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MICRO-RAMAN CHARACTERISATION OF SILVER CORROSION PRODUCTS: INSTRUMENTAL SET UP AND REFERENCE DATABASE

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While several databases with Raman spectra of interest to silver corrosion have been published already, we present a catalogue of Raman spectra of silver compounds, which can be found on corroded silver and silver alloy objects, i.e. not only concerning archaeological and artistic works but all kind of silver items exposed to the atmosphere. The collected Raman spectra of these highly pure (>99.99%) silver compounds have been useful as references in a project concerning the identification of silver corrosion products by micro-Raman spectroscopy in the early stages of atmospheric corrosion. The instrumental conditions and parameters, the most representative spectrum, and band assignments are reported for each selected silver compound followed by some detailed comments, unlike many other collections of spectra. Since some of these compounds show low vibrational frequencies and are highly photo-sensitive, micro-Raman spectroscopy has revealed to be a suitable and non-destructive tool for their analytical characterisation.

1 Introduction

Since the IV millennium B.C. silver and its alloys have been widely used for the manufacturing of precious objects, silver staining of glasses[e.g. ref. 1], photographic technology, and electric/electronic technologies, due to their optical, electrical and mechanical properties. On the other hand, these artefacts have a natural tendency to corrosion arising from exposure to the ambient atmosphere. In the perspective of conservation and restoration of silver artefacts, which are objects of cultural interest, the identification of corrosion products and their formation mechanisms are of great importance. During scientific diagnostic assessment, scientists depict the conservation state of an object and can also – with a thorough knowledge of physical and chemical degradation processes – propose ways in which the corrosiveness of an environment may be monitored or even reduced, and which artefacts can be protected from corrosive compounds.

Several papers have been published [e.g. refs. 2, 3] concerning the identification of corrosion products on metals, their formation mechanisms and the most suitable surface analytical tools. Recently, micro-Raman spectroscopy (RM) has been applied as a surface, qualitative and non-destructive analytical technique in order to identify silver corrosion products. Apart from its non-destructive character, there is no need of sample

preparation and it provides a high spatial resolution. Moreover, micro-Raman spectroscopy is suitable to detect oxides and sulfides, whose vibrational frequencies are in the near-IR range. In this case, the analyses are not affected by interfering species (e.g. H_2O, CO_2, glass), as is the case of IR spectroscopy. Finally, portable micro-Raman spectrometers are available, which fulfill two fundamental requirements of cultural heritage diagnostics: *in-situ* measurements and portability.

Since micro-Raman spectroscopy has never been considered as a primary surface analytical technique, one of the consequences of this is the lack of adequate databases of reference Raman spectra, i.e. spectra obtained from highly pure and certified chemical species. Due to the fact that the identification and characterisation of chemical species with RM is based on the comparison between the spectrum of an unknown material with reference ones (Raman spectral fingerprinting[e.g. ref. 4]), it is evident that a poorly-documented database would thus compromise any identification.

This work is part of a project dealing with the early stages (0-48 h) of atmospheric corrosion of silver substrates: highly pure silver substrates were exposed over 24 h and 48 h to test atmospheres simulating real world atmospheric conditions and then analysed with RM. Therefore, the silver compounds were chosen as possible corrosion products arising from the interaction of the silver substrate with the atmospheric agents (gas pollutants, humidity, UV radiation, airborne particulates etc).

2 Experimental

In order to fulfil the requirements of a standard, all selected silver compounds were provided as powders by Alfa Aesar®, which guarantees >99.99% purity determined by the company with ICP/AAS (Inductively Coupled Plasma - Atomic Absorption Spectroscopy). The selected silver compounds were: silver oxide (Ag_2O), silver chloride (AgCl), silver sulfide (Ag_2S), silver sulfite and sulfate (Ag_2SO_3, Ag_2SO_4), silver carbonate (Ag_2CO_3), silver acetate ($AgCH_3COO$), and silver nitrate ($AgNO_3$). Some of them have been already studied as mineralogical species (AgCl – chlorargyrite, Ag_2S – acanthite) but the others have no mineralogical names and are not known to be products of any natural geochemical processes.

Since RM does not require any special sample preparation, the silver standards were analysed by simply spreading the powder onto a microscope slide glass without any further treatment. The instrumental system used is an integrated confocal micro-Raman system (LabRAM ARAMIS – Horiba Jobin Yvon) equipped with three internal lasers as excitation wavelenght source: Nd:YAG (532 nm), HeNe (632.8 nm) and Diode (785 nm). The spectrometer is provided with notch and edge filters for the rejection of the excitation line; the confocal microscope (Olympus, BX41) is coupled to a 460-mm focal length spectrograph equipped with a four interchangeable gratings turret. The measurements were performed using radiation at 532 nm with a real output power of 148 mW; since some silver compounds are photo-sensitive to

laser irradiation, the provided set of six density filters was used to modulate the laser power on the samples. The Olympus BX41 microscope is equipped with Leitz objectives of 10x, 50x LWD (Low Working Distance), 50x, and 100x. The samples were observed with the 10x, 50x LWD, and 100x objectives which give laser spots with a diameter of 2.60 μm, 0.87 μm, and 0.72 μm, respectively; the analysed areas were pinpointed by using a TV camera attached to the microscope. The LabRAM Aramis micro-Raman is equipped with two front-illuminated CCDs (Charge-Coupled Device) detectors, both cooled at -70°C with a Peltier cooler: Andor DU420A CCD, optimised for visible and UV spectrum, and Andor iDus InGaAs CCD, for IR range (up to 1500 nm). Acquisition and basic treatment of spectra were performed with LabSpec software (Jobin Yvon-Horiba) and OriginPro 7.5: no baseline was subtracted, neither was any smoothing operation performed on the recorded spectra.

The evaluation of the Raman spectra and the catalogues of spectra are presented by introducing the main chemical properties of each silver compound, then the most representative Raman spectrum is shown, accompanied by the experimental instrumental conditions, and finally followed by a table with the characteristic Raman shift (cm-1) assignment to the relative molecular vibrational modes. The characteristic frequencies reported in the tables are described using abbreviations providing the relative intensity or the ratio with other bands: shoulder (sh), very strong (vs), strong (s), weak (w), very weak (vw). The evaluation of the Raman spectra was based on bibliographic research and experimental considerations arising from the comparison of similar species (e.g. Ag_2SO_3-Ag_2SO_4). Comments deal with the applicability of Raman spectroscopy and the evaluation of Raman shifts.

3 Results and Discussion

As explained in the introduction, the lack of reference Raman spectra of silver compounds required a first set of analyses focused on the optimum instrumental parameters to collect well resolved and useful spectra. Initially, the selected silver compounds were analysed with all the three laser wavelengths available in order to decide which laser would be the most suitable. Based on the appearance of the spectral bands of each compound and a good signal/noise (S/N) ratio, the best excitation radiation turned out to be the Nd:YAG laser (532 nm). Thus, the further spectra were collected using the 532 nm laser modifying only the output power using the provided density filters. The change of the laser output power – by a factor of 10-1 (14.8 mW) and 10-2 (1.48 mW) - was indeed necessary due to the high photo-sensitivity of the silver compounds and their consequent decomposition. This phenomenon is related both to the d9 electronic configuration of the Ag^+ ions and to the high predisposition of silver crystalline lattices to Frenkel defects.[5]

In the reported spectra the output power, the microscope magnification and the measuring time are given.

3.1   Silver(I) Oxide – Ag₂O

The standard Ag_2O is a fine black powder (CAS: 20667-12-3), highly photosensitive towards a wide range of light wavelengths similar to the majority of silver compounds. Due to this, it was decided to use a high density filter to reduce the laser power of the Raman spectrometer in order to avoid any decomposition the Ag_2O powder and the formation of secondary chemical species related to the photo-decomposition. However, it has been decided to select a quite long measuring time (40-50 s) in order to get well-defined spectra. This was possible due as fluorescence phenomena were not probable.

The most representative Ag_2O spectrum (Fig. 1) shows a very intensive band with two peaks at 95 and 146 cm^{-1} attributed to Ag lattice vibrational modes (i.e. phonons[6]). The range between 200-580 cm^{-1} is characterised by a broad band in which it is possible to define Raman shifts at 230, 248, 342, 430, 487 and 565 cm^{-1}. The other two quite broad bands in the range of 900-1200 cm^{-1} show peaks at 933, 950, 1072 and 1100 cm^{-1}.

All the Raman signals in both ranges can be related to oxygen species but the available literature is rather dissenting; significant agreement has been reached on the bands at 430 and 487 cm^{-1} assigning them to bulk Ag_2O stretching vibrations. The same assignment has been proposed for all the bands below

580 cm^{-1} while the Raman signals at 933 and 950 cm^{-1} are generally attributed to chemisorbed atomic/molecular oxygen species.[7-9] In order to distinguish which bands are due to the bulk Ag_2O and which ones could be related to the chemisorbed oxygen species it has been decided to collect Raman spectra at shorter measuring times. By reducing the exposure time of the Ag_2O powder to the Raman laser to a few seconds (5 s) the bands related to chemisorbed species are expected not to appear. The recorded Raman spectra with short exposure times show the same bands at 933-950 cm^{-1} and 1050-1070 cm^{-1}. With respect to the Raman shift at 1100 cm^{-1}, it is evaluated as a sum peak resulting from the combination of bands at 270 cm^{-1} (Ag–O_2) and 930-950 cm^{-1} (O–O)[10]. Thus, it is proposed to assigned them also to the Ag_2O vibrational modes (Tab. 1).

3.2   Silver(I) Chloride – AgCl

Standard AgCl is a white fine powder (CAS: 7783-90-6), highly photosensitive. The silver chloride occurs naturally as a mineral named chlorargyrite. This silver compound is widely used in photography (processing paper), glass industry as a colouring agent, and in the pharmaceutical industry. Moreover, it occurs as a typical corrosion product on artefacts exposed to particular environments (e.g. inshore areas, industrial zones) or buried in soils.[11]

The Raman spectrum of standard AgCl (Fig. 2) presents bands in the range of 90-400 cm^{-1}, in particular at 95, 143 (sh), 190 (sh), 233, 345 (w), and 409 (w) cm^{-1} (see Tab. 2). Since AgCl is an ionic metal-halide compound, with a face-centred cubic lattice structure in which each Ag^+ is surrounded by an octahedron of six
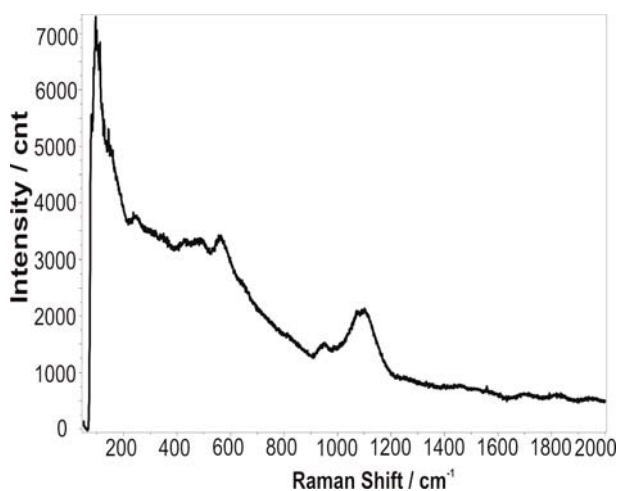

Figure 1: Raman spectrum of standard Ag_2O (14.8 mW, 10x, 40 s).

Characteristic Raman shift (wavenumber / cm-1)	Molecular bond and vibrational mode
85	Ag lattice vibrational mode
146 (sh)	
230-248	Ag-O stretching/bending modes
342	
430	
487	
565	
933-950	
1072	
1100	

Table 1: Proposed assignment for the main Raman frequencies for the standard Ag_2O powder.[7-9]
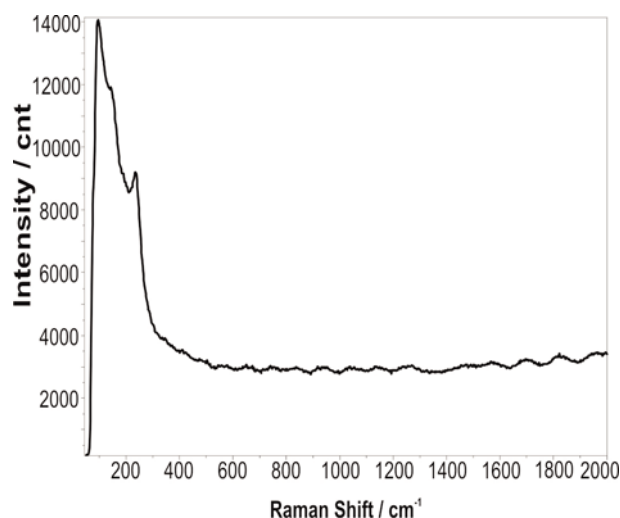

Figure 2: Raman spectrum of standard AgCl (1.48 mW, 50x lwd, 1 s).

Characteristic Raman shift (wavenumber / cm⁻¹)	Molecular bond and vibrational mode
95s	Ag lattice vibrational modes
143sh, 190sh	
233	Ag-Cl stretching modes
345	
409	

Table 2: Proposed assignment for the main Raman frequencies in standard AgCl powder-form.[7,8,13]

chloride ligands,[12] the halogen atoms may act both as bridging ligands between two silver atoms and as terminal atoms. In general, binuclear complexes such as AgCl exhibit two bands related to the stretching vibrations of the bridging halogen-metal and one due to the terminal halogen atoms stretching vibrations. It might be possible to distinguish terminal and bridging halogens since the bridging halogen has a lower stretching frequency.[7]

Possible band assignments are reported in Tab. 2.

3.3 Silver(I) Sulfide – Ag$_2$S

The standard Ag$_2$S is a fine black powder (CAS: 21548-73-2), highly photosensitive. At room temperature silver sulfide forms monoclinic crystals known to mineralogists as *acanthite*, one of the main silver ores for extracting metallic silver. On the other hand, acanthite and its phase transformations have been thoroughly studied as the most common advanced corrosion product of silver, arising from the corrosion phenomenon referred to as *tarnishing*. The corrosion mechanism for silver exposed under environments containing sulfur has been already established but the current practices to remove tarnished layers from silver items are still not satisfactory.[14]
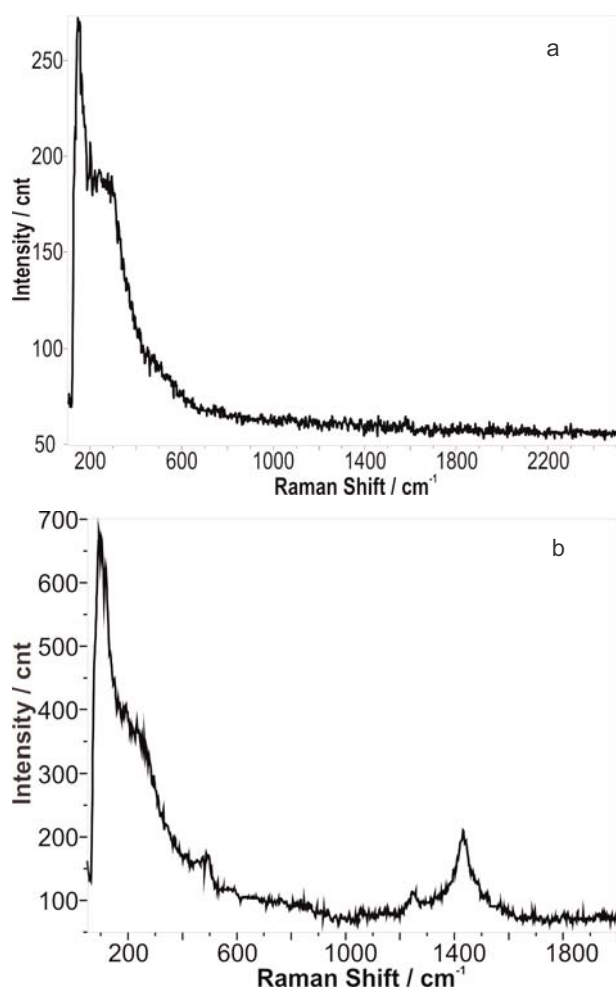
Characteristic Raman shift (wavenumber / cm^{-1})	Molecular bond and vibrational mode
93vs	Ag lattice vibrational modes
147	
188	Ag-S stretching modes
243	
273sh	

Table 3: Proposed assignment for the main Raman frequencies in standard Ag2S powder-form.[7,8,14]

With respect to the Raman spectra – since the Ag$_2$S molecule is triatomic and non-linear – the expected bands are related to the symmetric stretching mode, the only Raman-active one. The most representative Raman spectrum of Ag$_2$S is shown in Fig. 3a followed by some comments and the band assignments in Tab. 3.

The Raman spectrum of standard Ag$_2$S is characterised by intensive bands in the range of 90-300 cm^{-1}, in particular at 93, 188 and 243 cm^{-1} with a shoulder at 273 cm^{-1}. Apart from the bands related to silver lattice vibrations (i.e. phonons) at 93 and 147 cm^{-1}, the others can be assigned to Ag-S-Ag symmetric stretching mode (see Tab. 3).

An important remark has to be made about the photosensitivity of Ag$_2$S since the related photo-decomposition products could affect the Raman spectrum and the consequent evaluation. During the analysis it was observed that even changing the laser power by a factor of 10^{-2} (1.48 mW), the focused spot of the Ag$_2$S particle appeared 'burned'. In Fig. 3b another experimental Raman spectrum of Ag$_2$S collected with the laser at 532 nm, laser power 14.8 mW, and accumulation time of 7 s is shown. In comparison with the main Ag$_2$S spectrum the presence of other bands at 490, 1250, and 1435 cm^{-1} can be observed. Their appearance was noticed after analysis with high laser power or at relatively long measuring times. Thus it is proposed to assign these bands to photo-decomposition products of Ag$_2$S.

On the other hand, reducing the laser power by a lower factor implied that high resolution spectra could not be obtained (low intensities, highly noisy baseline, partial appearance of expected bands). To col-
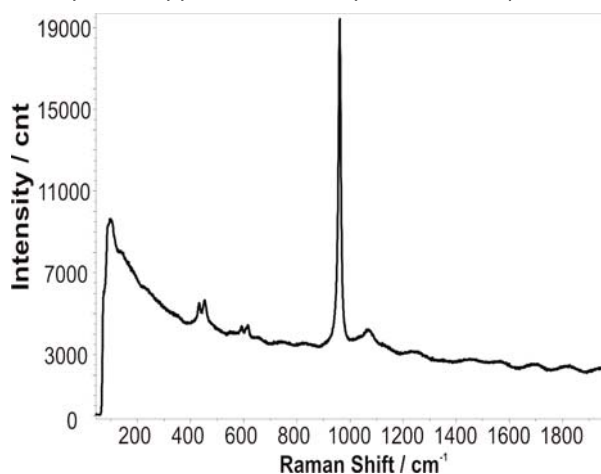

Figure 3: a) Raman spectrum of standard Ag$_2$S (1.48 mW, 10x, 5 s). Thumbnail graph: b) Ag$_2$S Raman spectrum with bands related to photo-decomposition products (14.8 mW, 10x, 7 s).

Figure 4: Raman spectrum of standard Ag$_2$SO$_3$ (14.8 mW, 50x lwd, 5 s).

Characteristic Raman shift (wavenumber / cm^{-1})	Molecular bond and vibrational mode
105s	Ag lattice vibrational modes
144sh	
460	O-S-O symm. bending (rocking)
602	O-S-O asymm. bending (scissoring)
964vs	S-O symm. stretching
1078	S-O asymm. stretching

Table 4: Proposed assignment for the main Raman frequencies in standard Ag$_2$SO$_3$ powder-form.[7,8,16]

lect useful Raman spectra a compromise between the laser power decrease (10^{-2} factor) and a short accumulation time (1-5 s) has to be struck.

3.4 Silver(I) Sulfite – Ag$_2$SO$_3$

The standard Ag$_2$SO$_3$ is a fine, white powder (CAS: 13465-98-0); the lattice primitive cell is constituted of pyramidal sulfite groups linked together by the silver atoms (ionic bonding). The coordination around one of the two non-equivalent silver atoms consists of three oxygen atoms from different SO$_3$ groups and one sulfur atom forming a tetrahedron. The other silver atom is surrounded by a very distorted tetrahedron comprising four oxygen atoms, each from a different sulfite group.[15]

As shown in Fig.4, the Raman spectrum of silver sulfite is very similar to the Ag$_2$SO$_4$ spectrum in terms of main vibrational frequencies: one intensive sharp band around 964 cm^{-1} and three other weak bands at 460, 602, and 1078 cm^{-1}. Furthermore, in the Ag$_2$SO$_3$ spectrum there is a quite strong band at 105 cm^{-1} with a shoulder at 144 cm^{-1}.

Due to this similarity it can be concluded that the Ag$_2$SO$_3$ vibrational modes are due to the presence of SO$_3^{2-}$ ions; moreover, no specific reference of Ag$_2$SO$_3$ vibrational modes was found so the analytical assignment (Tab. 4) of each band is based on other sulfite spectra,[16] counting that any shift in band position between the experimental Ag$_2$SO$_3$ spectrum and the references ones is due to the different cations bound to the SO$_3^{2-}$ group.
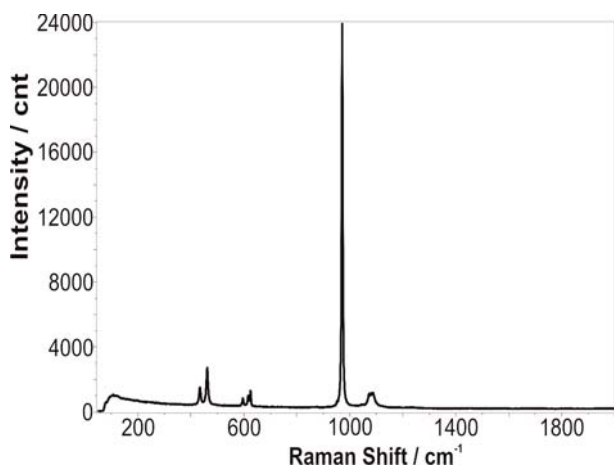

Figure 5: Raman spectrum of standard Ag$_2$SO$_4$ (14.8 mW, 10x, 1 s).

Characteristic Raman shift (wavenumber / cm^{-1})	Molecular bond and vibrational mode
432	O-S-O symm. in-plane bending (rocking)
460	
595w	O-S-O asymm. in-plane bending (scissoring)
623	
970vs	S-O symm. stretching
1079	S-O asymm. stretching

Table. 5: Proposed assignment for the main Raman frequencies in standard Ag$_2$SO$_4$ powder-form.[7,8,17]

3.5 Silver(I) Sulfate – Ag$_2$SO$_4$

The standard Ag$_2$SO$_4$ is a fine colourless powder constituted by rhombic crystals (CAS: 10294-26-5), which darken upon exposure to light. Besides its use as chemical reactant, silver sulfate occurs as corrosion product on silver substrates exposed to environments containing SO$_2$ species but the formation mechanism still has to be clarified (e.g. ref. 2). The comments about the photo-sensitivity, already introduced for the previous silver compounds, have to be considered also for silver sulfate.

The Raman spectrum of Ag$_2$SO$_4$ in Fig. 5 shows a sharp and highly intensive band at 970 cm^{-1}, two weak bands at 432 and 460 cm^{-1}, and a weak double band at 1079 cm^{-1}. In Tab. 5 the proposed band assignment is reported according to literature.[7,8,17]
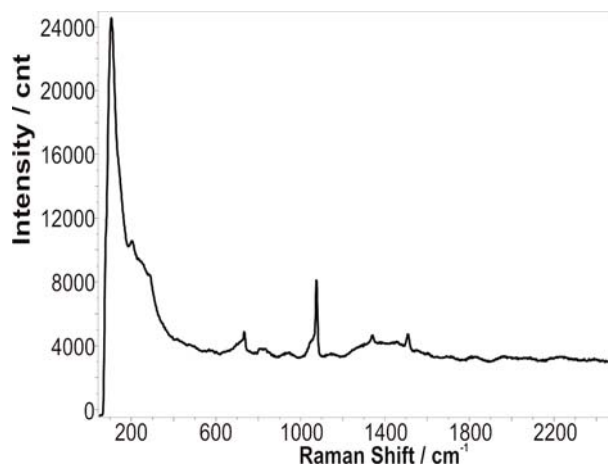

Figure 6: Raman spectrum of standard Ag$_2$CO$_3$ (1.48 mW, 50x lwd, 5 s).

Characteristic Raman shift (wavenumber / cm^{-1})	Molecular bond and vibrational mode
106vs	Ag lattice vibrational modes
204s	Ag-C stretching mode
283w	O-C-O asymm. in-plane bending
732	O-C-O in-plane bending
804	CO$_3$ out-of-plane bending (wagging)
853w	
1341	O-C-O symm. stretching
1507	O-C-O asymm. stretching

Table 6: Proposed assignment for the main Raman frequencies in the standard. Ag$_2$SO$_3$ powder-form.[7,8,19]

Due to its ionic bonds the fundamental frequencies of Ag_2SO_4 are due to the presence of SO_4^{2-} ions, while the Ag^+ ions produce a shift to lower frequencies in comparison to the unperturbed form of the anions.

3.6   Silver(I) Carbonate – Ag_2CO_3

Silver carbonate is an ionic compound (CAS: 534-17-7); in its solid state it appears as a light yellow powder when freshly precipitated, becoming darker on drying and exposure to light. This silver compound is mainly used as a reagent but it can occur also as a corrosion product, especially in combination with O_3 and UV light.[18]

Due to the ionic character of this compound, the expected bands are related to the CO_3^{2-} group and probably shifted to lower wavenumbers from the unperturbed form due to the presence of Ag^+ ions. Furthermore, the carbonate ions is a XY_3 planar molecule and has four normal modes of vibration: C-O symmetric stretching (v_1), CO_3 out-of-plane deformation (v_2, *wagging*), C-O asymmetric stretching (v_3), and CO_3 in-plane deformation (v_4, *rocking*). Differently from the previous case of the Ag_2SO_3 molecule – a pyramidal XY_3 molecule for which all four vibrations are Raman-active – the Raman-active modes of carbonate ions are v_1, v_3, and v_4.[7,8,19]

The Raman spectrum of Ag_2CO_3 in Fig. 6 shows an intensive peak at 106 cm^{-1} with a quite broad shoulder in the range of 200-300 cm^{-1}. Relatively less intensive peaks appear then at 732, 804-853, 1075, 1341 and 1507 cm^{-1}.

Apart from the bands at 106 cm^{-1} – silver lattice vibrational modes – and at 204 cm^{-1}, the other bands are related to the vibrational modes of CO_3^{2-} ions. In particular it is interesting to observe that even the band related to the CO_3 out-of-plane bending (804-853 cm^{-1}), which should be Raman-inactive, appears in the spectrum as a low intensive broad band. As already stated in the case of Ag_2SO_4, the characteristic frequencies of the CO_3^{2-} group are shifted from the documented position[7,8,19] due to the presence of the silver cations.

3.7   Silver(I) Acetate – $AgC_2H_3O_2$

Standard silver acetate occurs as a white-grayish powder (CAS: 563-63-3) constituted of needle-shaped crystals. The molecule of silver acetate is formed by the acetate ion covalently bonded to silver as an unidentate ligand; the primitive cell in the crystalline solid is a Ag_2(carboxylate)$_2$ dimer.[20] It is extensively used as a component in common pesticides, as industrial reagent and catalyst, in pharmaceutical industry and in the nanotechnology field. Moreover, silver acetate can occur as an advanced corrosion product in a galvanic corrosive process in which the acetic acid plays the role of electrolyte and the anode can be constituted by copper or lead, which are firstly affected by corrosion (e.g. silver soldered joints often suffer galvanic corrosion at the cost of copper).

As the majority of silver compounds, silver acetate is highly photo-sensitive; thus, the experimental conditions were set in order not to decompose it.
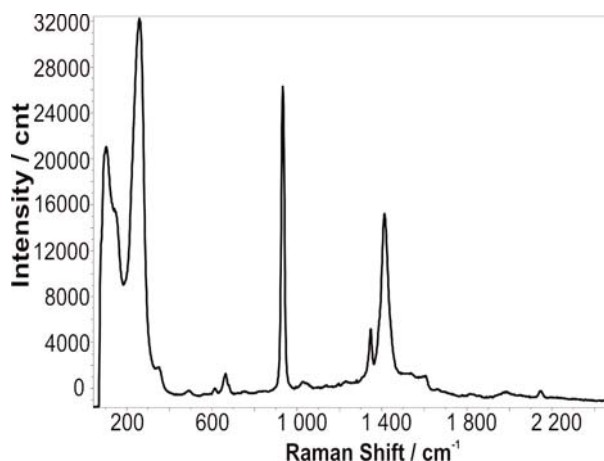

Figure 7: Raman spectrum of standard $AgC_2H_3O_2$ (1.48 mW, 50x lwd, 3 s).

Characteristic Raman shift (wavenumber / cm^{-1})	Molecular bond and vibrational mode
102s	Ag lattice vibrational modes
140sh	
258vs	C-O-Ag bending modes
341sh	
490w	
614w	C=O bending modes
664	
933s	C-CH$_3$ symm. in-plane bending (*rocking*)
1030w	CH$_3$ rocking mode
1133w	n.a.
1230w	CO-O stretching
1346	O-C-O symm. stretching
1410s	CH$_3$ symm. bending
1536	O-C-O asymm. stretching

Table 7: Proposed assignment for the main Raman frequencies in standard $AgC_2H_3O_2$ powder-form.[7,8,20,21]

The Raman spectrum of silver acetate in Fig. 7 is highly defined, showing intensive and sharp bands in the range between 100-400 cm^{-1}, related to the vibrational modes of silver lattice and to the covalent bond C-O-Ag. Further bands are related to the vibrational modes of the acetate ion but the characteristic shifts appear at lower frequencies in comparison with the unperturbed form, due to the presence of silver atoms. For instance, the symmetric (v_s) and asymmetric (v_a) stretching modes of the group COO in the unperturbed form are placed at ~1580 cm^{-1} (v_a) and at ~1415 cm^{-1} (v_s), while in the here reported Raman spectrum these vibrational modes appear at lower frequencies, such as 1536 cm^{-1} (v_a) and 1346 cm^{-1} (v_s).

3.8   Silver(I) Nitrate – $AgNO_3$

Silver nitrate is an ionic compound (CAS: 7761-88-8) in which Ag^+ ions are coordinated with the trigonal planar arrangement of NO_3 groups; in its solid state, $AgNO_3$ occurs as a white translucent powder charac-

terised by rhombic crystals. This silver salt has found application as a precursor of other silver compounds, in photographic technology, and as an antimicrobial in biological and medical field. The NO_3^- ions are isostructural to CO_3^{2-} thus the same Raman characteristic vibrational modes are expected: N-O symmetric stretching (v_1), N-O asymmetric stretching (v_3), and NO_3 in-plane deformation (v_4, *rocking*).
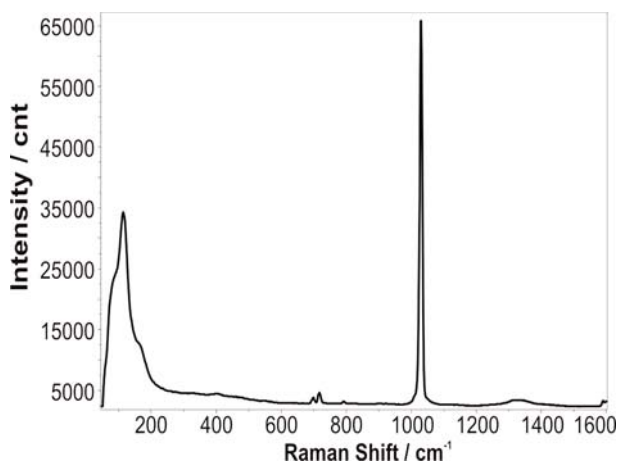

Figure 8: Raman spectrum of standard $AgNO_3$ (37 mW, 50x lwd, 1 s).

Characteristic Raman shift (wavenumber / cm^{-1})	Molecular bond and vibrational mode
95sh	
114s	Ag lattice vibrational modes
158sh	
698	Doubly degenerated N-O in-plane bending
717	
791w	N-O out-of-plane bending
1030vs	N-O symm. stretching
1330	N-O asymm. stretching

Table 8: Proposed assignment for the main Raman frequencies in standard $AgNO_3$ powder-form.[7,8,22]

Silver reference compound	Instrumental setup	Characteristic Raman shift (Wavenumber / cm^{-1})
Ag2O	14.8 mW, 10x, 40 s	95, 146, 239-248, 342, 430, 487, 565, 933-950, 1072, 1100
AgCl	1.48 mW, 50x lwd, 1 s	95, 143, 190, 233, 345, 409
Ag2CO3	1.48 mW, 50x lwd, 5 s	106, 204, 283, 732, 804-853, 1047, 1075, 1341, 1507
Ag2S	1.48 mW, 10x, 5 s	93, 147, 188, 243, 273
Ag2SO3	14.8 mW, 50x lwd, 5 s	105, 144, 460, 602, 964, 1078
Ag2SO4	14.8 mW, 10x, 1 s	432, 460, 595, 623, 970, 1079
AgNO3	37 mW, 50x lwd, 1 s	95, 144, 158, 698, 717, 791, 1030, 1330
AgCH3COO	1.48 mW, 50x lwd, 3 s	102, 140, 258, 341, 490, 614, 664, 933, 1030, 1133, 1230, 1346, 1410, 1536

Table. 9: Summary of the instrumental set-up and bands assignment for each selected silver compound.

In Fig. 8 the most representative Raman spectrum of standard silver nitrate is presented.

In Tab. 8 the proposed assignment[7,8,22] is based on the fact that any shift in the band positions is due to the Ag$^+$ ions. Apart from the intensive bands related to the Ag lattice vibrational modes and the N-O symmetric stretching mode, the v_4 double-peak appears around 700-717 cm^{-1} and, due to a clean baseline, also the v_2 peak at 792 cm^{-1} can be seen. In particular, the presence of the v_2 peak is interesting, which is Raman inactive in unperturbed NO_3^- that is caused by the high power of polarisability of Ag$^+$ on NO_3^- groups.

In Tab. 9, the proposed band assignments and the optimal instrumental set up are summarised for each selected silver compound. In particular, the possibility to collect Raman signals in the low-wavenumber region, <500 cm^{-1}, has been of fundamental importance to characterise and distinguish silver oxide, silver chloride and silver sulfide.

4   Conclusions

The corrosion products studied in this project were: Ag_2O, $AgCl$, Ag_2S, Ag_2SO_4, Ag_2SO_3, Ag_2CO_3, $AgC_2H_3O_2$, $AgNO_3$. Thus, these references can be used in future corrosion studies of both pure silver items and silver alloy ones.

It was possible to establish the most suitable instrumental parameters for the analyses of with silver powder compounds: the Nd:YAG laser (532 nm) has given the possibility to detect all the expected bands for each compound and no fluorescence occurred due to the inorganic nature of the compounds. Furthermore, it has clearly appeared that the photosensitivity of silver compounds requires a reduction of the laser output power in order to avoid the formation of secondary products related to photo-decomposition.

The collected spectra, the relative evaluation and the instrumental set-up turned out to be useful for characterisation of silver corrosion products formed on silver substrates degraded in test atmospheres. The experiments focussed on the initial stages of atmospheric corrosion, i.e. within 24-48 h of exposure. Micro-Raman spectroscopy is suitable for the detection of chemical species forming on silver substrates, giving the possibility to distinguish between the corrosion products (crystalline form) and chemisorbed species, related to the secondary processes of corrosion. Further work will focus on the extension of the reference compound library in order to deal with corrosion products and the formation mechanisms in different atmospheric conditions.

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8