

Introduction

- Mercury and arsenic compounds were often used to prevent damage of cultural heritage specimens, e.g. herbaria and paintings [1], and over time, Hg⁰ is formed by bacterial activity and released into the air. Furthermore, mirrors made before the end of the 19th century are mostly made of mercury [2] and can release Hg⁰ (g) as well (Fig. 1).
- Mercury was determined by Radioisotope Excited X-ray Energy Spectrometry (REXES) in nine museums directly on the exhibits [1] (Fig. 2). Portable mercury vapor indicator (MVI) [4,5], SEM, XRD, XPS and ICP-MS [4] and a portable analyzer using AAS [6] have also been used on a variety of samples.
- By using total reflection X-Ray fluorescence (TXRF), workgroups have determined Hg in samples like wastewater [7], seawater [8], and other liquid samples using Au-nanoparticles [9], and seafood samples by using Ag-nanoparticles (AgNPs) [10].
- There are no more references for the determination of Hg⁰ (g) by using TXRF.



Fig. 1: Mercury Mirror [3]

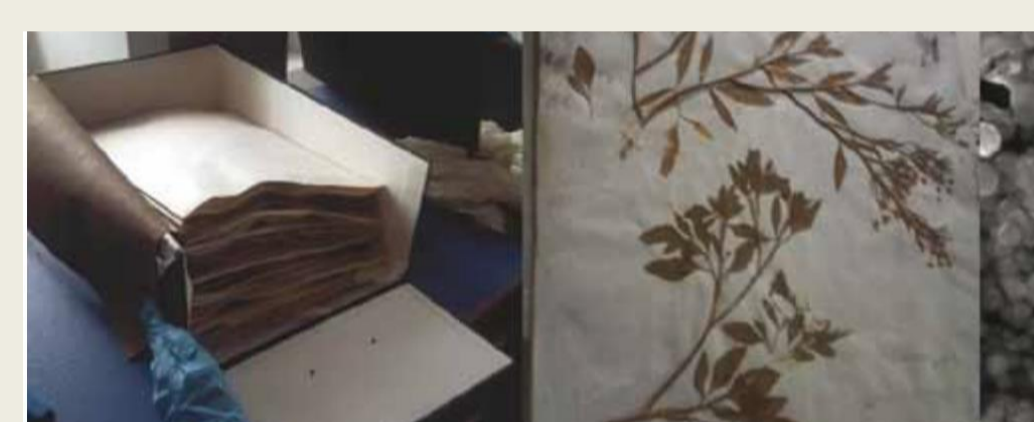


Fig. 2: Hg treated examples [2]

Objective and Experimental

- The aim is to develop a reliable, precise and accurate analysis of gas phase Hg⁰ using TXRF, a small footprint and efficient micro-analytical tool.
- Chemicals and instrumentation needed are in general already available in laboratories using TXRF for elemental analysis. A special set-up is not necessary.
- Applied was a procedure to enrich Hg⁰ (g) on AgNPs and determine its concentration by using TXRF.
- A S2 Picofox (Bruker, Germany) is used for TXRF. To optimize sample preparation procedures, as well as provide reliable and accurate determination, a custom built μ -XRF instrument was used [11].
- AgNPs are produced using AgNO₃ and NaBH₄. Different procedures of preparation and determination were tested: rinsing of deposits after the drying process; absolute determination and internal standards (i.e. Ga, Cr and Mo).

Specific aims and challenges

- Specific aim 1:
- reproducible production of AgNPs having good Hg capture efficiency.
- Specific aim 2:
- accurate determination of active Ag and absorbed Hg.
- Challenge:
- change of Ag surface due to pH change when Internal Standard (IS) is added (Fig. 3).

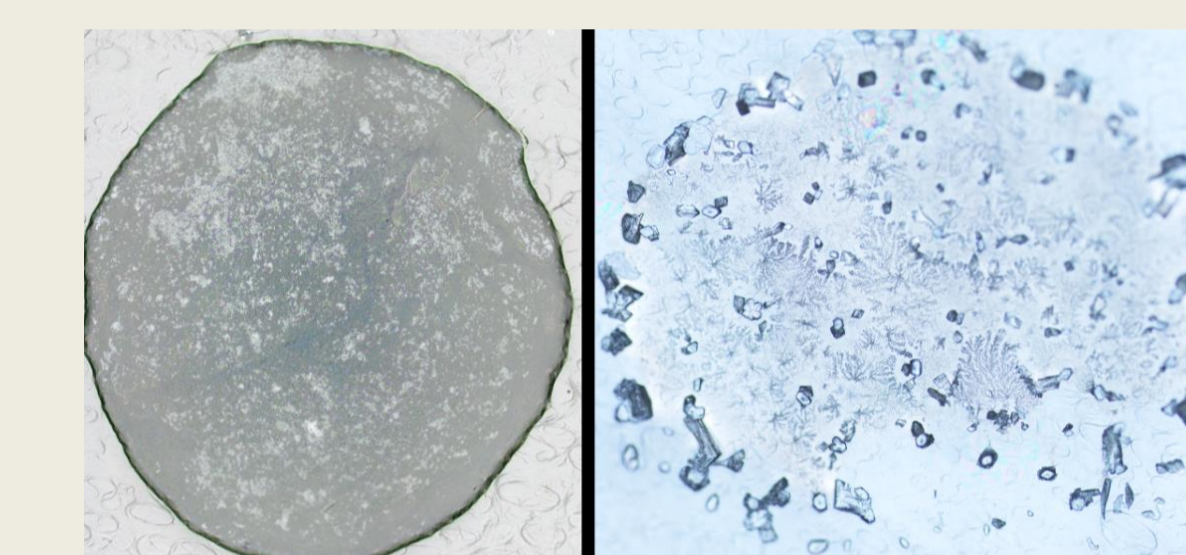


Fig. 3: Ag-NPs under light-microscope (left: Ag-NPs normal (10 μ L); right: Ag-NPs (9 μ L) + HNO₃ 3% (1 μ L))

Results: Optimization of the Ag-NP preparation method

- The Ag-NPs were dropped on a Quartz-carrier and left in a saturated atmosphere of mercury and left there for 24 h (Fig. 4).

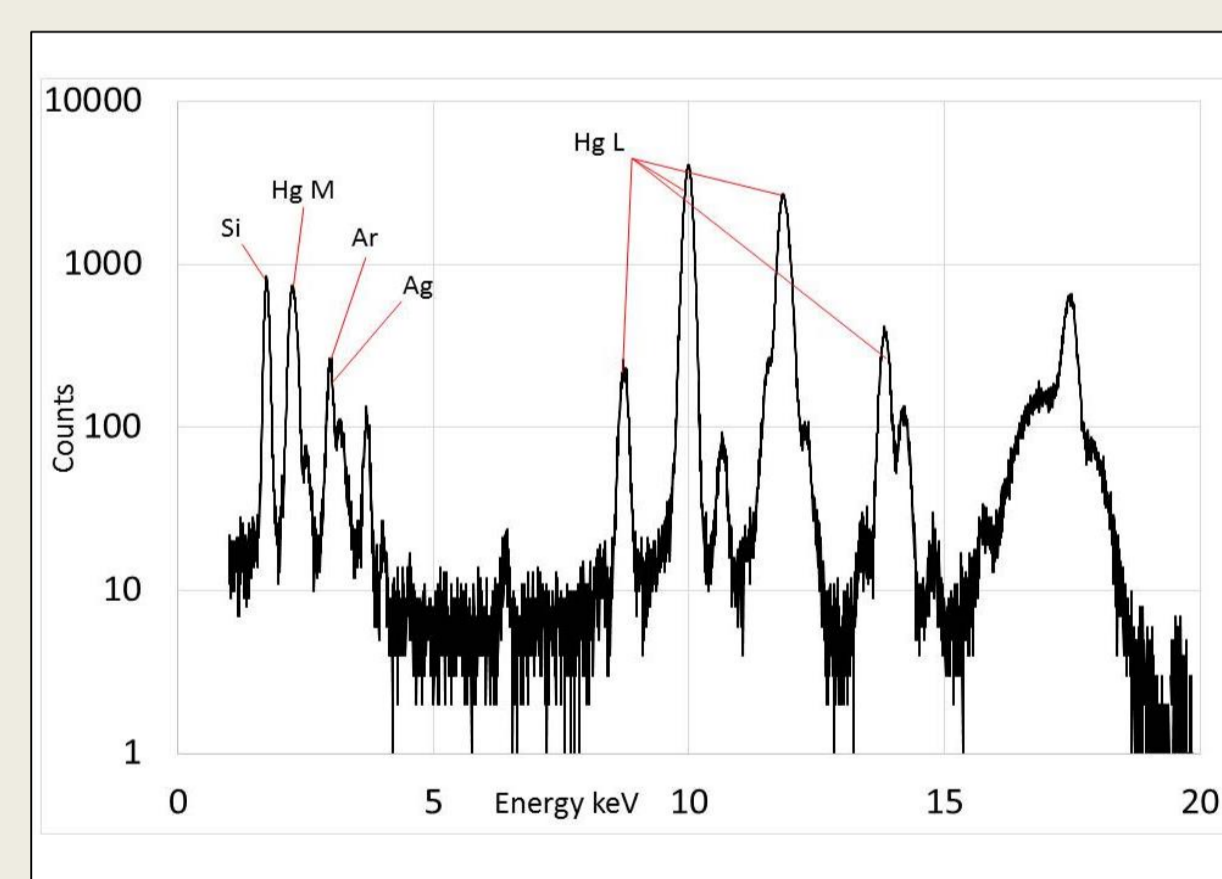


Fig. 4: Quartz-carrier left for 24 h in sat. atmosphere

Tab. 1: results relation of Hg and Ag

	Ave. Absolute Ag [ng]	Ave. Absolute Hg [ng]	Ave. Hg/Ag
Non-washed Ag-NPs	67	0.5354	0.00085
Washed Ag-NPs	45	6.09396	0.01379

- Efficiency and reproducibility of the Hg-capture of washed and non-washed AgNP-specimens were studied. Per batch, the standard deviation of Ag in average was about 10 %. Washed carriers had about 60% less Ag than non-washed specimens. Interestingly, Hg capture of the washed carriers was significantly higher than of the ones that were just dried (Tab. 1).

μ -XRF evaluation of internal standards & conclusions about homogeneity

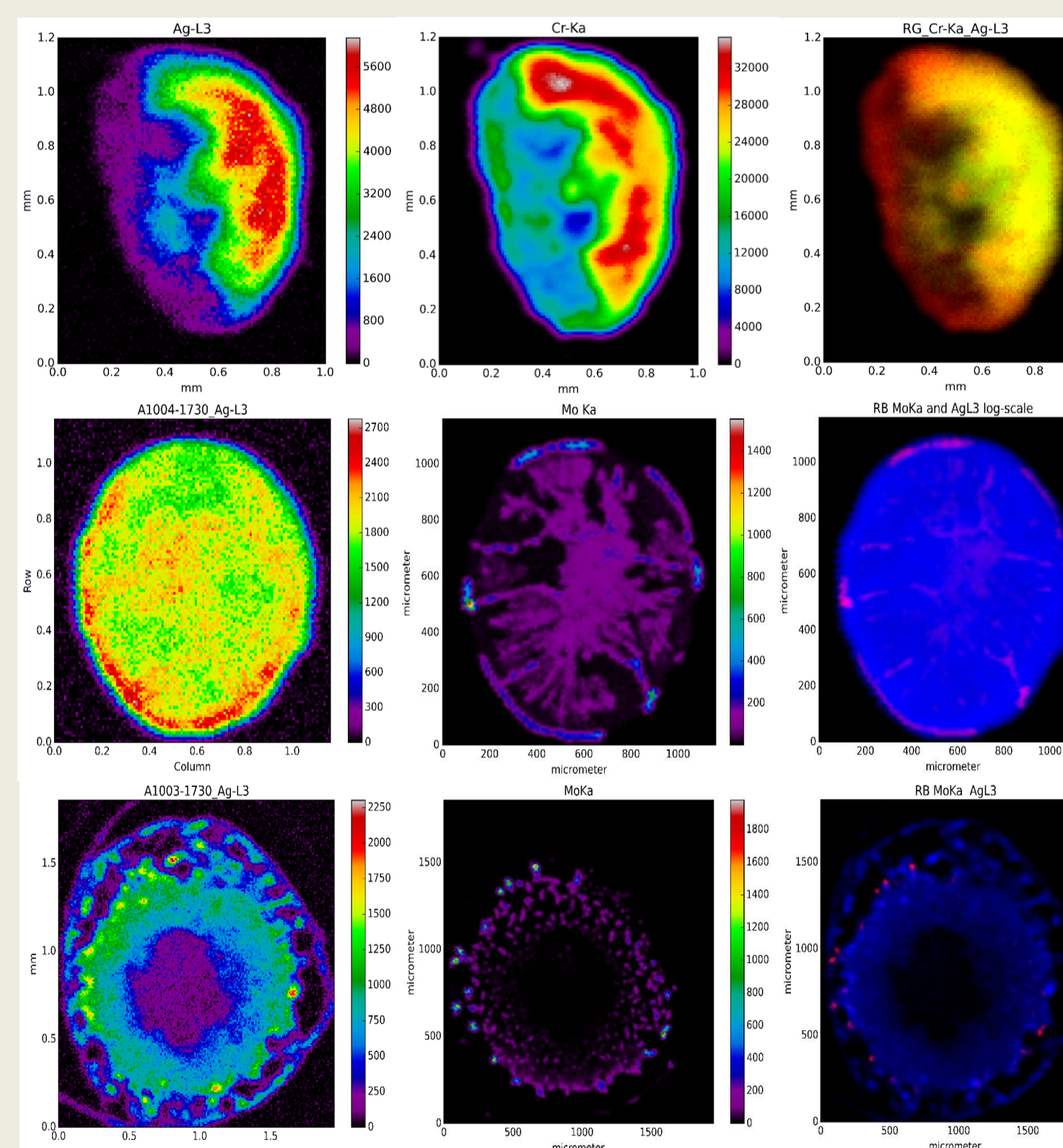


Fig. 5: micro-XRF images of elemental distribution first column of the Ag L-line, second of the internal standard (scale is given in counts) and third the RGB image of both elemental lines (the color intensity scaled between 5- and 80 % of the max. counts). First row Ag and Cr (not washed), second row Ag and Mo (not washed), third row Ag washed and Mo.

Tab. 2: relation Ag with Cr and Mo as internal Standard and deviation of different areas

	Ag/IS and amount of Ag [mg/L] total deposit	Ag/IS and Ag [mg/L] area A	Ag/IS and Ag [mg/L] area B	Ag/IS and Ag [mg/L] area C	Ag/IS and Ag [mg/L] area D	Max. Deviation from total [%]
Ag and Cr (not washed)	7.92; 113.7	12.2; 73.8	6.27; 143.6	7.88; 114.3	7.88; 114.2	35
Ag and Mo (not washed)	0.033; 962	0.033; 976	0.035; 924	0.035; 926	0.032; 987	4
Ag washed and Mo	0.041; 776	0.047; 683	0.03; 926	0.053; 607	0.035; 908	22

- The Cr-STD is not homogeneous and gives different results, dependent which side is irradiated (Tab. 2, Fig. 5, Fig. 6).
- The Mo-STD is more homogeneous and gives better results, than the Cr-STD (Tab. 2, Fig. 5).
- The washed AgNP deposit with successive Mo-STD addition shows higher inhomogeneity.

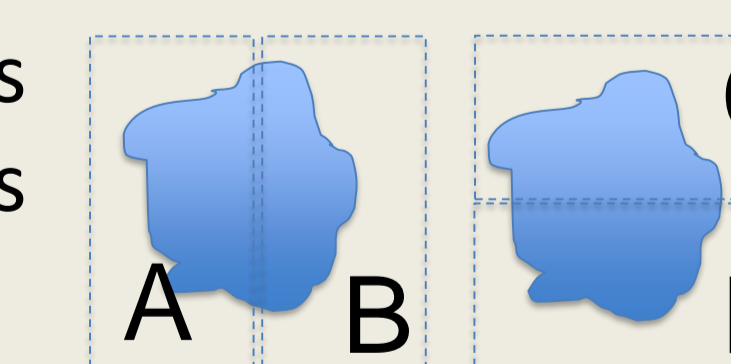


Fig. 6: different angles for the X-ray beam

Conclusion & Outlook

- As the washed deposit are very thin – using an external calibration curve (Ag) will be tested.
- Next aim is to correlate gas phase Hg concentration to Hg concentrations captured on the AgNPs in well-defined control environments.
- After that, the next step is to test a Hg-contaminated room (e.g. in a museum) and Hg-mirrors to determinate the Hg under field conditions.