

Determination of total mercury in solid environmental samples

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Abstract: The comparability of the results obtained for T-Hg in various solid environmental samples by different analytical methods, were investigated. Total digestion using mixture of acids including HF or the temperature high enough when applying non-destructive methods must be employed to completely release Hg included in the mineral lattice.

Key words: total mercury, analytical methods

INTRODUCTION

The first step in the frame of routine monitoring or risk assessment studies is to determine whether the total mercury (T-Hg) concentrations are within the range of background levels or over the concentration limits according to the national/international legislation. The analytical chemist is faced with several challenges when determining T-Hg in solid materials. These challenges include widespread contamination, both in the laboratory and the environment, possible losses of Hg during sample preparation, wide range of Hg values commonly observed, great matrix diversity, and sample heterogeneity. These factors can be naturally occurring or anthropogenic, but must be addressed to provide a precise and accurate analysis.

In this paper, comparison of the performance of two acid digestions (using mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3$ and $\text{HNO}_3/\text{HF}/\text{HCl}$, respectively) followed by CVAAS (HORVAT ET AL., 1991) and two independent non-destructive methods, k_0 -INAA (DE CORTE ET AL., 2001)

and RNAA (BYRNE and KOSTA, 1974) in different sample types is reported. For this purpose, diverse solid materials (sediment, soil and bauxite samples) of great matrix diversity and wide range of mercury concentrations were analysed.

RESULTS AND DISCUSSION

Characterisation of samples. Sediments originate from industrial polluted sites. Higher amounts of SiO_2 and Al_2O_3 on one hand and lower amounts of Ca, K and Na on the other indicate the aluminosilicate composition of these samples. Bauxite samples are composed primarily of one or more aluminium hydroxide minerals (gibbsite, boehmite, diaspore), plus various mixtures of silica, iron oxide and aluminosilicates. Soil samples originate from mercury polluted site in Idrija mercury mine region, Slovenia. According to their different agronomic parameters, soils can be divided into two groups; samples of alluvial plains

and others. Soils from alluvial plains contain less potassium, organic carbon and organic matter, have a higher C/N ratio and somewhat lower cation exchange capacity when compared with others. As regards texture, soils from alluvial plains are coarse grained, while fine-grained material prevails in other soil samples.

T-Hg results. Mean T-Hg concentrations and relative standard deviations (RSDs) obtained are listed in Table 1. Based on Table 1, the following is concluded, for probability level 95 % ($P=0.05$). ANOVA test revealed statistically significant results for all three sediment samples. Consequently, one or more of the performed methods differed significantly from the others. ANOVA is incapable of determining exactly which one of the performed

methods shows the highest or lowest results. Nevertheless, based on data in Table 1, it is almost sure that acid digestion method using strong hydrofluoric acid gives higher results than all the other methods. The reason for higher results obtained is probably mercury bound to the silicate lattice or crystalline iron and manganese oxides, which are not disintegratable in H_2SO_4/HNO_3 acids and by both neutron activation based methods.

Soil samples were analysed by AAS after both acid decomposition method. A F-test at a significance level of 0.05 detected significant differences between both decomposition methods in case of four soil samples out of seven. Method using mixture of $HNO_3/HF/HCl$ mixture revealed higher results for three soil samples, while method using mixture of

Table 1: Mean T-Hg concentrations and relative standard deviations obtained from sediments and soils by four different methods (ng/g)

Analyte	Method							
	H_2SO_4/HNO_3	RSD (%)	$HNO_3/HF/HCl$	RSD (%)	RNAA	RSD (%)	INAA	RSD (%)
SED 1	1596	3.4	1724	2.9	1575	7.2	1655	3
SED 2	243	10.1	288	9.5	137	9.8	188	21.6
SED 3	950	2.3	1000	3.9	915	2.9	858	3.4
SOIL 1	310	3.8	333	2.6	-	-	-	-
SOIL 2	50	8.1	47	9.8	-	-	-	-
SOIL 3	8.4	2.7	8.9	3.1	-	-	-	-
SOIL 4	338	21.2	369	8.5	-	-	-	-
SOIL 5	84	10.6	76	21.5	-	-	-	-
SOIL 6	174	3.4	175	14.9	-	-	-	-
SOIL 7	144	2.1	144	13.9	-	-	-	-
IAEA 405	0.8	1.0	0.8	6.7	0.84	4.8	0.86	2.7
BCR 580	129	4.3	134	0.42	-	-	138	1.5

^a BCR 580, Estuarine sediment (certified value 132 ± 3 mg Hg/kg).

^b IAEA 405, Estuarine sediment (reference value 0.81 ± 0.04 mg Hg/kg)

Table 2: Bauxite samples analyses results (ng/g)

Analyte	HNO ₃ /HF/HCl	RNAA	HNO ₃ /HF/HCl after 600 °C	HNO ₃ /HF/HCl after 900 °C	HNO ₃ /HF/HCl after 1200 °C	RNAA + HNO ₃ /HF/HCl after 600 °C
B1	202	97	164	46	0.89	261
B2	211	175	59	28	0.07	234
B3	431	310	139	35	0.97	449
B4	227	126	128	62	0.07	254
B5	314	91	153	87	1.01	244

H₂SO₄/HNO₃ revealed higher results for one sample. Other samples showed no significant differences between both acid decomposition methods. Considering very high T-Hg concentrations in these samples, mainly carbonate origin of these soils and the fact that “hot” cinnabar particles (soluble by both digestion technique) are representing more than 90 % of mercury in soils from the Idrija mercury mine region (KOCMAN ET AL., 2004), it can not be concluded which method gives better results. These results may reflect poor homogeneity of the samples (relatively high RSDs).

T-Hg in bauxite samples was determined by two methods: RNAA and AAS after digestion with the mixture of HNO₃/HF/HCl acids. It can be seen from Table 2 that strong HF acid decomposition revealed much higher (up to 3.5 times) results than RNAA method. Evidently there must be some mercury residues bound in the mineral lattice that was not released by RNAA method during the combustion of the samples at 700 °C. To confirm this assumption three sub-samples of each sample were combusted at three different temperatures (600, 900 and 1200 °C, respectively) for 1 hour. Afterwards samples were decomposed with mixture of HNO₃/HF/HCl acids and the residual mercury determined by CVAAS. The results revealed significant amounts of mercury remained

after the combustion at 600 and 900 °C, while only negligible amounts were left after the combustion at 1200 °C (Table 2). When the results obtained by HNO₃/HF/HCl method are compared with the sum of RNAA and residual concentrations after combustion at 600 °C, the concentrations are comparable.

CONCLUSIONS

The advantages and disadvantages of the techniques used and our observations can be summarized as follows: It was proved that, for difficult matrices like various sediments and bauxite matrices, insufficient recovery and bad reproducibility of the results are mostly attributed to unfit decomposition methods. Using wet digestion with the mixture of acids including hydrofluoric acid, significantly higher results were obtained in the case of this kind of materials. Considering the matrix of most environmental samples, a total digestion scheme must include the use of hydrofluoric acid to completely release mercury included in the aluminosilicate phase. Non-destructive methods based on combustion/pyrolyses techniques should use the temperature high enough (>1200 °C) to release all the mercury bound in the mineral lattice, when inorganic samples are investigated.

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