Mercury fractionation in soil using Diffusive Gradients in Thin-films coupled with thermal decomposition - atomic absorption spectrometry

Marin ŞENILĂ, Marius ROMAN, Bogdan ANGYUS

INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, 400293, Cluj-Napoca, Romania
Tel: +40-264-420590, Fax: +40-264-420667, Email: icia@icia.ro

INTRODUCTION

Mercury (Hg) is considered as one of the most toxic elements due to its impacts on the human and environmental health, thus its environmental monitoring needs a special attention. Hence, an accurate monitoring of mercury species in the environment is needed, and in addition to the determination of total metal concentration, the evaluation of its bioavailability provides very useful information for reliable risk assessment.

A variety of detection methods have been used for mercury determination. The most popular method for determining mercury in almost any type of sample has been based on cold vapour atomic absorption spectrometric measurement (CVAAS) and the technique is widely used. The way of liberating mercury from aqueous or digested samples is reduction, followed by volatilization and introduction of the mercury by aid of a gas stream. A gold amalgamation method to purify the mercury vapour can be used. After the organic vapour is purged out, mercury is released from the gold fibre trap by heating and then introduced into the spectrometer. The method can work not only for mercury purification but also for the collection and accumulation of mercury into a small volume which makes it possible to achieve elevated sensitivity.

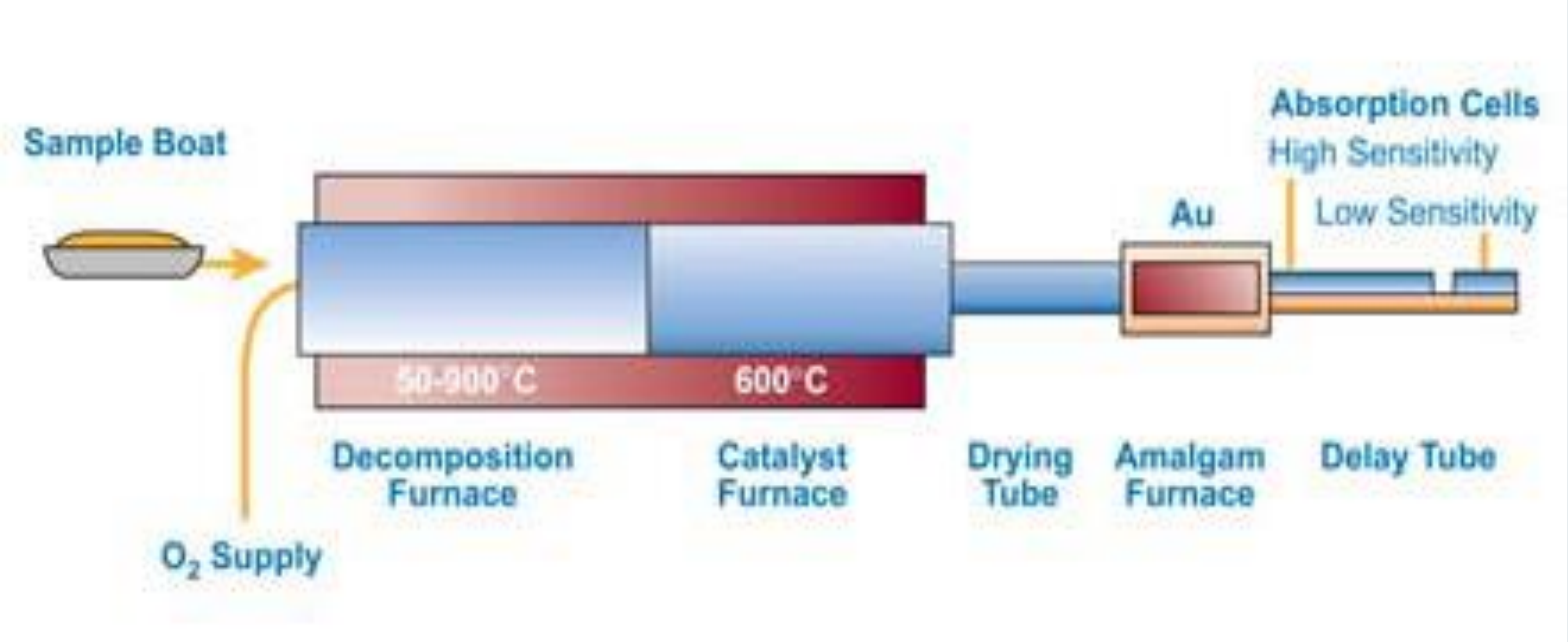
For solid samples, Hg determination is difficult due to the high volatility of these element, and the digestion methods suppose sample heating. Direct Hg determination from solid sample is very important to obtain accurate results.

The technique of diffusive gradients in thin films (DGT), developed by Davison and Zhang (1994), provides an in situ tool of measuring labile metal species in aqueous solutions. This is very important, because the labile species are better correlated with metals bioavailability. In several studies DGT and TD-AAS were used for Hg bioavailability assessment in environmental samples.

The present work describes the mercury determination in soil pore water collected from Baia Mare area, NW Romania using commercial DGT devices specific for Hg ions (Speron-Thiol resin gel) and TD-AAS technique.

INSTRUMENTATION

The Hydra-C Direct Mercury Analyzer (Teledyne Leemens Lab, USA) provides Hg analyses from solid samples without sample pretreatment.



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EXPERIMENTAL

Soils samples were sampled from private gardens from a village of Recea, located in the vicinity of Baia Mare, NW Romania, in an area with a long-history of ore mining and processing. Collected surface soil samples (0-10 cm) were transported to the laboratory, dried, crushed and sieved. For DGT determinations, amounts of 30 g of soil samples were mixed with ultrapure water until 100% water holding capacities (WHC), in plastic containers, and kept for 24 h at 25 ± 2 °C, for equilibration. The DGT devices were introduced into the soil slurries and kept for a known time at 25 °C. After retrieval, the DGTs were carefully washed with ultrapure water and the resin gels were introduced directly in Hg-analyser and the mass (M) of Hg accumulated in the resin was measured.

RESULTS AND DISCUSSIONS

Hg content in soil solutions (Hgsoln) ranged between 2.5 – 4.6 µg L-1, which generally represent less than 0.5 % of the total Hg content in soil. HgDGT concentrations were in the range of 2.2 – 3.8 µg L-1. In order to measure resupply from solid phase, the ratio R between HgDGT and Hgsoln was calculated. When R is higher than 0.95, the metal is present as mobile and kinetically labile species in the solid phase. That capacity of the solid phase to resupply the pore water is high. An R value approaching 0 suggests very limited or no metal resupply from the solid phase (DGT Research Ltd, Lancaster, UK). The R ratios in our case ranged between 0.76 - 0.92, indicating that Hg in solution is quickly replaced from the solid phase, where it is found in an available form.

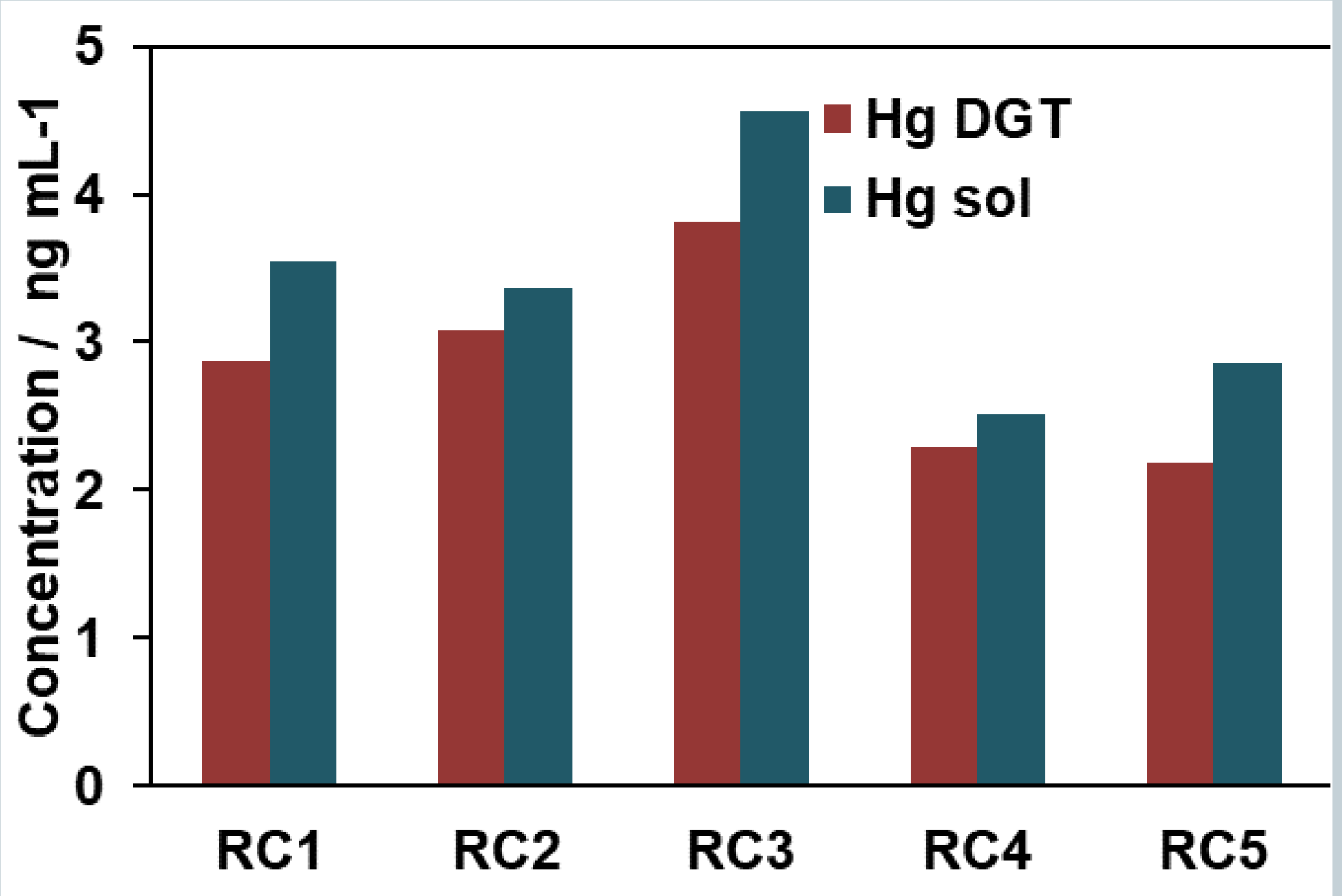

Fig. 1. Mercury in soil solution (Hgsol) and mercury measured by DGT (HgDGT) in soils

In Romanian legislation the normal value for Hg concentration in soil is 100 µg/kg. The alert threshold for sensitive areas is 1000 µg/kg. The total mercury concentration were in all analyzed samples, bellow the maximum admitted level of 1000 µg kg-1 dw for soils from residential and agricultural areas. From this, only a small part, less than 0.5%, was found to be in the soil solution. However, the high capacity of solid phase to resupply mercury to the soil solution and its high degree of bioavailability, explain the Hg hyperaccumulation in several plant species.

REFERENCES

Davison, W. & Zhang, H., 1994: In situ speciation measurements of trace components in natural waters using thin-film gels. Nature, 367, 546 – 548.