

### Introduction

- > Mercury and arsenic compounds were often used to prevent damage of cultural heritage specimens, e.g. herbaria and paintings, [1] and over time, Hg<sup>0</sup> is formed by bacterial activity and released into the air. Furthermore, mirrors made before the end of the 19<sup>th</sup> century are mostly made of mercury [2] and can release Hg<sup>0</sup> 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 other samples like wastewater [7], seawater [8] other liquid samples using Au-nanoparticles [9] and seafood samples by using Ag-nanoparticles (AgNPs) [10].
- $\succ$  There are no more references for the determination of airborne Hg by using TXRF.

## **Results: Optimization of the Ag-NP prepar**ation 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).



Tab. 1: results relation of Hg and A

	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

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

Efficiency and reproducibility of the Hg-capture of washed and nonwashed 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).



Europa-Universität Flensburg Institut für mathematische, naturwissenschaftliche und technische Bildung Abteilung für Chemie und ihre Didaktik



**Contact:** Sebastian Böttger

Dr. Ursula Fittschen ursula.fittschen@wsu.edu

# **Determination of airborne mercury using Ag-nanoparticles assisted TXRF**

### S. Böttger<sup>a,b</sup>, D. Rosenberg<sup>b</sup>, M. Busker<sup>b</sup>, W. Jansen<sup>b</sup>, U. Fittschen<sup>a\*</sup>



Fig. 1: Mercury Mirror [3]



Fig. 2: Hg treated examples [2]

## **Objective and Experimental**

- analytical tool.
- set-up is not necessary.

- standards i.e. Ga, Cr and Mo.

4	g	





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.

### **Acknowledgements and References:**

sebastian.boettger@uni-flensburg.de

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<sup>a</sup> Chemistry Departement, Washington State University, Pullman, WA 99163 <sup>b</sup> Departement of Chemistry and Chemistry Education, Europa-Universität Flensburg, Flensburg, Germany, 24943

> The aim is to develop a reliable, precise and accurate analysis of airborne Hg using TXRF, a small footprint and efficient micro-

 $\succ$  Chemicals and instrumentation needed are in general already available in laboratories using TXRF for elemental analysis. A special

> Applied was a procedure to enrich the airborne mercury 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  $\mu$ -XRF instrument was used [11].

 $\succ$  AgNPs are produced using AgNO<sub>3</sub> and NaBH<sub>4</sub>. Different procedures of preparation and determination were tested: rinsing of deposits after the drying process; absolute determination and internal

Specific aim 1:  $\succ$  reproducible production of AgNPs having good Hg capture efficiency.

Challenge: change of Ag surface due to PH change when Internal Standard (IS) is added (Fig. 3).

### **μ-XRF evaluation of internal standards & conclusions about homogeneity**

	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. Dev from tot
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

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

- > 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.

**B** 

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

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- [4] FELLOWES et al., Journal of Hazardous Materials, 189 (2011), 660-669

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### **Specific aims and challenges**

### Specific aim 2:

 $\succ$  accurate determination of active Ag and absorbed Hg.



Fig. 3: Ag-NPs under light-microscope (left: Ag-NPs normal (10 μL); right: Ag-NPs (9 μL) + HNO<sub>3</sub> 3% (1 μL)

### **Conclusion & Outlook**

- viation tal [%]
- > As the washed deposit are very thin – using an external calibration curve (Ag) will be tested.
- $\succ$  Next aim is to correlate Hg airborne concentration to Hg concentrations captured on the AgNPs in well-defined control environments.

 $\succ$  After that, the next step is to test a Hg-contaminated room (e.g. in a museum) and Hgmirrors to determinate the Hg under field conditions.

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