

Introduction

Mercury and arsenic compounds were often used to prevent damage to cultural heritage specimens, e.g. herbaria and paintings [1]. Over time, Hg⁰ air borne is formed. The pathway comprises bacterial activity and redox processes and is still subject of discussion.

Mercury has previously been determined by REXES directly on specimens [1]. Portable mercury vapor indicator (MVI) [3,4], SEM, XRD, XPS and ICP-MS [3], 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 [6], seawater [7], and other liquid samples using Au-nanoparticles [8], and in seafood samples by using Ag-nanoparticles (AgNPs) [9]. To the best of our knowledge no data is published for the determination of gas phase Hg by using the AgNP-TXRF approach.

Objective and Experimental

The aim was to develop a reliable, precise, and accurate analysis of gas phase Hg by using TXRF.

- Chemicals and instrumentation needed are generally already available in laboratories using TXRF for elemental analysis, and a special setup is therefore not necessary.
- Enrichment of the gas phase Hg on AgNPs was performed and Hg concentrations were determined using a S2 Picofox TXRF (Bruker, Germany).
- A custom built micro-X-ray fluorescence spectrometer (μ -XRF) was used [10] for the optimization of sample preparation procedures, as well as provide reliable and accurate Hg determination.
- AgNPs are produced using AgNO₃ and NaBH₄. Different procedures of preparation and determination were tested: rinsing of deposits after the drying process; absolute determination; internal standards and external calibration curves.

Results from AgNP method optimization

Optimization of the Ag-NP preparation method

The AgNPs were dropped on a Quartz-carrier and placed in a Hg saturated atmosphere and allowed to equilibrate for 24 h (Fig. 1).

Efficiency and reproducibility of the Hg-capture of washed and non-washed AgNP-specimens were studied (Table 1). The average standard deviation of Ag was ca. 10 % within a batch. Washed carriers contained ~60% less Ag than non-washed carriers. In addition to lower Ag levels, method optimization also resulted in increased Hg capture on washed carriers.

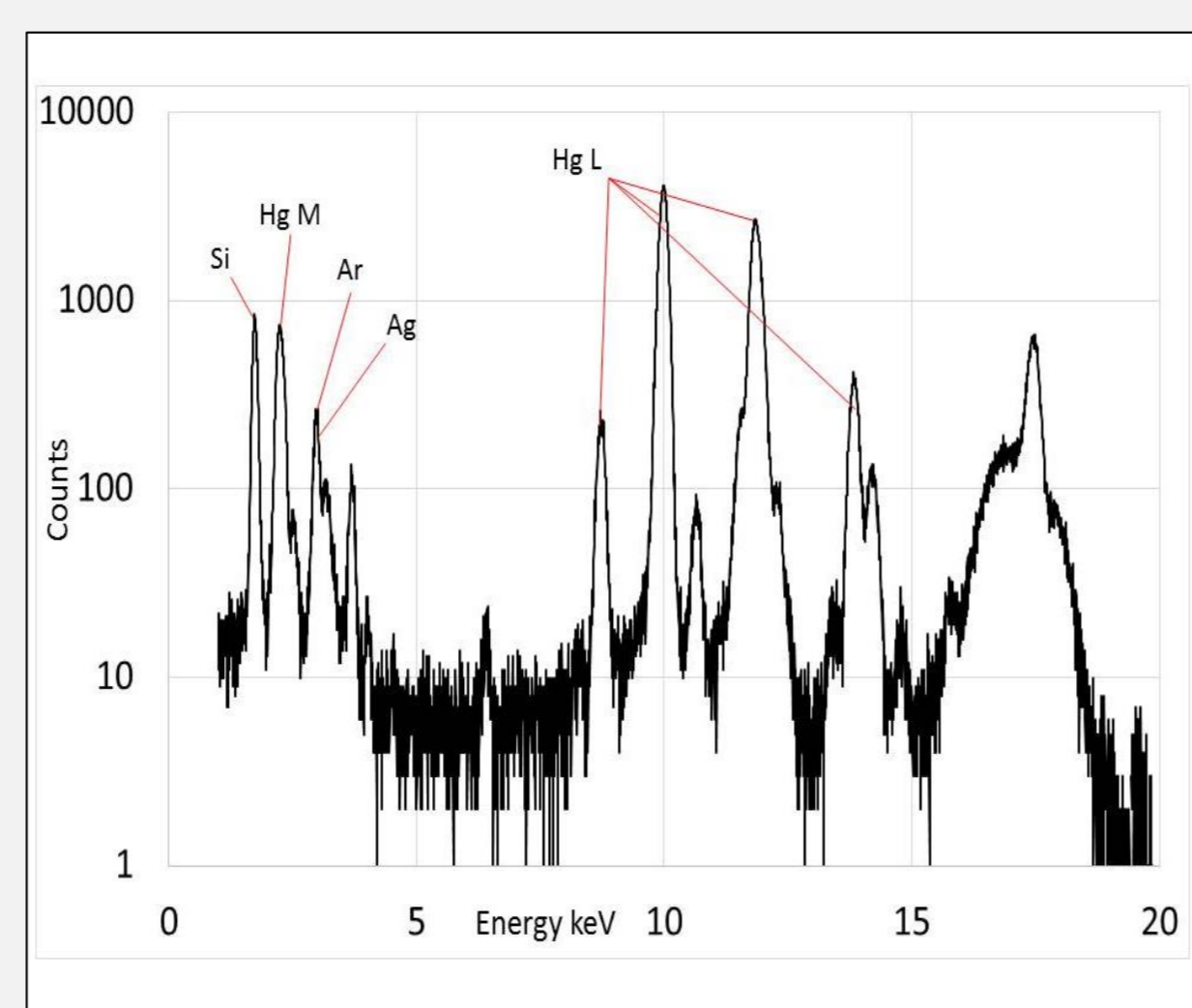


Fig. 1: Quartz-carrier with 10 μ L of the AgNP allowed to equilibrate for 24 h in an Hg-saturated atmosphere.

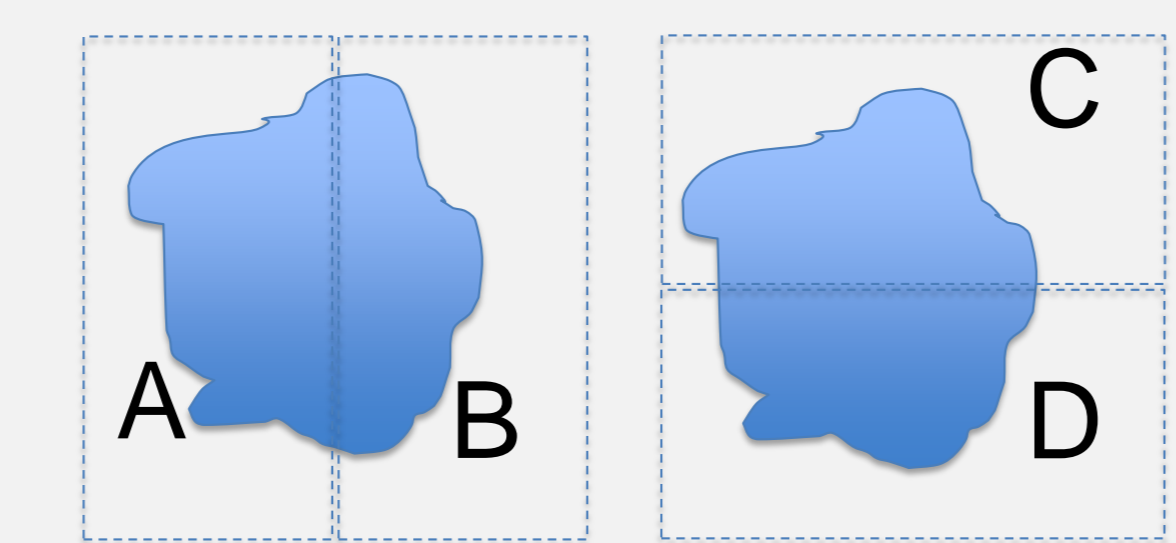


Figure 2: Different angles for the X-ray beam (Table 1).

Treatment	Ave. Absolute Ag [ng]	Ave. Absolute Hg [ng]	Ave. Hg/Ag
Non-washed AgNPs	67	0.5354	0.0085
Washed AgNPs	45	6.09396	0.01379

μ -XRF evaluation of internal standards and conclusions about homogeneity

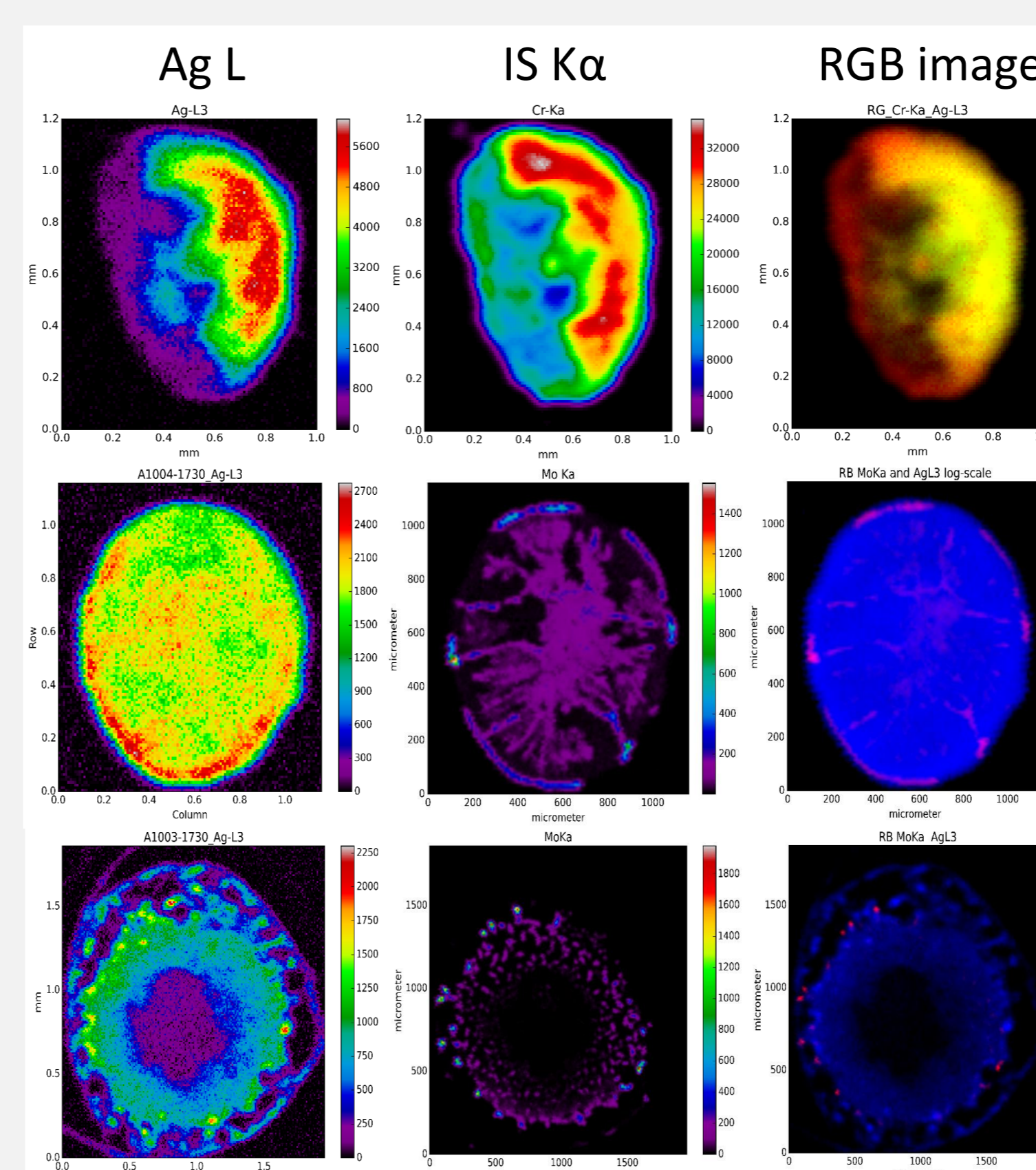


Figure 3: μ -XRF images of elemental distribution. Color intensity of RGB images is scaled between 5 and 80 % of the maximum number of counts. 1st row Ag and Cr (not washed), 2nd row Ag and Mo (not washed), 3rd row Ag washed and Mo.

Table 2: Results relating Ag to two internal standards, Cr & Mo, and the resulting deviation for 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-IS is not homogeneously distributed on the AgNPs and therefore gives highly variable results depending on the angle of irradiation (Table 2, Fig. 2, Fig. 3). The Mo-IS is more homogeneous and gives better results than the Cr-IS (Table 2, Fig. 3).

Results from External Calibration

Neither IS gave completely satisfactory results. A five-point calibration curve was used for external calibration. Since AgNP weights on the carriers fell in the range of 100 - 200 ng, two calibration ranges were selected for Ag: 100 – 500 ng and 60 – 250 ng.

- A linear regression analysis was performed following the calculation of the residuum and elimination of outliers (Fig. 4).
- Higher Ag masses (> 300 ng) resulted in higher variability between replicates.

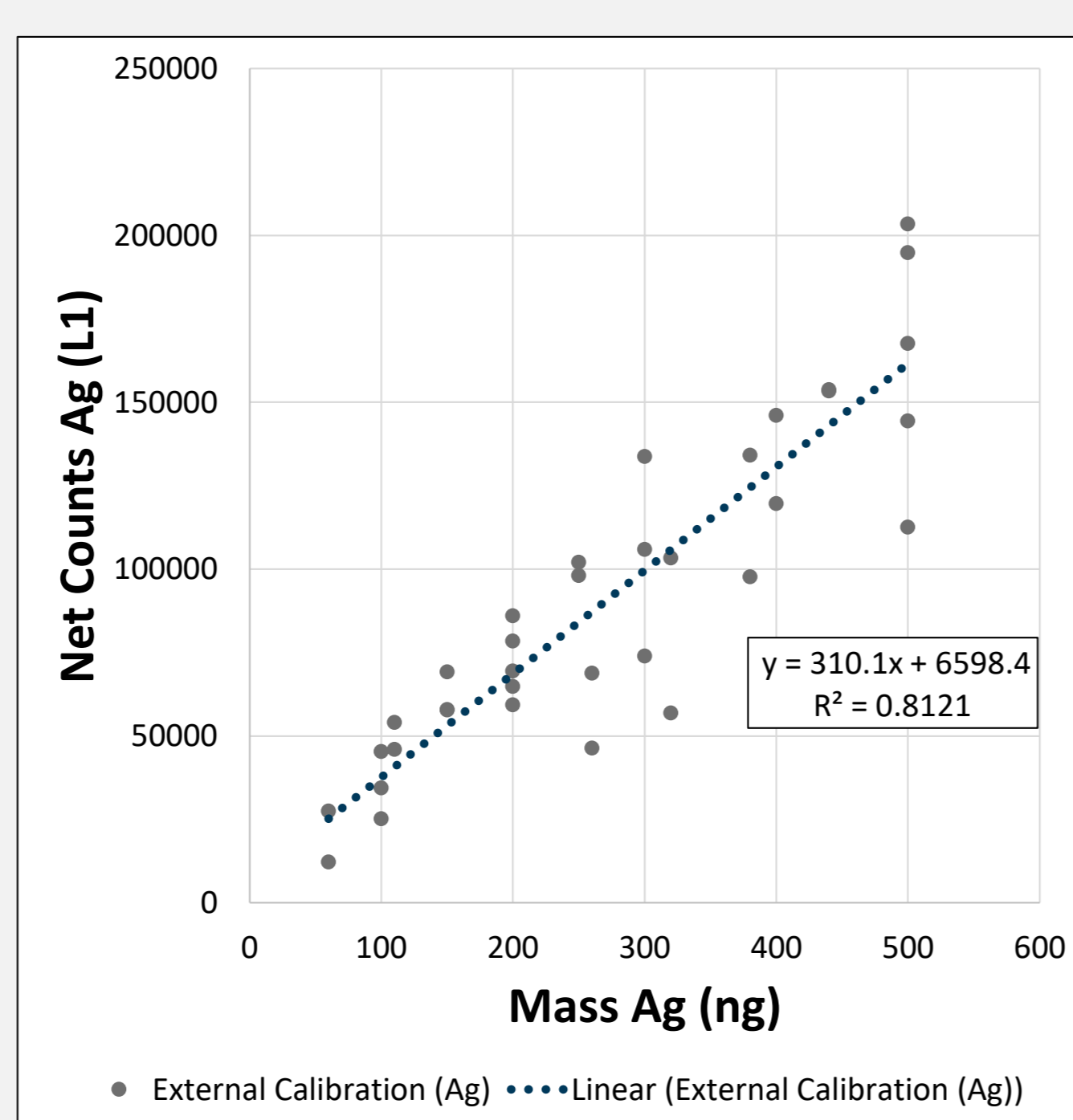


Fig. 4: External calibration of Ag.

- A five-point calibration range of 60 – 200 ng was used for Hg.
- A linear regression analysis was performed following the calculation of the residuum and elimination of outliers (Fig. 5).
- The results deviate from the absolute values measured by the program Spectra.
- The maximal allowable work-place concentration for Hg is 0.020 mg/m³, which corresponds to ca. 850 μ g absolute on the carrier. Since the actual concentrations in the museums were found to be around 0.002 mg/m³ (ca. 100 μ g on the carrier), a calibration curve range of 0.05 – 1 ng would be more suitable for quantification purposes. A lower calibration curve range is also expected to be less prone to errors due to absorption effects.

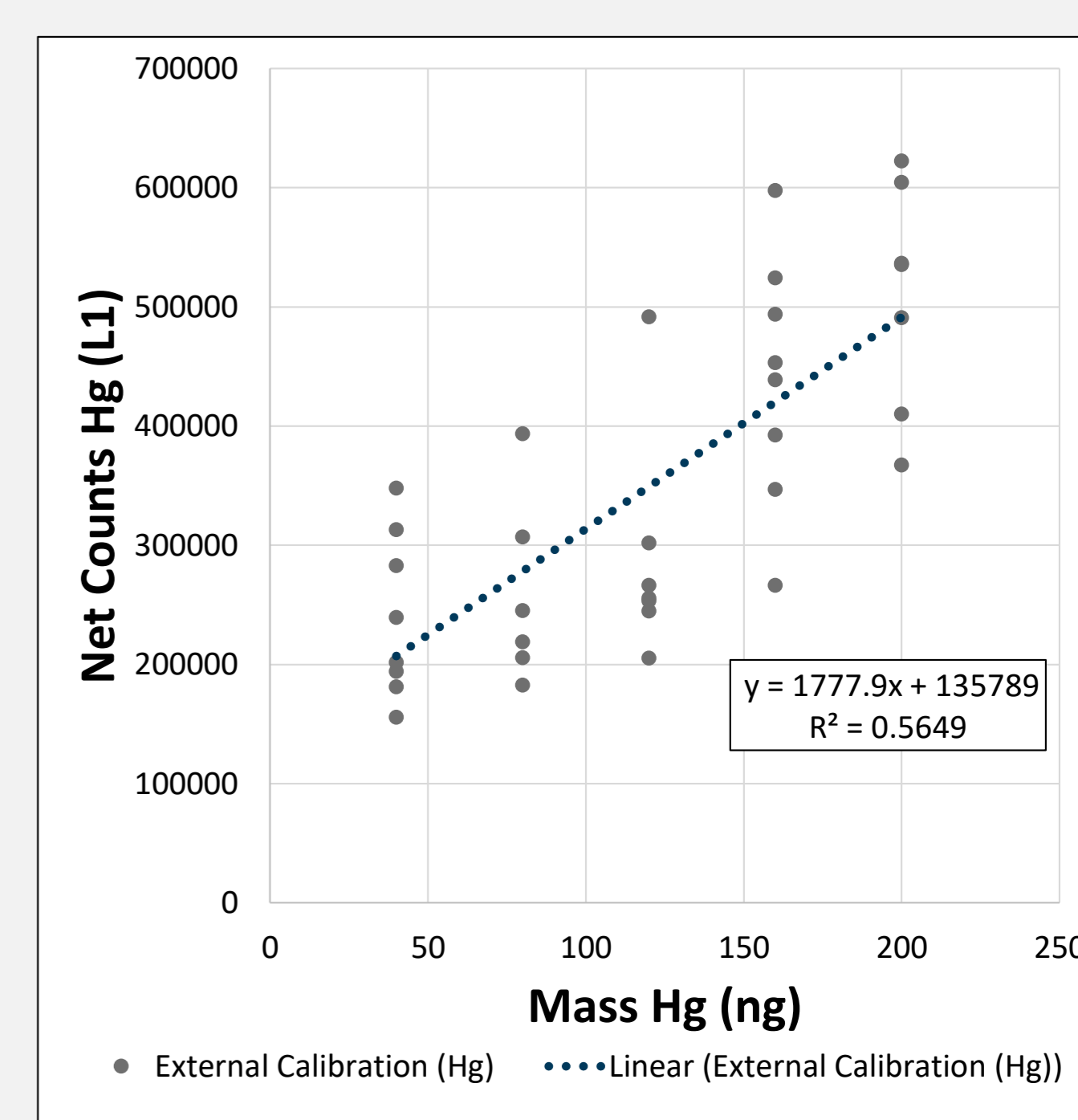


Fig. 5: External calibration of Hg.

Conclusions

- Lower limits of detection (LLD) for Ag and Hg were found to be 129 μ g and 4 μ g, respectively.
- The calibration of Hg needs to be performed in a significantly lower concentration range. Since the maximum allowable work-place Hg concentration is 0.020 mg/m³, and concentrations found in the Flensburg museum, as well as other museums, a calibration range from 50 μ g to 1 ng would be favorable. This would also significantly reduce matrix effects.

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