Determination of gas phase mercury – Experiments of saturation, determination, and storage life

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Introduction

Mercury and arsenic compounds were often used to prevent damage to cultural heritage specimens, e.g. herbaria and paintings [1], and over time, gas phase Hg is formed by bacterial activity, followed by photo reduction, and release into air [2,3]. Mercury has been determined by REXES directly on the specimens [1]. Portable mercury vapor indicator (MVI) [4,5], SEM, XRD, XPS, and ICP-MS [4], and a portable analyzer using AAS [3] 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 [6], water [7], seawater [8], and other liquid samples using Au-nanoparticles [9], and in seafood samples by using Ag-nanoparticles (AgNP) after converting organomercury into elemental Hg [10]. To the best of our knowledge, there have been no efforts in the determination of gas phase Hg using TXRF and AgNP. We have tested this approach and found it to be promising, allowing for convenient and sensitive analysis of gas phase Hg. Here we present the results from experiments evaluating Hg uptake of the AgNPs over time, the linearity of Hg capture on the AgNP in a well-defined control environment spiked with varying Hg concentrations, and the storage behavior of amalgamated samples.

Objective and Experimental

The aim: To develop a reliable, precise, and accurate analysis method for gas phase Hg by using AgNPs and TXRF.

The benefit: Chemicals and instrumentation needed are generally already available in laboratories using TXRF for elemental analysis; a special setup is not necessary. Hg is collected passively without the need of additional instrumentation.

Approach: Quartz-carriers were prepared with AgNP by an optimized method. Hg was collected passively for 24 h and subsequently analysed by a S2 Picofox TXRF (Bruker, Germany).

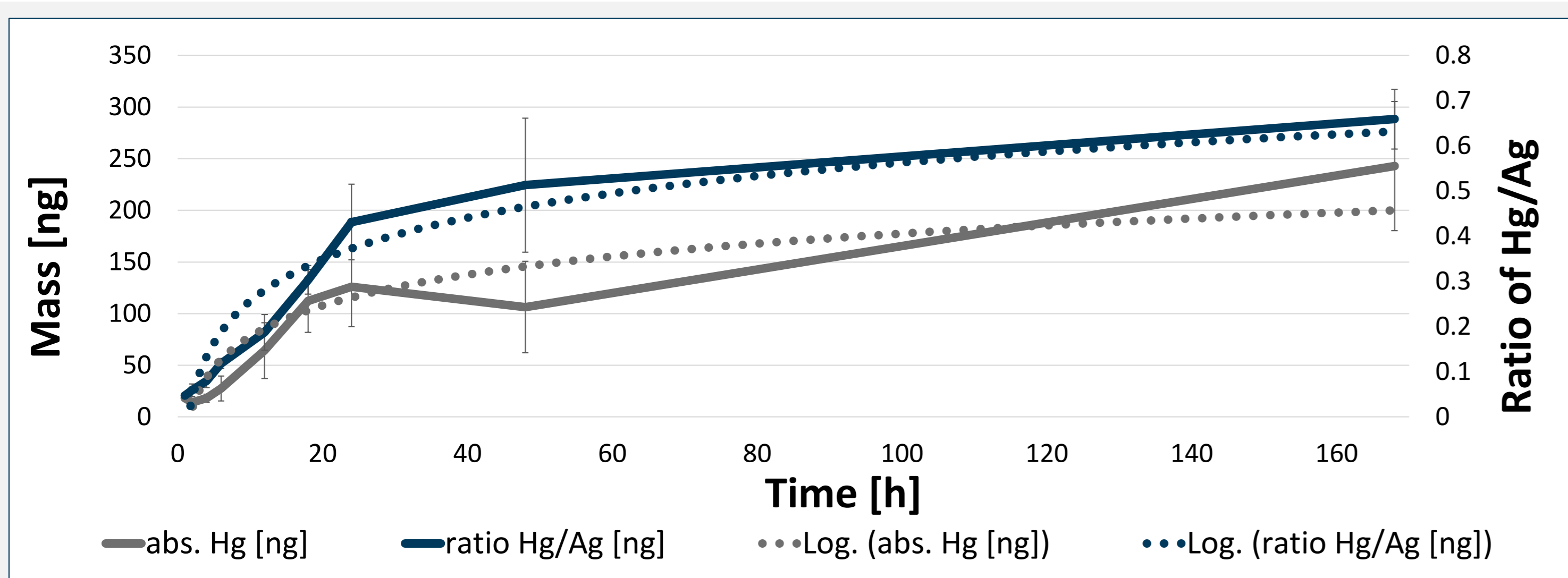## Results: Hg-uptake in a well-defined control environment

Figure 1: Hg-uptake onto AgNPs in a Hg-saturated atmosphere, with exposure times ranging from 1 – 168 h. TXRF measurements were performed for 500 s.
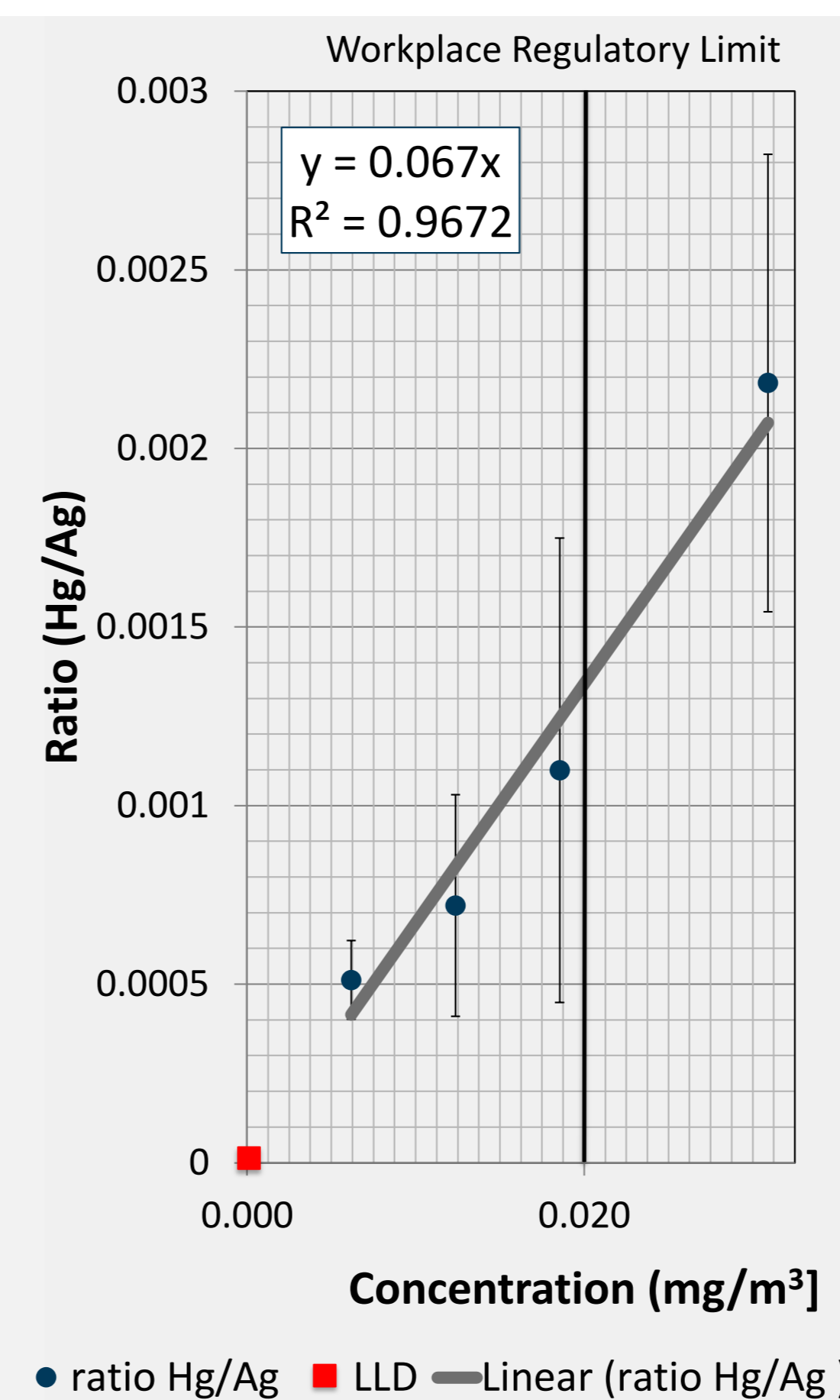

Figure 2: Hg in a well-defined control environment. Exposure time = 24 h; TXRF measurement time = 500 s; N = 5 at each concentration; LLD = lower limit of detection.

Figure 1 shows the increase in Hg concentrations over time on AgNP-carriers exposed to a Hg-saturated gaseous environment. Because the Hg uptake depends on the surface area available for amalgamation, which we considered to increase linearly with Ag concentration (first estimate), we normalized the mass of Hg to the mass of Ag (blue line). During the first 24 h, the Hg/Ag ratio increases linearly, followed by a decrease in rate of uptake after 24 h of exposure. Sampling times of about 110 h result in low deviation of Hg/Ag ratios. However, a 24 h amalgamation time was chosen to allow for more experiments.

To quantify gas phase Hg concentrations, Hg/Ag ratios obtained from a controlled environment were correlated to concentrations of Hg in mg/m³.

The following experiment was performed:

Carriers were placed in a plastic box (PP, 11 L) and, using a nozzle, Hg-saturated atmosphere from the desiccator was injected in well-defined concentrations (5-500 mL). The standard deviation at this time was unacceptably high. At the time of the experiment, AgNP production was not fully optimized and the deviation in available AgNP surface area has a significant influence on the amalgamation process. Further studies are ongoing. However, in general the method is capable to determine concentrations of interest lower than workplace limits of 0.02 mg/m³ [11,12]. We found detection limits to be around 1.18×10^{-4} mg/m³.
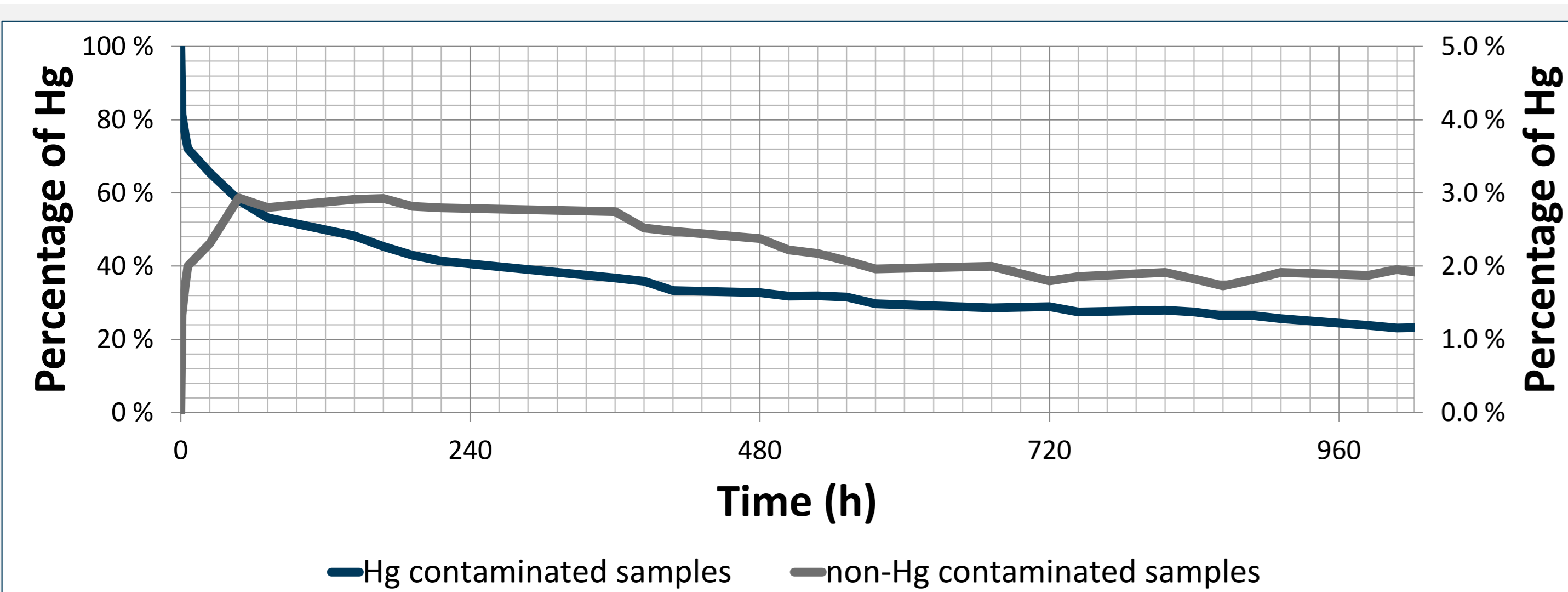
Storage life of Hg-samples

Figure 3: Cross-contamination between two carriers, one contaminated with Hg, while the other only contained AgNP (left y-axis for Hg-contaminated samples, right y-axis for AgNP only samples getting the Hg from the other sample).
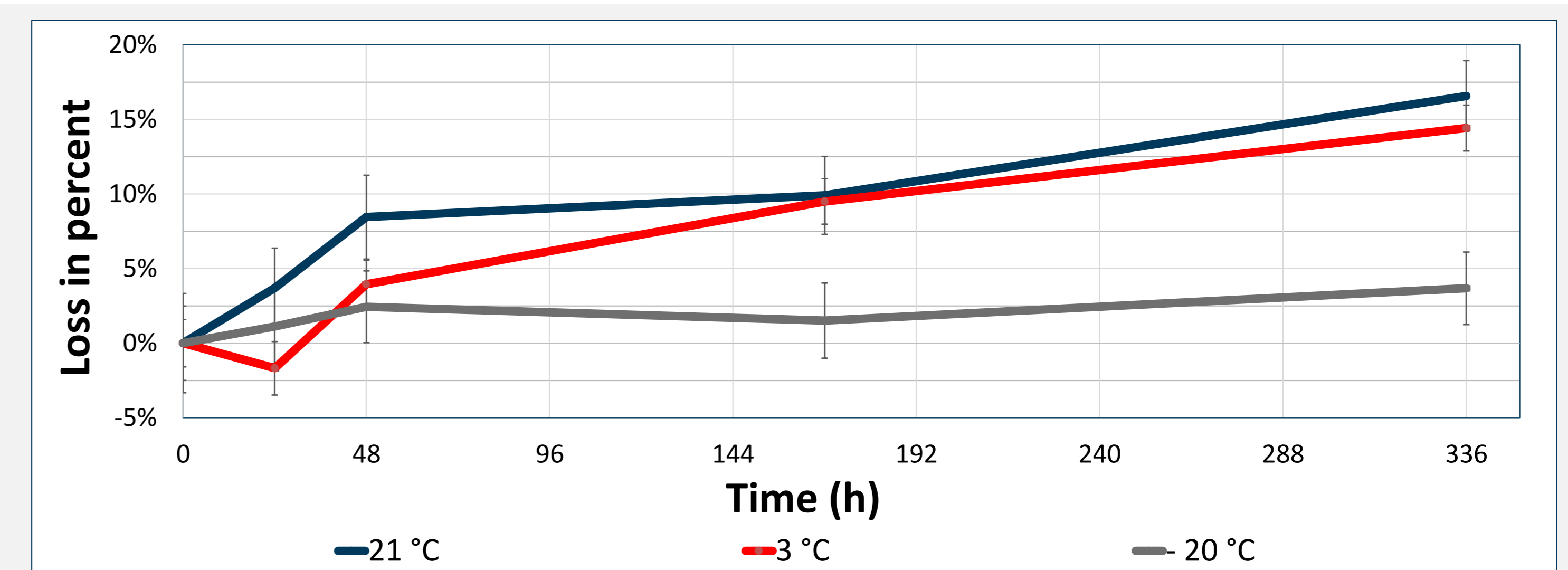

Figure 4: The loss of Hg depending on temperature (Amalgamation for 1 h in saturated atmosphere, measured for 500 s); each sample was stored in a petri dish and sealed using Parafilm®

To evaluate cross-contamination, a Hg contaminated carrier (10 ng) and a non-contaminated carrier (AgNP-only) were stored together in a petri dish (sealed using Parafilm®) at room temperature. Figure 4 indicates that the 78% of the Hg on the contaminated sample carrier evaporates, with an average Hg loss of 8 ng (N=3). The non-contaminated samples collect 0.3 ng Hg, on average, corresponding to an uptake of 2.2% of the Hg lost from the contaminated sample. This means that 97.8% of the Hg lost from the contaminated sample is unaccounted for, possibly due to a different count of photons from the X-Ray tube and the relatively low Hg concentration.

Cross-contamination is to be expected if samples are stored together. Every sample should therefore be stored in separate, sealed containers with small headspace volumes. The time between sampling and analysis should limited in order to reduce Hg loss from the sample carrier.

To further optimize storage conditions, the influence of the storage temperature was evaluated (Fig. 3). The loss at room temperature after 24 h was about 4%. Additionally, the loss of Hg during storage at -20 °C (freezer) was much lower than the others.

Conclusions: Hg can be conveniently enriched on carriers prepared with AgNPs. Preparation of thin film AgNP deposits, as well as the control room experimental procedure, need to be further improved to be able to precisely and accurately determine gas phase concentrations. Detection limits are found to be well below the regulated limits, in the order of 1.8×10^{-4} mg/m³. Storage at low temperatures is favorable to avoid Hg loss. In addition, the time between sampling and sample measurement should be limited. Individual storage of samples is advisable to avoid cross-contamination.

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