



Evaluating internal standards for the determination of gas phase mercury using silver nanoparticle assisted total reflection X-ray fluorescence[☆]



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ABSTRACT

Mercury was often used to protect cultural heritage specimens from damage by various pests. Over time, mercury is released into the air and access to archives may therefore need to be controlled due to the hazards associated with high gas phase concentrations of Hg. A procedure to analyze gas phase Hg using total reflection X-ray fluorescence (TXRF) was developed. TXRF is a small footprint instrument available in many laboratories. Silver nanoparticles (AgNPs) were prepared and used to sample Hg from air directly on the quartz carriers. The relative standard deviation (RSD) for the AgNP amount deposited on the carriers was on average about 10%. The efficiency and reproducibility of the Hg-capture on washed and non-washed AgNP-specimens was studied. Washed carriers had about 60% less Ag than non-washed specimens. Interestingly, the amount of Hg captured on washed carriers was significantly higher than on non-washed carriers. Calibration in TXRF is usually achieved using an internal standard (IS). However, acidic IS solutions like gallium (3% HNO₃) led to the formation of large Ag crystals and a rather poor reproducibility was observed for Ag determination using Ga as IS i.e. 10%. Alternative standard solutions having basic to neutral pH (i.e. chromate and molybdenum) were therefore tested. The TXRF results showed good reproducibility using Mo (L-lines) as IS, yielding a RSD of 2.6% mixing the standard with the AgNP solution before carrier preparation. A lower reproducibility was obtained using Cr as IS with a RSD of 4.0%. Micro-X-ray fluorescence studies on the spatial distribution of Mo and Ag in AgNP deposits with Mo IS showed a relatively even distribution of both elements over the entire area of the residue, although neither element correlated pixel by pixel. A web-like structure of Mo was overlaid by a space-filling Ag distribution, resulting in poor correlation ($r = 0.59$). The spatial distribution of Ag and Cr in AgNP deposits with Cr IS showed a significant inhomogeneity on a larger length scale. Half of the deposit was usually richer in Cr than the other half, however, the correlation ($r = 0.77$) was higher than for AgNPs with Mo IS. The addition of Mo to an already dried and washed AgNP deposits resulted in a more inhomogeneous sample ($r = 0.27$).

1. Introduction

Mercury and its compounds have often been used to prevent damage to historic or natural specimens and paintings by pests [1]. Corrosive sublimate solutions (i.e. HgCl₂) were used either saturated in sand for preparing skins [3], or as the pure chemical applied on the inside of the skin of specimens (e.g. birds) [2]. Fellowes et al. [4] reported that over time, Hg⁰ is formed from HgCl₂ and evaporates off the exhibits and herbaria, thereby releasing metallic mercury into the air [4–6]. The production of Hg⁰ originates from both bacterial activity and redox processes, but the exact pathways occurring are still subject to discussion. The mercury produced can be toxic to humans, i.e. curators and visitors, so it is necessary to analyze these exhibits and to determine

the gas phase concentrations of mercury.

Mercury has previously been determined in some museums, from gas phase sampling [4], directly on the specimens [1], and in collected dust [7]. Determination directly on specimens was carried out by using radioisotope excited X-ray energy spectrometry (REXES) [1]. Various other methods have been used on a variety of samples, including gold film [5], portable mercury vapor indicator (MVI), scanning electron microscope (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS) [4], a portable analyzer using atomic absorption spectroscopy (AAS) [8], AAS, and energy-dispersive X-ray spectroscopy (EDXRF) [7].

Briggs et al. [5] measured Hg⁰ concentrations of 25 µg/m³ at the Cambridge University Herbarium by using a MVI with a gold film, prior

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to the installation of new, improved ventilation. One year after the installation the concentrations had decreased to $4 \mu\text{g}/\text{m}^3$. The wooden cupboards where exhibits were stored was a major source of mercury, as well as the specimens themselves. Another problem is that the concentration of Hg vapor is temperature dependent. Oyarzun et al. [8] analyzed the Faculty of Pharmacy Herbarium in Madrid (Spain) during two different seasons and discovered that concentrations of Hg^0 rose significantly from late winter (23°C , $404\text{--}727 \text{ ng}/\text{m}^3$) to early summer (31°C , $748\text{--}7797 \text{ ng}/\text{m}^3$) [8]. About 80% of specimens in natural history collections evaluated by Sirois [1] have been found to be contaminated with arsenic, mercury, or both. However, only 5% of those specimens tested positive for mercury.

The toxicity of mercury is based on its physical state, with elemental liquid mercury being less toxic for humans than in the gaseous state [9]. The maximum allowed workplace concentration of gas phase mercury according to European work place regulation is $0.02 \text{ mg}/\text{m}^3$ [10].

Total reflection X-ray fluorescence (TXRF) is a small footprint, efficient micro-analytical tool currently available in many laboratories. By using TXRF, workgroups have developed different procedures to determine mercury. Ionic mercury from aqueous samples have been immobilized from wastewater using various additives [11], collected from seawater using Hg-ion selective membranes [12], and electro-deposited on niobium coated-carrier [13]. Amalgamation on a silver film was attempted to capture Hg from an aqueous solution by direct contact without adding reducing agents [15]. Silver nanoparticles (AgNPs) have been used to determine Hg in seafood samples. A reducing agent was added to the digested samples and the gas phase Hg was amalgamated on carriers prepared with AgNPs [16]. Amalgamation on gold, which is a common procedure in Hg sampling and AAS analysis, results in low sensitivities in TXRF because of spectral interferences [14].

Both internal and external calibration have previously been used for the determination of Hg with TXRF. Margui et al. [11] have used yttrium as an internal standard (IS) for the determination of Hg in waste water and external calibration curves have been used by Koulouridakis et al. [12]. Ritschel et al. [13] used a combination of both an external calibration curve and tellurium IS for the determination of Hg in water samples. Romero et al. [16], who applied the use of AgNPs as a pre-concentration step in the analysis of seafood samples, used gallium as an IS. Problems with either path of standardization were not discussed in the aforementioned studies. External calibration in TXRF usually requires full illumination of the specimens, which restricts the linear range of measurable concentrations. Prerequisite for a reliable internal calibration is the homogeneous distribution of analyte and IS, in order to be able to compensate for effects like partial illumination, dispersion of the beam, and uncovered solid angle by the detector. Here we present the optimization of AgNP synthesis and evaluation of internal standardization.

The overall aim of this work was to develop a reliable, precise, and accurate method for the analysis of gas phase mercury by using TXRF. Due to the promising results of Ag amalgamation, this method was chosen as the approach for the current study. To the best of our knowledge, no data is currently published on the determination of gas phase mercury by using amalgamation of Hg to AgNPs combined with analysis via TXRF.

2. Experimental

2.1. Chemicals

Silver nitrate (AgNO_3 , $\geq 99.9\%$) and sodium borohydride (NaBH_4 , $\geq 96\%$) used for the synthesis of AgNPs were obtained from Carl Roth GmbH & Co KG, Karlsruhe, Germany, and Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany, respectively. Aqueous solutions of AgNO_3 and NaBH_4 were prepared fresh daily. Standard solutions containing gallium ($1000 \mu\text{g}/\text{L}$ in $7\% \text{ HNO}_3$), molybdenum ($1000 \mu\text{g}/\text{L}$ in trace NH_4OH), and chromium(VI) ($1000 \mu\text{g}/\text{L}$ in H_2O) were obtained

from Inorganic Ventures (Christiansburg, Virginia, USA). HNO_3 (OmniTrace, $67\text{--}70\%$, Millipore, Darmstadt, Germany) was used for pH adjustments. All working solutions were prepared using ultrapure water ($> 18.2 \text{ M}\Omega\text{-cm}$, Purelab Flex 3, Elga Veolia, High Wycombe, UK).

2.2. Sample preparation and analysis

2.2.1. Synthesis of silver nanoparticles

For the synthesis of AgNPs, silver nitrate and sodium borohydride, were used. The synthesis of AgNPs was based on a method by Lee and Meisel [18] and modified by Romero et al. [16].

In short, aqueous AgNO_3 ($300 \text{ mg}/\text{L}$) and NaBH_4 ($400 \text{ mg}/\text{L}$) solutions were prepared. NaBH_4 (1 mL) was added to a 15 mL conical tube ($76 \times 20 \text{ mm}$, PP, Sarstedt, Nümbrecht, Germany) containing a small magnetic stir bar (Rotilabo® – mag. Stirring rods, cylindrical. PTFE-coated, $\varnothing 2 \text{ mm}$, length 5 mm , Carl Roth GmbH & Co KG, Karlsruhe, Germany). The tube was held in an ice bath (about 2°C) placed on a stir plate. The ice bath contained a second magnetic stir bar in order to prevent temperature gradients in the bath. The aqueous AgNO_3 solution was added drop by drop to the cooled NaBH_4 during stirring. When a total of 1 mL of the AgNO_3 solution had been added, the tube was closed and underwent vigorous stirring until the reaction was complete (6 min) yielding a solution with AgNPs. It is important, that the solutions are made freshly as it remains stable over one day. About 200 carriers can be prepared with one batch and can be stored for future use. The NaBH_4 is used as the reducing agent and a large excess is needed for the reducing and stabilization of the AgNPs [16,19].

After synthesis, $10 \mu\text{L}$ of the AgNP solution was placed on a quartz carrier (Bruker, Berlin, Germany) and dried at room temperature for 30 min in a clean bench to avoid contamination; these carriers were considered non-washed. Washed carriers were made in order to test if removing the non-bonded AgNPs from the carriers would change the amalgamation process. These carriers were made by taking dried carriers containing AgNPs and rinsing them cautiously with deionized water before undergoing further drying.

2.2.2. Internal standards

For the preparation of the Hg-samples, we used the AgNPs preparation method from above and prepared $n = 5$ samples. Amalgamation time was 24 h .

Three standards and HNO_3 (3%) were tested to determine the best IS for use with AgNPs adhered to quartz carriers and influence of pH on the AgNP size. An aliquot ($900 \mu\text{L}$) of the AgNP solution was added to a microfuge tube followed by the addition of a Ga standard ($100 \mu\text{L}$ of $1000 \mu\text{g}/\text{mL}$) and mixed. Ten microliters of this solution were placed on quartz carriers and dried as described above (Section 2.2.1). This was repeated for Cr(IV) ($100 \mu\text{g}/\text{mL}$) and Mo ($100 \mu\text{g}/\text{mL}$) to test their potential as IS. An additional method tested involved the addition of $1 \mu\text{L}$ Mo standard to the top of a washed carrier (after drying). For Mo in TXRF analysis, the L-line was used for quantification.

Silver nanoparticle samples with IS for micro-XRF analysis were prepared on mylar foil using the same method as for the quartz carriers, followed by mapping to obtain spatially resolved elemental distribution, with one exception: the Ga IS concentration for micro-XRF measurements was $100 \text{ mg}/\text{L}$. After measuring, the dried AgNP droplets were cut out of the foil and fixed on a quartz carrier for TXRF measurement.

2.2.3. Hg-atmosphere

2.2.3.1. Saturated atmosphere. A desiccator (DN 150, Duran Group GmbH, Germany) with two valves, one on top and one on the side, was used in order to obtain a Hg-saturated atmosphere (see Fig. S1). A pool of mercury was placed on a watch-glass at the bottom of the desiccator and mercury was allowed to evaporate into the atmosphere within the desiccator. Quartz carriers ($n = 5$) with AgNPs were then placed on the porcelain plate (DN 150, Duran Group GmbH, Germany) within the desiccator and exposed to the saturated Hg atmosphere

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