APPLICATION OF ICP-OES FOR DETERMINATION OF MERCURY SPECIES IN ENVIRONMENTAL SAMPLES

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ABSTRACT

Direct determination of mercury species in real environmental samples is challenging due to their trace concentrations and low ionisation energy. In this investigation, a microwave-assisted and aqua regia digestion method is proposed for the analysis of trace inorganic mercury. Measurements were performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) method in soil, digestate and waste samples. The detection limits of the proposed method were found to be 0.03 and 0.115 mg/kg for mercury at 184.9 and 194.2 nm, respectively. The accuracy of the method with respect to the systematic and constant errors was confirmed by the analysis of certified reference material (CRM) (> 95 % recovery with < 15 % relative standard deviation RSD). The method was successfully applied for the determination of mercury in solid wastes listed in the Decree on Burdening of Soil with Waste Spreading and the Decree on the Treatment of Biodegradable Waste and the Use of Compost or Digestate in the Republic of Slovenia (Official Gazzette of the Republic of Slovenia, No. 34/08 and 61/11 and No 99/13, 56/15 and 56/18).

Keywords: *mercury, inductively coupled plasma optical emission spectroscopy, soil, digestate, waste*

INTRODUCTION

Mercury (Hg) is found mainly in cinnabar and coal [1]. The largest mercury emissions come from coal combustion. Elemental mercury represents 53 % of total mercury emissions. However, the major source of organic mercury found in ecosystems is methylmercury ion ($MeHg^+$) [2]. Potential sources of organic mercury include emissions from fossil fuels, medical waste incineration, dental amalgam, and various commercial products such as skin creams, germicidal soaps, vaccinations, thermometers, barometers, light bulbs, and batteries. Other sources of organic mercury include phenylmercury compounds and ethylmercury compounds that were components of latex paints used before the 1990s [3]. Among the most dangerous mercury compounds is dimethylmercury

((CH$_3$)$_2$Hg), which is toxic enough to cause death if only a few microliters get on the skin or even latex gloves [4]. The long-term effects of California gold mining on the redistribution of mercury and consequently on human health have been observed [5]. Mercury poisoning can lead to death.

Hg in environmental samples can be analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), cold vapour atomic absorption spectroscopy (CVAAS), cold vapour atomic fluorescence spectroscopy (CVAFS) and direct analysis by thermal decomposition [6].

Numerous mercury-contaminated and mercury-free soil and plant samples were digested and analysed [7]. ICP-AES with wavelength selection at 194.2 nm resulted in reliable detection of mercury in plant and soil samples. Currently, mercury is discharged into the environment in inorganic form. Mercury generally has low mobility in soil [8]. Extensive soil samples were collected from the site of the former roasting plant of Idrija mine, Slovenia [9]. The study showed that the predominant environmental problem related to this site remains inorganic Hg in unroasted cinnabar ore. In addition to soil and plants, Hg analyses were carried out in different types of samples. Impurities in liquid pharmaceutical samples were analysed by inductively coupled plasma optical emission spectrometry (ICP OES) [10].

A preliminary study showed that the inductively coupled plasma optical emission spectroscopy ICP-OES method is not suitable for the determination of mercury in wastewater samples due to trace concentrations. The aim of the study was to determine the applicability of the simplified sample preparation and to validate mercury detection in real contaminated soil, digestate and waste samples using ICP-OES.

As indicated by the various authors, ICP-OES has advantages over atomic absorption spectrometry. It has high selectivity and sensitivity, improved detection limits for refractory elements, improvement of productivity and reduction of matrix interferences [11 - 13]. Improving productivity is extremely important in practice, and ICP-OES makes this possible due to its multi-element analysis capability and wide dynamic range.

MATERIALS AND METHODS

Instrumentation

Inductively coupled plasma optical emission spectroscopy ICP-OES from Spectro ciros vision (USA) was used to determine Hg concentration in environmental samples. The instrument is equipped with Smart Analyzer Vision for method programming. The instrument settings are shown in Table 1. Two spectral lines were selected: the mercury emission line at wavelength 194.2 nm may be a better choice than the more intense line at 184.9 nm to avoid spectral interference from iron [14].

Table 1. Inductively coupled plasma (ICP) parameters settings

Conditions	Value
RF power	1500 W
Auxiliary flow	1.7 L/min
Plasma flow	12 L/min
Nebulizer flow	0.75 L/min
Torch	Radial view
Pump mode time Wash time	24 s 30 s
Spectral lines selected	Hg 184.9 nm Hg 194.2 nm

Sandy soil C (CRM-SA-C) certified reference material (CRM1) was obtained from High-Purity Standard, Inc. (Charleston, SC, USA), with certified Hg concentration of 5.0 ± 0.2 mg/kg. The certified reference material (CRM2), ERM-EC680k (European reference material sample with certified values) was obtained from Sigma-Aldrich (Steinem, Germany). The CRM2 was prepared from low density polyethylene granulate spiked with inorganic pigments, including HgS. The certified concentration is 4.64 ± 0.2 mg/kg Hg.

Samples

Various environmental samples were selected for analyses, and those without detectable Hg concentrations were spiked. All samples were sampled according to Characterization of Waste - Sampling of Waste Materials - Framework for the preparation and application of a sampling plan SIST EN 14899:2006.

In accordance with the standard, a sampling plan was prepared and, as necessary, adjusted to the actual situation in the field before sampling. List of samples is presented in Table 2.

Table 2. List of samples

Samples	Sample
Environmental samples	Compost
	Excavated contaminated soil
	Ground coal, spiked with 0.75 mg/L Hg (Coal)
	Soil, spiked with 24 mg/L and diluted with factor 200 (Soil)
Industrial samples	Industrial sludge
	Shredded light fraction
	Waste wood, spiked with 0.25 mg/L Hg (Waste wood)
	Digestate, spiked with 0.3 mg/L Hg (Digestate)
	Ground electronic scrap
	Ash
	Plastic material doped with 0.5 mg/L Hg (Plastic)

Sampling of industrial sludge, shredded electronic waste, shredded light fraction, ash, waste wood, shredded coal and plastics was done at landfills or intermediate storage facilities of waste handling companies. Sampling of compost was done in the composting plant and the digestate was sampled at the biogas plant. Excavated contaminated soil was sampled in the area of origin in the same way as the soil sample.

Sample preparation

Procedure 1: Powdered samples (2.5 - 3 g) were mixed with 21 mL HCl (37 %, Emparta) and 7 mL HNO$_3$ (65 %, Fluka) and heated for 2 h under reflux. The sample was then filtered through a cellulose filter into a 100 mL flask and diluted to the mark with deionized water. A drop of defoamer was added and stirred vigorously for 30 s before measurement. Procedure 1 is also known as aqua regia digestion.

Procedure 2: Waste samples (0.25 - 0.5 g) were homogenized and crushed to a diameter of 250 μm. The sample was placed in teflon reactors. 6 mL of HCl (37 %, Emparta), 2 mL of HNO$_3$ (65 %, Fluka) and 2 mL of HF (40 %, AppliChem) were added. The reactors were placed in a microwave cooker (800 W) for 15 min with a ramp of 5 (n = 3) at a temperature of 120 °C (holding time: 10 min), 160 °C (holding time: 5 min), and 180 °C (holding time: 10 min). After the reactors had cooled down, they were carefully opened, and 0.65 g boric acid (AppliChem) was added. The reactors were then resealed and placed back in the microwave oven where the program was repeated. The residue was transferred to the volumetric flask (50 mL) and diluted to the mark with deionized water. Procedure 2 is also called microwave digestion.

Determination of LOD and LOQ

Limit of detection (LOD) refers to the lowest concentration that can be detected with a certain degree of confidence, and limit of quantification (LOQ) refers to the lowest analyte concentration that can be quantitatively analysed by a given method with a reasonable degree of confidence [15]. These definitions represent the principle of the 3σ and 10σ approaches (σ = population standard deviation), which are now normative approaches for defining the values of LOD and LOQ. The approaches use the mean blank signal value, as the reference point value for the calculation of LOD and LOQ.

RESULT AND DISCUSSION

Results of LOD and LOQ determination

During the development of the ICP-OES method, a series of standards of decreasing

concentration were used to determine the limit of detection (LOD) and limit of quantitation (LOQ) for the detection of mercury. These results were obtained using a blank-based calibration and five calibration standards (concentrations of 0.01, 0.025, 0.05, 0.1, and 0.5 mg/L) in 5 % nitric acid. Standard deviation (s_0) and relative standard deviation (RSD) were calculated.

The results of determination of LOD and LOQ in samples prepared by procedure 1 and procedure 2 are shown in Table 3. The results are presented at two wavelengths (λ), 184.9 nm and 194.2 nm. It can be seen that LOD and LOQ are the same at two different λ (procedure 1).

Table 3. Limit of detection (LOD) and limit of quantification (LOQ) of digested samples prepared by procedure 1 and procedure 2

	Procedure1 at		Procedure2 at	
	184.9	194.2	184.9	194.2
Average of blank [mg/L]	0.0058	0.0030	0.0025	0.001
s_0	0.0030	0.0030	0.0042	0.0015
LOD [mg/L]	0.009	0.009	0.013	0.004
LOQ [mg/L]	0.030	0.030	0.042	0.015
LOD [mg/kg d.m.]	0.1520	0.1520	2.112	0.742
LOQ [mg/kg d.m.]	0.5069	0.5069	7.042	2.472

Determination of the working range

The blank samples have been measured along with calibration standards, 3 times at 6 concentrations which were evenly distributed over the linear range. Interferences did not cause non-linear responses, and the ability of the method to extract/recover the analyte varied with the sample matrix [16].

I in Figure 1 refers to the Intensity in counts per second (cps) in correlation with mercury concentration c (mg/L). As seen in Figure 1, the range for both λ were determined from 0.03 to 1 mg/L for procedure 1. For procedure 2, the working range was determined from 0.04 to 1 mg/L and from 0.015 to 1 mg/L at 184.9 and 194.2 nm, respectively. The results are consistent with another study in which the working range was determined from 20 µg/L to 1 mg/L without the need for dilution [7].

Precision and accuracy

A certified reference soil standard containing mercury (CRM1) was analysed to verify the accuracy of the method. The certified value of mercury in soil was 5.0 ± 0.2 mg/kg. This certified standard was digested in triplicate and analysed by ICP-OES. The preformed analyses following procedure 1 gave an average result of 4.27 ± 0.05 mg/kg at 184.9 and 4.76 ± 0.26 mg/kg at 194.2 nm, giving a mercury recovery of 92.1 % with a relative error of 7.9 % at 184.9 nm, and mercury recovery of 102.6 % with a relative error of 2.7 % at 194.2 nm. These ICP-OES results are in statistical agreement with the certified value at a confidence level of 95 % at 194.2 nm [7].

A certified reference standard containing mercury (CRM2) was analysed to verify the accuracy of the method following procedure 2. The certified value of mercury was 4.64 ± 0.2 mg/kg. The preformed analyses following procedure 2 gave an average result of 4.94 ± 0.33 mg/kg at 184.9 and 5.32 ± 0.27 mg/kg at 194.2 nm, giving a mercury recovery of 106.4 % with a relative error of 6.4 % at 184.9, and mercury recovery of 114.6 % with a relative error of 14.6 % at 194.2 nm. This ICP-OES result does not statistically agree with the certified value at the 95 % confidence level at 194.2 nm.

Therefore, interlaboratory reproducibility was checked using the same method. 6 replicates (N) were made, and average value was calculated. The samples were treated according to procedure 1. The results are presented in Table 4. RSD_{pool} was calculated based on all four samples (waste wood, digestate, coal and soil) measurements.
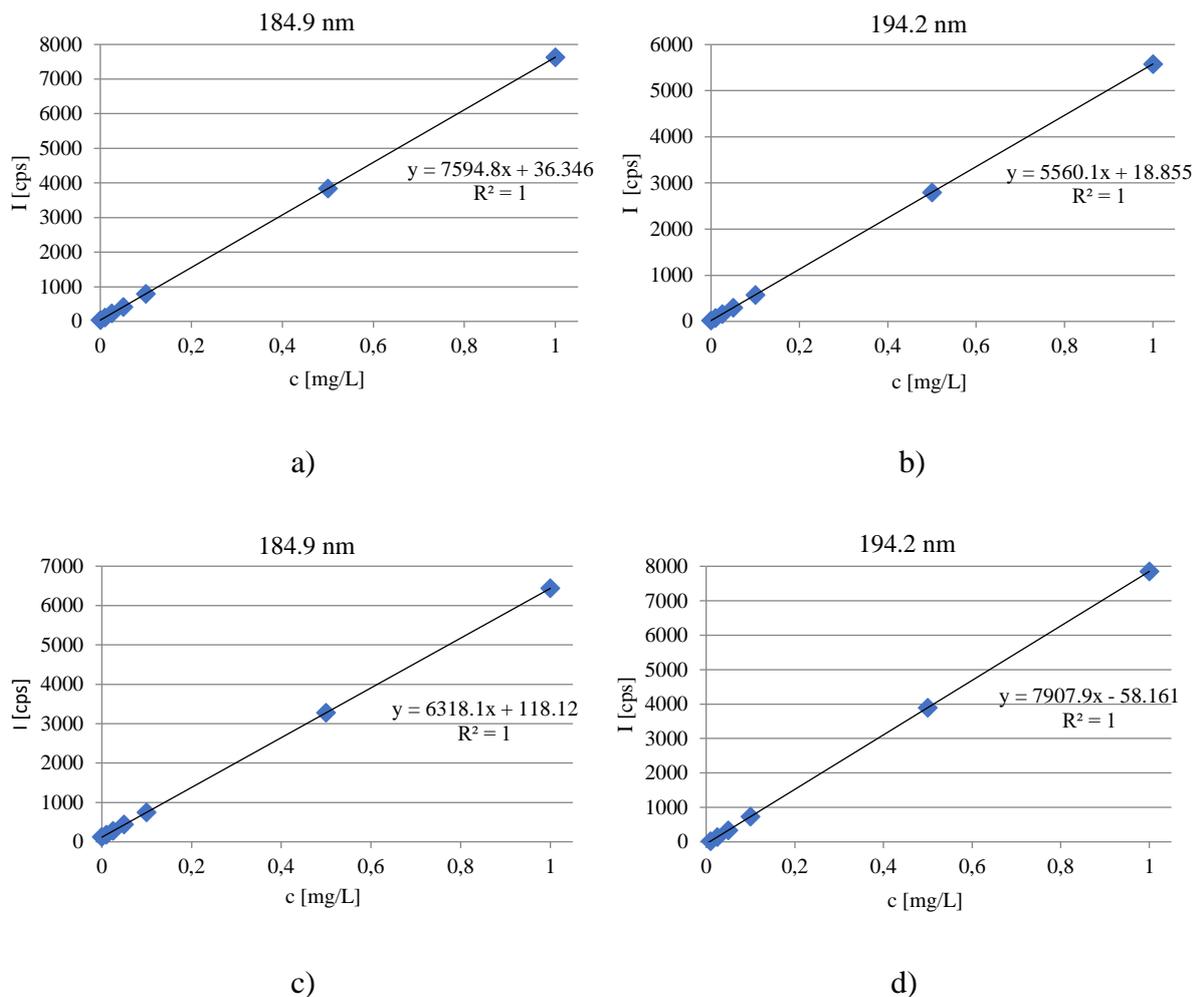
Figure 1. Linear weighted regression for samples treated with procedure 1 (a, b) and procedure 2 (c, d)

It can be seen that $R^2 = 1$, while the condition is $R^2 > 0.9999$.

Table 4. Reproducibility results (RSD_{pool}) of samples after procedure 1

λ [nm]	184.9				194.2			
Sample	Waste wood	Digestate	Coal	Soil	Waste wood	Digestate	Coal	Soil
Average of measurement [mg/L]	0.024	0.242	0.771	0.118	0.025	0.291	0.763	0.119
s_o	0.003	0.021	0.015	0.002	0.004	0.023	0.010	0.007
RSD [%]	10.918	8.797	1.924	1.895	13.987	7.857	1.321	6.265
N	6	6	6	6	6	6	6	6
RSD_{pool} [%]	7.139				8.637			

The reproducibility results for the samples treated with procedure 2 are shown in Table 5. RSD_{pool} was calculated based on ERM-EC680k and plastic samples. The RSD_{pool} is slightly worse compared to those in Table 4. However, the RSD_{pool} is below the limit of 15 %.

Table 5. Reproducibility results (RSD_{pool}) of samples after procedure 2

λ [nm]	184.9		194.2	
Sample	ERM-EC680k	Plastic	ERM-EC680k	Plastic
Average of measurement [mg/L]	0.059	0.478	0.063	0.458
s_o	0.006	0.062	0.004	0.066
RSD [%]	9.505	12.928	5.723	14.458
N	6	6	6	6
RSD_{pool} [%]	11.346		10.995	

Results in Tables 6 and 7 were calculated as sampled basis from calibration curve and recalculated based on dry matter to mg/kg. As shown in Tables 6 and 7, most Hg concentrations in environmental samples are below the LOQ, but above the LOD. However, in some specific wastes, such as industrial sludges or soil wastes, Hg concentrations are high enough to be assessed with some confidence.

Table 6. Results of Hg concentration in environmental samples treated by procedure 1

Procedure 1 digestion	184.9 nm [mg/kg]		194.2 nm [mg/kg]	
	Average measurement	s_o	Average measurement	s_o
Compost	0.08	0.05	0.13	0.04
Industrial sludge	0.47	0.095	0.86	0.092
Excavated contaminated soil	0.20	0.05	0.56	0.07
Ground electronic scrap	13.67	0.07	13.65	0.07

Table 7. Results of Hg concentration in environmental samples treated by procedure 2

Procedure 2 digestion	184.9 nm [mg/kg]		194.2 nm [mg/kg]	
	Average measurement	s_o	Average measurement	s_o
Shredded light fraction	0.17	0.27	1.6	1.4
Ash	0.17	0.26	1.7	0.43

The LOQ was determined to be 0.5 mg/kg soil using procedure 1. The LOQ was higher using procedure 2, above 2.4 and 7 mg/kg at 194.2 and 184.9 nm, respectively. The applicability of sample preparation by procedure 1 for ICP-OES determination in different environmental samples in terms of regulation was evaluated. Several legally defined limits were found, which are summarised in Table 8.

Table 8. Limit values from different statutory documents

Hg limits (Decree on soil)	Limit immision	Warning immision	Critical immision
Value [mg/kg]	0.8	2	10
Digestate (Decree on the recovery)	1st quality (< 20 % dry matter)	1st quality (> 20 % dry matter)	2nd quality
Value [mg/kg]	1	1	3
Compost (Decree on the recovery)	1st quality	2nd quality	
Value [mg/kg]	1	3	

Regarding the Decree on Burdening of Soil with Waste Spreading [17], the statutory limits are below the LOQ for the application of procedure 1.

According to the legally determined values written in the Decree on the Treatment of Biodegradable Waste and the Use of Compost or Digestate and the Decree on Soil Pollution by Waste Input [18, 19], the LOQ of the method after procedure 1 was low enough that this procedure could be applied to the entire spectrum of environmental sample

measurements, while the LOQ determined after procedure 2 was not.

CONCLUSION

In summary, it has been shown that the simple method according to procedure 1 allows rapid determination of mercury in soil and hazardous waste samples by applying ICP-OES. Mercury emission line at a wavelength 194.2 nm was chosen instead of the more intense line at 184.9 nm to avoid spectral interference from iron.

An LOQ of 50 μg/L and a linear working range of 30 μg/L to 1 mg/L were calculated. The study showed that the described method is suitable for the determination of Hg in soil samples, digestate and hazardous waste, where quite high Hg concentrations were measured. The method is not suitable for municipal waste. Proper sample preparation can save time, cost and effort in the analysis of Hg in environmental samples compared to other methods. In practice, this is extremely important because it enables the productivity of the analytical laboratory to be increased. The increase in productivity is mainly reflected in the profitability of the company. The study confirms the applicability of the described method for samples with concentrations in the mg/L range, while standardized methods are more suitable for samples with Hg concentrations in the trace range.

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Acknowledgements