

Erratum to the Influence of Gaseous Pollutants on Silver Artifacts Tarnishing, Vol. 6 (2017), 135-148

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The original online version of this article Salem, Y. (2017) The Influence of Gaseous Pollutants on Silver Artifacts Tarnishing. *Open Journal of Air Pollution*, 6, 135-148. doi: 10.4236/ojap.2017.64011 unfortunately contains grammar mistakes. The author wishes to correct the errors.

Abstract

The present work investigated the effect of common gaseous pollutants on silver artifacts. The study was carried out on coupons made of a silver alloy (91 silver and 9% copper) with chemical composition similar to ancient Egyptian silver artifacts. These coupons were exposed to gaseous pollutants such as sulfur dioxide, nitrogen dioxide, carbon dioxide, hydrogen sulfide and chlorine, each gas separately. The exposure period was four weeks inside a climate chamber with 10 PPM concentration of each gas. After each test, examinations by SEM and PM were used to evaluate the effect of each gas and observe the formed tarnish layers. The results revealed that all gases reacted with the surface except carbon dioxide. The formed tarnish layers varied in coverage and density rate, and the heaviest layer was of H₂S coupons. The tested coupons were analyzed by XRD and the results revealed Ag₂S, AgCl, Ag₂SO₄, Ag(NO₃)₃(NO)₃, AgO and Ag₂O as corrosion products.

Keywords

Silver, Artifacts, Atmospheric Corrosion, Gaseous Pollutants

1. Introduction

Archaeological silver and its alloys have relatively high resistance against atmospheric environment corrosion compared to copper and iron objects. Nevertheless, silver is susceptible to tarnish and corrosion in the atmospheric envi-

ronment especially in the presence of sulphur containing pollutants and humidity. Many corrosion products such as Ag_2S , Ag_2SO_4 , and AgCl have been identified on silver objects whether in museum environment (displayed in showcases and stored in cabinets) or excavated from the burial environment. Silver objects corrosion in the atmospheric environment attributes to the reaction with the gaseous pollutants such as chloride anions, sulfates, carbonates, and sulfides that lead to the metal dissolution [1].

Among the family of ancient metals, silver has received the fewest number of studies related to the laboratory and field exposure of the gaseous pollutants. Previous laboratory exposure tests have often focused on silver tarnish with sulfur-containing pollutants [2]-[7]. These studies were in agreement with their results which confirmed the formation of silver tarnish as a black layer of Ag_2S as a main corrosion product and Ag_2SO_4 in a negligible quantity. Few laboratory studies have included the effect of other gaseous pollutants such as Cl , NO_2 , and CO_2 , whereas the results were different and varied. The differences were as follow:

- Results of previous studies indicated that nitrogen dioxide is not considered a corrosion factor for silver and does not react with it [8] [9] [10] [11] [12]. Conversely, a previous study identified silver nitrate Ag_2NO_3 as corrosion products on exposed silver to 1.2 ppm NO_2 for 40 hours [2].
- Ag_2SO_4 as corrosion product was detected on silver coupons exposed to outdoor environment [13], although some studies indicated that silver sulfate (Ag_2SO_4) forms only in artificially high levels of sulfur dioxide [14] [15].
- Silver is sensitive to chloride and chlorine, and silver chloride is formed as a result of the reaction [10] [11] [12] [15] [16] [17]. On the other hand, a study revealed that silver chloride product was not identified on silver coupons after the exposure to an ASTM B117 salt spray chamber [18]. other previous studies mentioned that silver does not react directly with chlorine gas and the presence of silver chloride as a corrosion product is due to burial in a chloride-enriched environment [19] [20].
- Laboratory studies of the effect of CO_2 gas on silver artifacts are very few. although CO_2 is found as natural constituent and artificial pollutant in the atmospheric environment surrounding of silver artifacts. Ag_2CO_3 is distinguished as corrosion product of silver as result of the reaction with CO_2 . the formation mechanism of Ag_2CO_3 depends on the presence of strong alkaline solutions [21]. Ag_2CO_3 product has not been detected as corrosion product on the silver artifacts, whereas it was identified in a recent study on the silver coupons exposed to various outdoor environments and this product was detected only in one site distinguished as frozen desert environment [1].

The current study, the effect of H_2S , SO_2 , NO_2 , Cl , and CO_2 on silver was presented as a laboratory study and the results were compared with previous studies. NO_2 , Cl , and CO_2 gases did not undergo sufficient laboratory studies to evaluate their effect on the silver artifacts although they were common gaseous

pollutants in outdoor and indoor atmospheric environments. Hydrogen sulfide and sulfur dioxide were tested as they are the main gases in tarnishing process of silver and lead to a silver sulfide product which is distinguished as a predominant corrosion product of silver artifacts.

2. Experimental Procedures

2.1. Coupons Preparation

Silver coupons should be similar to archaeological silver of ancient Egypt civilization. Various chemical compositions were found in Ancient Egyptian Silver. The elemental analysis of a number of Egyptian silver artefacts showed that the concentration of silver was between 83% to 90% of 10 objects and between 90% to 95% of 19 other objects [22] [23]. Also analyses of Babylonian coins from a silver copper alloy were about 87% - 90% purity [21]. Therefore, the chemical composition of the experimental coupons was Ag 89.4% and Cu 10.5%. This concentration was not artificially available and was obtained by alloying a mixture of silver (pieces from the pure silver) and pure copper pieces. This mixture was melted in a crucible and then poured into a rectangular mold. The thick rectangular rod was obtained after solidification. Therefore, successive processes of annealing and drawing on a metal rolling machine were performed to obtain thin thickness about 0.8 mm (**Figure 1**) [24]. The dimensions were 3 cm × 5 cm × 0.08 cm and all coupons were holed for hanging in the test chamber, **Figure 2**. XRF analysis was used to determine the chemical composition. Five coupons were used for each test of gas.

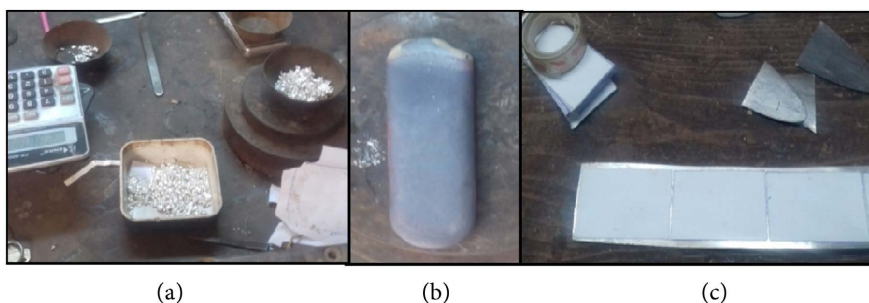


Figure 1. The preparation of silver coupons: (a) pure silver pieces, (b) the shape of the resulting rod after casting and (c) cutting the coupons after drawing and hammering processes.

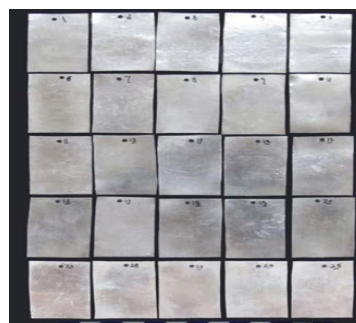


Figure 2. Silver alloy coupons before the tests.

Thin thickness of the coupons about 0.8 mm will be suitable and similar to silver artifacts thickness. Many silver artefacts were manufactured from sheets whether thick or thin such as slippers, crowns, thin sheets for royal garments, hollow statues, horse saddles items, jewellery items, funeral items, cosmetic items, and Household items of daily life including spoons, jugs, cups, vessels, pots, covered wooden object, and bowls [21].

2.2. Design and Preparation of Climate Chamber

The Climate chamber was designed according to ASTM [25]. It is made of glass with dimensions of 1 cubic meter.

Humidity inside the chamber was controlled gradually by a cup of saturated salt solution. Approximately 85% RH was obtained with a saturated solution of potassium chloride [26] and the chamber was only opened to remove the coupons. A cartridge heater was placed inside the room to heat the air if necessary. The air inside the chamber was distributed by a fan, which was hanged from the ceiling of the chamber. The temperature and relative humidity inside the chamber are continuously measured by a data logger device [27] [28]. Few studies were presented on the silver deterioration tests inside climate chamber, these studies used two types of the deterioration factors: high relative humidity [10] [29] or gaseous pollutants in the presence of high relative humidity [2] [25] [29]. Most studies of silver deterioration were carried out with corrosive solutions as deterioration factors, such as BaS 5 g/l solution for 24 hours [18], and Na₂S that was used as tarnish solution [30] [31]. Acetic acid solutions were used as simulation of emissions vapors in wooden cabinets. CuCl₂ 50 g/l for 20 min and NaCl [29] were used for AgCl patina [19].

2.3. The Test Gases

The studied gases were as follows: sulfur dioxide SO₂, nitrogen dioxide NO₂, carbon dioxide CO₂, chlorine gas Cl and hydrogen sulfide H₂S. The gas was mixed with the air inside chamber. Those gas types are the most effective in the deterioration of silver artefacts.

2.4. Test Procedures

Five coupons were exposed to humidified air (85%) containing a concentration of 10 ppm for each gas. The procedures for each test were as shown in Table 1. The test period and proportion of relative humidity, temperature, and gas concentration were chosen after a survey of such previous studies concerning ancient metals family (copper, bronze, silver, steel and lead) as shown in Table 2. Most tests shown in Table 2 were performed at room temperature (22°C - 5°C)

Table 1. Conditions and procedures of the tests.

Period	T	RH	Concentration
8 weeks	25°C	85%	10 ppm

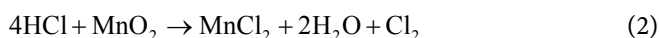
Table 2. Summarizes the laboratory exposure conditions for gaseous pollutants with ancient metals in previous studies.

Ref.	Gas	Time	Concentration	C	RH	Coupons
[32]	(OCS), H ₂ S, (SO ₂)	5 week	2.5 - 0.26 ppm 2.66 - 3.64 ppm	22°C	50%	Silver
[33]	SO ₂ , NO ₂	30 hours	10 - 22 ppm, 1.8 ppm	25°C	80% - 90%	Tin
[34]	H ₂ S	22-77 days	50 ppb, 2 ppm	30°C, 80°C	40%	Copper
[35]	(SO ₂ + NO ₂)		75 ppb SO ₂ + 120 ppb NO ₂			Copper
[36]	Acetic and formic acid vapors	One, two and four weeks.	formic acid 160 ppb, acetic acid, 170 ppb, CO ₂ 350 ppm	22°C	95%	Lead
[37]	H ₂ S, NO ₂ , Cl ₂	4, 10 days	10, 200, 10 ppb	30°C	70%	Copper
[38]	Mixture of NO ₂ , SO ₂ , O ₃		200 ppb SO ₂ , 200 ppb O ₃ , NO ₂ ppb	25°C	80%	Copper
[39]	Vapor HNO ₃	7 days	325 µg/m ⁻³	25°C	65%	Copper
[40]	Mixture of SO ₂ , H ₂ S		SO ₂ 75, H ₂ S 50 (ppb)	25°C	75%	Copper
[41]	Mixture of SO ₂ , NO ₂	10, 30, 60 hour	SO ₂ 75, NO ₂ 120 (ppb)	25°C	75%	Copper
[42]	Formaldehyde, Acetic and formic acid	135 days	0.04, 0.4, 4, ppmv	25°C	54%, 75%	Copper, lead
[43]	formic and acetic acid	21 days.	100, 200 and 300 (ppm)	30°C	100%	Copper
[44]	HNO ₃	2 weeks	126 (ppb)	25°C	65%	Copper
[45]	NO ₂ , NO ₂ + SO ₂	2 weeks	800, 800 + 800 (µg/m ⁻³)	30°C	90%	Zinc
[46]	SO ₂	4 week	10 (ppm)	25°C	90%	Copper
[47]	SO ₂ + O ₃	4 week	476 ppb + 500 (ppb)	30°C	70%	Copper
[48]	NO ₂ + SO ₂	4 week	200 + 3000 (ppb)	25°C	90%	Steel
[49]	H ₂ S	4 week	50 - 200 (ppb)	25°C	80%	Copper
[50]	SO ₂ + NO ₂	14, 21, 28 days	200 and 800 (µg/m ⁻³)	35°C	70%, 90%	Copper
[29]	O ₃	24 h	500 ppb	25°C	50%, 90%	Silver

and relative humidity between 80 - 90, whereas the gases concentration and the exposure period were various.

Cylinders with 99% concentration were used to obtain CO₂, SO₂ and NO₂ gases. The gas has flowed from cylinder into the exposure chamber after the calculation of the flow and time of the required concentration. H₂S and Cl⁻ were prepared in lab, H₂S was prepared by the reaction of hydrochloric acid with ferrous sulfide (Equation (1)) [51] and Cl⁻ prepared by the reaction of concentrated hydrochloric acid with manganese dioxide (Equation (2)) [52]. For the required concentration of H₂S and Cl, it was obtained according to the molar

volume of this concentration inside the test chamber. According to the law of Avogadro and Lussac, The molar volume occupied by the required concentration (10 ppm) inside the chamber can be calculated, Where molecular weight (one mole) of any gas under standard conditions occupies 22,400 ml (molar volume), Equation (3)) [53], Based on the molecular weight of H_2S Equation (4) which occupies 22,400 ml, the volume molar of H_2S can be calculated Equation (5).



$$1 \text{ mole of a gas at STP} = 22.4 \text{ liters of a gas} \quad (3)$$

$$2 \times 1 + 32 = 34 \text{ g} = 22400 \text{ ml} \quad (4)$$

$$10 \text{ ppm} (19 \text{ mg/m}^3) = X \quad (5)$$

Gas syringe was used to obtain the required volume and inject its into inside the chamber **Figure 3** and a small fan was used to distribute the gas inside the chamber.

3. Results and Discussion

3.1. Examination of the Samples after the Test

All coupons reacted with the gases from the first week, except the exposed coupons to carbon dioxide. The reaction behavior inside the chamber and the growth rate of the tarnish layer were similar among Cl , H_2S , and NO_2 . The reaction began as a very thin tarnish layer on the surface. The surface appearance of the coupons converted to dark gray then black film, finally. The tarnish layers of H_2S and Cl were heavy, whereas were slight with SO_2 , NO_2 as shown in **Figure 4**.

The coupons were examined after each test by visual examination, polarizing microscope, and scanning electron microscope to observe the formed tarnish

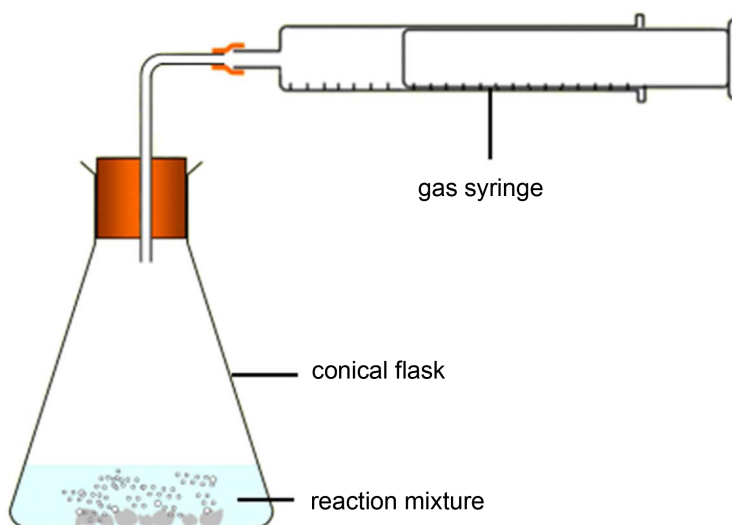


Figure 3. The syringe and the method for taking the required volume of the gas resulting from the reaction.

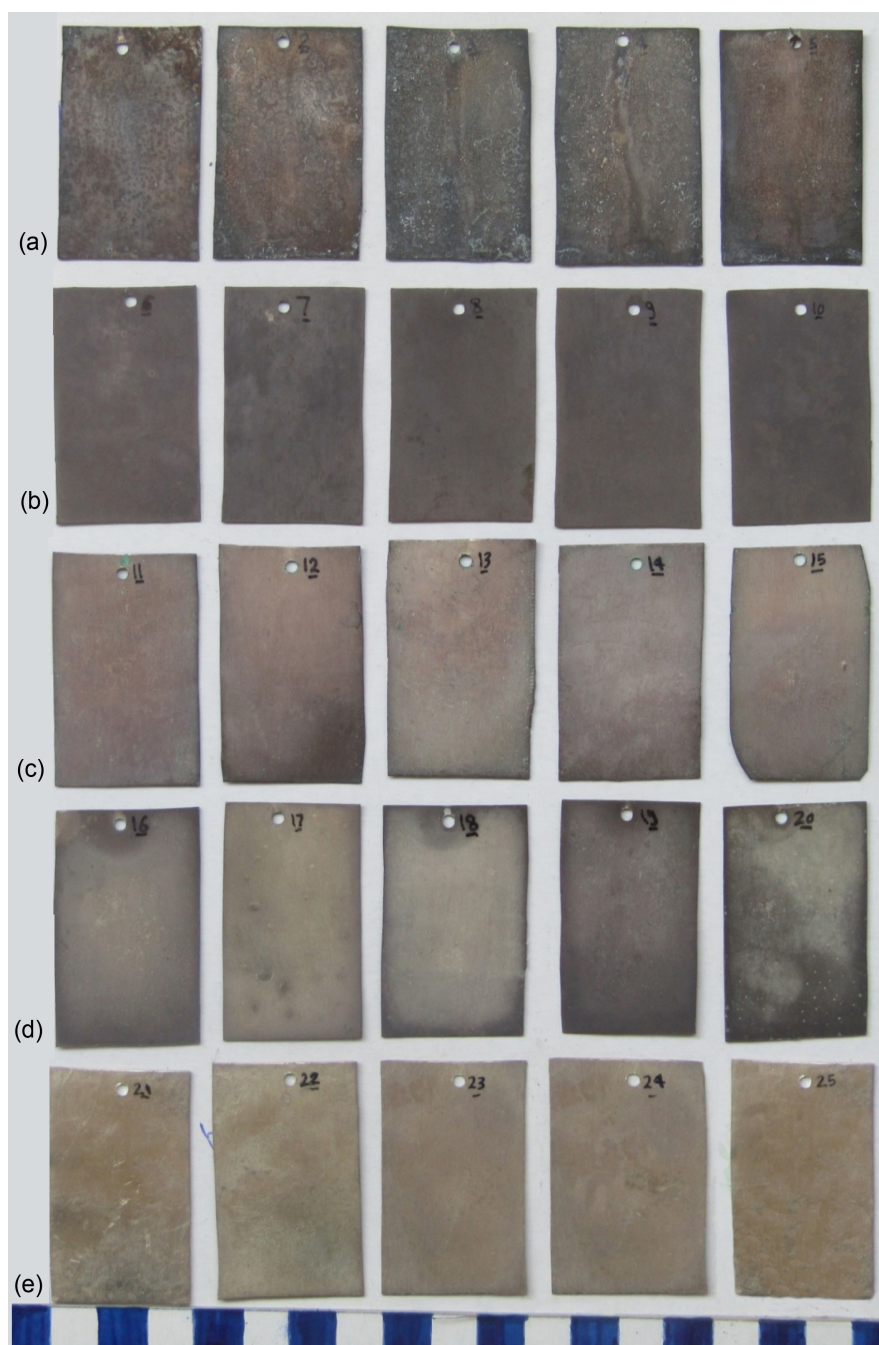


Figure 4. The coupons after the tests: (a) H_2S coupons, (b) Cl coupons, (c) SO_2 coupons, (d) NO_2 coupons and (e) CO_2 coupons.

layer and evaluate the reaction between the coupons surface and the test gases. The investigation results revealed that the thickness, density and coverage of the formed tarnish layer on the surface were differed among the coupons as shown in **Figure 5**. H_2S coupons showed heavy tarnish layer and complete coverage of the surface. Moreover, H_2S caused pitting on the coupons surface. Cl coupons were completely covered by a uniform dense layer of silver tarnish. CO_2 coupons revealed very weak effect of the gas. A slight tarnish layer with green spots was

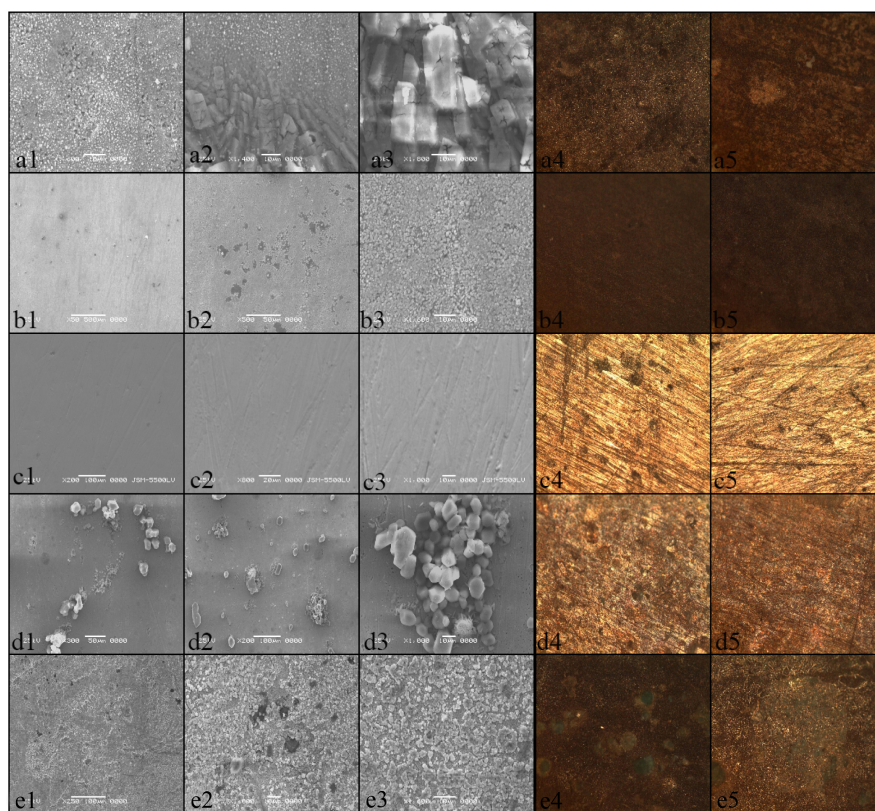


Figure 5. Investigation by SEM and polarizing microscope $\times 500$ show the most important characteristics of tarnish layer on the surface such as H_2S coupons are covered by dense tarnish layer (a1)-(a5); Cl coupons reveal a uniform and thick tarnish layer (b1)-(b5); CO_2 coupons reveal very weak effect of the gas (c1)-(c5); SO_2 coupons reveal the crystal structure of product of tarnish (d1)-(d5); Green spots on the surface of NO_2 coupons (e1)-(e5).

observed on the surface of NO_2 and SO_2 coupons and the reaction was very slow [35].

3.2. The Analysis of Corrosion Products by X-Ray Diffraction and Raman Spectroscopy

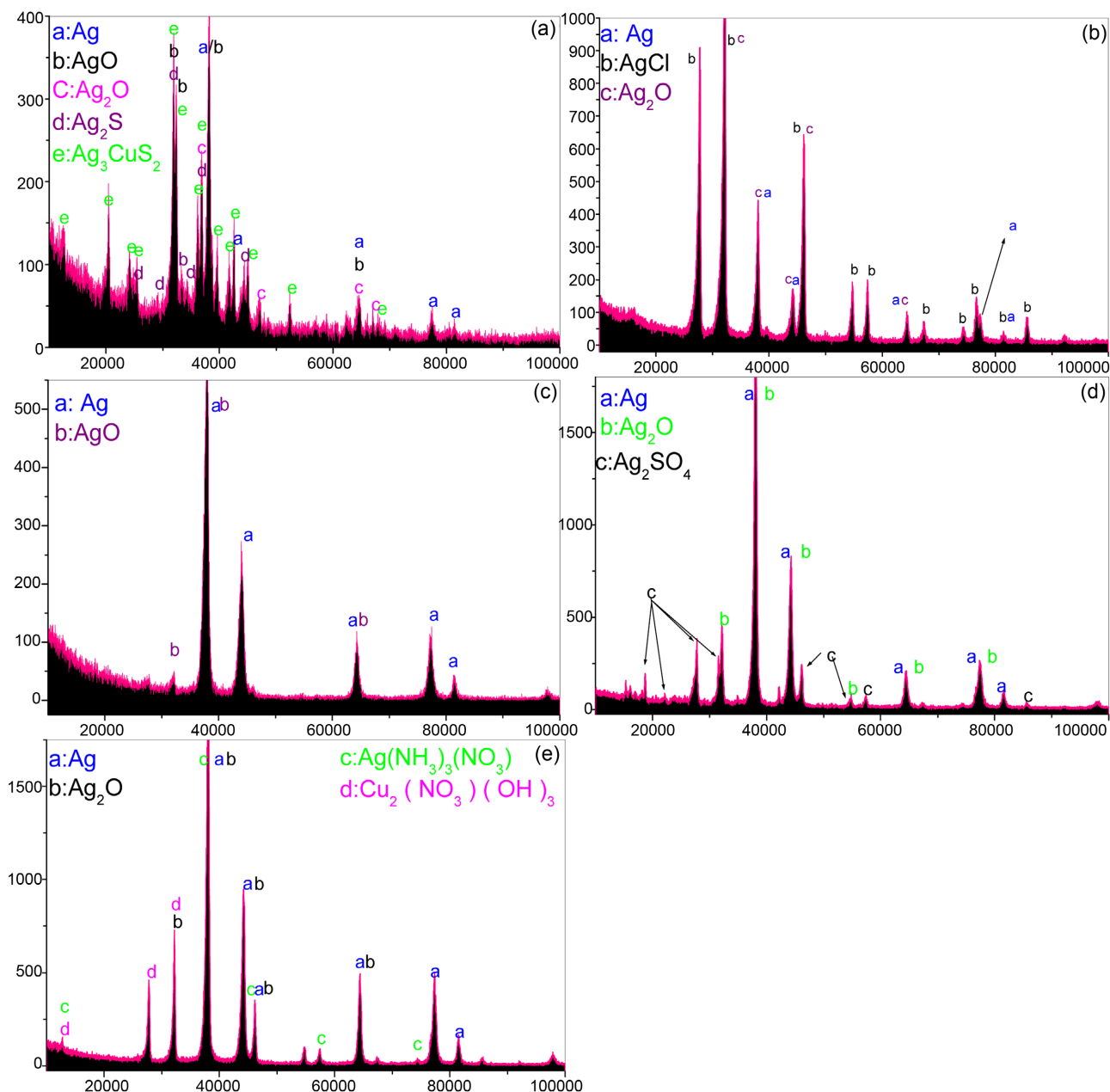
The coupons were exposed to X-ray diffraction to analyze the formed tarnish layer.

XRD results showed many of the corrosion products as shown in **Figure 6** and **Table 3**. The Raman spectrum of the tarnish formed of H_2S gas showed four intensive bands in the range of $80 - 274 \text{ cm}^{-1}$. The bands related to silver lattice vibrations were shown at 93 and 147 cm^{-1} , the others can be assigned to Ag-S-Ag symmetric stretching mode in particular at 93 , 188 and 243 cm^{-1} with a shoulder at 273 cm^{-1} [54]. The Raman spectrum confirmed XRD result because the bands revealed acanthite product **Figure 7(a)**.

The Raman spectrum of Cl gas coupon showed a sharp and high intensive band at 236 cm^{-1} and two weak bands at 145 and 349 cm^{-1} **Figure 7(b)**. These beaks are in agreement with the main beaks of AgCl bands, as reported in ref.

Table 3. Corrosion products on the coupons after the test.

SO ₂	Cl	CO ₂	H ₂ S	NO ₂
Ag Ag ₂ O Ag ₂ SO ₄	AgCl Ag ₂ O Ag	Ag AgO	Ag AgO Ag ₂ O Ag ₂ S Ag ₂ CuS ₂	Ag Ag ₂ O Ag(NO ₃) ₃ (NO) ₃ Cu ₂ (NO ₃)(OH) ₃

**Figure 6.** XRD patterns of tarnish layers on the coupons: (a) H₂S, (b) Cl, (c) CO₂, (d) SO₂ and (e) NO₂.

[54]. The tarnish layer of other gas coupons was so slight that it was not identified by Raman.

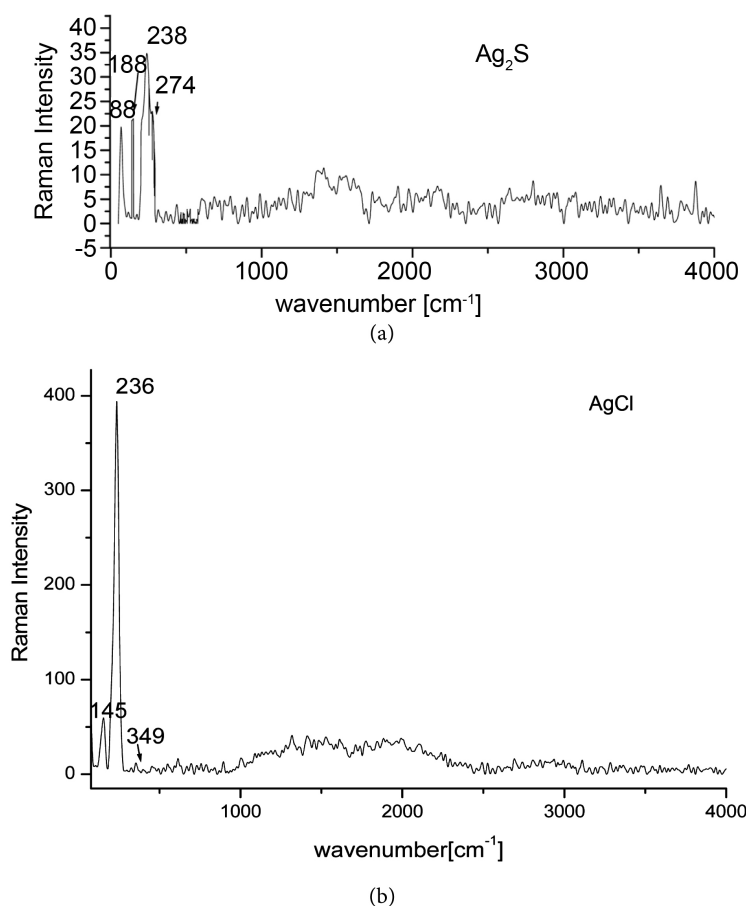
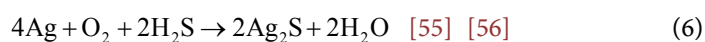
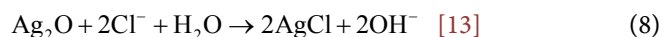


Figure 7. Raman spectrum of tarnishing of H_2S (a) and Cl (b).

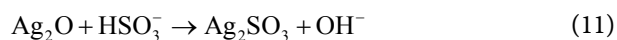
Silver sulfide (Ag_2S acanthite) is predominant product of silver artifacts and it often forms as a result of the reaction between gas H_2S and the silver surface, as shown in Equations (6) and (7).



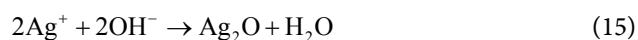
Silver chloride (AgCl Cerargyrite, chlorargyrite): the prevailing theory interpreting the formation mechanism of chloroargyrite AgCl is the transformation of Ag_2O to AgCl as shown in Equation (8) [13] [14]



Silver sulfite (Ag_2SO_3): This product was identified in a previous study as a corrosion product of silver [1]. The Equations (9)-(12) were suggested for the formation mechanism of Ag_2SO_4 on the coupons surface.



Silver oxide Ag_2O : Silver artifacts react with oxygen whether by the electrochemical reactions in the presence of humidity (Equations (13)-(15)) or in the absence of humidity (Equation (16)). Therefore, Ag_2O and AgO are often formed on silver artifacts surfaces.



Silver ammine nitrate ($\text{Ag}(\text{NO}_3)_3(\text{NO})_3$): a previous laboratory study of silver coupons exposed to NO_2 gas identified Ag_2NO_3 product as a corrosion product of silver from nitrates anions [2], Therefore, Ag_2NO_3 was expected to be a corrosion product of the tarnish layer of NO_2 gas, whereas analysis showed a Silver ammine nitrate product ($\text{Ag}(\text{NO}_3)_3(\text{NO})_3$).

Copper Nitrate Hydroxide (Rouaite, $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$): Silver and copper are the coupons alloy elements. The formation of rouaite corrosion product is contributed to selective corrosion of copper by the reaction of with NO_2 gas.

4. Conclusions

In atmospheric environment, the silver artifacts are susceptible to the reaction with several air pollutants and a black tarnish layer is formed on a surface. The tarnish layer is heavily formed in the presence of sulfur containing pollutants and other gaseous such as Cl and NO_2 .

Except for the CO_2 coupons, all tested gas coupons showed a tarnish layer which was formed on the surface as a blackish tarnish layer. The coupons of H_2S and Cl showed a sever tarnish layer, whereas the coupons of SO_2 and NO_2 showed slight tarnish layer. The XRD analysis revealed several corrosion products and Raman confirmed the identification Ag_2S and AgCl .

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Founding

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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