílico de parte soluble en agua

Eiris: la ventaja es que utilizando este, después de pintar mucho con el resto abres la ventana y se va.

Thaïs: bueno si os llevais las marcas y tal, podéis buscarlos.

Massimo: pero bueno en internet no dicen nada.

Eiris: bueno en las fichas de seguridad

Massimo: si es lo que iba a decir que, en las hojas de seguridad si. Pon la marca y el código que hay ahí en la esquina. Bueno esto lo hacen en Porriño ¿no?.

Eiris: si, quería yo ir un día por allí.

Massimo: si, que tienen un montón de producciones allí.

Eiris: bueno ahora descubrí unas cosas que son como una especie de esmaltes, que es como un esmalte sintético, pero natural, digamos que es todo a base de aceite de linaza y son más caros, pero se extienden mucho más, y ahora la gente los están utilizando para pintar las casas.

Thaïs: ¿para pintar las casa?

Eiris: si, tardan un poco más en secar, pero secan bien, en tres días más o menos.

Massimo: si, si a base de aceite tardan más en secar.

Thaïs: bueno ya me dirás cuando te acuerdes de la marca.

Eiris: si, además yo quería mirar una cosa que es como una cera, para hacer algo más así.

Massimo: más espeso.

Thaïs : si, además eso tiene que ser carísimo, tal y como lo estás contando

Eiris: si, si.

Thaïs: esto, es ¿betum de judea?

Eiris: Si.

Video 5 Minutos 0:00 a 13: 38

Massimo: ¿le echaste alguna otra cosa? ¿Aceite o algo?

Thaïs: algo le tuviste que echar para que te quedase así.

Eiris: si, para que me quedará así.

Thaïs: si algo, le tuviste que echar para que te quedase así.

Eiris: estos son así...

Thaïs: está muy bien.

Eiris: uhm, pues ese era curioso porque

Thaïs: tendrías que perderle el miedo.

Eiris: ¿a este ? ah no, yo creo que lo que tiene este yo sé lo que es.

Thaïs: si, era es , era ese,

Eiris: este es...

Massimo: si bueno, pero a este sí que queda pegajoso.

Thaïs: pero no, este no está pegajoso.

Eiris: no, ese craquela y el primal no craquela , pero bueno

Daniela: ¿tu siempre haces pinturas, nunca esculturas?

Thaïs: audiovisual también tienes

Eiris: uhhh, si que tiene que ver con eso de las capas.

Thaïs: tiene que ver con las capas y los videos que tenemos nosotros en la colección tiene que ver sobre las capas y el aplicar y quitar pintura .

Eiris: y ahí hay un tema, que es que, yo creo que eso si que es más tal, porque esas las paredes las decapaba a veces con una radial, y son casa antiguas y entonces tú no sabes que pintura

Massimo: uhm, y hay muchas capas además ¿ no?

Eiris: y estás volatilizando el pigmento y entonces ¿esos pigmentos? yo no sé que pueden ser, prefiero no pensarlo mucho

Massimo: si hay cosas viejas, pueden ser cualquier cosa.

Eiris: si, supongo, claro, porque yo que sé o no pero bueno, hombre este yo creo que no porque esto yo creo que es hierro no es plomo.

Massimo: si, pintura metálica.

Thaïs: acero reciclable pone

Massimo: ah vale, perfecto

Eiris: y ahora descubrí que en bricomark o algo así en el polígono

Thaïs: ah si en el polígono

Eiris: que no me lo sabían decir, pero bueno que hay unos botes así enormes que es de bitumen y es al agua

Thaïs: ¿al agua?

Massimo: algo sintético seguro.

Thaïs: claro

Eiris: claro y yo le decía al chico

Massimo: tú piensa que eso no es compatible.

Thaïs: es algo para dar color como el bitumen, pero no es bitumen.

Eiris: bueno es que eso era, para venía en un cubo así.

Massimo: si, y algo barato me imagino.

Eiris: barato y era para asfaltar.

Thaïs: hombre eso es algo industrial.

Massimo: si, si semi-industrial.

Eiris: claro yo es que estoy buscando un producto que no huela mucho y que sea gordo.

Massimo: pero negro ¿no?

Eiris: no, que no huela mucho y que sea así una capa.

Thaïs: y, ¿ que de consistencia?

Eiris: claro.

Massimo: y que seque además.

Eiris: claro, porque el acrílico cuando seca.

Thaïs: mengua.

Eiris: mengua, porque no es lo mismo dar muchas capas de óleo que dar muchas capas de acrílico.

Thaïs: pero, es lo que te estoy diciendo al acrílico le puedes echar el carboximetil.

Eiris: pero, ¿que da fluido?

Thaïs: a ver el carboximetil depende de la cantidad que le eches, si lo mezclas con agua acaba siendo un gel, y dependiendo de la cantidad de agua puede ser un gel más espeso o un gel más fluido.

Massimo: pero tú, ¿buscas algo muy espeso?

Eiris: ehmm pero que quede fluido de manera que se pueda trabajar.

Daniela: como, ¿yeso por ejemplo?

Eiris: no, porque el yeso lo que le da es carga.

Thaïs: él lo que quiere es algo que le dé cuerpo, pero que a la vez sea fluido, prueba con el carboximetil, el carboximetil mezclado con agua simplemente y tú ya le das la consistencia que quieras luego le das con el acrílico, que ves que te queda demasiado líquido, le echas más carga de carboximetil, es un polvo pero que con el agua mezclado se vuelve gel.

Eiris: ahaaam, ¿y que también vale para el óleo?

Thaïs: para los dos, tú, ¿sabes para que se utiliza el carboximetil?, como espesante en las comidas

Eiris: ostras

Thaïs. los donuts y todo eso lo llevan.

Eiris: ósea, que no es tóxico.

Thaïs: no, no, pero se utiliza por ejemplo en restauración como adhesivo de papel, porque es un adhesivo que tiene una baja adhesividad lo suficiente como para pegar papel. También se utiliza como consolidante de pinturas como acuarela o el gouache pero le dan demasiado brillo, para que no le den brillo nosotros utilizamos unas algas que se llaman Funori, unas algas japonesas que es un adhesivo que queda mate.

Massimo: carísimo.

Eiris: con es, ¿queda mate?.

Thaïs: sí, pero bueno el trabajo con el Furoni es complicado porque tienes que hervirlo, luego cocerlo, colarlo, y nada te durará dos o tres días en la nevera.

Eiris: y, ¿no le puede aportar hongos?

Thaïs: no, porque le puedes echar una gotita de alcohol o de ácido acético para que no...

Eiris: o de ... hay como j

Thaïs: y si trabajas con el tiempo adecuado, no dejándolo 15 días y así no pasa nada, es como la cola de conejo y esas cosas.

Eiris: pues, genial porque a ver con el tema de olores este para mi es lo que sería el límite ideal, poder trabajar con trementina y aceite de linaza, pero claro ya cuando te metes en sintéticos y eso...

Massimo: bueno hay tantos productos que al final uno no sabe ni lo que está usando, esa es la duda que tengo yo.

Eiris: y es que ademásj es vestíal lo que huele un bote de esmalte sintéticos.

Thaïs: a ver el problema que tenemos ahora es que la industria te ofrece tanto, tanto tanto que nos podemos encontrar de todo, a ti porque yo te conozco y puedo hablar contigo y trabajar en colaboración, pero yo muchas veces me encuentro obras que no sé lo que tienen, y es imposible saberlo.

Massimo: bueno, en este caso específico tú nos contestes lo que usaste, pero no suele ser así.

Thaïs: no, no, no, tú eres una persona muy accesible pero hay muchos artistas que son muy impermeables con el tema de sus materiales y obras entonces en ese sentido es mucho más complicado

Eiris: uhm, ya.

Thaïs: o... que no se acuerdan.

Massimo: o que nunca supieron lo que usaron.

Thaïs: por ejemplo Moldes, Moldes no se acuerda de lo que le metió a sus obras, yo me acuerdo cuando tuve que restaurar las monjas de Pontevedra y yo jpe ro Manuel ¿que

le metiste aquí?, porque yo tengo confianza con él y me decía, yo que sé, ya no me acuerdo, entonces yo me encontraba con una obra que está pintada sobre una lona impermeabilizada de camión, y cada vez que yo intentaba tensar aquello j era imposible porque le metía humectación y me la escupía era tal cual, le dabas agua para meterle vapor y te salían las gotitas, complicado... pero bueno.

Eiris: uhmj Uhmm . Pero bueno...

Thaïs: también estamos hablando de obras de los 70 e, con lo cual, de aquellas para conseguir una lona de esas dimensionesj

Massimo: si, tenía que ser muy caro, y difícil de encontrar y de mala calidad seguro.

Thaïs. Si

Massimo: será más facil por un lado y más complicado por el otro, porque puedes encontrar un montón de materiales pero nunca sabes lo que estás usando.

Eiris: si, en ese sentido si.

Thaïs: y Manuel, Moldes nunca fue cocinillas, es un hombre que utiliza los materiales segúnj , no le importa los materiales como los puedes trabajar tú, él es más de improvisación.

Eiris: claro.

Massimo: yo tengo curiosidad por lo que contaste del bitumen, esej

Eiris: si, vienen en unos ehm no me acuerdo como le llamabas pero viene en unos bidones asíj

Massimo: uuhmm pero para impermeabilización ¿ o para...?

Eiris: le tiene una carga de piedras, y lo utilizan para el terreno.

Thaïs: ¿para el suelo? ¿Para carretera y cosas así?

Eiris : si, pero debe ser a nivel más doméstico yo creo.

Massimo: sí, sí, si tienes algo pequeño.

Thaïs: ósea que deben de ser bidones de 25L.

Eiris: de 50 kg

Thaïs: de 50? Carai.

Massimo: sí , no sé lo que puede ser.

Eiris: lo que claro es más barato que esto, pero no sé si comprarlo allí, porque claro este se lo que es y lo otro no.

Massimo: lo busco y te digo, que tengo curiosidadj

Thaïs: bueno.

Massimo: okey te dejamos trabajar.

7. ANNEXES TO THE RESULTS AND DISCUSSION

ANNEX 3.1: MITIGATING THE EFFECTS OF OXIGEN DIFFUSION

(Coated ABS: mitigating the effects of oxygen diffusion). As a side project, a small amount of time (eight months) was devoted to deepening the comprehension of the mechanisms of permeability and diffusion of oxygen in ABS films. WP4 of NanoRestArt on coatings gave the opportunity to test the effectiveness of new customized passive coatings formulations. The base of ABS films was identical to that of uncoated films.

In general, coatings are meant to reduce the oxygen permeation from the surface of the material inwards. The oxygen uptake is intentionally reduced through the barrier created by the coating and, as a consequence, the OIT prolongs. The study of ABS photoaging behavior was performed by removal of the coating with a scalpel prior to ATR-FTIR spectral acquisitions from 150 h onward, following the same aging ranges of uncoated films. Two oxygen barrier coatings (WSP grade 1, 2), respectively silica-based and carbon nanoparticle-bearing by ARK/CEA were tested. In addition, WB6 and WB9 coatings, respectively a polyurethane-based formulation and acrylate-based formulation by NIC were also tested. The main challenge with the new formulations was the risk to permanently altering the appearance of the films (*e.g.*, dark, insoluble and thick coatings are not recommended).

Small molecules diffuse into the polymeric layers as gases, and might be of interest to retain oxygen permeation. In some applications, such as packaging, the ability to tailor such permeability is crucial to service life of the material. Gas and liquid small molecules travel through voids within the material diffusing, hence the structure of the molecules (*e.g.* crystalline, amorphous rubbery) affects the diffusion rate. As anticipated in the main text, BR component in ABS is that where the oxidation reactions initiate. Further, ABS is highly hygroscopic: water moisture uptake is 0.3 % wt. in 24 h. The thickness of the films affects the permeability of oxygen, and the uptake is reduced for deeper penetrations.

The most important aspect to consider for the formulation of an effective barrier coating is the oxygen permeability rate. Gas transport follows the Henry's law (Annex Equation 3.1.1) and first (Annex Equation 3.1.2) and second Fick's laws (in the main text in section 1.3.2).

$$\Delta c = -D\nabla p \quad (3.1.1)$$

Where c is the concentration of the gas, S is the solubility and p the partial pressure, and provide the coefficient of diffusion of the gas in the polymer.

$$j = -D\nabla c \quad (3.1.2)$$

Gradients of concentration, time and spatial distribution of defects rule the diffusion of gases through the polymeric matrix. Surface roughness and ratio between area and radius of the defects also affect the gas flow through the polymer. Barrier coatings enable to reduce to some extent the permeability of the gas, hence the flow rate, increasing the density of the microstructure and changing its porosimetry.

It is anticipated that the application of WB6 and WB6 revealed ineffective for the protection of the ABS films, as confirmed by the evidence of ATR-FTIR, SEC, and DSC characterizations showing data similar to that of uncoated ABS films at comparable time ranges. On the contrary, WSP grade 1 showed to have a slight effect in lowering the oxidation rate; however, also for oxygen barrier-type coatings color changes were comparable to those of ABS uncoated samples. Overall, the **paradox** of using polymeric coatings on polymer-based artworks was confirmed. Aging and yellowing behavior of the coatings makes such formulations aesthetically/chemically not suitable for conservation purposes.

ANNEX 3.2: COLOR CHANGES IN ABS

(Color changes: yellowing, darkening and loss of transparency of uncoated and coated ABS).

Discoloration in ABS is caused by the presence of surface photoproducts of oxidation that present high rates of UV-light absorption. Intrinsically, ABS weathers in a heterogeneous manner: initially the PB segments rubber oxidize, and then the radical species and photoproducts initiate oxidation of the styrene segments that produce highly absorbing species. To be highlighted that such ABS features make stabilizers less effective. UV absorbents, coatings or laminated capping are best to lower degradation rates in ABS.

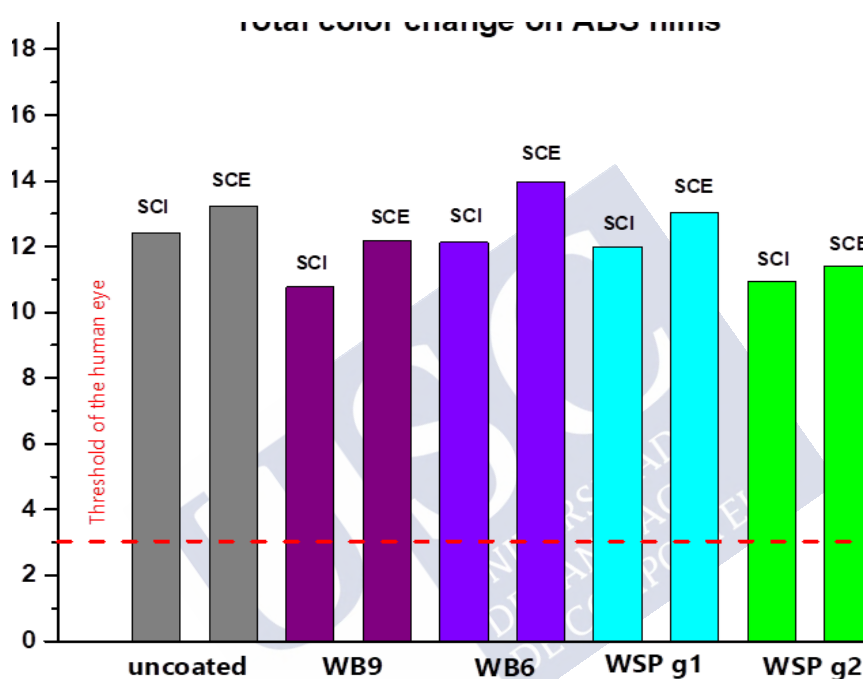
Reflectance (%) is the ratio between the light spectrum reflected and incident on the surface; it is presented either with the coordinates of the specular component included (SCI) or excluded (SCE). Intuitively, the latter value represents the real color of the object, since it excludes the gloss due by the nature of the material itself. However, the SCI is the color perceived by the human eye, therefore prioritized for the aim of this discussion. Overall, the human eye can detect color changes starting from $\Delta E \geq 3$ (Annex Equation 3.3), and all color space coordinates contribute to its shifting (ΔL , Δa^* , Δb^*).

$$\Delta E_{ab}^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (3.2.1)$$

Bearing in mind the color sphere of the CIE $L^*a^*b^*$ system, ΔL is the shift on the **lightness-darkness** axis, Δa^* on the **redness-greenness** axis, and Δb^* on the **yellowing-blue** axis. Heritage science research focuses on changes in the aspect of objects, or on color change before/after conservation treatments. Natural weathering and conservation treatments should not modify the human-eye experience of the object. In the current experiments, typical color changes of clear films were associated to chemical and mechanical degradation. For example crosslinking can be associated to becoming opaque and yellow. ΔL values describe

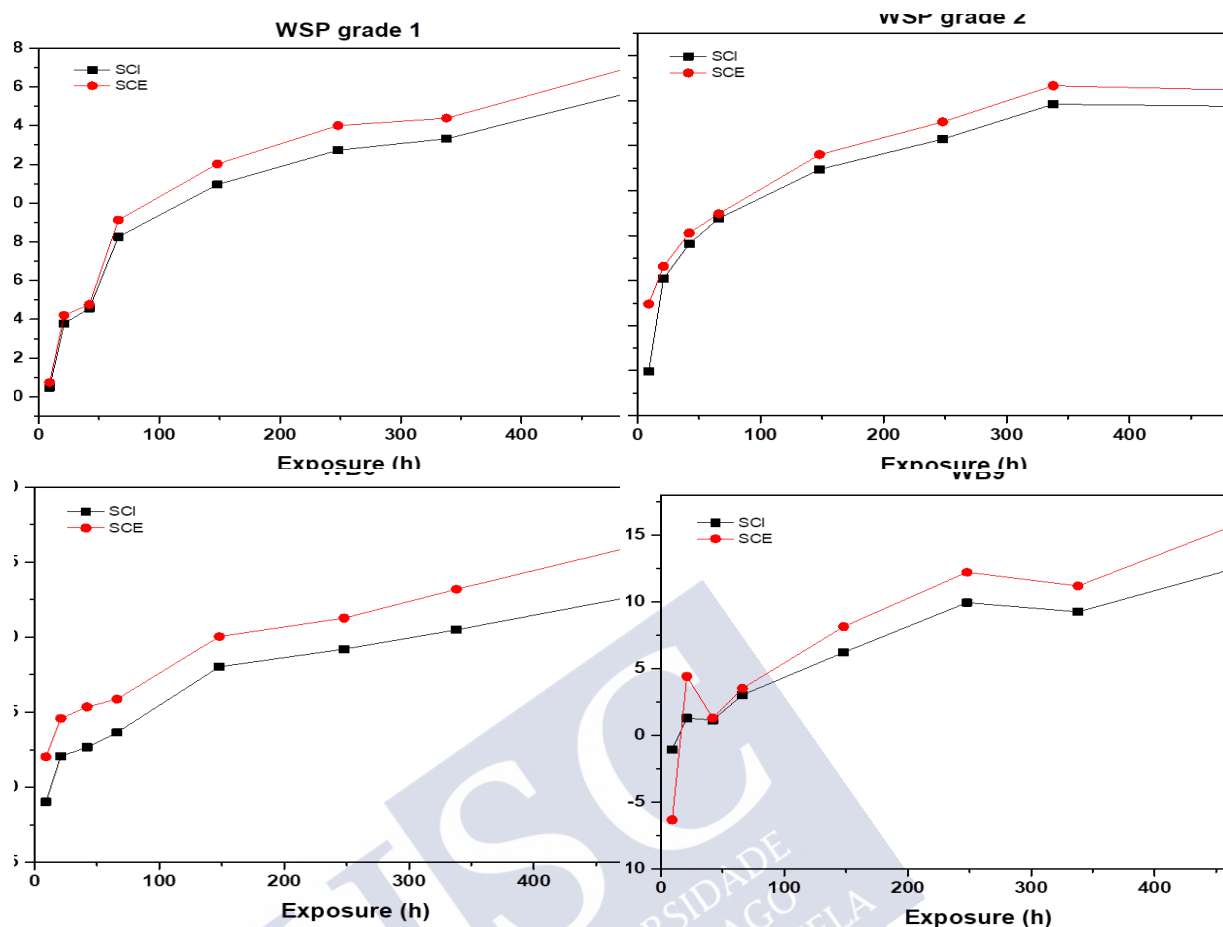
opaqueness, whereas Δb^* values describe the increase of yellowness. Overall, yellowing, darkening and loss of transparency increased in coated and uncoated ABS films in the first stages of photoaging (~50 h).

ΔE values of coated and uncoated ASB samples treated up to 415 h are presented in Figure Annex 3.2.4. Measurements resulting were taken at different stages of photoaging, although only initial (0 h) and final (415 h) values are presented. It can be noticed that ΔE_{SCI} values for all coated samples is slightly higher or similar to uncoated ABS (~12). Therefore, it could not be appreciated an enhancement of the overall color performance of the films using coatings.



Annex Figure 3.2.4 Histograms of color changes in uncoated and coated ABS films photo-aged with irradiance ≥ 300 nm, ΔE calculated for each sample at 0h and 415h treatment.

As far as **darkening** is concerned, the performance of the coatings was comparable or better than that of uncoated ABS films, being $\Delta L_{SCI} \sim -7$ for samples up to 415 h. Similarly, WB6 and WB9 showed $\Delta L_{SCI} \sim -7$ and -5 , respectively. WPS grade 1 and 2 darkened less presenting $\Delta L_{SCI} \sim 2$ and ~ -2 , respectively. As far as **yellowing** is concerned, a preliminary reference, Δb^* for uncoated ABS photo-aged up 415 h was calculated for the two components as 9.30 (SCI) and 9.42 (SCE). Figure Annex 3.2.5 shows the scattered lines for Δb^* of WSP grade 1(a), WSP grade 2(b), WB6 (c) and WB9 (d). Overall the use of coatings worsens the yellowing performance of the ABS films compared to uncoated ABS. In particular, WSP grade 1 and WSP grade 2, reached $\Delta b^*_{SCI} \sim 16$ and ~ 12 , respectively. Furthermore, WB6 and WB9 similarly poorly, presenting respectively $\Delta b^*_{SCI} \sim 13$ and ~ 14 .

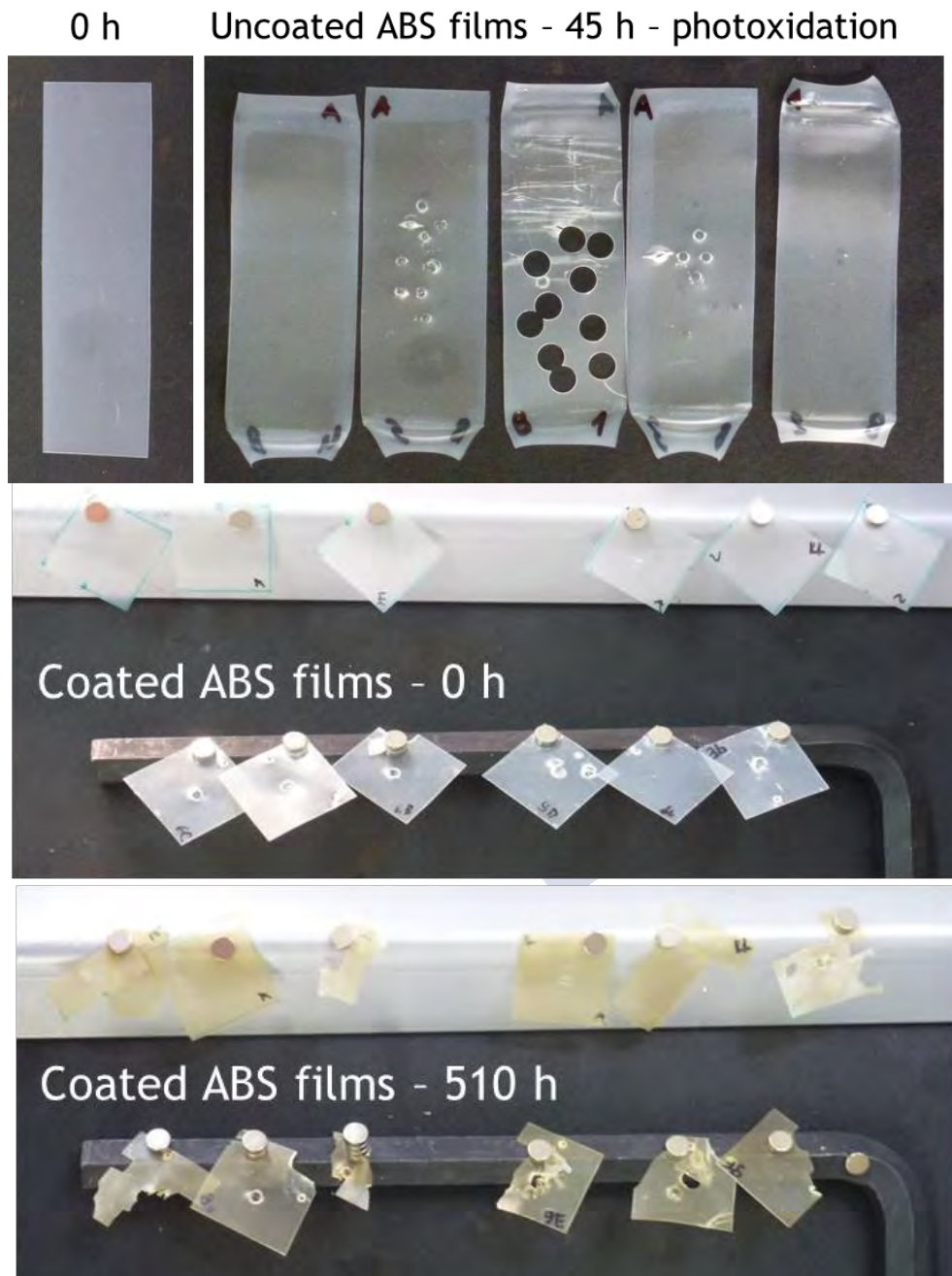


Annex Figure 3.2.5. Scattered lines showing mostly exponential growth of Δb^* values up to 100 h treatment, following at lower rate up to 515h. Curves are reported for ABS films coated with WPS grade 1 (a), WPS grade 2 (b), WB6 (c), WB9 (d).

Similar colorimetric data were collected for thermally aged uncoated ABS samples (500 h at 80°C) that did not show substantial yellowing, due to the absence of superficial products of photooxidation and photolysis. Although their mechanical strength was compromised as demonstrated by early aging rigidity, samples did not turn opaque and yellow. Overall (SCI) color changes were calculated as $\Delta E = 2$, $\Delta L = 2$, $\Delta a = -1$, $\Delta b = -15$.

ANNEX 3.3: PHOTOAGED ABS

Photographs of uncoated and coated ABS films are reported below as an example of color change and mechanical damage.



Annex Figure 3.3: ABS films uncoated (top row) and coated (middle and down rows), before and after photoaging tests.

ANNEX 3.4: ATR-FTIR SPECTROSCOPY ON COATED ABS

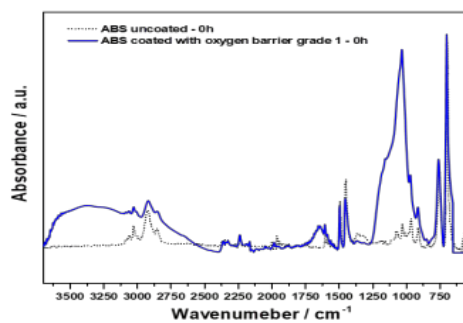
Annex Figures 3.4 (a-i) report ATR-FTIR normalized spectra from ABS coated with oxygen-barrier **WSP grade 1**. The area of the nitrile vibration at 2237 cm^{-1} was used for normalization. The spectrum of uncoated and unaged ABS (0 h) was compared to all photoaged coated films (a – 0h, b – 10h, c – 24h, d – 42, e – 70h, f – 150h, g – 250, h – 350h, i – 500h, approximately). Spectra of uncoated photoaged films are embedded in the graphs to quickly assess the formation of carbonyl species under the coating at similar time ranges.

The presence of hydroxyl species with a maximum at (3375 cm^{-1} at 0 h treatment) should not be overlooked as a feature of oxidative weathering, rather a component of the coating. From 150 h treatment on, spectra were collected on the surface of the coating and underneath after grinding the outer layer. The grinding was functional to assess of the oxygen permeation through the coating during aging.

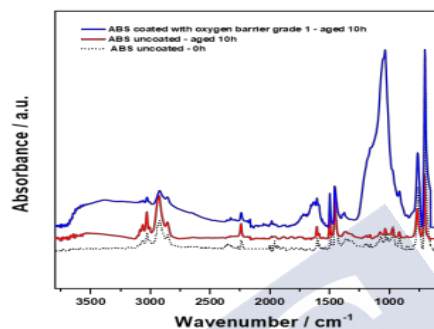
Carbonyl species were recorded underneath the surface of the film coated with WSP grade 1 in Figure Annex 3.4 (c 1), showing features at 1718 and 1370 cm^{-1} . Spectral comparison revealed that WSP grade 1 presented the **best protecting performance** because the formation of carbonyl species initiated in later stages compared to all the others coatings tested. Figure Annex 3.7 (c) shows **WSP grade 2** coated films in Figure Annex 3.4 (a - c 2): the formation of a band centered at 1740 cm^{-1} started at 148 h treatment. Polyurethane (**WP6** in Figure Annex 3.4 (a - c 4) and acrylate (**WP9** in Figure Annex 3.4 (a - c 3) coatings confirmed as well the ABS degradative behavior, showing the increase of bands in the carbonyl and hydroxyl regions after around 150 h treatment. WB6 coating was slightly more effective than the WB9 and reduced the permeability to oxygen up to 250 h treatment, for then showing similar degradative behavior as uncoated ABS films.

Spectra collected on WP9 coated films in Figure Annex 3.4 (c 3) show the typical decrease of the C-H peaks and C=O associated to broadening of the latter. In addition, in the hydroxyl region $3600 - 3100\text{ cm}^{-1}$ there was an increase with a broad band, further to appearance of a band at 2600 cm^{-1} . The band at 3250 cm^{-1} was assigned to the decomposition of the laterals butyl groups, whereas that at 2600 cm^{-1} to bonded –OH groups. In the carbonyl region, bands centered at 1804 , 1762 , 1705 cm^{-1} appeared. The band centered at 1745 cm^{-1} increased and broadened due to the formation of carboxylic acids and other C=O bearing molecules. Similarly ketones and C=C bonds crosslinking occurs. WB9 coating was not effective to reduce oxygen permeability and resulting analysis with ATR-FTIR showed to be closely similar to those of uncoated ABS films.

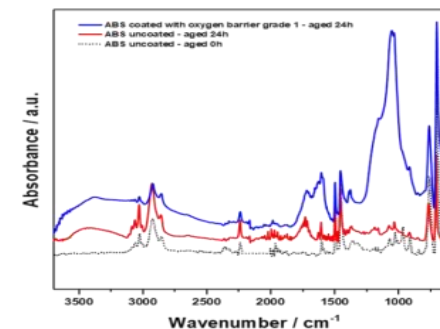
Overall, lowering of carbonyl through oxygen barriers did not prevent ABS from yellowing. Photolysis is another degradation mechanism that might be responsible for the yellowing. Different analytical methods, such as Electron Paramagnetic Resonance (EPR), could reveal the presence of radicals forming in very fast photo-chemical reaction involving, small reaction intermediates responsible of color changes.



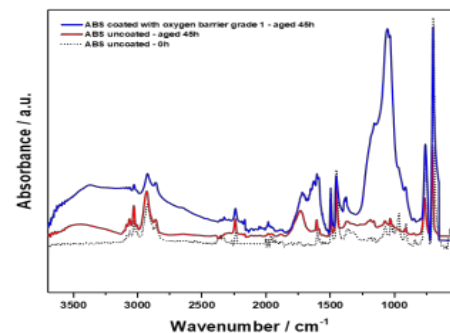
Annex Figure 3.4 (a 1): WSP grade 1 - 0 h



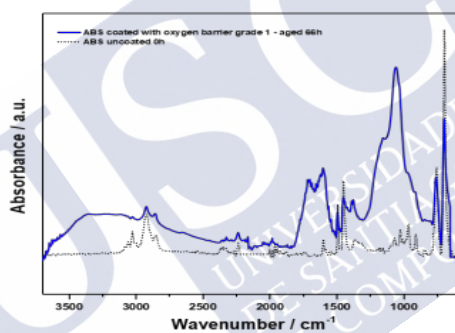
Annex Figure 3.4 (b 1): WSP grade 1 - 10 h



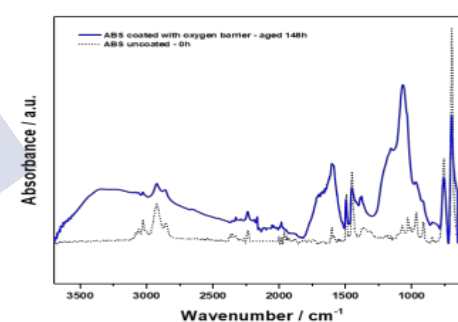
Annex Figure 3.4 (c 1): WSP grade 1 - 24 h



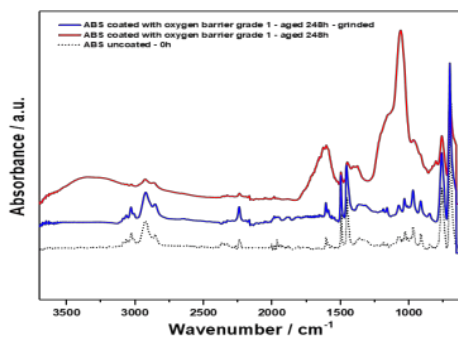
Annex Figure 3.4 (d 1): WSP grade 1 - 45 h



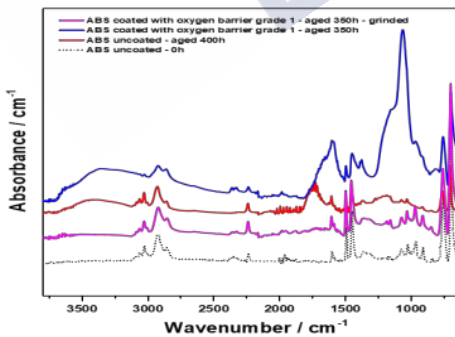
Annex Figure 3.4 (e 1): WSP grade 1 - 66 h



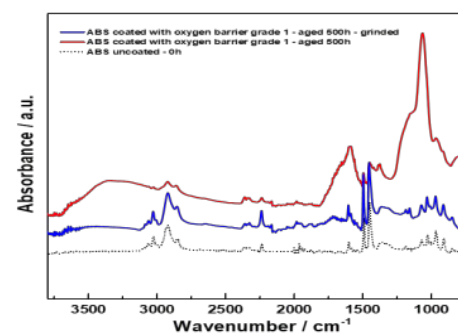
Annex Figure 3.4 (f 1): WSP grade 1 - 148 h



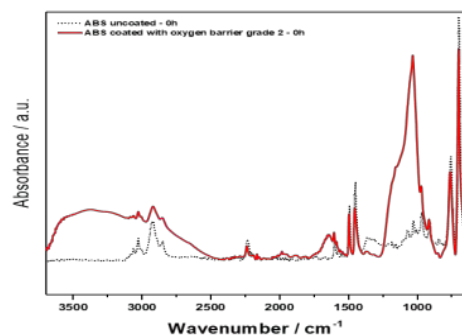
Annex Figure 3.4 (g 1): WSP grade 1 - 248 h



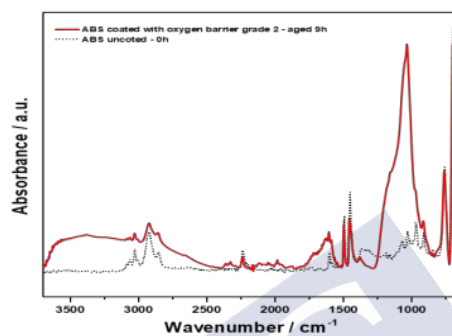
Annex Figure 3.4 (h 1): WSP grade 1 - 350 h



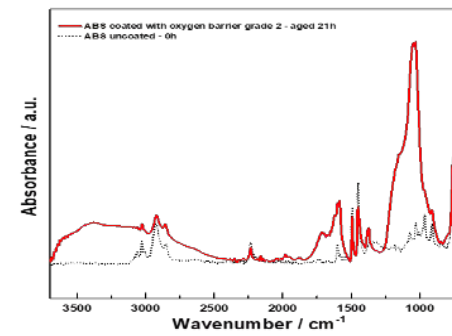
Annex Figure 3.4 (i 1): WSP grade 1 - 500 h



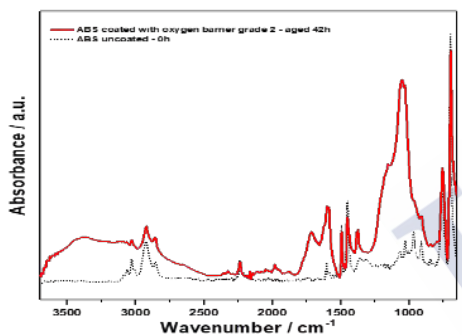
Annex Figure 3.4 (a 2): WSP grade 2 - 0 h



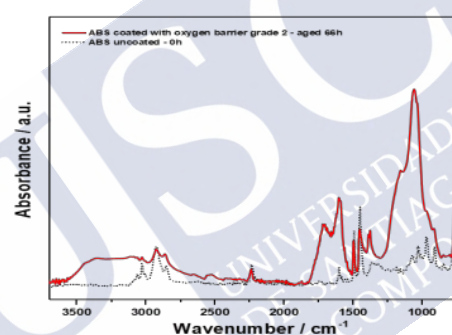
Annex Figure 3.4 (b 2): WSP grade 2 - 10 h



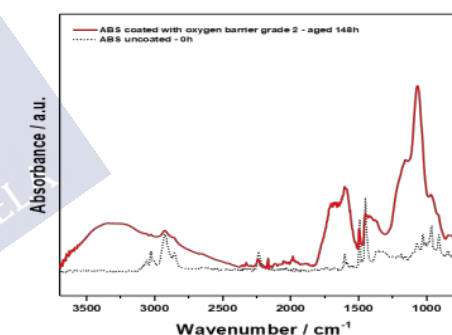
Annex Figure 3.4 (c 2): WSP grade 2 - 24 h



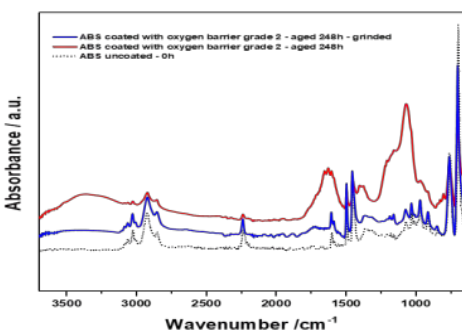
Annex Figure 3.4 (d 2): WSP grade 1 - 45 h



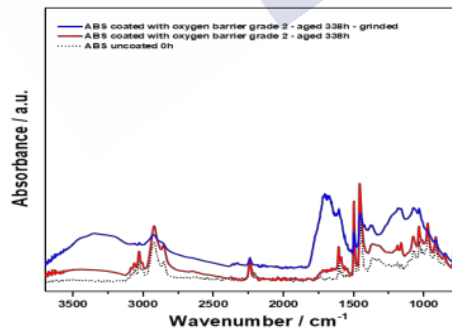
Annex Figure 3.4 (e 2): WSP grade 2 - 66 h



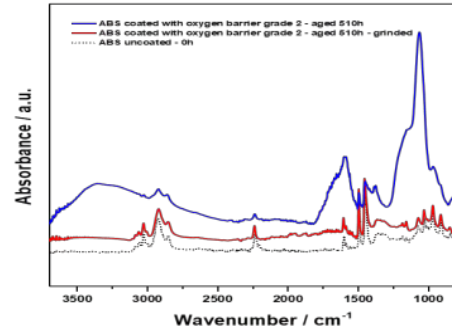
Annex Figure 3.4 (f i): WSP grade 2 - 148 h



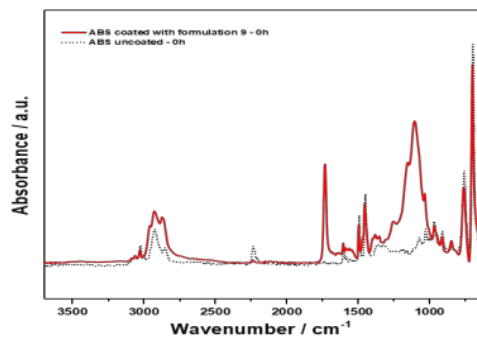
Annex Figure 3.4 (g 2): WSP grade 2 - 248 h



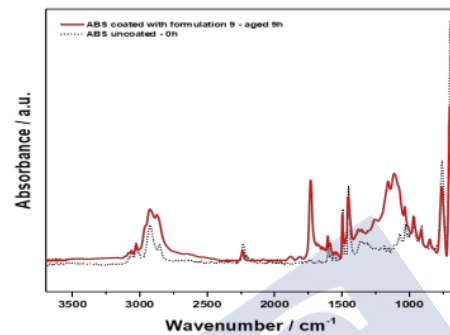
Annex Figure 3.4 (h 2): WSP grade 2 - 350 h



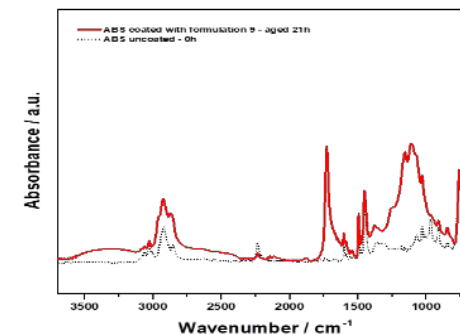
Annex Figure 3.4 (i 2): WSP grade 2 - 500 h



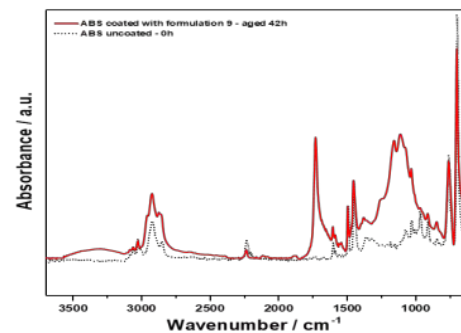
Annex Figure 3.4 (a 3): WB9 - 0 h



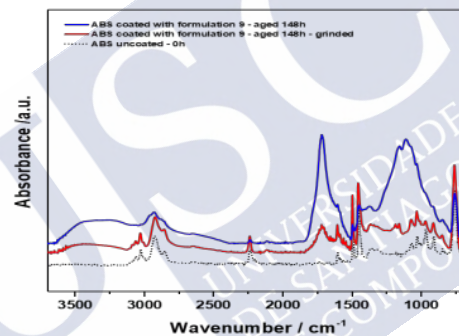
Annex Figure 3.4 (b 3): WB9 - 10 h



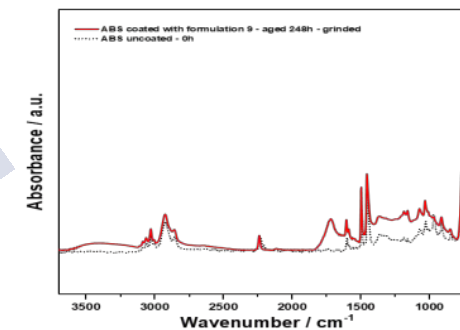
Annex Figure 3.4 (c 3): WB9 - 21 h



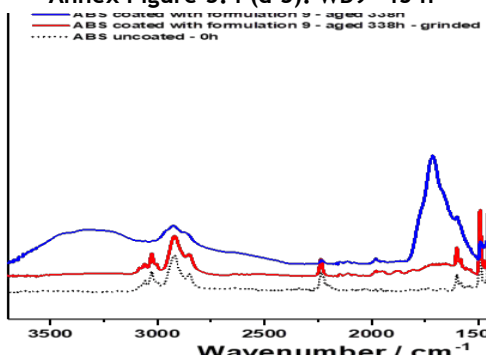
Annex Figure 3.4 (d 3): WB9- 45 h



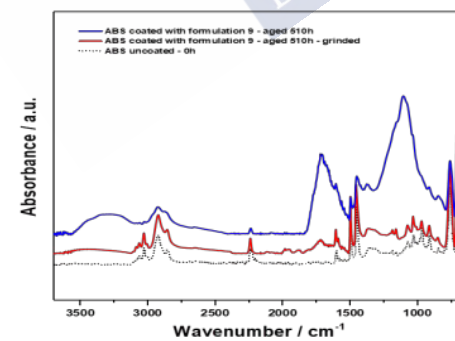
Annex Figure 3.4 (e 3): WB9 - 148 h



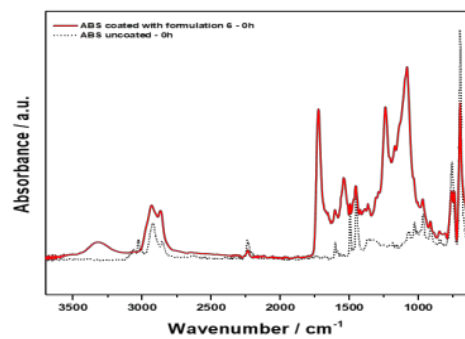
Annex Figure 3.4 (f 3): WB9- 248 h



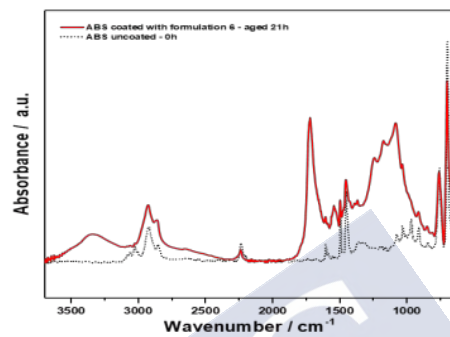
Annex Figure 3.4 (g 3): WB9- 338 h



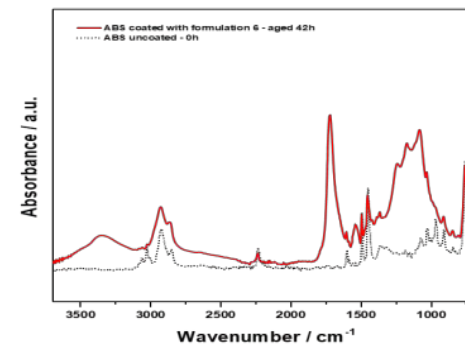
Annex Figure 3.4 (h 3): WB9 - 500 h



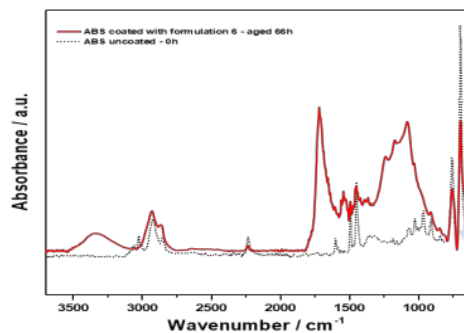
Annex Figure 3.4 (a 4): WB6 - 0 h



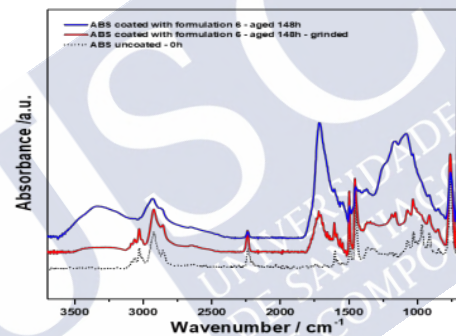
Annex Figure 3.4 (b 4): WB6 - 20 h



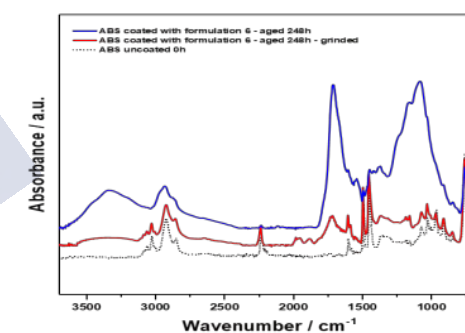
Annex Figure 3.4 (c 4): WB6 - 42 h



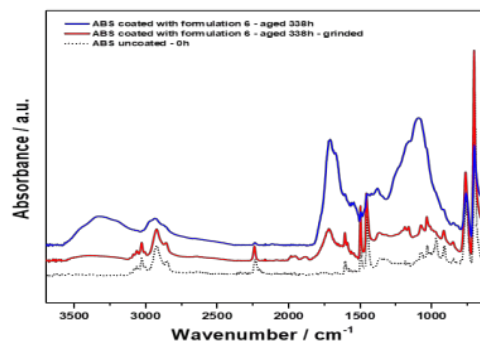
Annex Figure 3.4 (d 4): WB6 - 64 h



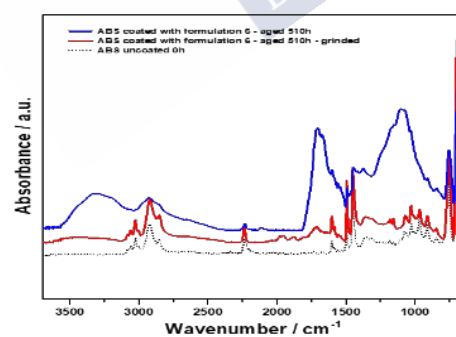
Annex Figure 3.4 (e 4): WB6 - 148 h



Annex Figure 3.4 (f 4): WB6 - 248 h

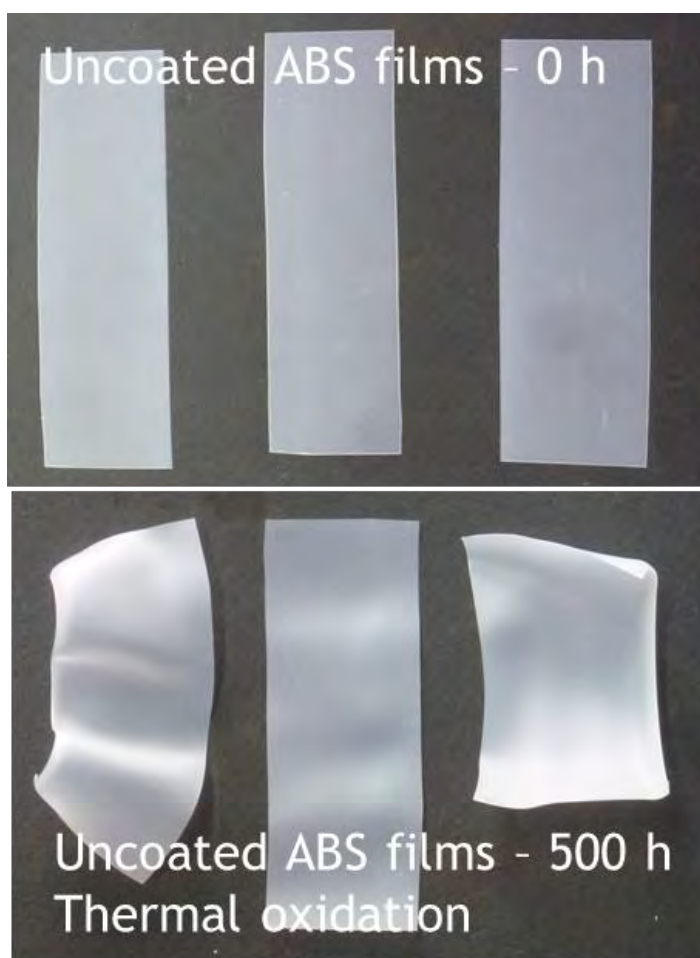


Annex Figure 3.4 (g 4): WB6 - 338 h



Annex Figure 3.4 (h 4): WB6 - 500 h

ANNEX 3.5: THERMALLY AGED ABS



Annex Figure 3.5: photographs of thermally aged ABS films.

ANNEX 3.6: SEC ON UNCOATED AND COATED ABS

SEC measurements on the soluble fractions of ABS coated and uncoated films (sample size ~2 mg). M_n (number averaged), M_w (weight averaged) and PD (polydispersity) values inform us on the molecular weight distribution on photoaged ABS.

Annex Table 3.6 a: SEC on photooxidized uncoated ABS

Sample Name	M_n	M_w	PD
ABS 0 h	77916	243139	3.13
ABS 24 h	30782	133772	4.35
ABS 64 h	31841	131079	4.12
ABS 44 h	37120	144474	3.89
ABS 106 h	34534	140020	4.05
ABS 391 h	17546	135909	7.75

**Annex Table 3.6 b: SEC on photooxidized coated ABS
WSP grade 1 and grade 2**

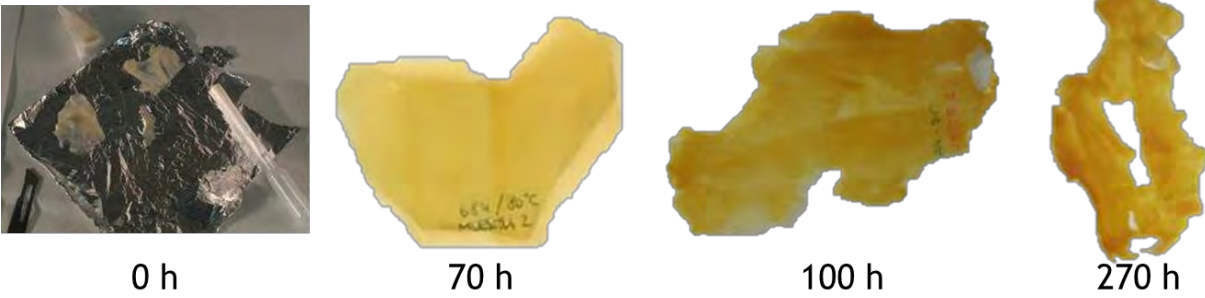
Sample Name	M_n	M_w	PD
ABS- WSP grade 1 -0 h	--	--	--
ABS- WSP grade 1 -100 h-150 μ L	62164	267610	4.30
ABS- WSP grade 1 -248 h-200 μ L	70636	264751	3.75
ABS- WSP grade 1 -510 h-200 μ L	21008	244320	11.63
--	--	--	--
ABS- WSP grade 2 - 0 h-200 μ L	32590	132084	4.05
ABS- WSP grade 2 - 100 h-200 μ L	54882	238026	4.34
ABS- WSP grade 2 -248 h-200 μ L	46099	236139	5.12
ABS- WSP grade 2 - 510 h-150 μ L	41843	109502	2.62

**Annex Table 3.6 c: SEC on photooxidized coated ABS
polyurethane (WB6) - acrylate (WB9)**

Sample Name	M_n	M_w	PD
ABS-WB6-0 h-150 μ L	35460	143851	4.05
ABS-WB6-100 h-200 μ L	58923	250694	4.25
ABS-WB6-248 h-200 μ L	41220	292617	7.09
ABS-WB6-510 h - 150 μ L	39891	258677	6.48
--	--	--	--
ABS-WB9-0 h-200 μ L	450877	684488	3.74
ABS-WB9-100 h-200 μ L	561679	854565	3.63
ABS-WB9-248 h-200 μ L	479128	754499	4.01
ABS-WB9-510 h- 150 μ L	300542	510876	3.16

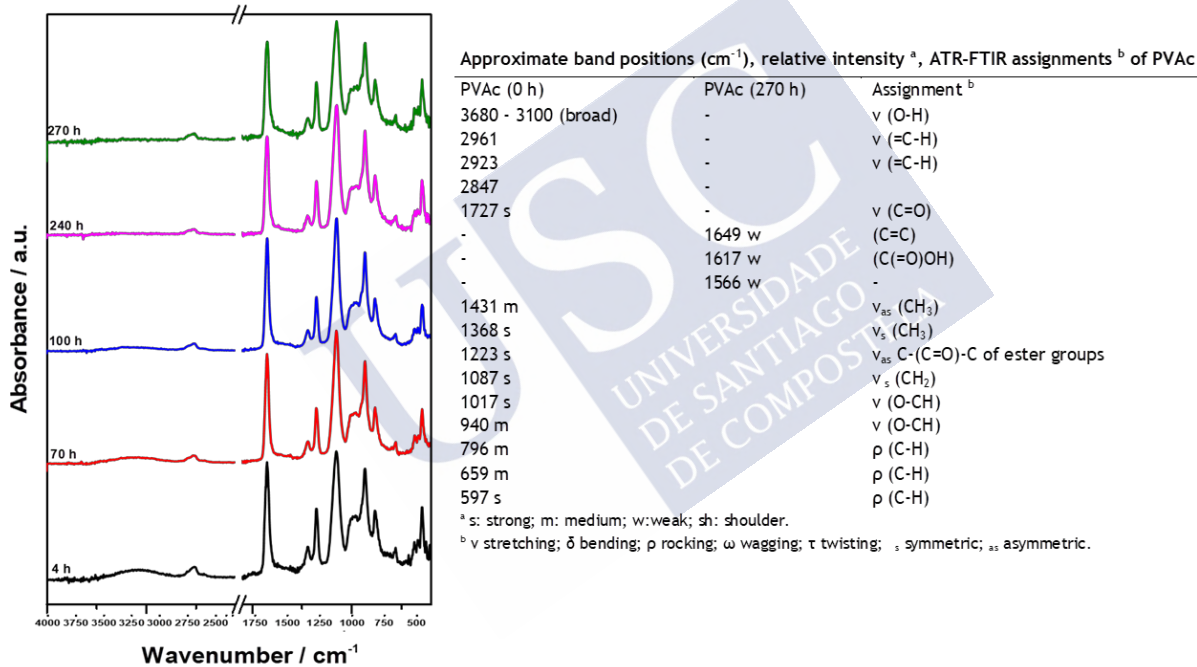
ANNEX 3.7: THERMALLY AGED PVAc

PVAc films - Thermal oxidation

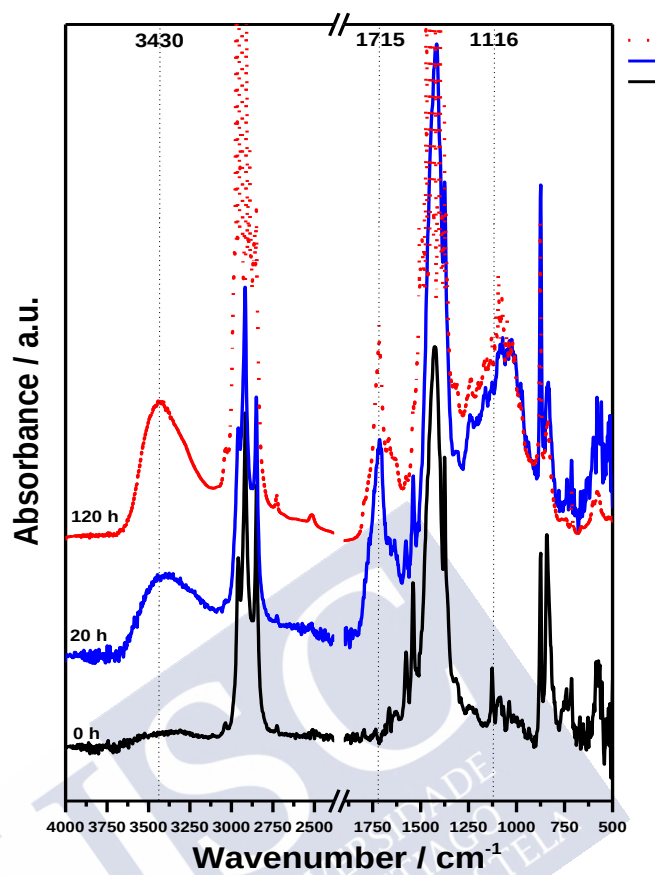


Annex Figure 3.7: photographs of PVAc samples at different thermal aging steps

ANNEX 3.8: ATR-FTIR SPECTROSCOPY ON PVAc



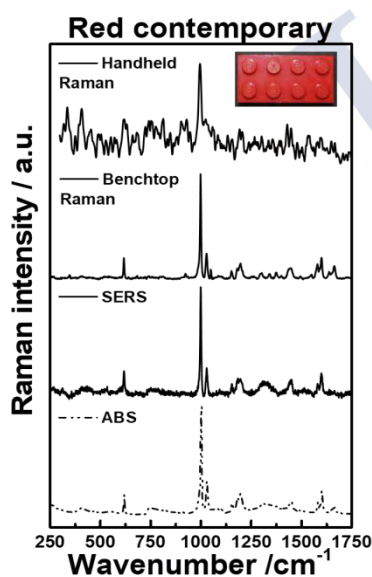
Annex Figure 3.8: ATR-FTIR spectra on the left at different aging stages, table with band assignment on the right.

ANNEX 3.9: ATR-FTIR SPECTROSCOPY ON PHOTOAGED PI

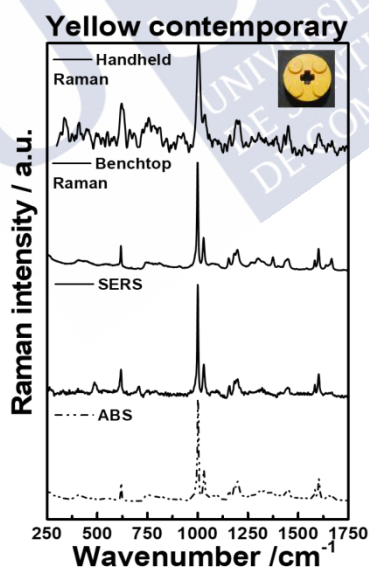
Annex Figure 3.9: ATR-FTIR spectra on PI photoaged up to 120 h.

ANNEX 3.10: RAMAN SPECTROSCOPY ON LEGO® BRICKS**Annex Table 3.10.1: Raman spectroscopy assignment of ABS bands**

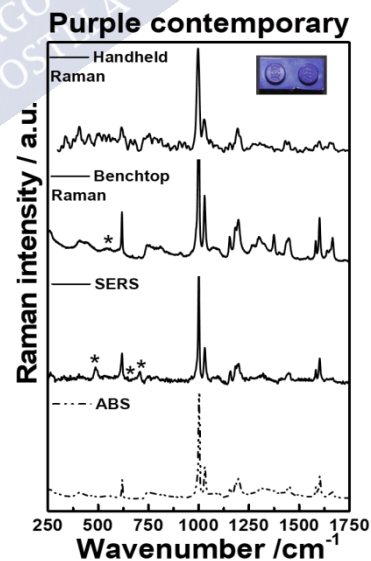
Band/ cm^{-1}	Assignment
624	δ aromatic ring in styrene
750	ω CH_2 aromatic ring in styrene and ring deformation
1005-1035	ν aromatic ring in styrene
1154	δ (C-H) out-of-plane
1196	ν (C-C) in-plane
1189	ν (C-H) out-of-plane of benzene ring
1208	ν_s (C-C)
1330	δ (CH_2)
1449	ν_{as} (C-C) of benzene ring
1451	δ_s (CH_2)
1587	ν_{as} (C-C) of benzene ring
1605	ν_s (C-C) of benzene ring
1668	ν (C=C trans) in butadiene
2240	N (C $\equiv$ N) in acrylonitrile



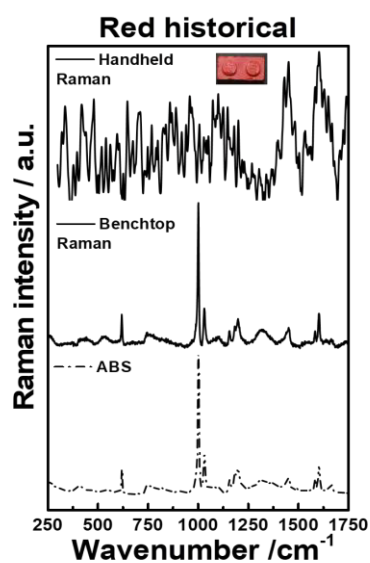
Annex Figure 3.10 a: Raman spectra on red brick



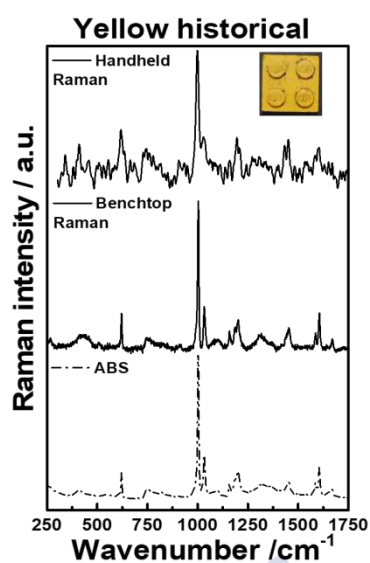
Annex Figure 3.10 b: Raman spectra on yellow brick



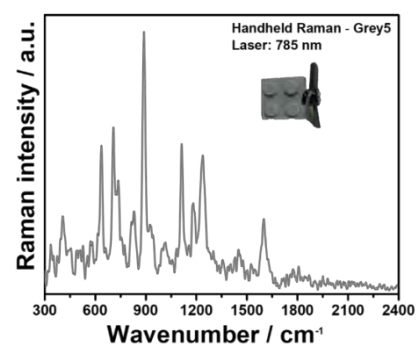
Annex Figure 3.10 c: Raman spectra on purple brick



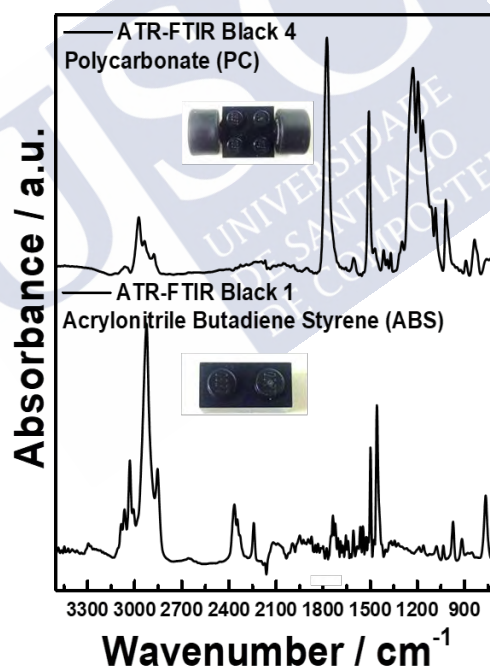
Annex Figure 3.10 d: Raman spectra on red brick



Annex Figure 3.10 e: Raman spectra on yellow brick

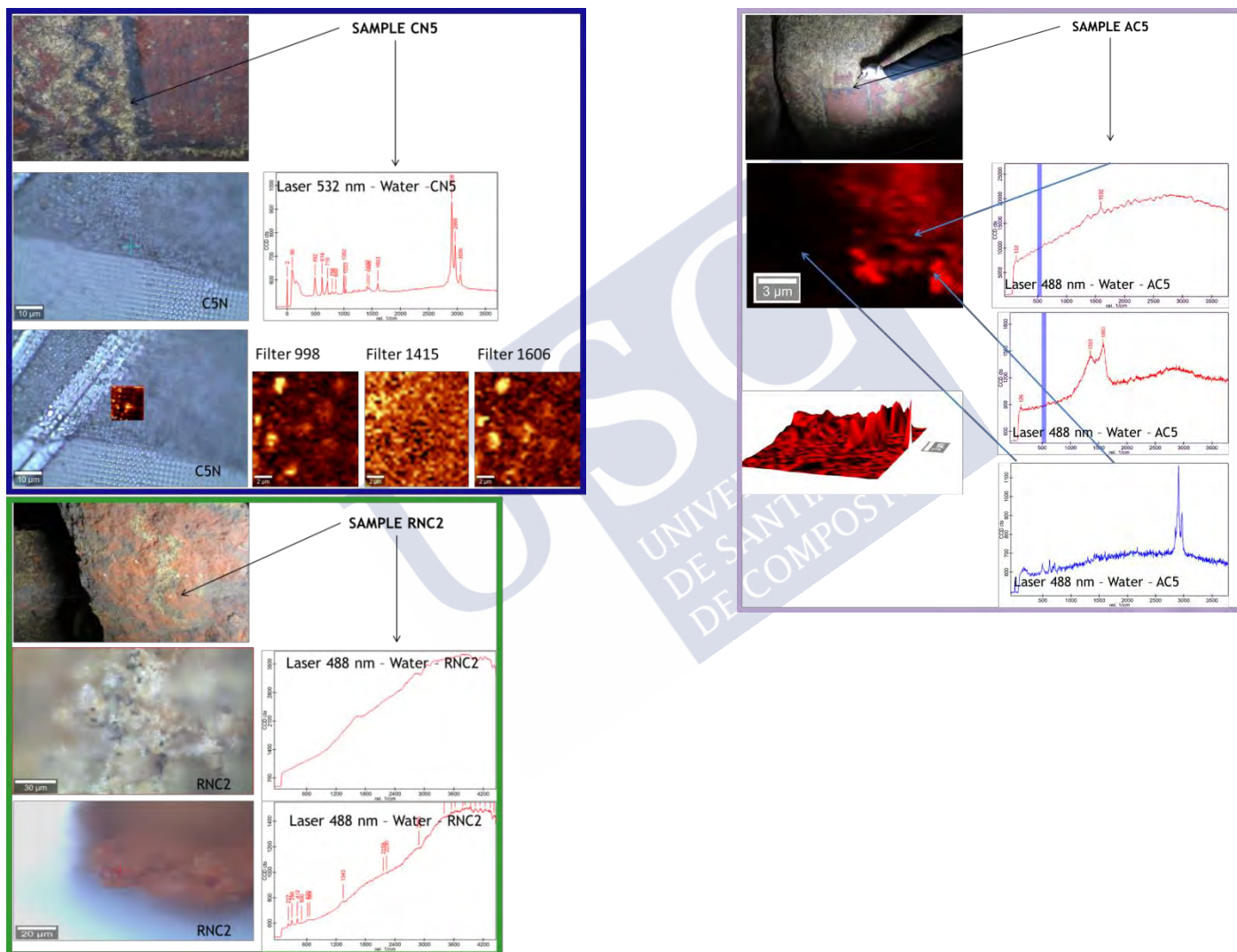


Annex Figure 3.10 f: Raman spectra on grey brick

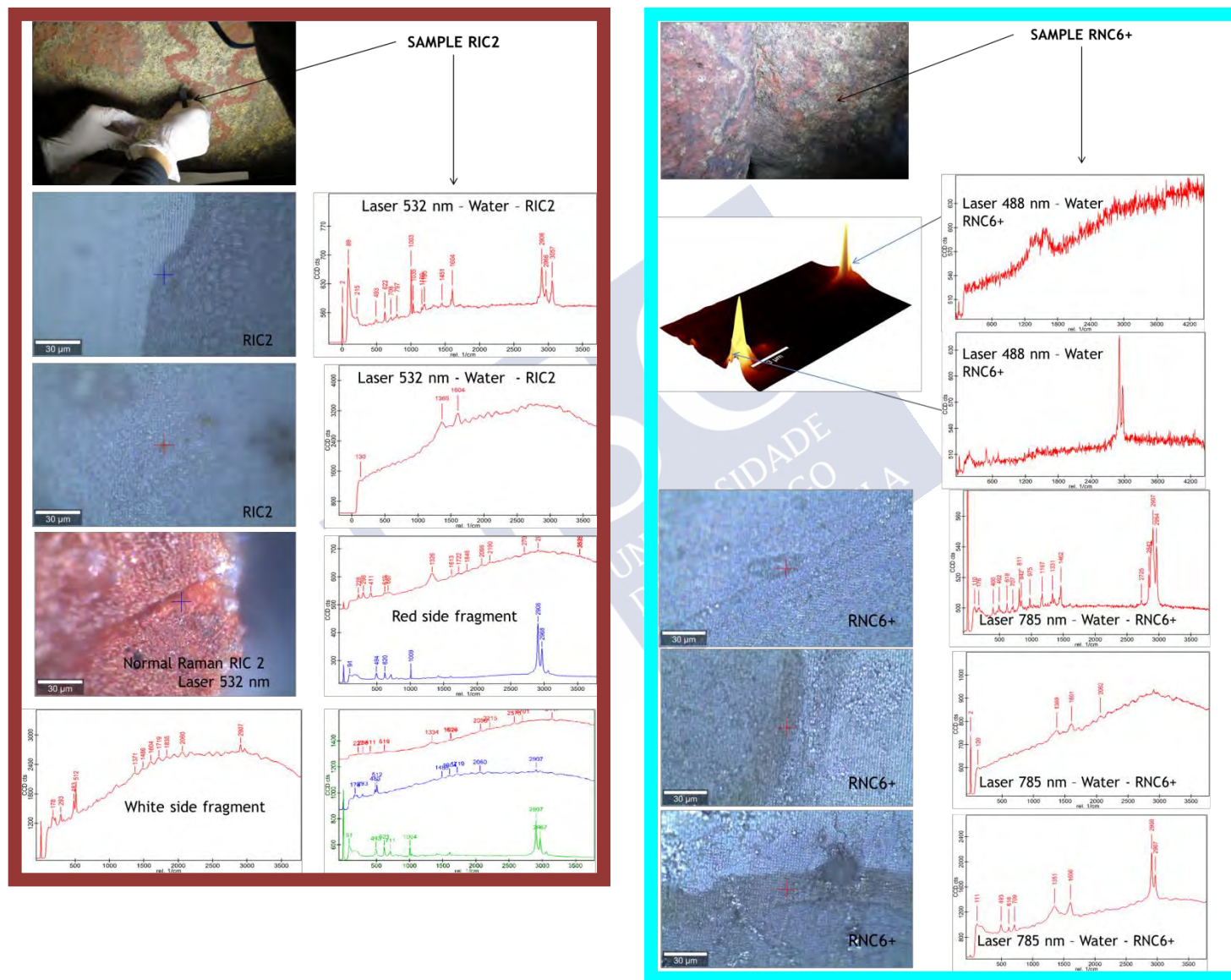


Annex Figure 3.10.2: ATR-FTIR spectra on black contemporary bricks

ANNEX 3.11: 3D RAMAN IMAGING AND SERS ON WALL PAINTINGS

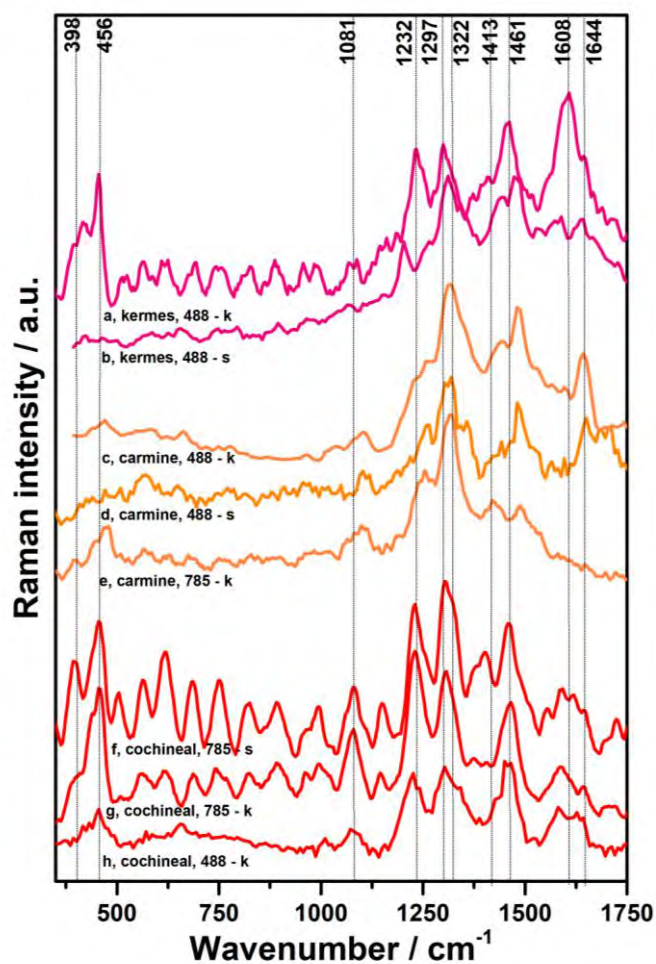


Annex Figure 3.11.1: photographs, spectral data and Raman mapping on samples from the Antelas Dolmen (PDMS sampling method).



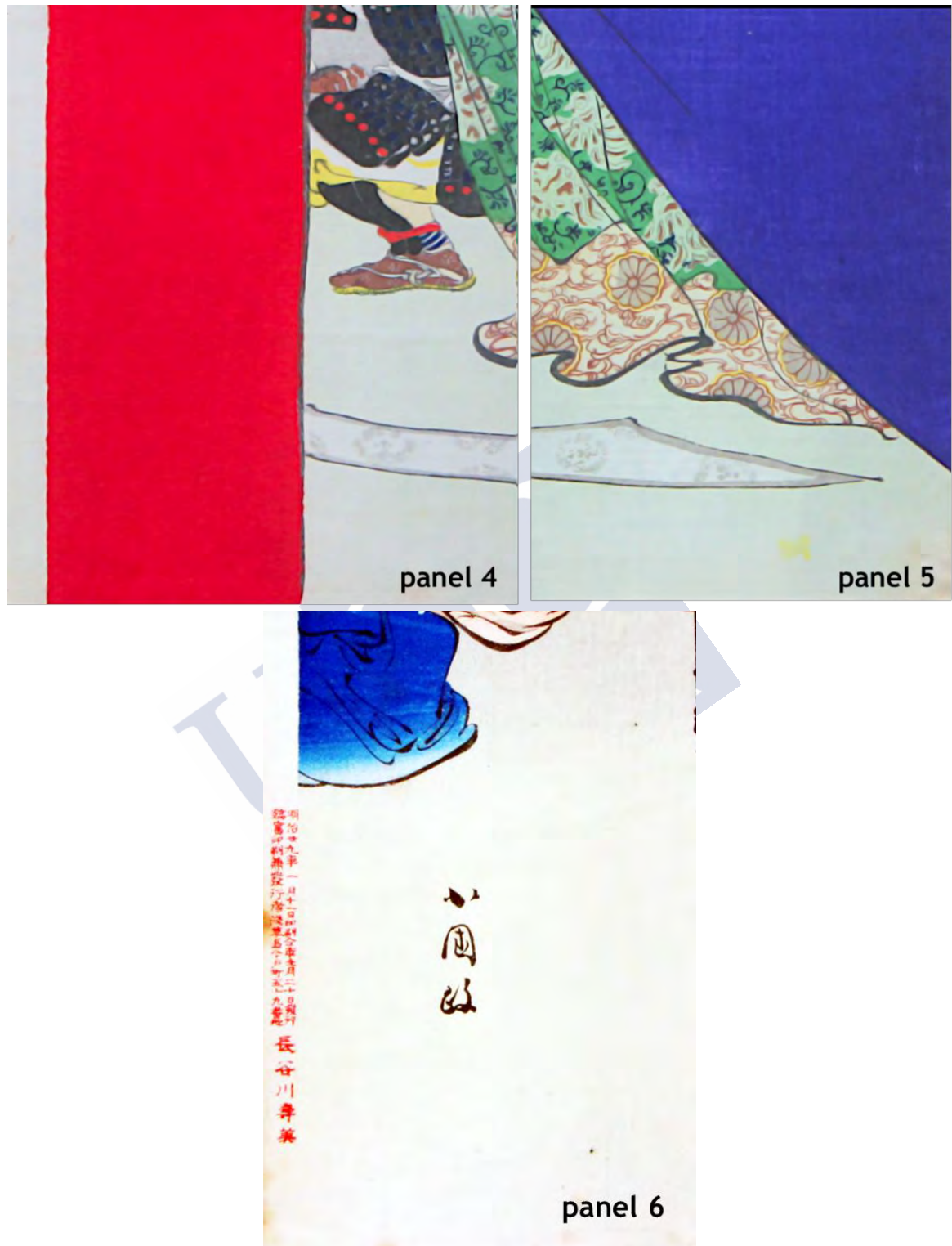
Annex Figure 3.11.: photographs, spectral data and Raman mapping on samples from the Antelas Dolmen (PDMS sampling method).

ANNEX 3.12: SERS MICROEXTRACTS ON REFERENCE NATURAL DYES



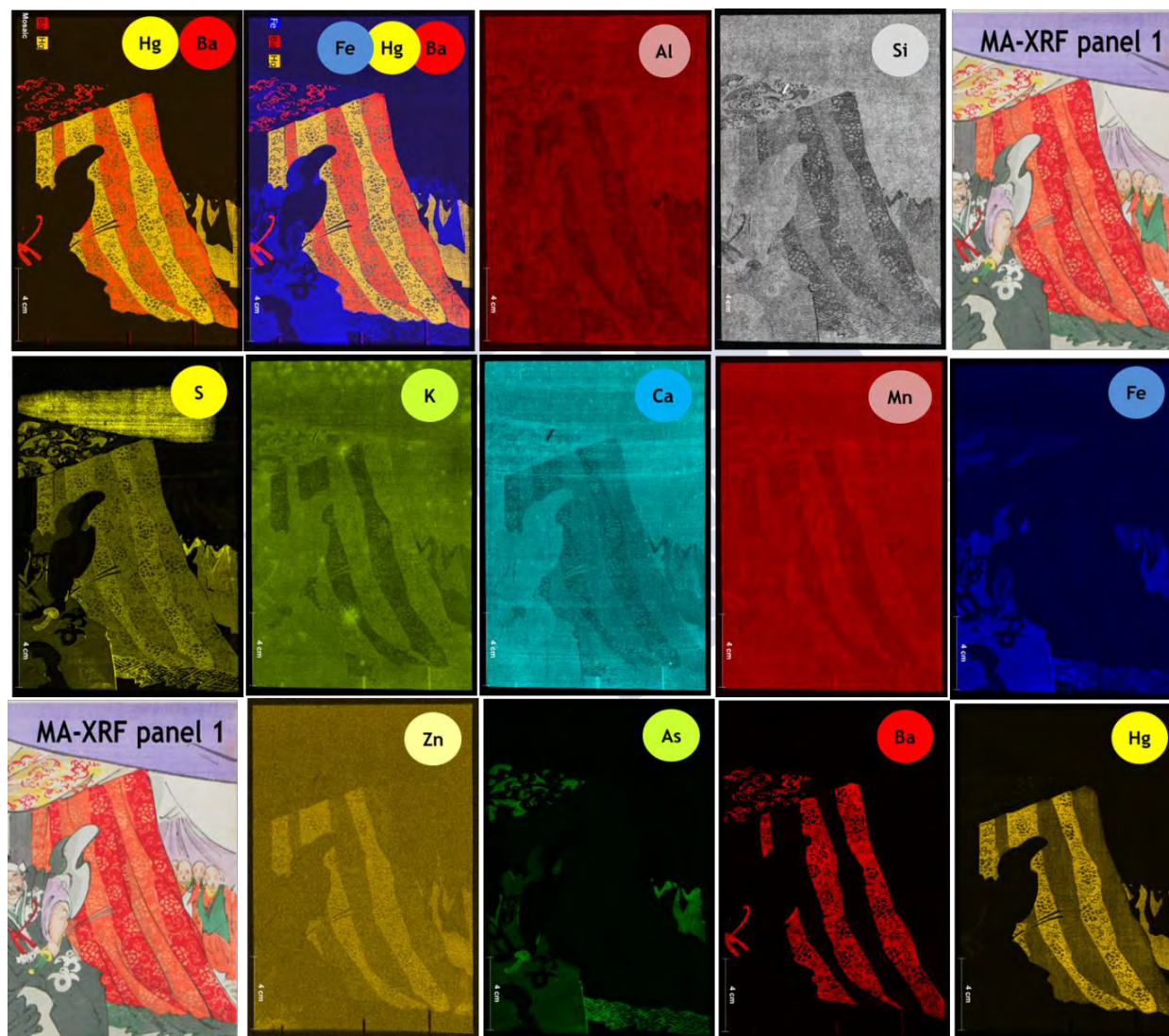
Annex Figure 3.12: SERS microextracts on historical references of kermes, carmine and cochineal

ANNEX 3.13: JAPANESE WOODBLOCK PRINTS

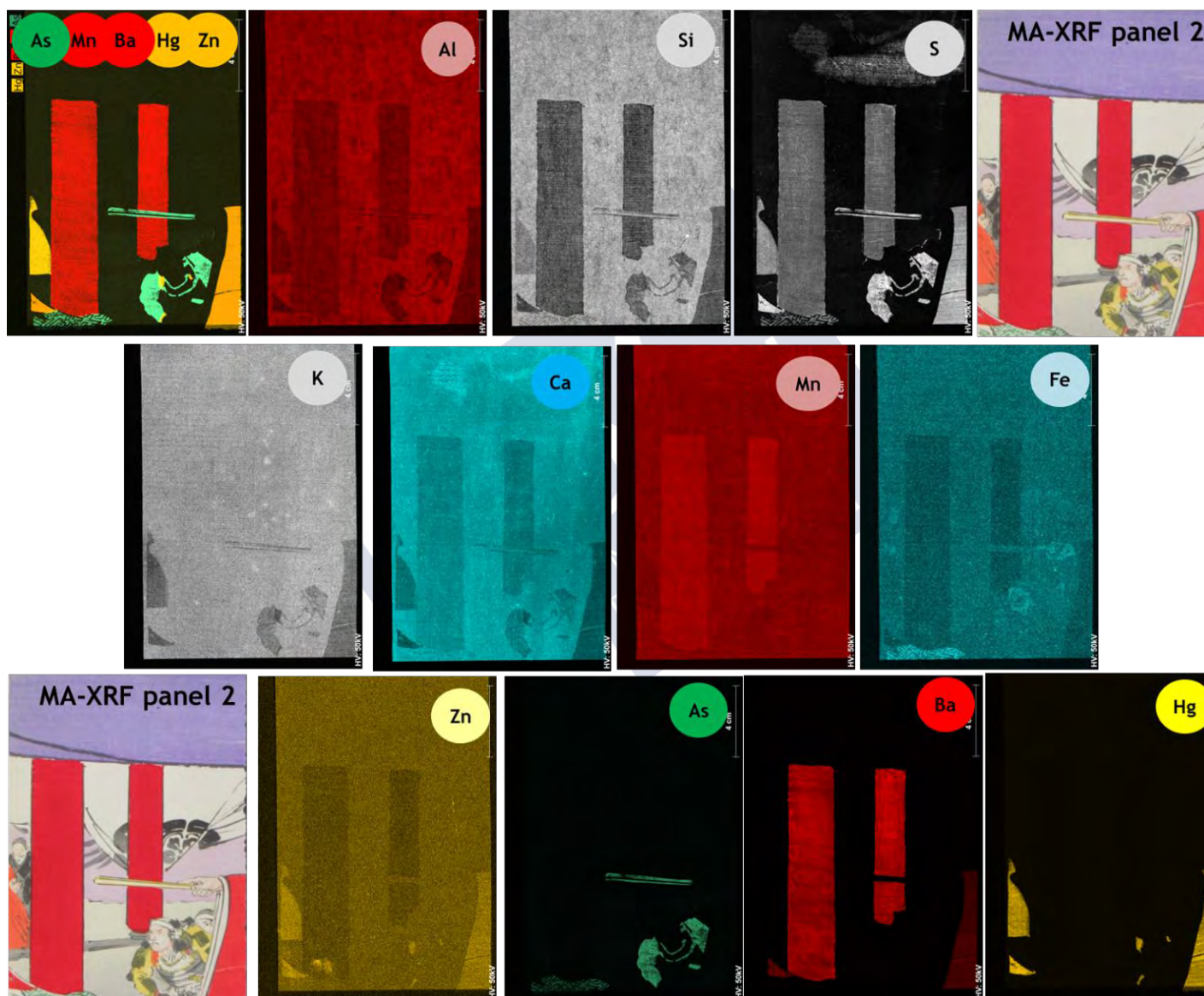


Annex Figure 3.13: photographs of woodblock prints panels.

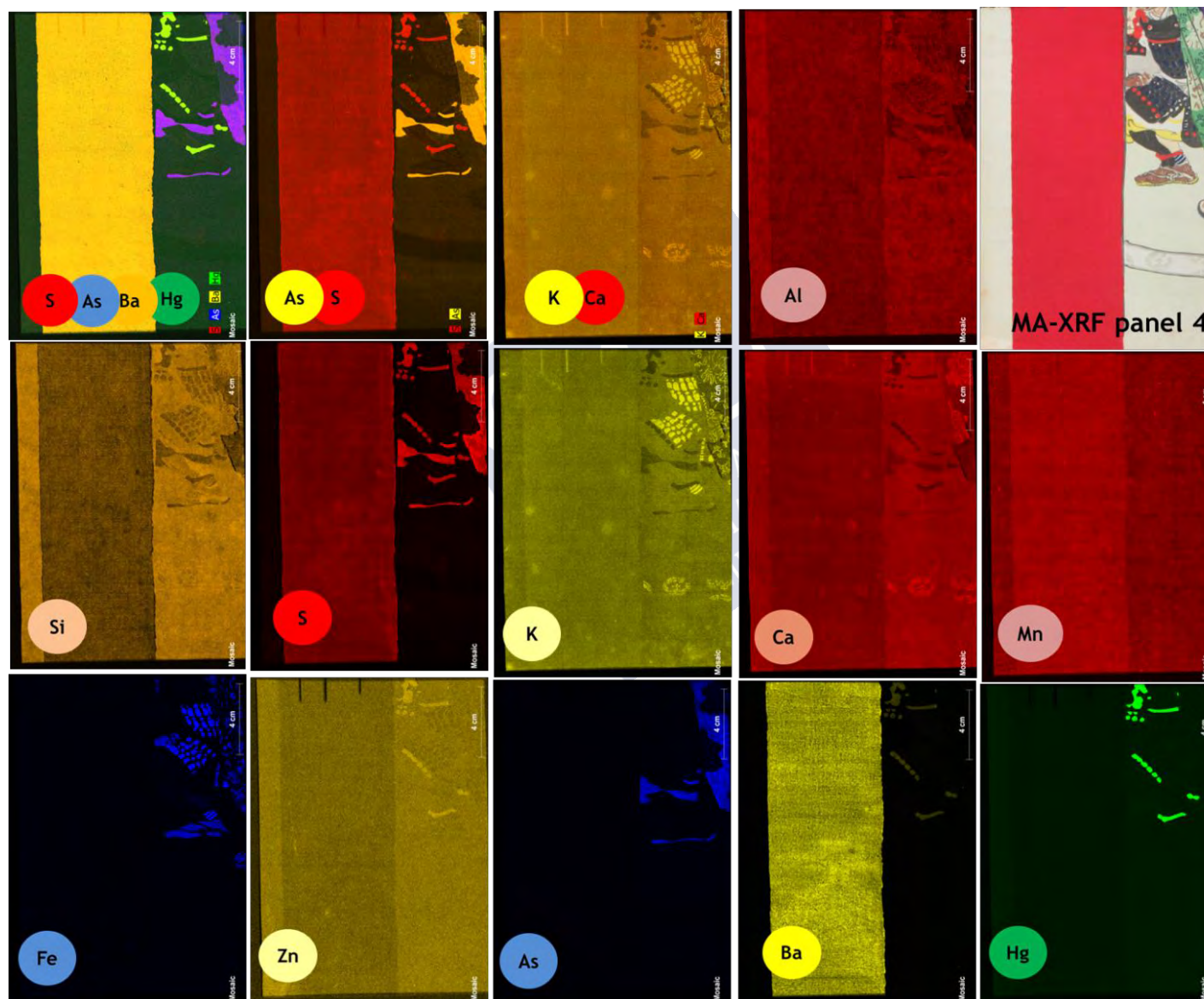
ANNEX 3.14: MA-XRF ELEMENTAL MAPPING ON PRINTS



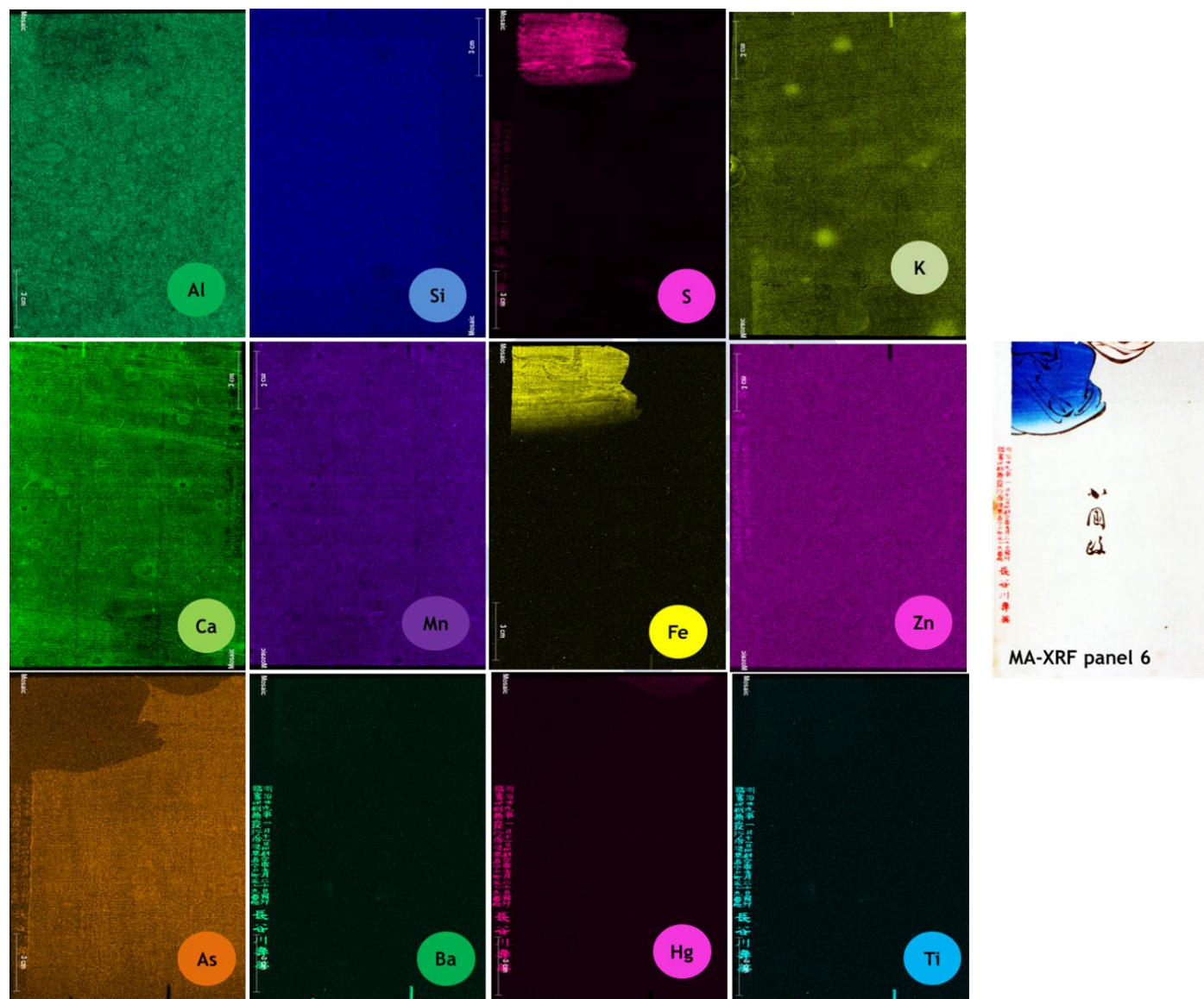
Annex Figure 3.14.1: MA-XRF elemental imaging on panel 1.



Annex Figure 3.14.2: MA-XRF elemental imaging on panel 2.



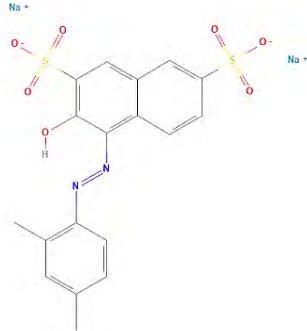
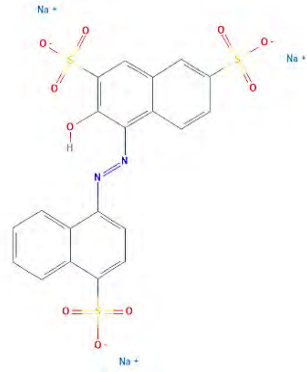
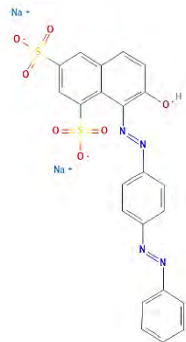
Annex Figure 3.14.3: MA-XRF elemental imaging on panel 4.



Annex Figure 3.14.4: MA-XRF elemental imaging on panel 6.

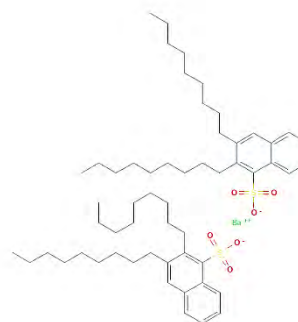
ANNEX 3.15: SMALL MOLECULES IDENTIFICATION

Annex Table 3.15: color grouping and chemical structures of the main synthetic dyes and pigments from the Japanese woodblock prints

Color	Molecular ID and molecular weight	Structure
Red (dark/light/orange)		
	Pigment Red 106 Vermilion <i>mercuric sulfide</i> 232.66 g/mol	$S \equiv Hg$
	Acid Red 26 Ponceau 2R <i>azo β-naphthol dye</i> 480.4 g/mol	
	Acid Red 27 Amaranth <i>azo β-naphthol dye</i> 604.5 g/mol	
	Acid Red 73 Cotton Scarlet <i>azo β-naphthol dye</i> 556.5 g/mol	



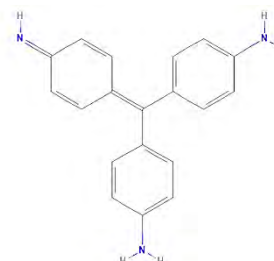
Pigment Red 60:1
Sunbrite Red
naphthalene sulfonic acid pigment
lake (barium salt)
1056.7g/mol



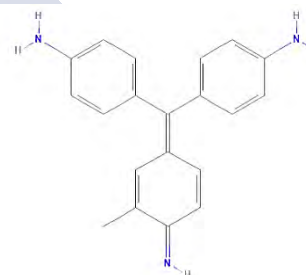
Purple
(dark/light)



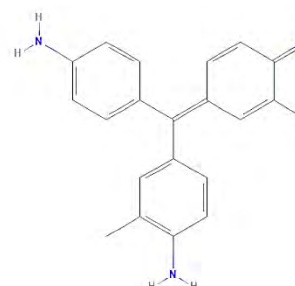
Basic Red 9
Pararosaniline (magenta)
triarylcarbonium pigment
323.8 g/mol



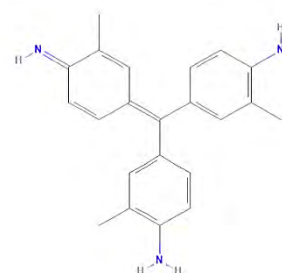
Basic violet 14
Rosaniline (fuchsine)
triarylcarbonium pigment
337.8 g/mol



Dimethyl fuchsine
(magenta II)
triarylcarbonium pigment
351.9 g/mol



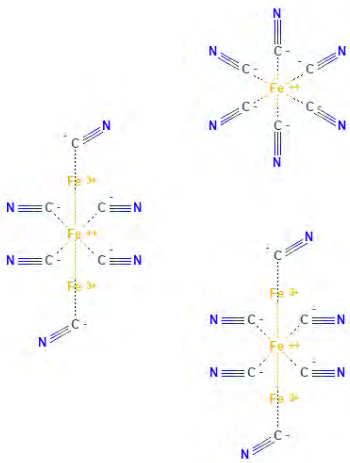
Basic Violet 2
New fuchsine (magenta III)
triarylcarbonium pigment
365.9 g/mol



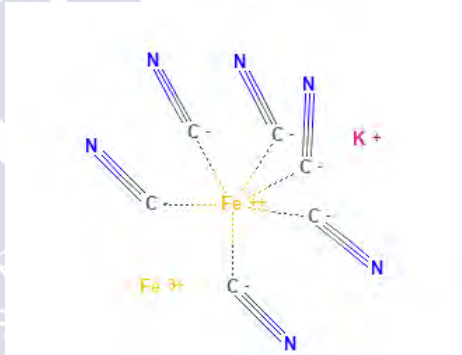
Blue



Pigment Blue 27
Prussian blue
ferric ferrocyanide
(insoluble)
859.2 g/mol



Pigment Blue 27
Prussian blue
ferric ferrocyanide
(water-soluble)
306.89 g/mol



Green
(olive/bright)



Glass arsenic sulfide + Prussian blue



Yellow



Glass arsenic sulfide
(synthetic orpiment)
252.1 g/mol

Pink



Vermilion + hematite + glass
arsenic sulfide

Brown

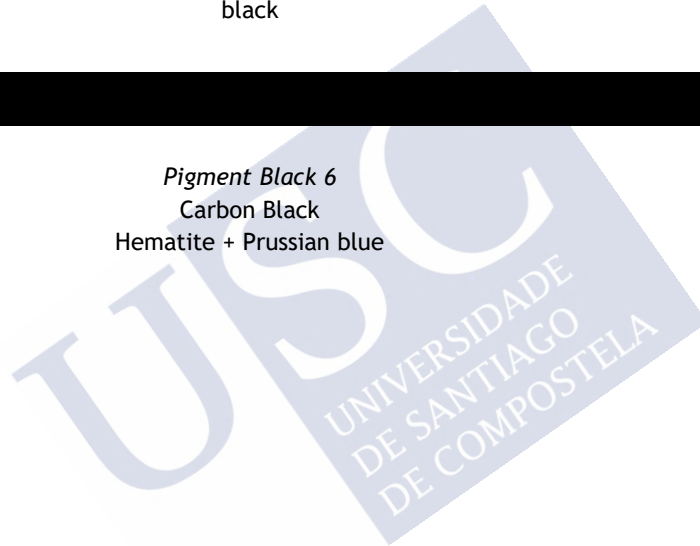


Hematite + Prussian blue + carbon
black

Black



Pigment Black 6
Carbon Black
Hematite + Prussian blue



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Figure 1.2



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Publication Title	Chemical communications	Rightsholder	Royal Society of Chemistry
Article Title	Surface enhanced Raman scattering (SERS) in the visible range on scalable aluminum-coated platforms.	Publication Type	e-Journal
Author/Editor	Royal Society of Chemistry (Great Britain)	Start Page	10638
Date	01/01/1996	End Page	10641
Language	English	Issue	75
Country	United Kingdom of Great Britain and Northern Ireland	Volume	54
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Title	Testing, validation and optimization of SERS sensors for the detection of small molecules in cultural heritage materials	Institution name	Univerdidade de Santiago de Compostela
Instructor name	Massimo Lazzari	Expected presentation date	2021-10-01
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Title, description or numeric reference of the portion(s)	Surface enhanced Raman scattering (SERS) in the visible range on scalable aluminum-coated platforms	Title of the article/chapter the portion is from	Surface enhanced Raman scattering (SERS) in the visible range on scalable aluminum-coated platforms.
Editor of portion(s)	Gómez, Manuel; Kadkhodazadeh, Shima; Lazzari, Massimo	Author of portion(s)	Gómez, Manuel; Kadkhodazadeh, Shima; Lazzari, Massimo
Volume of serial or monograph	54	Issue, if republishing an article from a serial	75
Page or page range of portion	10638-10641	Publication date of portion	2018-09-18

Figure 1.5

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Publication Title	Plastics materials	Country	United Kingdom of Great Britain and Northern Ireland
Author/Editor	BRYDSON, J. A.	Rightsholder	Elsevier Science & Technology Journals
Date	01/01/1999	Publication Type	Book
Language	English		

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Instructor name	Massimo Lazzari	Expected presentation date	2021-10-01

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Title, description or numeric reference of the portion(s)	Effect of structure regularity, molecular stiffness and intermolecular attraction on polymer properties	Title of the article/chapter the portion is from	Relation of Structure to Thermal and Mechanical Properties
Editor of portion(s)	N/A	Author of portion(s)	BRYDSON, J. A.
Volume of serial or monograph	N/A	Issue, if republishing an article from a serial	N/A
Page or page range of portion	60	Publication date of portion	1999-01-01

Figure 1.6

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Figure 1.14

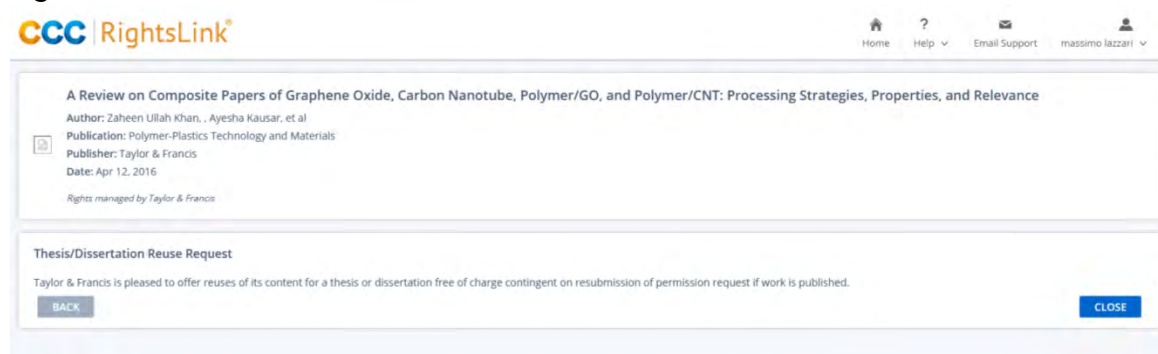


Figure 1.15



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Article Title	Rutile and its applications in earth sciences	Start Page	1
Date	01/01/1966	End Page	28
Language	Dutch	Issue	1-2
Country	Netherlands	Volume	102
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Instructor name	Massimo Lazzari		

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Editor of portion(s)	Meinhold, Guido	Author of portion(s)	Meinhold, Guido
Volume of serial or monograph	102	Issue, if republishing an article from a serial	1-2
Page or page range of portion	1-28	Publication date of portion	2010-09-01





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Article Title	A review on the synthesis of the various types of anatase TiO ₂ facets and their applications for photocatalysis	Publication Type	Journal
Date	01/01/1996	Start Page	123384
Language	English, French, German	Volume	384
Country	Netherlands		
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Title, description or numeric reference of the portion(s)	Crystal structure of anatase, rutile, and brookite	Title of the article/chapter the portion is from	A review on the synthesis of the various types of anatase TiO ₂ facets and their applications for photocatalysis
Editor of portion(s)	Jiangyong, Hu; Farahani, Mohammad Hossein Davood Abadi; Tanhaei, Mohammad; Masudy-Panah, Saeid; Katal, Reza	Author of portion(s)	Jiangyong, Hu; Farahani, Mohammad Hossein Davood Abadi; Tanhaei, Mohammad; Masudy-Panah, Saeid; Katal, Reza
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Page or page range of portion	123384	Publication date of portion	2020-03-15

Figure 1.16

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Publication Title	Physical chemistry chemical physics	Publication Type	e-Journal
Article Title	Bulk and surface phases of iron oxides in an oxygen and water atmosphere at low pressure	Start Page	1114
Author/Editor	Royal Society of Chemistry (Great Britain)	End Page	1122
Date	01/01/1999	Issue	6
Language	English	Volume	3
Country	United Kingdom of Great Britain and Northern Ireland	URL	http://firstsearch.oclc.org/journal=1463-9...
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Editor of portion(s)	Ketteler, Guido; Weiss, Werner; Ranke, Wolfgang; Schlögl, Robert	Author of portion(s)	Ketteler, Guido; Weiss, Werner; Ranke, Wolfgang; Schlögl, Robert
Volume of serial or monograph	3	Issue, if republishing an article from a serial	6
Page or page range of portion	1114-1122	Publication date of portion	2001-01-01

Figure 1.17

Functional Phthalocyanine Molecular Materials

Publication type: Book
Article: Functional Phthalocyanines: Synthesis, Nanostructuration, and Electro-Optical Applications

ISBN-13: 9783642047527
Publication Year: 2010
Publisher: Springer Berlin Heidelberg
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Language: German
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Figure 1.19

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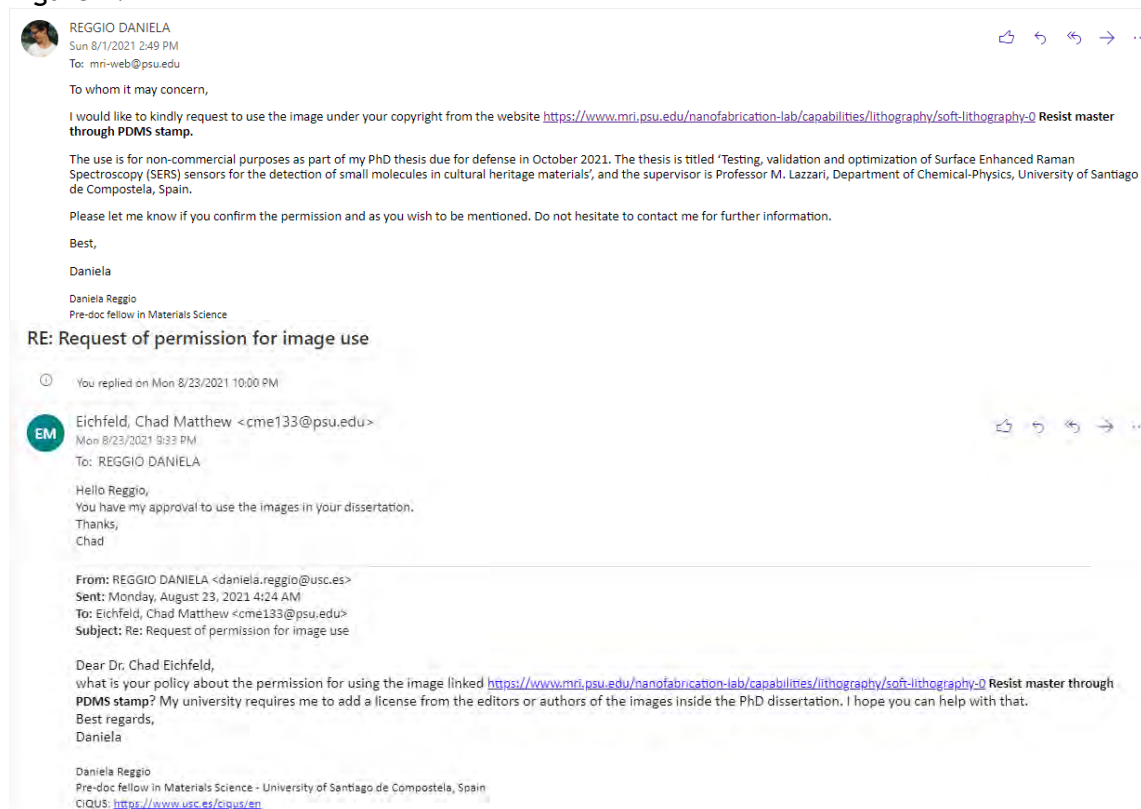


Figure 2.2

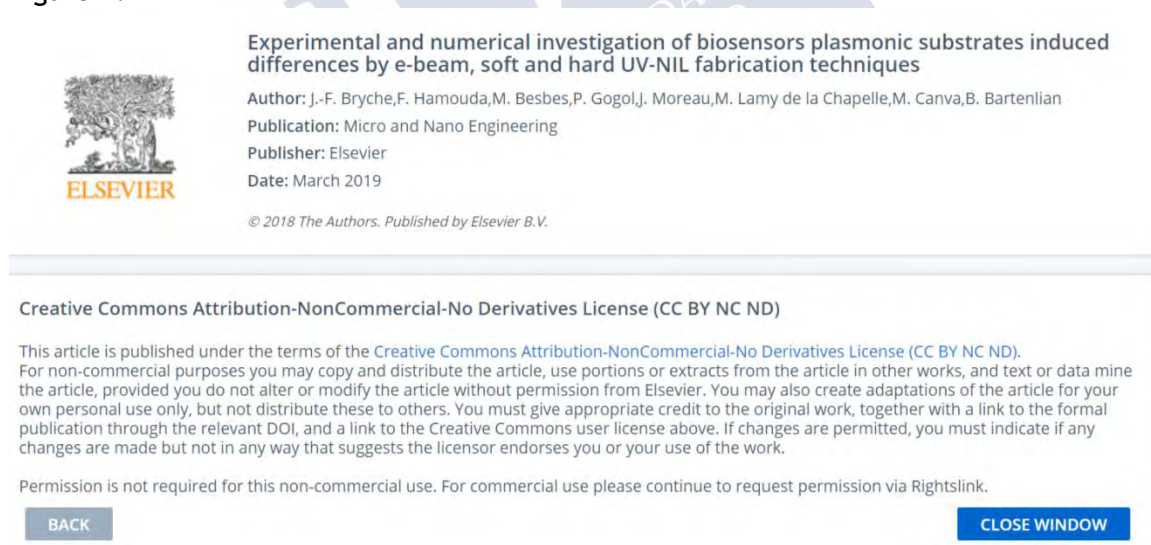


Figure 2.5

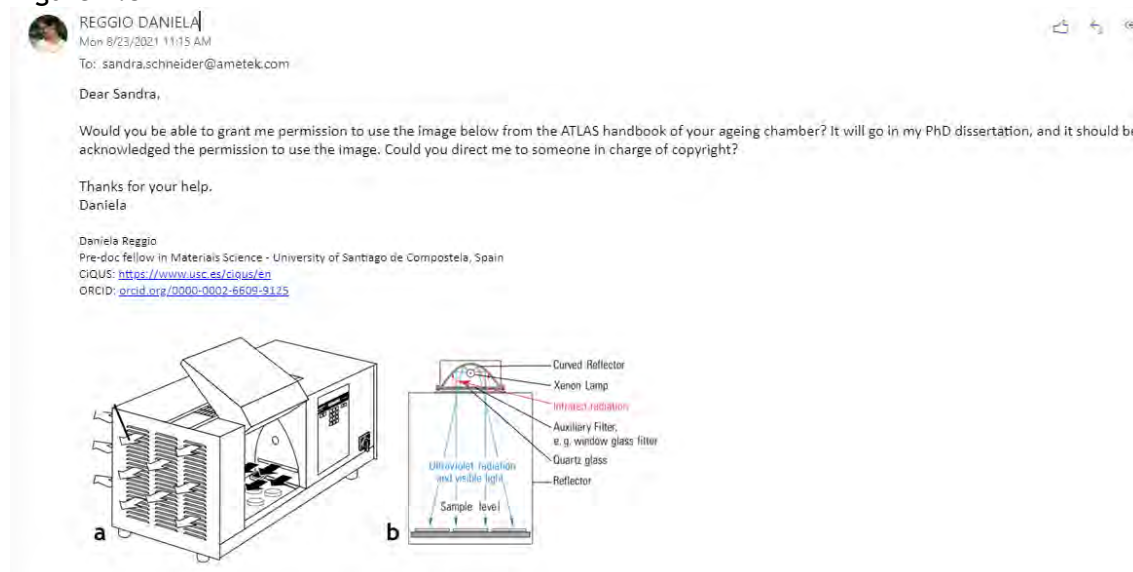


Figure 3.1



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Publication Title	European polymer journal	Publication Type	Journal
Article Title	Photopolymerization of a perfluoropolyether oligomer and photolithographic processes for the fabrication of microfluidic devices	Start Page	1118
		End Page	1126
		Issue	6
Date	01/01/1965	Volume	48
Language	English, French, German, Italian		
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Instructor name	Massimo Lazzari		
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Editor of portion(s)	Vitale, Alessandra; Quaglio, Marzia; Cocuzza, Matteo; Pirri, Candido Fabrizio; Bongiovanni, Roberta	Author of portion(s)	Vitale, Alessandra; Quaglio, Marzia; Cocuzza, Matteo; Pirri, Candido Fabrizio; Bongiovanni, Roberta
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Publication Title	ChemSusChem	Publication Type	e-Journal
Article Title	Carbon Dioxide Capture Adsorbents: Chemistry and Methods.	Start Page	1303
Author/Editor	EU ChemSoc., Società chimica italiana.	End Page	1317
Date	01/01/2008	Issue	7
Language	English	Volume	10
Country	Germany	URL	http://www3.interscience.wiley.com/jour...
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Volume of serial or monograph	10	Publication date of portion	2017-04-10
Page or page range of portion	1303-1317		

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Detection of degradation markers from polymer surfaces by a novel SERS-based strategy
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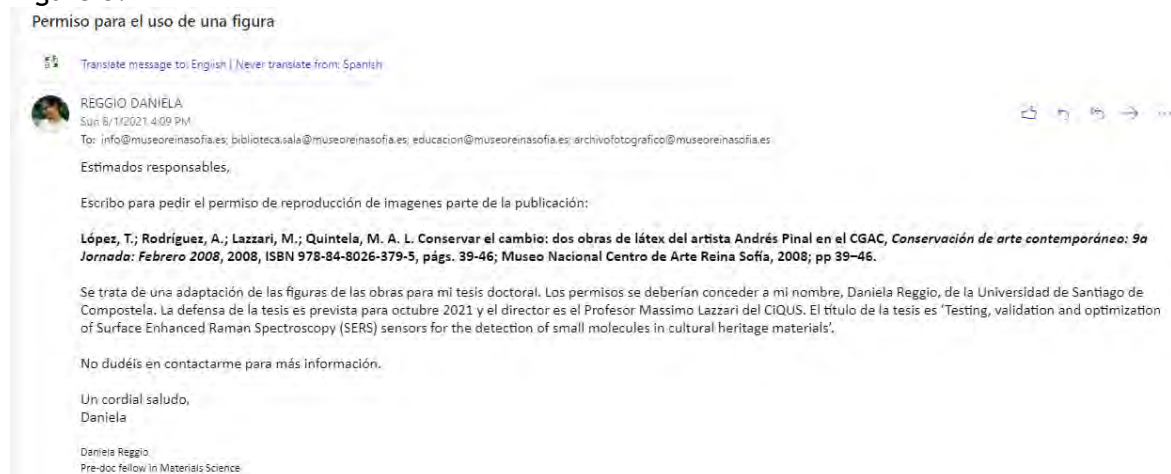


Figure 3.28 - 3.32



Figure 3.33

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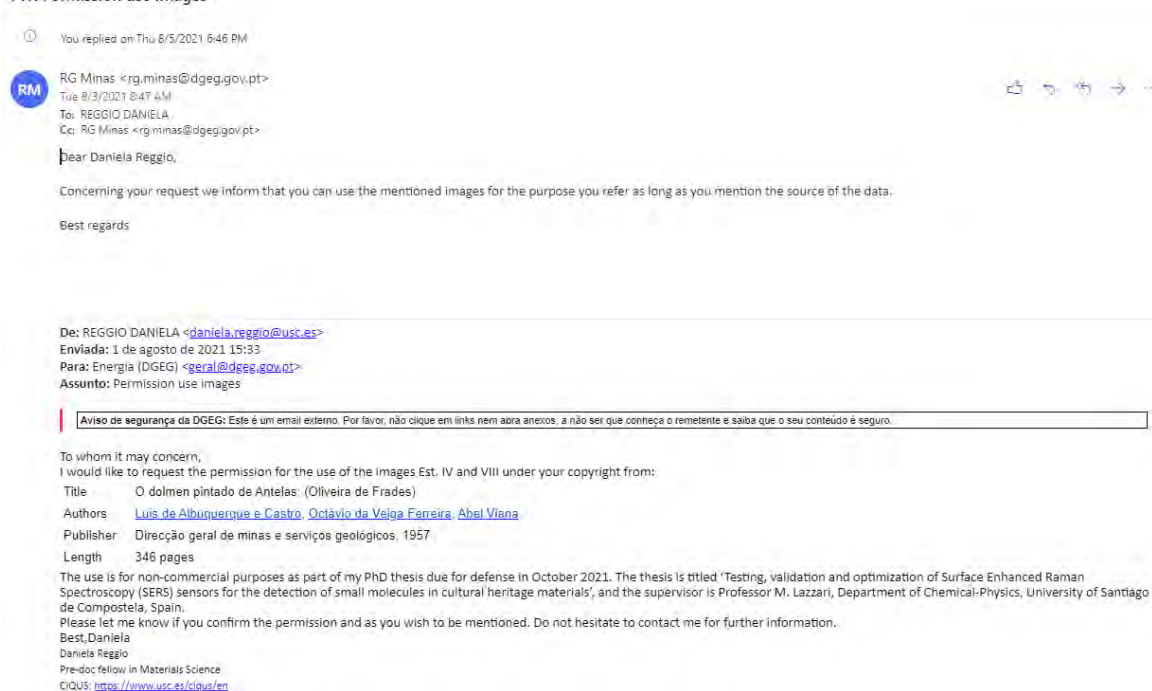


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11. LIST OF PRESENTATIONS AND PUBLICATIONS

Presentations and participations to national and international conferences:

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2. D. Reggio, D. Iacopino, M. Lazzari. ‘Multipurpose SERS substrates for nanodestructive detection of heritage collections materials‘, 10th international congress on the application of Raman spectroscopy in art and archaeology, Potsdam, Germany, <https://doi.org/10.25932/publishup-43269> (abstract), (**invited moderator & oral presentation**), Sept., 3-7, 2019.
3. D. Reggio, R. Gómez-García, M. Lazzari, Novel surface enhanced Raman spectroscopy (SERS)-active substrates for the detection of low molecular weight degradation products of polymers, 33rd The Polymer Degradation Discussion Group Conference, Malta, Sept., 1-5, 2019.
4. D. Reggio, Rapid test kit for heritage science research, VII Encontro Mocidade Investigadora, Galician University Union, Science and Technology Section, Faculty of Journalism, University of Santiago de Compostela, <https://doi.org/10.15304/9788417595289> (abstract), (**oral presentation**), May, 27-29, 2019.
5. D. Reggio, Multipurpose SERS substrates for non-destructive molecular detection in heritage collections, 6th DOC Meet Talk – Faculty of Physics, University of Santiago de Compostela, (**oral presentation**), Feb., 20, 2019.
6. D. Reggio, M. Gómez, A. Mirabile, M. Lazzari, Detection of dyes in Japanese woodblock prints and felt-tip pen drawings by a novel SERS-based strategy, NanoRestArt final conference of the EU project ‘Nanomaterials for the Restoration of Works of Art‘, National Museum of Denmark, Copenhagen, (**poster presentation**), Nov., 29-30, 2018.
7. M. Lazzari, M. Gómez, D. Reggio, ‘Aluminum-coated SERS substrates for the detection of deterioration products in plastic artworks‘, 3rd international conference on innovation in art research and technology, Parma, Italy, Mar., 26-29, 2018.

8. D. Reggio, M. Gómez, M. Lazzari, ‘SERS for polymers degradation’, 9th International congress on the application of Raman spectroscopy in art and archaeology, Evora, Portugal, **(oral presentation)**, Oct., 20-25, 2017.
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2. D. Reggio, C. Garcia, M. Gómez, M. Lazzari, and T. López-Morán, “Contemporary paints: Materials identification and fabrication techniques,” in *Conserving Cultural Heritage*, doi: 10.1201/9781315158648-47, CRC Press, 2018.
3. M. Gómez, D. Reggio, M. Lazzari, I. Rodríguez-Arias, and M. A. López-Quintela, “Nanotechnologies for contemporary art conservation: Some applications on plastics,” in *Conserving Cultural Heritage*, doi: 10.1201/9781315158648-46, CRC Press, 2018.
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