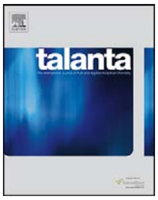
Talanta 82 (2010) 1325–1331

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta



Comparison of action of mixed permanent chemical modifiers for cadmium and lead determination in sediments and soils by slurry sampling graphite furnace atomic absorption spectrometry

Ryszard Dobrowolski*, Agnieszka Adamczyk, Magdalena Otto

Maria Curie-Sklodowska University, Faculty of Chemistry, Department of Analytical Chemistry and Instrumental Analysis, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland

ARTICLE INFO

Article history:
Received 25 February 2010
Received in revised form 22 June 2010
Accepted 28 June 2010
Available online 4 July 2010

Keywords:
Cadmium and lead determination
Slurry sampling atomic absorption spectrometry
Permanent modifiers
Soils
Sediments

ABSTRACT

Slurry sampling atomic absorption spectrometry with electrothermal atomization was used to the determination of cadmium (Cd) and lead (Pb) in soils and sediments using permanent modifiers. Comparison of action of mixed permanent modifiers niobium (Nb)/iridium (Ir) and tungsten (W)/iridium (Ir) were studied in detail. The effect of amount of Ir, W and Nb on analytical signals of Cd and Pb was examined. The optimal amounts of modifiers for Cd and Pb determination were stated. Niobium carbide formation on graphite surface was studied for different pyrolysis temperatures. Finally for Cd determination in sediments and soils 200 μg of Nb mixed with 5 μg of Ir was used as permanent modifiers and 15 μg of Nb mixed with 200 μg of Ir for Pb determination. Suspensions were prepared in 5% HNO_3. The analytical procedure was optimized carefully basing on data from pyrolysis and atomization curves studies. Ammonium dihydrogen phosphate was used additionally as matrix modifier during Cd determination in samples in order to prevent interferences coming from matrix components. The analysis of CRMs confirmed the reliability of the proposed approach. The precision and accuracy of Cd and Pb determination by the described method for soils and sediments were acceptable.

1. Introduction

Determination of heavy metals in sediments and soils by available analytical methods is often a very difficult task because of its low content and interference effects. The conventional methods of trace metals determination in sediments or soils involves acid digestion step, but to bring those samples to the solution is time consuming and includes the use of concentrated acids such as hydrochloric acid, nitric acid, fluoric acid. Slurry sampling graphite furnace atomic absorption spectrometry is a very rapid and convenient method for determination of Cd and Pb in various samples [1–6]. In opposite to this methodology sample contamination and analyte losses may occur if the sample is decomposed before analysis by wet-decomposition or dry-ashing procedures. The slurry sampling technique has been extensively employed to simplify sample preparation procedures. This technique also allows introducing of a small sample mass into electrothermal atomizer, using the same devices available for liquid sampling, such as autosamplers and pipettes [7].

Because of molecular interferences in this technique, the use of chemical modifiers has become an important part of the analytical procedure, in order to obtain interference-free measurement conditions [8]. Generally, the modifiers allow applying high pyrolysis temperature and eliminating at least partially the matrix before atomization, reducing interferences and background signals. A mixture of palladium and magnesium nitrates is the most frequently used chemical modifier in GFAAS. This modifier is universal for more than 20 analytes [9]. The action of modifiers in GFAAS technique for injection of solution, as well as slurry introduction into electrothermal atomizer is different [10]. Chen and Jackson used a palladium/magnesium modifier for the determination of Pb in slurries of sediments by GFAAS [11]. Authors stated that the modifier behaved differently depending on whether the analyte and modifier were premixed or were injected on the separate place into the platform. Therefore, aqueous standards can be used for slurry analysis.

Determination of Pb in sediment slurries by GFAAS was also the subject of the study by Lopes and Arruda [1]. For Pb determination, a 7% (v/v) HNO_3 plus 0.02% (v/v) Triton X-100 solution and conventional modifier magnesium nitrate were used. The extraction of Pb into the liquid phase (7%, v/v HNO_3) was ca. 56% in spite of long time of sonification.

Slurry sampling GFAAS for Cd and Pb determination in soils and sediments were the subject of a study by Lopez-Garcia et al. [6]. For cadmium and lead determination in soils 5% (v/v) hydrofluoric acid was used as the suspension medium. No other modifier

---

* Corresponding author. Tel.: +48 81 5375704; fax: +48 81 5333348.
E-mail address: rdobrow@poczta.umcs.lublin.pl (R. Dobrowolski).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.06.049

than hydrofluoric acid was required. This methodology was used for Cd and Pb determination in soils and sediments of SRM materials. The author applied a fast-heating program to shorten the time of analysis by replacing the conventional pyrolysis step by a modified drying stage at 400 °C. Thanks to action of hydrofluoric acid strong interference effects coming from the presence of chloride was reduced significantly. However, for soils with higher contents of organic materials, drying stage at 400 °C temperature seems to be insufficient for carbonization of organic substances. Additionally, hydrofluoric acid is aggressive for graphite tube and considerably decreases tube lifetime.

Recently, the platinum group metals (PGM), mainly platinum (Pt), rhodium (Rh), ruthenium (Ru) and Ir, have been used as permanent modifiers alone or mixed for the determination of trace elements. Surface modification by permanent modifiers can be realized by thermal treatment, sputtering or electrodeposition techniques [10]. During thermall treatment, the volatile impurities of permanent modifier are eliminated and for this it is not required to employ a high purity permanent modifier. The most important advantages of using of permanent over conventional modifiers include: extended tube lifetime, lower reagent blank and lower limit of the detection. Carbide forming elements such as W, zirconium (Zr) and Nb alone or combined with noble metals have also been used as permanent modifiers [12].

Since the topic is of practical interest, it has been the subject of study by several authors. Lima et al. used single modifiers, such as Rh, Ir, W, Ru and mixed modifiers W/Rh, W/Ir, W/Ru for the determination of Cd and Pb in environmental samples (soils, sediments, sludges) by slurry sampling GFAAS [3–4]. Barałkiewicz and Gramowska described application of W/Rh combined with conventional modifier $NH_4H_2PO_4$ for the Cd determination in lake sediments by slurry sampling GFAAS [2]. Authors described that application of mixed modifier stabilized Cd to 1300 °C but any additional method for real temperature measurements of graphite furnace was applied.

Pereira et al. [13] studied the influence of chosen permanent modifiers on Cd signal for marine sediment using slurry sampling GFAAS technique but the optimization data on used masses of permanent modifiers are not available.

Bianchin et al. [14] applied W/Ir as permanent modifier for the determination of Cd in coal by introduction of slurries into electrothermal atomizer. He suggested that in contrast to some published results, the mixed W/PGM permanent modifiers indicated worse stabilizing power compared to the pure PGM modifiers.

Borges et al. [15] used the classical modifiers and the permanent modifiers: Ru and Ir for Cd determination in sediments and sewage sludge by slurry sampling GFAAS. Authors observed that the thermal behavior of Cd in the presence or without the studied modifiers depends on the sample of the matrix. Finally they chose Ir as the favorable modifier for Cd determination in sediments and sewage sludge.

Permanent modifiers have been successfully used for the determination of Pb by slurry sampling GFAAS in biological matrix such as marine plankton [16], botanical samples [17], plants controlling phytoremediation processes [18], human teeth [19], food [20] and in different biological materials [21]. Acar [17] found that application of mixed permanent modifier W/Ir combined with the classical modifier $NH_4H_2PO_4$ were preferable for Pb determination in slurries of botanical and biological samples by GFAAS technique.

Application of permanent modifiers seems to be a very promising approach, because of the simplicity of the analytical procedure – comparing to use of classical modifiers – relying on introducing of the modifier once into the graphite tube just before the measurements. Moreover, the permanent modifiers act against corrosive tube effecting in increasing the tube lifetime. However for specific and difficult matrixes application of combination of the permanent and the classical modifiers seems to be still necessary.

Table 1
Instrumental parameters and operational conditions for the determination of Cd and Pb in soil and sediment slurries by ETAAS.

	Cd	Pb
Wavelength (nm)	228.8	283.3
Lamp current (mA)	4	5
Slit (mm)	0.2	0.2
Injection volume (μL)	20	20
Intergration time (s)	5	5

Taking into account chemical resistance of transition metal carbides NbC is more thermostable than WC (melting point for NbC is 3500 °C, for WC is 2870 °C) and what is more important NbC shows higher resistance against concentrated mineral acids.

The aim of this study was to compare the action of W/Ir and Nb/Ir permanent modifiers for cadmium and lead determination in sediments and soils samples by application of slurry sampling GFAAS technique. The preliminary studies include: the influence of the amount of modifiers on analytical signal of cadmium and lead in respect to peak shape, comparison of atomization efficiency and stability of niobium carbide with temperature. Basing on preliminary study, the favorable modifier was chosen for cadmium and lead determination in studied samples taking into account optimal time-temperature programme. Additionally, examination of stability of the suspensions in respect to time and analyte partitioning for liquid media were carried out.

2. Experimental

2.1. Instrumentation

Measurements were carried out using AAS-3 (Carl Zeiss, Jena, Germany) atomic absorption spectrometer equipped with a deuterium-lamp background corrector, an EA-3 electrothermal atomizer and a MPE autosampler. Pyrolytically coated graphite tubes and pyrolytically coated L'vov platforms were obtained from PerkinElmer. Measurements were performed using Cd and Pb hollow cathode lamps (PerkinElmer). Pure argon was used as the purge gas with the flow rate of 280 mL min^{-1} in all steps except the atomization stage, where stop-flow was used. Background-corrected integrated absorbance was used as the analytical signal. Instrumental parameters and operational conditions for the determination of Cd and Pb in soil and sediment slurries by ETAAS are given in Table 1. Temperature programs for the determination of Cd and Pb in soil and sediment slurry samples using permanent modifiers are presented in Table 2.

Standard solutions and slurries were prepared using Transferpette micropipets (Brand, Wertheim, Germany), a Sartorius R – 200D balance (Gottingen, Germany), a Vortex agitator and a MPW – 50 separator (Mechanika Precyzyjna, Warszawa, Poland).

Table 2
Temperature programs for the determination of Cd and Pb in soil and sediment slurry samples using Nb/Ir permanent modifier.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow (mL min^{-1})
Drying I	80	20	3	240
Drying II	105	2	40	240
Ashing	700[a,b]	100	5	240
Cooling	120	–	10	240
Atomization	2200[a,b]	1000	5	0
Cleaning	2600	1000	2	280

[a] Nb/Ir permanent modifier combined with $NH_4H_2PO_4$ for Cd determination.
[b] Nb/Ir permanent modifier for Pb determination.

Eppendorf's polyethylene vessels were used for preparing and storing the solutions and the slurries. They were filled with nitric acid for 24 h and flushed with double-distilled water before use. The X-ray diffractograms of modified graphite platform were recorded using the HZG-4 diffractometer (Carl Zeiss, Jena, Germany).

2.2. Reagents and certified reference materials

Spectral purity nitric acid (Merck, Darmstadt, Germany) was used for preparing standard solutions and slurries. Iridium (SCP Science, Quebec, Canada) and niobium (CPI International, Santa Rosa, USA) standard solutions diluted in appropriate way in 5% (v/v) HNO_3 and tungsten standard solution (Fluka, Buchs SG, Switzerland) diluted in double-distilled water with a resistivity of 18 MΩ cm were used for modification of tubes. The calibration standards were obtained from standard solution of cadmium and lead (Merck, Darmstadt, Germany) by dilution with 5% (v/v) nitric acid. Ammonium dihydrogen phosphate was obtained from Merck (Darmstadt, Germany).

Marine sediments certified reference materials (PACS-1, MESS-1) were obtained from National Research Council of Canada (Ottawa, Canada). San Joaquin Soil 2709 obtained from National Institute of Standards and Technology (Gaithersburg, USA) and SL-1 obtained from International Atomic Energy Agency (Vienna, Austria) were used as soils certified reference materials. Samples of estuarine sediment coming from Ume (Ümea, Sweden) and Baltic sediment (BSS) collected by National Institute of Geology (Warszawa, Poland) were studied. The three Polish soils were collected from the polish agriculture area: Felin (Loess Soil), Parczew (Lithic Rendolls) and Bezek (Entic Rendolls).

2.3. Sediment and soil slurries preparation

For slurry preparation the soil and sediment samples were ground using MM-2 vibrational mill (K. Retsch, Haan, Germany), equipped with the chambers and balls made of tungsten carbide. The effectivity of grinding was examined by monitoring slurries prepared in alcohol by means of scanning electron microscopy. It was experimentally stated that after 15 min of grinding, about 80–85% of the particle had sizes below 25 μm. Than the soil and sediment samples were dried at 105 °C in laboratory oven to constant weight. The slurries were prepared by the balance method in clean polyethylene vessels. After weighting of sediment or soil powder 2 mL of 5% nitric acid was added. Then the slurries were homogenized using Vortex agitator before each measurement, which reduced drastically the error caused by the lack of stability of slurries.

3. Results and discussion

3.1. Optimization of amounts of permanent modifier

The action of permanent modifiers is different comparing to classical and slurry sampling techniques. Optimization of proper amounts of permanent modifiers was carried out by study their influence on analytical signal of Cd and Pb, first for increasing amount of W, then for constant amount of W in respect to the highest signal of Cd or Pb with increasing amount of Ir. Similar studies were carried out for Nb/Ir modification. Optimization of Nb mass was carried out first for increasing amounts of Nb, then for constant amount of Nb in respect to the highest signal of Cd or Pb with increasing amount of Ir. In Fig. 1A, the influence of W/Ir and Nb/Ir permanent modifiers on analytical signal for Cd is shown. With increasing tungsten mass the integrated absorbance for Cd rose slightly with plateau around 250 μg of W. In the case of mixed modifier W/Ir integrated absorbance for Cd at the beginning is stabilized (plateau around 80 μg) and then slightly decreases. In case of graphite surface modification by Nb integrated absorbance for Cd is almost double higher than for W. With increasing amount of Nb integrated absorbance for Cd at the beginning decreases slightly and then arises, plateau started from 200 μg of Nb. Quiet surprising for mixed modifier Nb/Ir integrated absorbance increases for small amount of Ir then, reaches maximum around 5 μg of Ir and then decreases rapidly with respect to Ir mass. Basing on above consideration 250 μg of W + 80 μg of Ir and 200 μg of Nb + 5 μg of Ir have been found as efficient amount and proportion of modifiers for Cd determination. In Fig. 1B, the influence of W/Ir and Nb/Ir permanent modifiers on analytical signal for Pb is shown. With increasing W mass the integrated absorbance for Pb rises slightly, then decreases and rises with plateau around 250 μg of W. In the case of mixed modifier W/Ir integrated absorbance for Pb at the beginning rapidly rises and then is stabilized starting from 50 μg of Ir. With increasing Nb mass the integrated absorbance for Pb rises rapidly (maximum integrated absorbance around 15 μg of Nb) and then slightly decreases with plateau started from 100 μg of Nb. In case of graphite surface modification by mixed Nb/Ir modifier integrated absorbance for Pb is almost 1.5 times higher than for W. At the beginning integrated absorbance increases for small amount of Ir then is stabilized (plateau around 100 μg of Ir). Basing on described data and relation shown in Fig. 2, 300 μg of W and 15 μg of Nb have been found as proper amount for Ir optimalisation. However, the double peak of signal of Pb was observed as a result of the graphite tube modification, primarily by 15 μg of Nb or 300 μg of W and then modification by the smallest amount of Ir for which the plateau for Pb signal was observed (Fig. 1B). In Fig. 2, the absorbance-time profiles for the atomization of 0.4 ng Pb in aqueous solution in the presence of different combination of Nb alone

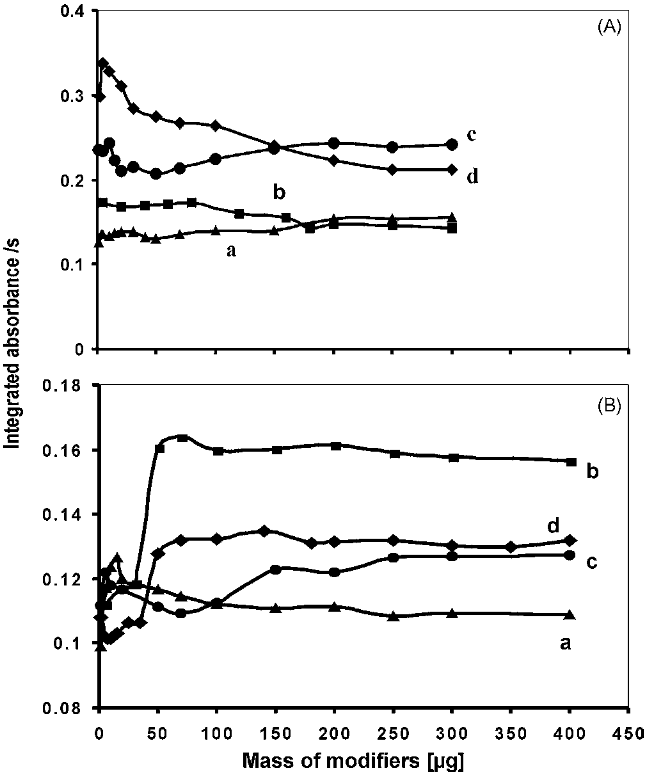


Fig. 1. (A) W (a) and 250 μg W + Ir (b), Nb (c) and 200 μg Nb + Ir (d) masses influence on Cd (0.02 ng) analytical signal. Pyrolysis temperature 400 °C, atomization temperature 2000 °C; (B) Nb (a) and 15 μg Nb + Ir (b), W (c) and 300 μg W + Ir (d) masses influence on Pb (0.4 ng) analytical signal. Pyrolysis temperature 600 °C, atomization temperature 2000 °C.

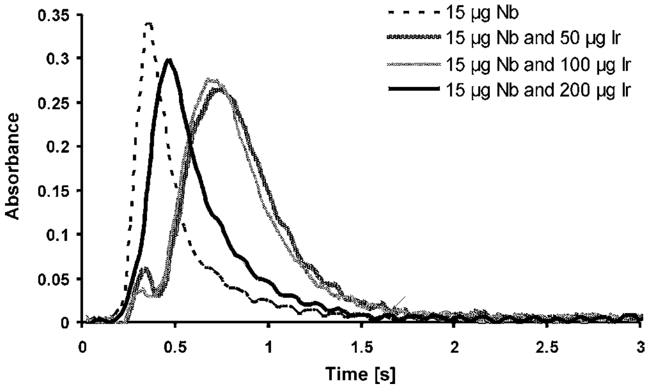


Fig. 2. Absorbance-time profiles for the atomization of 0.4 ng Pb in aqueous solution in the presence of appropriate amounts of Nb alone and Nb with increasing amounts of Ir permanent modifier. Pyrolysis temperature 600 °C and atomization temperature 2000 °C.

and Nb/Ir permanent modifier are shown. The absorbance profile for Pb in aqueous solution in the presence of 15 μg of Nb alone is distinctly different from the peak for Pb when a mixed modifier was used. In the presence of 15 μg of Nb alone the signal appeared earlier than when the mixed modifier Nb/Ir was used. In case of application of mixed modifier the absorbance signal becomes broader, decreasing the peak high and showing double maxima. This behavior can be explain by the different extent niobium-iridium and tungsten-iridium interaction and surface distribution. Similar effect for iridium-tungsten and iridium-zirconium modification of the graphite surface for study of bismuth, silver and tellurium vaporization was observed by Slaveykova et al. [22]. For such high amount of Ir as 200 μg, one maximum of signal was observed. Basing on above study 15 μg of Nb + 200 μg of Ir have been found as efficient amount and proportion of modifiers for Pb determination. Experimentally it was stated that for W/Ir modification peak with double maxima was observed. For this reason 300 μg of W and 400 μg of Ir were chosen for graphite tube modification for which peak with one maximum was observed. Comparing the action of mixed W/Ir and Nb/Ir modifiers (Fig. 1A and B) it is clear that Nb/Ir modification result in higher efficiency of atomization of both Pb and Cd. In order to compare the formation of niobium and tungsten carbides onto graphite surface XRD studies were studied in particular.

3.2. XRD study of carbide formation

Particular study on tungsten carbides formation was reported earlier [23]. It was observed that crystals of W_2C and metallic W were formed at 1250 °C. At the temperature of 1500 °C formation of WC took place, simultaneously the peak for crystals of metallic tungsten decreased on X-ray diffraction pattern. For the temperature higher than 2000 °C W_2C and WC existed whereby the conversion of W_2C to WC took place. In this paper particular study on niobium carbides formation was done. Taking into account the fact that the synthesis of NbC and Nb_2C depends mainly on carbide temperature formation [24], the L'vov platform treated by 1 mg of Nb was heated according to the procedure described by Dobrowolski [23]. The process involved four stages of thermal treatment: at 1250 °C for 10 min, 1550 °C for 10 min, 2050 °C for 10 min and 2500 °C for 100 s. After each heating the structural changes on the platform were investigated by X-ray diffractograms using the HZG-4 diffractometer.

In Fig. 3 part of X-ray diffraction patterns of the graphite/niobium platform surface in respect to modification temperature is shown. Decomposition of niobium pentachloride at the temperature 1250 °C results in Nb_2O_5 formation (Fig. 3A). Formation of stable α-Nb_2O_5 at the temperature 1120 °C was reported earlier by Bansal [25]. At the temperature of 1550 °C formation of NbC takes place (Fig. 3B). Further thermal treatment of modified platform at temperature 2050 and 2500 °C do not result in changes of X-ray diffractograms. It is clear that NbC formed on graphite surface is stable in higher temperature and does not convert into Nb_2C opposite to W_2C. It can be expected that action of NbC comparing to WC and W_2C as permanent modifier should be more stable in respect to temperature and firing numbers.

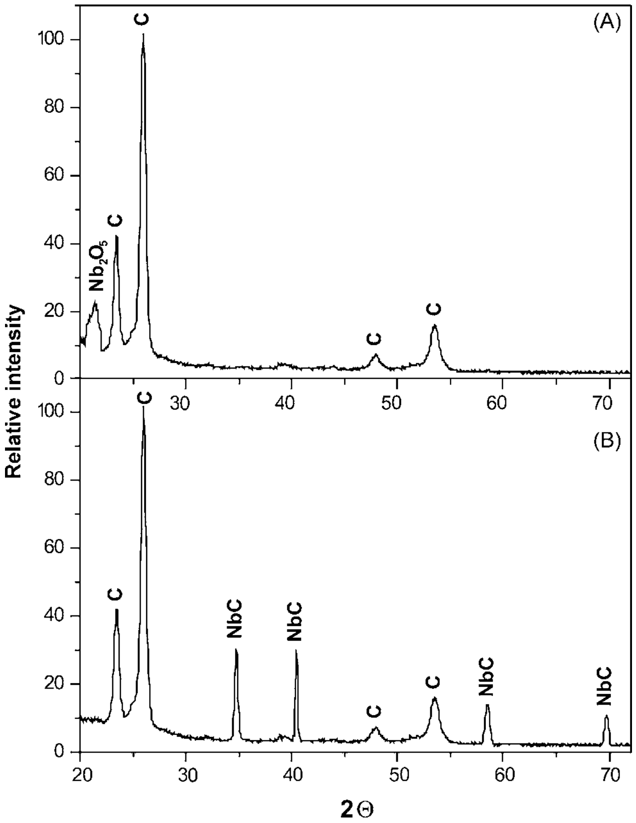


Fig. 3. Part of X-ray diffraction patterns of the graphite/niobium nitrate system heated at (A) 1250 °C and (B) 1550 °C for 10 min.

3.3. Optimization of the time-temperature programme

The action of permanent modifiers for slurry sampling GFAAS technique seems to be more composed in comparison to aqueous solutions. It can be expected that matrix components interact with an analyte and different species are formed. Moreover, in the case of soils and sediments the strong interaction of silica on graphite surface at the temperature higher than 2450 °C can be expected. The influence of matrix components using proposed modifiers on Cd and Pb signal was studied in particular depending on the relation of pyrolysis and atomization curves.

Fig. 4A presents comparison of pyrolysis and atomization curves for 0.4 ng Pb in aqueous solution and for slurry prepared from NIST 2709 using 15 μg Nb + 200 μg Ir as permanent modifiers. Comparing pyrolysis curves for the slurry and aqueous solution for Pb it is visible that matrix of NIST 2709 causes a decrease of maximum temperature of pyrolysis curves for Pb from 1000 °C for solution to 700 °C for slurry. On the other hand the shape of atomization curves is very similar for slurry and aqueous solution for Pb. Because of influence of matrix components from NIST 2709 the optimal temperature for pyrolysis is 700 °C and for atomization 2200 °C. In Fig. 4B comparison of pyrolysis and atomization curves for 0.4 ng

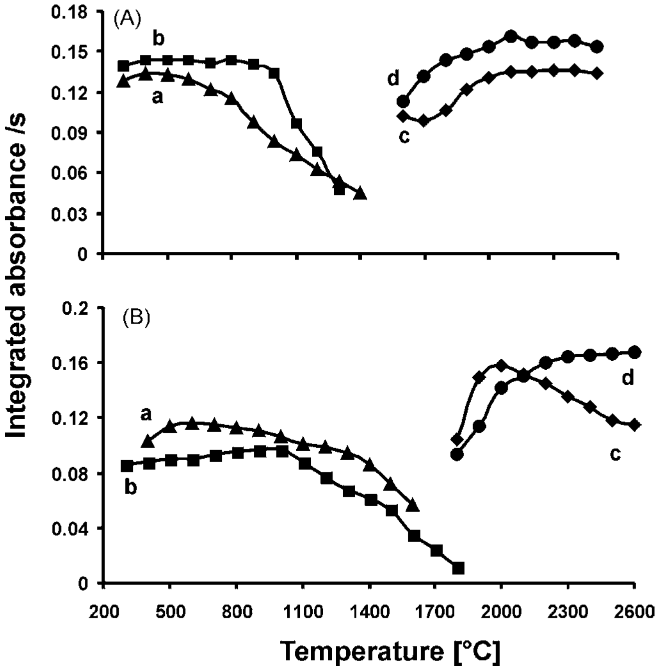


Fig. 4. Comparison of pyrolysis and atomization curves for 0.4 ng Pb in aqueous solution and in NIST 2709 (10 mg/mL 5% HNO_3): (A) using Nb/Ir permanent modifier (a and b – pyrolysis curves for the slurry of NIST 2709 (a) and 0.4 ng Pb in aqueous solution (b), atomization temperature 2000 °C); (c and d – atomization curves for slurry of NIST 2709 (c) and 0.4 ng Pb in aqueous solution (d), pyrolysis temperature 1000 °C); (B) using W/Ir permanent modifier (a and b – pyrolysis curves for 0.4 ng Pb in aqueous solution (a) and the slurry of NIST 2709 (b), atomization temperature 2000 °C); (c and d – atomization curves for 0.4 ng Pb in aqueous solution (c) and the slurry of NIST 2709 and (d), pyrolysis temperature 600 °C).

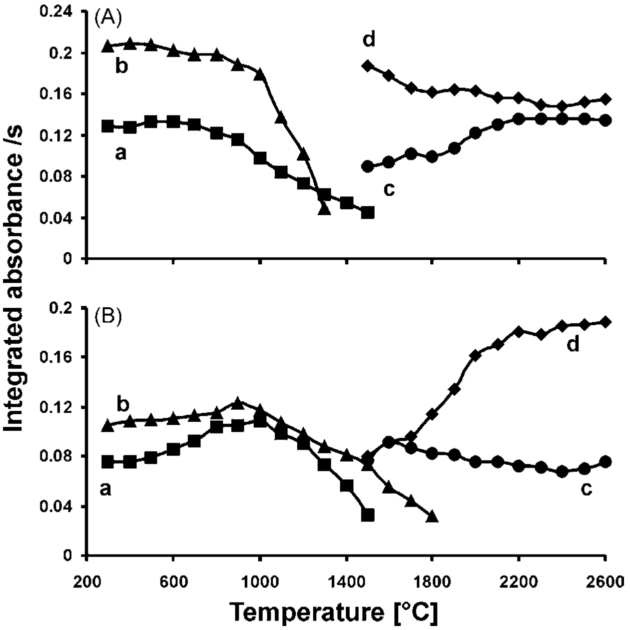


Fig. 5. Comparison of pyrolysis and atomization curves for 0.02 ng Cd in aqueous solution and in NIST 2709 (30 mg/mL 5% HNO_3): (A) using Nb/Ir permanent modifier with conventional modifier $NH_4H_2PO_4$ (a and b – pyrolysis curves for the slurry of NIST 2709 (a) and 0.02 ng Cd in aqueous solution (b), atomization temperature 2000 °C); (c and d – atomization curves for the slurry of NIST 2709 (c) and 0.02 ng Cd in aqueous solution (d), pyrolysis temperature 700 °C); (B) using W/Ir permanent modifier with conventional modifier $NH_4H_2PO_4$ (a and b – pyrolysis curves for 0.02 ng Cd in aqueous solution (a) and the slurry of NIST 2709 (b), atomization temperature 2100 °C); (c and d – atomization curves for 0.02 ng Cd in aqueous solution (c) and the slurry of NIST 2709 (d), pyrolysis temperature 1000 °C).

Pb in aqueous solution and for slurry prepared from NIST 2709 using 300 μg W + 400 μg Ir as permanent modifiers are shown. Opposite to action of Nb/Ir modifier, atomization curves for slurry and aqueous solution for Pb show a different shape. For aqueous solution a maximum around 2000 °C is observed. In case of slurry prepared from NIST 2709 increase of integrated absorbance for Pb with respect to temperature is noted. Pyrolysis curves for Pb show different shape and characteristic. For slurry prepared from NIST 2709 integrated absorbance for Pb monotically increases up to temperature 1000 °C then decreases rapidly. In case of pyrolysis curves for Pb in aqueous solution integrated absorbance decreases monotically from the temperature of 600 °C. Basing on above observation the optimal temperature of NIST 2709 for pyrolysis is 600 °C and for atomization 2000 °C. Comparing the action of two studied modifiers the optimal atomization temperature is a very critical parameter for W/Ir modification.

Using both Nb/Ir and W/Ir modification of graphite surface the maximum pyrolysis temperature for Cd was only 300 °C. This temperature is too low for the effective carbonization of organic materials in soil and sediment samples. It means that high background may occur for atomization step especially for soils rich in organic materials. In order to apply high temperature the application of conventional modifier ammonium dihydrogen phosphate was used. In Fig. 5A, comparison of pyrolysis and atomization curves for 0.02 ng of Cd in aqueous solution and for slurry prepared from NIST 2709 using 200 μg of Nb + 5 μg of Ir as permanent modifiers with addition of $NH_4H_2PO_4$ are shown. Pyrolysis curves for cadmium in aqueous solution as well as in slurry prepared from NIST 2709 are very similar with maximum pyrolysis temperature around 700 °C. Integrated absorbance in respect to temperature for Cd in aqueous solution slightly decreases with growth of temperature. Opposite in case of slurry prepared from NIST 2709 integrated absorbance increases in function of temperature with plateau started from 2200 °C. Basing on above statement the optimal temperature of NIST 2709 for pyrolysis is 700 °C and for atomization 2200 °C. In Fig. 5B pyrolysis and atomization curves for 0.02 ng Cd in aqueous solution and for slurry prepared from NIST using 250 μg of W + 80 μg of Ir as permanent modifiers in combination with $NH_4H_2PO_4$ are shown. Pyrolysis curves for Cd in aqueous solution as well as in slurry prepared from NIST 2709 are very similar with maximum pyrolysis temperature around 1000 °C. Atomization curves for Cd in aqueous solution and for slurry prepared from NIST 2709 are completely different. For the temperature of 2200 °C integrated absorbance of Cd for slurry prepared from NIST 2709 is 2.5 times higher than for aqueous solution. It means that standard calibration method cannot be used. Worth to mention is that the signal obtained for atomization temperature of 2200 °C comes from 20 pg of Cd in aqueous solution as well as in slurry prepared from NIST 2709. Basing on above observation for W/Ir modification of graphite surface with addition of $NH_4H_2PO_4$ the optimal pyrolysis temperature for Cd is 1000 °C. On the other hand using the atomization temperature around 2200 °C will be resulted in application of standard addition as a method of calibration. It can be suspected that the slurry concentration can influence on efficiency of Cd atomization for above described system and will make calibration difficult.

3.4. Long term performance investigation

The role of permanent modifiers in slurry sampling GFAAS technique seems to be very complex. Carbides of transition metals influence on mechanism of atomization as well as reduce interference effects [26]. Platinum group metals (PGMs) as permanent modifiers additionally protect graphite surface against corrosion, especially in the case of soils and sediments analysis where a lot

Table 3
Certified and determined concentrations of Cd and Pb in CRM's and in 'real' samples obtained by slurry sampling GFAAS.

Element	Certified reference material	Certified value (μg/g)	Determined value (μg/g) modifier Nb/Ir	Sample	Determined value (μg/g) modifier Nb/Ir
Cd	San Joaquin			Loess Soil	0.261 ± 0.003
	Soil 2709	0.38 ± 0.01	0.371 ± 0.019	Lithic Rendolls	0.173 ± 0.003
	SL-1	0.260 ± 0.050	0.248 ± 0.004	Entic Rendolls	0.321 ± 0.008
	PACS-1	2.38 ± 0.20	2.120 ± 0.057	Umea sediment	0.589 ± 0.046
	MESS-1	0.59 ± 0.10	0.599 ± 0.009	BSS[a] sediment	0.305 ± 0.042
Pb	San Joaquin			Loess Soil	14.21 ± 0.82
	Soil 2709	18.9 ± 0.5	19.93 ± 0.42	Lithic Rendolls	10.48 ± 0.42
	SL-1	37.7 ± 7.4	41.9 ± 1.8	Entic Rendolls	10.64 ± 0.34
	PACS-1	404 ± 20	409 ± 17	Umea sediment	27.3 ± 1.6
	MESS-1	34 ± 6.1	26.14 ± 0.68	BSS[a] sediment	66.7 ± 2.9

[a] Information value for Cd in BSS sediment <0.4 μg/g and for Pb 69.9 μg/g.

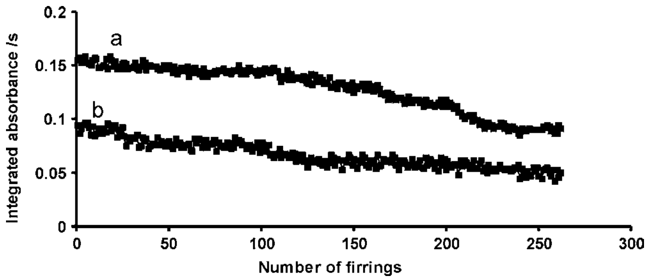


Fig. 6. The relation of number of firings and integrated absorbance of Pb signal in NIST 2709 (10 mg/mL 5% HNO_3) in the presence of (a) Nb/Ir as modifier, pyrolysis temperature of 700 °C, atomization temperature 2200 °C, and (b) W/Ir as modifier, pyrolysis temperature of 600 °C, atomization temperature 2000 °C.

amount of silica is presented on the surface during atomization step. This assumption was verified by investigation of influence of proposed modifier on tube lifetime in respect to slurry sampling GFAAS technique for Pb and Cd determination.

In Fig. 6 the relation of number of firings and integrated absorbance of Pb for both proposed graphite surface permanent modification is shown. In each series of measurements the slurry prepared from NIST 2709 (1 mg/1 mL in 5% HNO_3) was injected into the graphite tube modified previously by the appropriate amounts of Nb/Ir and W/Ir modifiers and signals of Pb were measured up to the end of the tube lifetime. The shape of obtained diagrams is very similar however for Nb/Ir modification integrated absorbances are around 50% higher. Reproducibility of signal of Pb is better for Nb/Ir modification especially in the beginning part of the relation up to 30 firings. After 200 firings the reproducibility decreases. Experimentally it was stated that after 120 firings the integrated absorbance of Pb dramatically decreased for measurements for slurry prepared from NIST 2709 and application of $NH_4H_2PO_4$ as classical modifier. Moreover reproducibility for this approach was worse comparing to apply Nb/Ir as permanent modifier. Those observations and higher number of firings for Nb/Ir as permanent modifier, with respect to the stability of Cd and Pb, reassured us in decision to use Nb/Ir as permanent modifier with samples.

3.5. Determination of Cd and Pb in samples

To exam the range of matrix different kind of certified reference materials (CRM) and real samples were taken for the determination for Pb and Cd. Real samples selected for Cd and Pb determination differ mainly of geological background matrix composition and contents of carbon, which are between range 1.2% and 8%. CRMs vary interferent components especially sulphur, chloride, silica and other elements forming carbides with graphite. The last group acts corrosive on graphite surface. The chloride contents in studied CRMs are in the range 10–23,900 mg/kg, the iron contents: 3.05–6.74%, the arsenic contents: 10.6–211 mg/kg and the sulphur content 0.089–1.67 mg/kg. Fe (228.903, 228.725 and 228.763 nm) and As (228.02 nm) are potential interferents in Cd determination. By carried out additional experiments no spectral interference effects were observed both for Fe and As for artificial samples containing Cd and interferents at the highest content in respect to studied samples. On the other hand the absorbances of Cd were changed depends on Ir content but integrated absorbance of Cd was constant and the same for the sample without interferent. Because of the high contents of chloride and sulphur in some studied samples the conventional modifier $NH_4H_2PO_4$ was applied for determination of cadmium. Table 3 shows final results of determination of Cd and Pb in soils and sediments by slurry sampling GFAAS technique using graphite tubes modified by Nb/Ir for certified reference materials and for real sediment samples (Ume estuarine sediment, BSS Baltic sediment, Loess Soil, Lithic Rendolls and Entic Rendolls). The precision of Pb and Cd determination by the method presented can be regarded as acceptable for this application. Relative standard deviations (RSD %) for five replicate measurements were less than 5%. The characteristic masses accounted for studied slurries (1%, m/v) were 0.79 and 19.5 pg for Cd and Pb, respectively.

4. Conclusions

This study proved that the amounts of Ir, W and Nb should be carefully optimized as permanent modifiers for Pb and Cd determination using slurry sampling GFAAS technique. It was stated that NbC formed on graphite surface is stable at higher temperature and does not convert into Nb_2C opposite to W_2C. Application of Nb/Ir modification for determination of Cd and Pb by slurry sampling GFAAS resulted in prolong tube lifetime. It was pointed out that Nb/Ir is a favorable permanent modifier for Pb and Cd determination from the group of refractory metals. To prevent interferences during Cd determination in soils and sediments samples and stability of Cd in pyrolysis step ammonium dihydrogen phosphate was used.

References

[1] A.S. Lopes, M.A.Z. Arruda, Microchim. Acta 164 (2009) 445–451.
[2] D. Barałkiewicz, H. Gramowska, Anal. Chim. Acta 510 (2004) 249–256.
[3] E.C. Lima, F. Barbosa Jr., F.J. Krug, M.M. Silva, M.G.R. Vale, J. Anal. Atom. Spectrom. 15 (2000) 995–1000.
[4] E.C. Lima, F. Barbosa Jr., F.J. Krug, J. Anal. Atom. Spectrom. 14 (1999) 1913–1918.
[5] D. Barałkiewicz, Talanta 56 (2002) 105–114.
[6] I. Lopez-Garcia, M. Sanchez-Merlos, M. Hernandez-Cordoba, Anal. Chim. Acta 328 (1996) 19–25.
[7] N.J. Miller-Ihli, J. Anal. Atom. Spectrom. 9 (1994) 1129–1134.
[8] W. Slavin, D.C. Manning, G.R. Carnrick, Atom. Spectrosc. 2 (1981) 137–145.
[9] B. Welz, G. Schlemmer, J.R. Mudakavi, J. Anal. Atom. Spectrom. 7 (1992) 1257–1271.
[10] A.B. Volynsky, Spectrochim. Acta Part B 55 (2001) 103–150.
[11] G. Chen, K.W. Jackson, Spectrochim. Acta Part B 51 (1996) 1505–1515.

[12] D.L. Tsalev, V.I. Slaveykova, L. Lampugnani, A. D'Ulivo, R.B. Georgieva, Spectrochim. Acta Part B 55 (2001) 473–490.
[13] L.A. Pereira, I. Amorim, J.B.B. da Silva, Talanta 68 (2006) 771–775.
[14] L. Bianchin, D. Nadvorny, A. Furtado da Silva, M.G.R. Vale, M.M. da Silva, W.N.L. dos Santos, S.L.C. Ferreira, B. Welz, U. Heitmann, Microchem. J. 82 (2006) 174–182.
[15] D.L.G. Borges, L.F. Dias, M.A.M.S. da Veiga, A.J. Curtius, J. Braz. Chem. Soc. 14 (2) (2003) 291–296.
[16] Z. Arslan, J.F. Tyson, Microchem. J. 86 (2007) 227–234.
[17] O. Acar, Microchim. Acta 151 (2005) 53–58.
[18] D. Barałkiewicz, M. Kózka, H. Gramowska, B. Tomaszewska, K. Wasinkiewicz, Int. J. Environ. Anal. Chem. 84 (12) (2004) 901–908.
[19] D. Santos Jr., F. Barbosa Jr., A.C. Tomazelli, F.J. Krug, J.A. Nobrega, M.A.Z. Arruda, Anal. Bioanal. Chem. 373 (2002) 183–189.
[20] D. Santos Jr., F. Barbosa Jr., S.S. de Souza, F.J. Krug, J. Anal. Atom. Spectrom. 18 (2003) 939–945.
[21] E.C. Lima, F. Barbosa Jr., F.J. Krug, Fresen. J. Anal. 369 (2001) 496–501.
[22] V.I. Slaveykova, L. Lampugnani, D.L. Tsalev, L. Sabbatini, E. De Giglio, Spectrochim. Acta Part B 54 (1999) 445–467.
[23] R. Dobrowolski, Anal. Bioanal. Chem. 374 (2002) 1294–1300.
[24] T.B. Massalski, Binary Alloys Phase Diagrams, 2nd ed., ASM International, Metals Park, Ohio, 1991.
[25] N.P. Bansal, J. Mater. Sci. 29 (1994) 4481–4486.
[26] R. Dobrowolski, M. Otto, A. Adamczyk, Microchim. Acta 168 (3–4) (2010) 355–362.