

Optimisation of cold vapour atomic absorption spectrometry for determination of high levels of total mercury in activated carbon

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Abstract: The relative efficiency of digestion/leaching procedures for the determination of high mercury concentrations in activated carbon obtained from natural gas treatment facilities was investigated. The method is based on acid digestion/leaching, reduction by SnCl₂, gold amalgamation and detection by cold vapour atomic spectrometry. Sample decomposition was carried out in sealed Pyrex ampoules and closed Teflon vials, as well as in "cold finger" vessels. We used various combinations of acids (HNO₃/H₂SO₄, HNO₃, HNO₃/HCl, HNO₃/HF/HCl and HCl), digestion time, temperature and filtration. The efficiency of decomposition was obtained by comparison with results obtained by the Eschka method, radiochemical neutron activation analysis (RNAA) and k₀-instrumental neutron activation analysis (k₀-INAA). Our results showed that for samples of activated carbon containing up to 6 % of mercury, good results could be obtained using various digestion procedures (HNO₃/HCl, HNO₃/HF/HCl and HCl) with the exception of HNO₃ or HNO₃/H₂SO₄, which resulted in lower values. In addition, for samples of activated carbon with more than 6 % of mercury, efficient digestion/leaching can be obtained by treating the activated carbon in a "cold" finger vessel with 20 mL of concentrated HCl or aqua regia (HCl:HNO₃ (3:1)).

Key words: atomic absorption spectrometry, mercury, activated carbon

INTRODUCTION

Many analytical techniques have been developed for the determination of total mercury, especially for low mercury levels in environmental samples, using CV AAS. When samples with very high mercury concentrations (e.g., in the mg/g concentration range) are to be analysed by such a sensitive technique the major source of error may be

due to large dilution factors. Also, preparation of such contaminated samples in trace analysis laboratory may lead to contamination of the laboratory and/or the measurement system. The activated carbon studied in this work originates from natural gas treatment facilities, where it is used for removal of mercury from the natural gas stream. On average, the concentrations of Hg in such carbon can reach up to 30 % (w/w) of mer-

cury. The second problem is the preparation of a homogeneous and representative sample of activated carbon, and the third important problem to be mentioned is related to the efficiency of digestion/leaching procedures. In order to overcome these difficulties the granules of activated carbon were ground in a stainless steel mixer.

The classical approach to determine Hg at high concentration is based on the gravimetric principle that was for centuries used in the Hg mining industry (the Eschka method). There are a number of alternative methods that can also be used, such as radiochemical neutron activation analyses (RNAA) or instrumental NAA (INAA), but these methods are only available in specialized institutions. The goal of this study was to investigate the relative efficiency of digestion/leaching procedures for subsequent determination of high mercury levels in activated carbon using gold amalgamation and detection by cold vapour atomic absorption spectrometry (CV AAS)^[1, 2]. Sample decomposition was carried out in sealed Pyrex ampoules and closed Teflon vials, as well as in “cold” finger vessels. We used various combinations of acids ($\text{HNO}_3/\text{H}_2\text{SO}_4$, HNO_3 , HNO_3/HCl , $\text{HNO}_3/\text{HF}/\text{HCl}$ and HCl), digestion time, temperature and filtration. The efficiency of decomposition was compared with results obtained by Eschka method^[5], radiochemical neutron activation analysis (RNAA)^[3, 4] and k_0 -instrumental neutron activation analysis (k_0 -INAA)^[4] as reference methods.

EXPERIMENTAL

The activated carbon studied in this work originated from natural gas treatment facili-

ties, and was received in granulated form. Since the efficiency of wet digestion and leaching of mercury from the sample also depends on the size of the particles, the granules of activated carbon were ground in a stainless steel mixer. About 50-100 mg of ground activated carbon was weighed directly in a Teflon vial, Pyrex ampoule or “cold” finger digestion vessel. After addition of different acids the vessel was closed, Pyrex ampoules were sealed and the mixture was left to react at room temperature for 1 hour. Digestion/leaching was finished by heating the mixtures in an Al block at 100 (135) °C for 3 or 12 hours on a hot plate. Some digests were filtrated through Whatman GF/C filter prior dilution. To the digest was added 10 mL of BrCl and Milli-Q water to the desired volume. An aliquot of the digest was added to the reduction vessel and after reduction with SnCl_2 , mercury was swept from the solution by aeration and concentrated on a gold trap. Mercury was then released from the gold trap by heating and measured by cold vapor atomic absorption spectrometry (CV AAS).

The Eschka method is used for fast quantitative determination of Hg in the ores and is based on amalgamation process on a pure-golden pot. Ground and dried sample was weighed in a porcelain dish and 3 g of iron chips and 30 g of ZnO were added. The porcelain dish was covered with a previously weighed pure-golden pot and heated on an electric furnace at 600-800 °C for 30 minutes. Meanwhile fresh deionized water was constantly added on the surface of the golden pot, so the temperature of water did not exceed 40 °C. When the reaction was finished, the porcelain dish was left to cool down for 10 minutes. The golden pot was dried with a

filter paper and weighed again. The % of Hg was calculated from the difference between the mass of a golden pot before and after the amalgamation process, and divided with the mass of the sample.

RESULTS AND DISCUSSION

Samples of activated carbon were analyzed in both granulated form and in powder form,

obtained by grinding. The acid digestion/leaching involved 6 mL of an $\text{HNO}_3/\text{H}_2\text{SO}_4$ (4:2) mixture and heating in an Al-block on a hot plate at 100 °C for 3 hours. Before dilution with Milli-Q water 1.0 ml of BrCl was added. The measurement proceeded as described above. The differences in homogeneity and digestion/leaching efficiency between the granulated and powder form of activated carbon in 9 parallel aliquots are presented in Table 1. Table 2 presents results

Table 1. Comparison of results for total mercury (%) in granulated and powder forms of activated carbon, determined by CV AAS

Parallel	Hg (%)								
	1	2	3	4	5	6	7	8	9
Sample form:									
1. Granulated	1.24	0.916	0.666	0.463	0.536	0.421	-	-	-
2. Powder	4.23	3.42	3.56	3.59	3.87	3.82	4.22	3.84	4.41

Table 2. Results for total mercury (%) in four samples of activated carbon (A, B, C, D) obtained by the Eschka method, RNAA, k_0 -INAA, and CV AAS after different digestion/leaching procedures

	Method	Sample			
		A	B	C	D
	Eschka method	30.7	5.5	5.7	18.2
	RNAA ^[3, 4]	25.6	5.2	6.1	15.0
	k_0 -INAA ^[4]	31.9	5.9	-	18.9
CV AAS	6 mL $\text{HNO}_3:\text{H}_2\text{SO}_4$ (2:1) 100 °C, 3 hrs, Teflon vial	19.8	4.0	2.7	5.7
	6 mL $\text{HNO}_3:\text{H}_2\text{SO}_4$ (2:1) 100 °C, 3 hrs, Teflon vial, filtered (GFC)	18.0	4.9	-	14.3
	10 mL $\text{HNO}_3:\text{HF}$ (2:1) + 1.5 mL HCl 135 °C, 12hrs, Teflon vial	15.7	-	5.8	13.1
	3 mL HCl: HNO_3 (4:1) 100 °C, 12hrs, Pyrex tube, filtered (GFC)	24.6	-	5.3	12.6
	20 mL HCl: HNO_3 (3:1) 100 °C, 3hrs, cold finger vessel	33.5	-	-	-
	20 mL HCl 100 °C, 3 hrs, cold finger vessel	31.4	-	-	-
	5.0 mL HCl 100 °C, 12 hrs, Teflon vial, filtered (GFC)	22.4	-	6.1	17.6
	20 mL HNO_3 100 °C, 3 hrs, cold finger vessel	3.9	-	-	-
	3.0 mL HNO_3 100 °C, 12 hrs, Pyrex tube, filtered (GFC)	-	-	3.5	1.9

for total mercury (%) in four samples of activated carbon obtained by the Eschka method, RNAA, k_0 -INAA, and CVAAS with different digestion/leaching procedures.

In the granulated form of activated carbon concentrations of mercury were of only about 10-35 % of those found for the powdered form of the sample. The granulated sample was also non-homogeneous. Results from Table 1 show that the size of the particles of activated carbon is extremely important for more efficient acid digestion and leaching of mercury from the sample. Samples of activated carbon with high Hg concentrations of the order of 300,000 mg/kg (30 %), digested with HNO_3 as the major acid, showed about 40 % - 90 % lower results compared to the results obtained by RNAA, k_0 -INAA, and the Eschka method. After digestion/leaching in sealed Pyrex ampoules or Teflon vials using aqua regia (HCl/HNO_3 (4:1)) or concentrated HCl for 12 hours mercury concentrations were underestimated by about 25 %. These results may reflect inefficient decomposition of the sample and losses with Hg volatilisation during longer extraction. Slightly higher Hg concentrations compared to results obtained by RNAA, k_0 -INAA and the Eschka method were found after digestion/leaching in a "cold" finger vessel using 20 mL of aqua regia (HCl/HNO_3 (3:1)) for only 3 hours. Samples of activated carbon with Hg concentrations in the order of 60,000 mg/kg (6 %) digested with HNO_3 as the major acid showed

about 50 % lower results than those obtained by RNAA, k_0 -INAA and the Eschka method. Results obtained by digestion/leaching with $\text{HNO}_3/\text{HF}/\text{HCl}$, aqua regia or HCl alone showed good agreement with the results obtained by these other methods.

CONCLUSIONS

For determination of mercury in very contaminated samples of activated carbon containing more than 6 % of mercury the CVAAS method can be applied, if appropriate wet digestion/leaching of the sample is used. The efficiency of wet digestion/leaching depends on the size of the particles. Grinding before wet digestion/leaching is therefore a very important step. However, by far the best method in laboratories routinely analyzing very contaminated samples is based on gravimetry (Eschka method), while radiochemical methods are useful as reference methods for occasional quality control.

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