

ANALYSIS OF SELECTED MERCURY COMPOUNDS IN ENVIRONMENTAL SAMPLES USING THERMO-DESORPTION TECHNIQUE

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Keywords: Mercury, fractionation, thermal desorption

Introduction

Mercury is one of the most hazardous elements. Its transformation and transport in the environment strongly depend on its chemical form. Information about Hg form is also important for understanding the bioavailability as well as toxicity of this element. Published methods for Hg speciation include sequential chemical extraction (Wallschlager et al., 1998), X-ray adsorption fine structure spectroscopy (Kim et al., 2000) and thermo-desorption atomic absorption spectroscopy (Biester and Scholz, 1997). Each of this methods has advantages and disadvantages. However, the large number of various procedures used by different authors results in a large quantity of non-comparable data. The objective of this research was to develop and validate a simple thermo-desorption technique for mercury fractionation in environmental samples using the direct mercury analyzer. It allow to standardized the operational conditions to get reproducible results in different laboratories.

Methods

The direct mercury analyzer DMA-80 (Milestone, Italy) was used for the detection of Hg. The instrument was develop for determination of the total Hg by combustion of sample and CV AAS detection using oxygen as a carrier gases. For temperature fractionation the same instrument was used, only the temperature of catalytic tube heating was changed. In this case the temperature at which Hg was released from the samples was controlled. Each sample was heated from 50°C to 750°C and result was presented as a thermo-desorption curve. The Hg species were characterized by the temperature range at which they were release. Twelve synthetic standard material were used in this work. HgCl₂, Hg₂Cl₂, Hg(NO₃)₂, HgSO₄, HgO (red), HgBr₂, HgI₂, HgF₂, HgS, (CH₃COO)₂Hg, Hg(SCN)₂, Hg(CN)₂ were purchased from Sigma Aldrich. Hg concentration in this materials were too high to be measured directly, therefore they were dry diluted with beach sand (<90% SiO₂) heated by 24h in 800°C. Additionally, the decomposed plant collected from the composter was used as a humus-like standard. The method was tested on a certified reference material (BCR-414; NCS DC 87103) as well as on natural samples: soil (with high organic matter content), beach sand, marine sediment, plankton and aquatic plant (*Lemna minor*).

Results

First step of the development of the thermo-desorption method for mercury fractionation was optimization of the heating time. Two aspects were checked for each temperature: time to reach the target temperature and time in which the highest Hg concentration was measured. The first one was crucial to avoid overheating the sample, because it could disturb the next measurement. The second one was important because of the recovery. The next step was the analysis of Hg concentration in the certified reference material and natural samples. The results from Hg fractionation were compared to total mercury concentration in those samples. In soil sample with total mercury concentration about 90 ng g⁻¹ d.m. recover was more than 95% but in samples with total Hg concentration less than 20 ng g⁻¹ d.m. recover ranged from 60%

to 75%. The next step was the analysis of Hg standards. The obtained results showed that Hg halides, nitrate, cyanide, thiocyanate and acetate had desorption peak at the lowest temperature (fig. 1). The exception was HgF₂, which had main peak at 450°C. After Hg halides, at 250°C sharp peak belongs to the humic-like substances could be seen. Between 275°C and 350°C there is wide peak for HgS. The desorption profile obtained for HgSO₄ showed a maximum in 450°C, while red form of HgO had wide peak with maximum in 475°C. Comparison of the thermograms obtained for Hg standards and for soil sample indicated that in this sample Hg was associated mainly with humic-like organic matter.

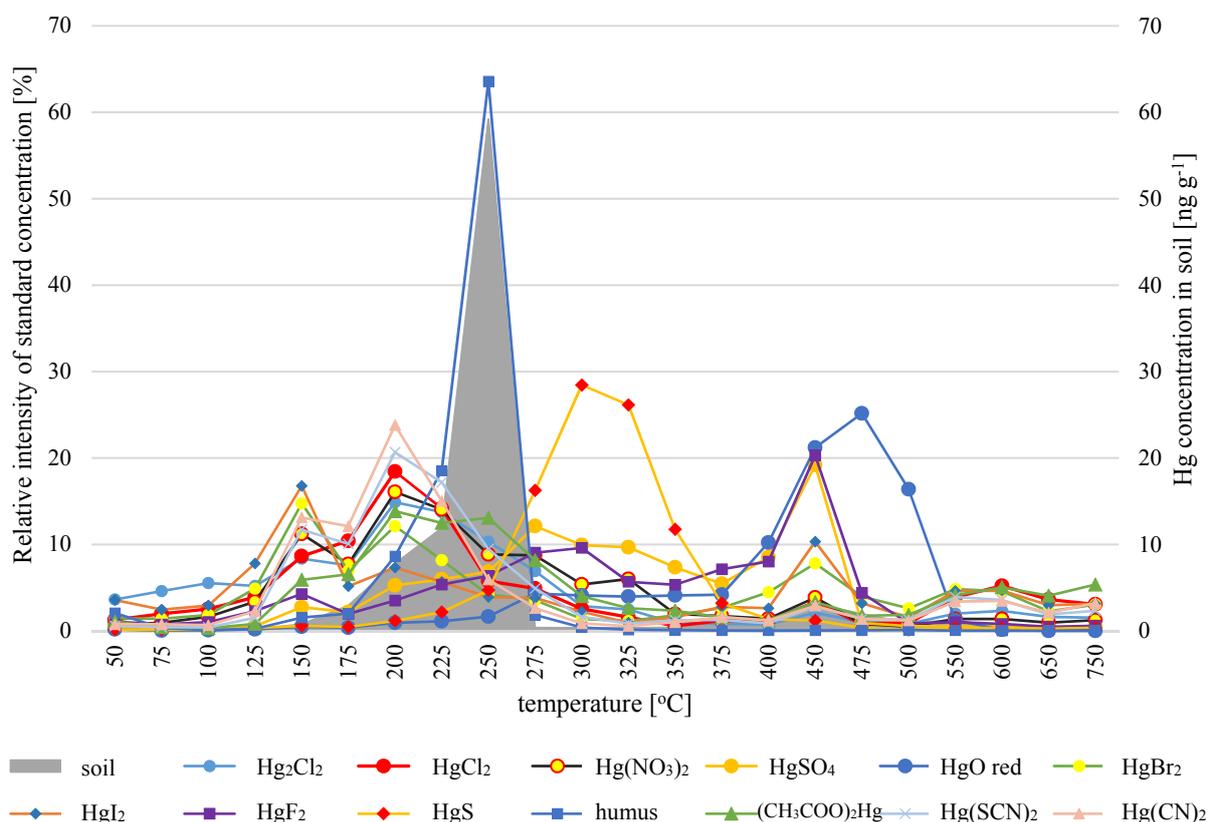


Figure 1. Thermograms of mercury standards (right axis) and soil sample (left axis).

Conclusion

The obtained results show that the thermo-desorption method does not allow for precise determination of single Hg compounds. However, this method can be considered as a screening technique for the evaluation of the percentage contribution of certain groups of Hg compounds with similar properties in solid samples with Hg concentration about hundred ng g⁻¹ and higher. This could be a valuable basis for discussion about Hg transformation in the environment. The research is still in progress.

References

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