Determination of lead in contaminated soils by graphite furnace atomic absorption spectrometry for environmental risk assessment

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Abstract. A simple and rapid graphite furnace atomic absorption spectrometric (GF-AAS) technique was developed for the determination of lead in soil samples taken from a skeet shooting area. The method was evaluated by measuring some of the samples by inductively coupled plasma atomic emission spectrometry. Water and nitric acid extraction were used to determine the easily soluble lead and the total lead in order to evaluate the mobility of lead in the ground. The precision (RSD) of the GF-AAS analysis ranged from 1.1% to 3.2%. The method was tested with determining the lead in the reference materials CANMETC-Cu, PACS-2, and CRM 320. The results obtained were in good agreement with the recommended values.

Key words: lead determination, contaminated soils, GF-AAS, ICP-AES, environmental risk assessment.

INTRODUCTION

It has been realized recently that lead in the skeet shooting ranges may cause environmental problems. The annual load of lead is thousands of kilograms per range, and in some cases the skeet shooting ranges are situated in regions with high groundwater levels. The mobility of lead in soil is determined mainly by the pH and cation exchange capacity [1]. The threshold value of lead in the soil for

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pollution in Finland is 300 mg/kg [2]. If the threshold value is exceeded, generally evaluation of pollution risk and possible actions to minimize it are required.

According to the quality requirements for drinking water in Finland the maximum concentration of lead may be 0.01 mg/L [1]. In nature lead is accumulated in soil and tissues of water organisms. In human beings lead poisoning causes lack of appetite, anaemia, stomach pain, and partial paralysis. For children a too high lead concentration in blood may cause misbehaviour and it may slow down their mental development [3].

The determinations from samples with high lead concentrations are usually performed in addition to flame atomic absorption spectrometry by inductively coupled plasma atomic emission spectrometry, photometry, and X-ray fluorescence [4–11].

Few techniques of chemical analysis enjoy the same position as atomic absorption spectrometry. This is based on its good sensitivity, low detection limits, relatively low costs of the technique, and high speed of analysis. In the determinations of lead by the flame atomic absorption technique the detection limit is about 0.19 mg/L and the dynamic range up to 20 mg/L when the most popular wavelength of 217.0 nm is used [12, 13]. For the graphite furnace technique the detection limit is 0.012 ng/mL [13]. For the determination of trace levels of lead in environmental samples an advantageous flow injection on line co-precipitation–pre-concentration systems for flame atomic absorption measurement was recently published [14]. This technique is good when the trace levels of lead have to be measured in different kinds of samples.

The decomposition methods used for the determination of various metals in environmental samples are total decomposition, strong acid extraction, or determination of available metals. Total decomposition is performed by using hydrofluoric acid with nitric, sulphuric, perchloric, and hydrochloric acids in various combinations. Strong acid-extractable metals have been determined using aqua regia, hydrochloric, nitric, sulphuric, and perchloric acids, or a combination of these. Available metals have been determined by extraction using weak acids or chelating agents [15–17]. On the basis of these techniques various sequential extraction procedures have been developed [18–20].

The aim of this study was to develop a rapid analytical method for the determination of lead in shooting areas in order to evaluate the risk caused by high lead concentrations to groundwater. That is why the dissolution procedures should be as simple as possible. This technique can also be used if more elegant and more expensive methods are used for risk assessment.

EXPERIMENTAL

Instrumentation and operating technique

All samples were analysed with a Perkin Elmer Zeeman 3030 atomic absorption spectrometer, equipped with the graphite furnace HGA 600. A lead hallow

Table 1. GF-AAS operating conditions for lead determination

Method parameters			
Wavelength	283.3 nm	Sample volume	20 μL
Slit	0.7 mm	Furnace type	Pyrolytically coated
Replicates	2		L'vov platform
Integration time	5 s	Inert gas	Argon
Signal mode	Peak area		

Furnace programme				
Step	Temperature, °C	Ramp, s	Hold, s	Gas flow rate, mL/min
Drying 1	90	1	1	300
Drying 2	130	20	15	300
Pyrolysis	700	20	15	300
Atomization	1900	0	5	0
Cleaning	2500	1	5	300
Cooling	20	1	5	300

Table 2. ICP-AES instrumental parameters and conditions

Injector tube (quartz)	1.50 mm i.d.
Plasma power	1.0 kW
Coolant argon flow	13.0 L/min
Nebulizer argon pressure	280 kPa (40 psi)
Sample uptake	1.0 mL/min
Sample read delay	60 s
Autosampler wash delay	20 s
Integration time	3 s
Number of integration	3
Wavelength Pb (I)[a]	280.199 nm

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[a] Atom line.

cathode lamp (HCL) was used. The sample introduction system included a Model AS-60 autosampler.

The results were evaluated by analysing some of the samples with a sequential PU 7000 Philips (Unicam Analytical System, Cambridge, UK) inductively coupled plasma-atomic emission spectrometer (ICP-AES). The ICP-AES includes a 40.68 MHz free-running oscillator for driving the plasma, an echelle grating for wavelength separation, and a grid nebulizer for sample aspiration. Instrumental parameters for the graphite furnace atomic absorption spectrometer (GF-AAS) and ICP-AES are presented in Tables 1 and 2. For microwave dissolution a Milestone MLS 1200 microwave oven was used.

Reagents and standards

All the reagents used were pro analytical or suprapure grade of Merck. The stock solution containing 1000 mg/L (Reagecon) of lead was used for the

preparation of standards. For all dilutions Milli-Q water (16–18 MΩ/cm) was used. For the microwave decomposition 65% nitric acid (suprapure) was used.

Sample preparation

The samples were taken from each soil horizon. The distance of the six sample points varied from 50 to 200 m from the shooting place covering the different types of ranges where the lead bullets fall down. Two control samples were taken at about 100 and 200 m distance outside the shooting range.

Symbols of horizons and sampling depth: A_0 (humus layer), 0.5–1.5 cm; A (leached layer, white mineral soil), 3–10 cm; B (enriched layer, dark brown mineral soil), 10–17 cm; C (basic soil layer, yellowish brown mineral soil), 40–60 cm.

For the determination of water-soluble lead 5 ± 0.0002 g soil samples having the original humidity were weighed into polyethylene bottles. Distilled water (50 mL) was added and the bottles were shaken for 24 h. The moisture content of different sample materials was determined from separate samples in order to avoid the influence of the drying process on the solubility of the lead. For the evaluation of the total concentration of lead 2.5 g of soil sample was weighed into the fluoroplast microwave digestion vessel and 10 mL 65% nitric acid was added. The digestion time was 5 min used at a power of 1200 W for 12 vessels. After the digestion the samples were filtered and diluted by distilled water to the volume of 100 mL.

RESULTS AND DISCUSSION

The microwave digestion by nitric acid was chosen for the dissolution because this seemed to dissolve lead totally from the studied types of environmental samples. The extraction by distilled water was chosen in order to directly see the amount of already solved or very easily solved lead. The measurement procedure was developed for graphite furnace atomic absorption so that no matrix modifier was needed. After the dissolution of the samples, the sample solutions were either dilute water or acid solutions being of the same type so that an exact furnace program could easily compensate for the absence of the matrix modifier. The method was tested by analysing selected samples by the ICP-AES method. The differences of the results obtained by the two methods were tested by Student's t-test and F-test [21] to ascertain whether the difference between the two methods was significant. The statistical tests applied showed that the method developed is accurate and there is no significant difference between it and the results obtained by the ICP-AES method.

Table 3 presents the results as relative standard deviations for different concentrations of samples. The table shows that the precision and the repeatability of the method are good. The reference materials were also analysed (Table 4). A good agreement with certified values of reference materials was obtained

Table 3. Relative standard deviations (RSD, %) obtained on the determination of different lead concentration levels after nitric acid leaching procedure

Sample[a]	Soil layer	GF-AAS, mg/L		ICP-AES, mg/L	
		$\bar{c}$ [b] $\pm$ SD	RSD, %	$\bar{c}$ [b] $\pm$ SD	RSD, %
S1	A_0	18.5 ± 0.36	1.92	18.6 ± 0.24	1.3
S2	A_0	10.2 ± 0.19	1.81	10.0 ± 0.15	1.5
S3	A_0	14.5 ± 0.10	0.69	14.3 ± 0.23	1.6
S4	A_0	68.2 ± 2.15	3.15	68.4 ± 0.62	0.9
S5	A_0	667.0 ± 21.34	3.20	665.6 ± 6.00	0.9
S6	A_0	62.4 ± 1.02	1.64	62.7 ± 0.88	1.4
C1	A_0	0.30 ± 0.003	1.07	0.32 ± 0.006	1.8
C2	A_0	0.20 ± 0.003	1.44	0.18 ± 0.003	1.7
S1	B	0.26 ± 0.007	2.75	0.27 ± 0.005	1.9

[a] S stands for shooting range and C is control from the background outside the shooting range.
[b] Mean concentration of five replicates.

Table 4. Results of GF-AAS determination of lead in reference materials

Reference material	Certified value, %	Found[a] , %	
	$\bar{c} \pm$ SD	$\bar{c} \pm$ SD	RSD, %
CANMETC – Cu	0.364	0.333 ± 0.0113	3.39
PACS – 2	0.0183 ± 0.0008	0.0188 ± 0.0007	3.72
CRM 320	0.0043 ± 0.0002	0.0041 ± 0.0001	2.44

[a] Five replicates.

[22, 23]. This proves that the developed AAS method provides a precise and accurate technique for the determination of the lead concentration in skeet shooting areas.

Analytical results obtained in the shooting range

The skeet shooting range situated in the town of Raahe in central Finland was selected as the test area. The shooting area is situated on a dry sand moor, where the groundwater is several meters below the ground level. Skeet shooting has been practised there for about 10 years. The lead bullets used cause an environmental risk when the metallic lead is dissolved. Thus it is important to know the mobility of lead in this type of soil.

The concentration of lead in the samples decreases from the A_0 towards the C horizon as expected. Water-soluble lead varied from 0.14 to 3.1 mg/kg in the A_0 horizons and from <0.01 to 0.96 mg/kg in the other horizons (Fig. 1). Total lead varied from 536 to over 10 000 (26 300) mg/kg in the humus layers and from 1.26 to 163 mg/kg in the mineral soil layers (Fig. 2). The ratio of water-soluble and total lead was from <0.01 to 0.0018 in the A_0 layers and from <0.01 to 0.037 in the mineral soil layers (Fig. 3). This shows that lead is not absorbed in the enrichment
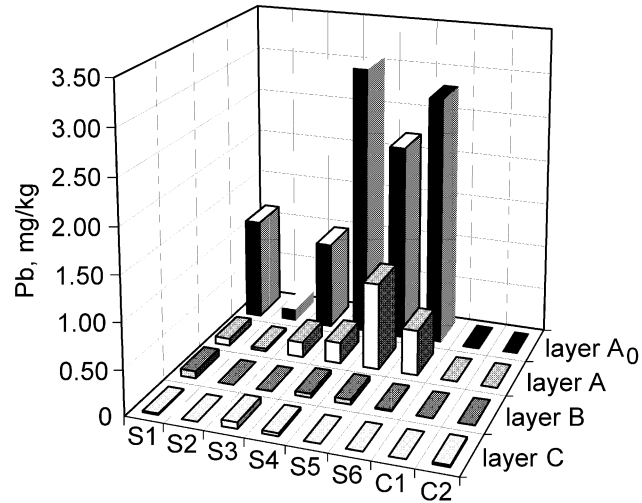
Fig. 1. Water-soluble lead concentration in soil samples from A_0 to C horizons. Samples S1–S6 were taken from the skeet shooting range and control samples C1 and C2 from background outside the shooting range.
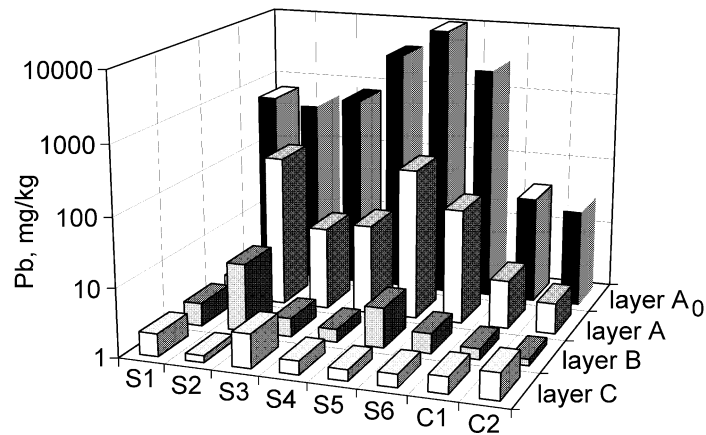

Fig. 2. Total lead concentration in soil samples determined after microwave leaching procedure with HNO_3.

layer but it continuously goes deeper in the ground (see Figs. 1 and 2). This mobility can also be verified by observing the ratio of water-soluble and total lead in the different layers of the ground. Figure 3 demonstrates that the ratio of water-soluble lead to total lead is increasing towards deeper layers. However, these observations also show that the mobility of lead is slow and the soil is binding lead effectively. The concentration of water-soluble lead is so low in the shooting range investigated that there is no danger for groundwater pollution if the soil is cleaned in some years. Still, lead is slowly leached through the soil and
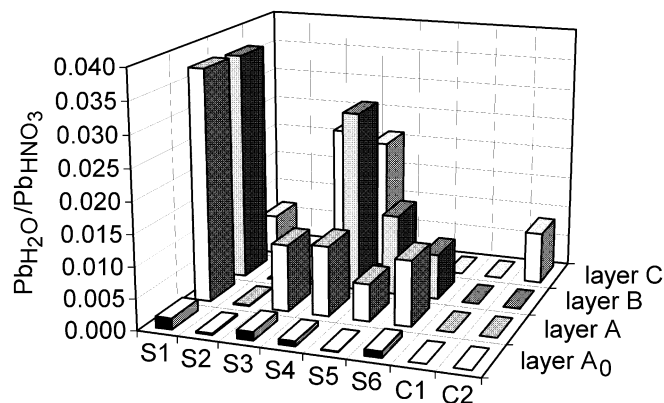
Fig. 3. The ratio of water-soluble and total lead in samples collected from different horizons.

this may cause environmental problems in the future, which makes the follow-up of the concentrations necessary. Also different factors like acid rain or possible formation of insoluble sulphates may have an important role by increasing or decreasing the mobility of lead in the future.

CONCLUSIONS

The developed two-step extraction procedure together with atomic absorption determination offers a quick and economical tool for the evaluation of the mobility of lead and pollution risk for groundwater. This simple method contains dissolution by distilled water and total dissolution by nitric acid. By following the concentrations and the ratios of lead in these two solutions estimates on the state of lead in the ground can be obtained. Shooting ranges are very often situated in the vicinity of large villages and towns, which makes it necessary to evaluate the risk for the environment by following the mobility of lead in the ground. The technique described can be also used to evaluate the time periods after which the cleaning of the area should be performed.

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Grafiitküvetiga aatomiabsorptsioonspektromeetriline plii määramine saastunud muldades keskkonnariski hindamiseks

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Arendati kiire ja lihtne GF-AAS-metoodika plii määramiseks saastunud muldades, mis oli kogutud laskeraja ümbrusest (Raahe, Soome). Metoodika võrdluseks kasutati induktiivselt sidestatud plasma aatomiemissioonspektromeetrilist (ICP-AES) meetodit. Plii eraldati muldatest ekstraheerimisel lämmastikhappega (mikrolaine lagundamine) ja vesiekstraktina, et määrata plii liikuvust maapinnas.

Metoodikat testiti mitmete standardmaterjalide analüüsil. GF-AAS-analüüsi täpsus (RSD, %) kõikus 1,1 ja 3,2 protsendi vahel.