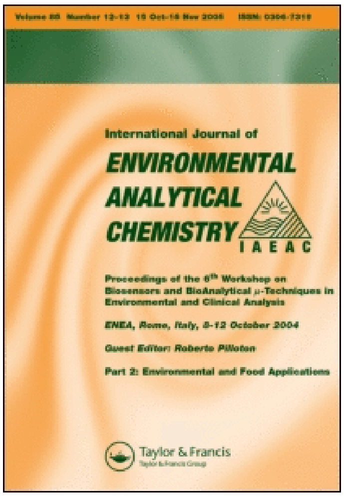

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DETERMINATION OF CADMIUM AND LEAD IN PLANT MATERIALS BY FLOW INJECTION – FLAME ATOMIC ABSORPTION SPECTROMETRY. ELIMINATION OF THE MATRIX EFFECT IN THE PRECONCENTRATION STEP

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The determination of cadmium and lead in plant samples by flame atomic absorption spectrometry with analyte preconcentration in a flow injection system was studied. Preconcentration of Cd and Pb from solution after wet digestion was performed by the use of C_{18} column, as sorbent, ammonium diethyldithiophosphate (DDPA) at pH = 1 as complexing agent, and methanol as eluent. A strong column clogging effect of the iron and copper was successfully eliminated by the use of masking agents. Oxalic acid 0,4 M and thiourea 0,06 M are sufficient for masking of iron and cooper in solutions obtained after digestion of various plant samples. The enrichment factors obtained at 30 s loading time were 42 for cadmium and 38 for lead. Detection limits (3σ) were 0,5 μg/l and 4,4 μg/l respectively, for cadmium and lead.

Keywords: Preconcentration; flow injection; cadmium and lead determination; plant materials; flame atomic absorption spectrometry

INTRODUCTION

Flame atomic absorption spectrometry (FAAS) has for many years been used in the analysis of various materials, including environmental samples[1,2]. However, in some cases of direct determination of trace heavy metal analytes, the sensitivity and detection limits offered by FAAS are insufficient. Preconcentration eliminates this problem, but if carried out manually it can lead to an additional

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interference effect or contamination of the sample material. It is time and reagent consuming as well. The flow injection (FI) technique is one possibility offering on-line sample preconcentration and matrix separation. The principles and application of the FI separation and preconcentration technique combined with FAAS have already been described[3,4]. Such techniques as liquid-liquid extraction, sorption, gas-liquid separation, dialysis, and precipitation, performed using FI, have also been thoroughly discussed[5] or considered individually for sorbent extraction[6–11].

The FI-FAAS system applied to preconcentration and determination of cadmium and lead consists usually of the solid reversed phase sorbent C_{18} (silica bonded with octadecyl functional groups) and diethylammonium-N,N-diethyldithiocarbamate (DDTC)[6,12–14] or ammonium diethyldithiophosphate (DDPA)[14] as complexing agents. It has been successfully used to analyze various water samples, including sea-water samples[12], and also biological[13] and environmental[14] samples.

The composition of solutions of the environmental samples digested, such as plant materials, is very complex. Except for main matrix components, concentrations of most analytes are very low. There are two reasons why two types of matrix effects may appear in the preconcentration step: either the main element and analyte react with the complexing agent or their complexes compete on the sorbent surface[12]. In some cases such effects which influence the signal, can be eliminated by masking agents[13,14], but other effects, such as precipitation, can block and damage the microcolumn[14,15].

When determining cadmium, copper, and lead in the environmental samples with the use of DDDC (as complexing agent) Ma, et al.[14] found that iron had a strong effect on the signal. The sensitivity was reduced, and back pressure in tubes caused by plugging of the column increased; sometimes the columns were permanently damaged. Their conclusion was that the determination of Cd, Cu and Pb using DDDC without masking agent plus a controlled pH was not possible. In addition, it was found that citric acid, used for iron masking, acts insufficiently in some cases: iron still was able to influence copper and cadmium. Using DDPA with 0.1 M citric acid at pH = 1, the authors observed stepwise reduction of loading that was caused by gradual clogging of the column. With a diluted solution of the river sediment sample the sampling rate and peak area were not influenced, and only a small depression of the cadmium signal was observed. After extraction, with addition of 1.0 M citric acid, it was found that a relatively high percentage of iron remained in the column. Similar but less noticeable effects were observed when analytes were extracted for determination by means of graphite furnace AAS[15].

In addition to citric acid (added to DDPA) – used most often as masking agent especially for iron – other masking reagents were studied for analysis of the biological and environmental samples[15–18].

Under conditions recommended by Ma et al.[14] we noticed the strong column clogging effect that lead to extensive damage of the columns during analysis of plant samples[19]. In our examinations we attempted to detect sample components responsible for this effect and to eliminate it by using suitable masking agent(s) in proper concentrations. All tests were carried out using a sample of grass *(Poa annua)* but the results are generalized to other plant materials.

EXPERIMENTAL

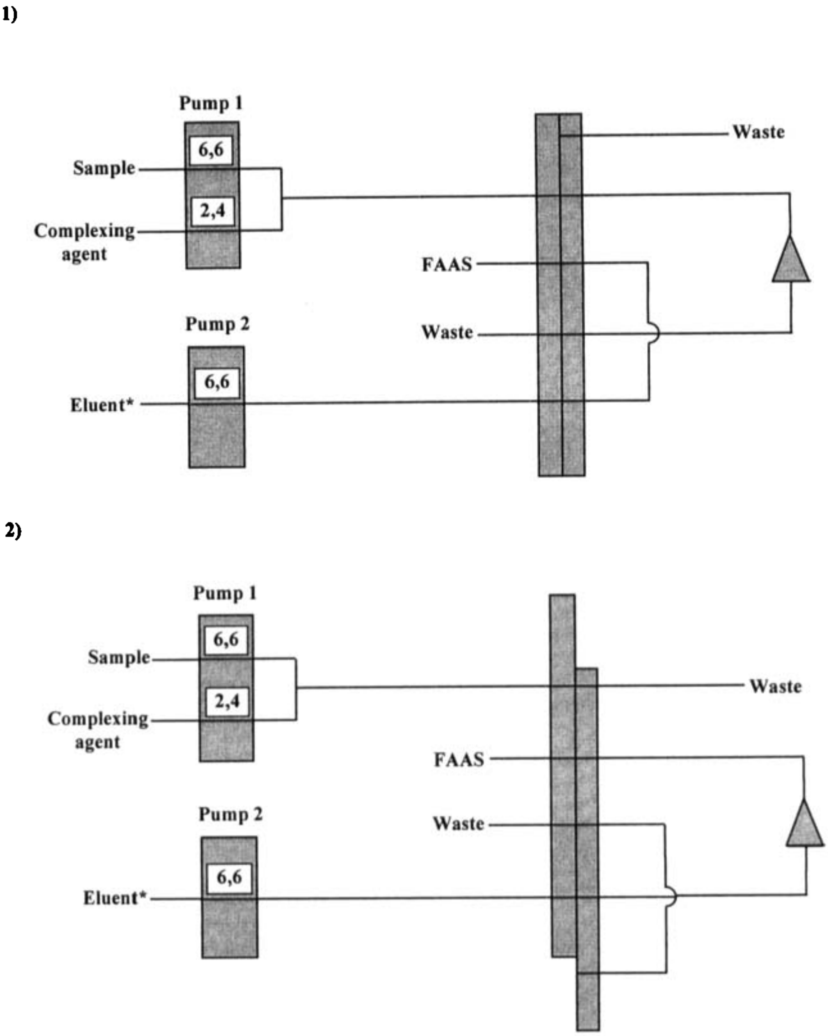
Apparatus

An AAnalyst 300 atomic absorption spectrometer and a FIAS-400 flow injection system - both from Perkin Elmer – were combined. Flame air/acetylene was used. The air flow was set at the recommended value 10 l/min. The acetylene flow was optimized to achieve maximum sensitivity, precision and stability of the flame and was finally set at 1.8 l/min for lead and 2.0 l/min for cadmium. The flow spoiler was used in the spray chamber with an eluent uptake rate by the nebulizer of 5 ml/min. Hollow cathode lamps were used. Lead and cadmium were measured at 217.0 nm at 228.8 nm respectively. Deuterium background correction was used for all measurements.

TABLE I FIAS – 400 working program

Step	*Time*	*Pump speed rpm*		*Valve*		*Read*
No	*s*	*pump 1*	*pump 2*	*loading*	*elution*	*s*
prefill	20	80	80	+		
1	20	80	0	+		
2	10	80	80	+		
3	2	80	80		+	+
4	18	0	80		+	
5	1	0	0		+	

Figure 1 illustrates the flow injection on – line preconcentration system. The column C_{18} of particle size approximately 40 μm was used. The column was initially activated with methanol.



• A solvent resistant Isoversenic tubes were used for methanol.

FIGURE 1 Diagram of flow injection on-line preconcentration system for FAAS : 1) loading, 2) elution

The spectrometer and FIAS analyzer worked under the control of AA WinLab software. The sequence of steps is given in Table I. Total loading time was 30 s and elution time including washing step was 20 s.

Reagents

Stock solutions of lead, copper and iron were prepared by dissolution of appropriate metal (Specpure, Johnson Matthey) in nitric acid (Merck), and the stock solution of cadmium was prepared by dissolution of the cadmium (Specpure, Johnson Matthey) in hydrochloric acid (Merck) according to the procedure by Perkin Elmer (20). Methanol (Merck) was used as eluent. The DDPA solution 0.2 % (w/v) (Aldrich, 17, 779 – 2) was adjusted to pH = 1 with 65 % nitric acid (Merck) and was prepared daily for use as a complexing agent. Citric acid (POCh, Poland), oxalic acid (POCh, Poland), tartaric acid (FOCh, Poland), thiourea (POCh, Poland) and ammonium thiocyanate (POCh, Poland) of analytical grade were added to DDPA solutions as masking agents. Standard solutions were prepared by dilution from the stock solutions with 1 % (v/v) nitric acid. Re-distilled water was used throughout all the experiments.

Sample preparation

A sample of polluted plant material (grass – *Poa annua*) was collected from the side of the road. The analytical sample was dried at approximately 120 °C and then milled. Test portions from the analytical sample were used for all experiments. A test portion of approximately 0.8 g was digested in the PTFE bomb with 10 ml of concentrated HNO_3. The temperature and time of heating were optimized and set at 190 °C and 2 h, respectively. The solution was transferred onto a PTFE evaporating dish and evaporated in a water bath almost to dryness. The residue was dissolved in 1 % HNO_3 and made up to 50 ml.

RESULTS

Preliminary study

In the preliminary study the analysis of the grass was performed by FAAS and the precipitation effects of DDPA and each element at its real concentration level were checked. Among elements examined such as Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Sr, Zn at quite different concentrations, only iron 272 μg/l and copper 1,16 μg/l precipitates with DDPA.

As the first step in the elimination of the precipitation, the masking agents for copper and iron were tested by manual off-line procedure[19]. Using the same phase ratio of sample and DDPA solution as in the on-line method, the concentrations of masking agents were optimized to avoid precipitation or to delay it at least for a 15 minute period, i.e., long enough for safe analysis without clogging of the column. Cu and Fe solutions of concentration 1.16 and 272 μg/l, respectively, i.e. as determined previously in the digested grass sample, were used.

First of all, it was noticed that thiourea (0.1 M) was especially effective for masking both Cu and Fe and the masking effect of citric, oxalic and tartaric acids (all 0.1 M) on iron were similar. Cu and Fe masking by various pairs of these reagents showed that only the solution containing thiourea and oxalic acid was able to prevent precipitation for 15 minutes. When this test was carried out on the real sample solution it was found out that 0.06 M thiourea and 0.4 M oxalic acid were sufficient.

Concentrations 0.3 M of thiourea and 0.5 M of oxalic acid prevent the precipitation throughout for more than 90 minutes. Otherwise, for other plant materials of higher Cu and Fe contents, necessary concentrations of masking agents were established as follows:

- 0.4 M oxalic acid prevents for DDPA – Fe precipitation up to 400 mg/l of Fe,
- 0.06 M thiourea prevents DDPA – Cu precipitation up to 4 mg/l of Cu.

Examination of the developed procedure

The comparison of calibration graphs with and without the addition of masking agents showed that thiourea and oxalic acid had no significant influence on the sensitivity of cadmium or lead determination (the significances of differences were tested at $\alpha = 0.05$ level by the use of Student's t test). The enrichment factors (EF) calculated from the appropriate calibrations graphs, with and without preconcentration, after optimization of flame, burner position and uptake rate conditions, were 42 for cadmium and 38 for lead respectively. Detection limits found were 0.5 μg Cd/l and 4.4 μg Pb/l, respectively.

In order to check the resistance of the method to the matrix effect and/or analytes losses, the analyte recovery procedure was applied. Determinations of the analyte were carried out in two ways, namely when it was spiked into the grass sample before digestion and into the sample solution obtained after digestion.

In the first procedure four equal portions of the grass were weighed on an analytical balance. Three of them were spiked with one, two or three portions of analytes and then all separately digested. The solutions of unspiked and spiked portions were analyzed and recovery was calculated. Results for cadmium and lead are presented in Table II and Table III, respectively.

TABLE II The recovery of Cd added to the sample before digestion

Sample	*Mean detected concentration of Cd** μg/l	*Standard deviation of the mean* μg/l	*Recovery %*	*Significance of differences** %*
unspiked	3.3	0.7	-	-
spiked 21.2 μg/l	26.6	1.3	106.6	no
spiked 42.4 μg/l	50.1	0.4	110.8	no
spiked 63.6 μg/l	74.1	1.5	108.1	no

*4 replicates were taken for each sample.
**The Student's t test at $\alpha = 0.05$.

TABLE III The recovery of Pb added to the sample before digestion

Sample	*Mean detected concentration of Pb** μg/l	*Standard deviation of the mean* μg/l	*Recovery %*	*Significance of differences** %*
unspiked	203.6	4.4	-	-
spiked 100 μg/l	307.6	2.8	104.6	no
spiked 200 μg/l	412.1	7.4	104.5	no
spiked 300 μg/l	501.8	5.0	89.5	no

*4 replicates were taken for each sample.
**The Student's t test at $\alpha = 0.05$.

The second procedure was carried out as follows: the solution after digestion of the grass sample was divided into three equal portions. The first portion was not spiked, and one or two spikes of the standard solutions were added into the second and third portions. All portions were made up to the same volume with 1 % HNO_3, then the solutions were analyzed and recovery was calculated. Results for cadmium and lead are presented in Table IV and Table V, respectively. On the basis of 8 sets of results of the cadmium determination with 4 repetitions and 11 sets for lead with 4 repetitions the mean concentrations, standard deviations, and relative standard deviations of analytes in the test sample of grass were calculated. The results are presented in Table VI.

TABLE IV The recovery of Cd added to solution after sample digestion

Sample	*Mean detected concentration of Cd* µg/l*	*Standard deviation of the mean µg/l*	*Recovery %*	*Significance of differences** %*
unspiked	4.4	0.4	-	-
spiked 21,0 µg/l	25.9	0.3	102.4	no
spiked 42,0 µg/l	50.0	0.2	114.8	no

*4 replicates were taken for each sample.
**The Student's t test at $\alpha = 0.05$ was used.

TABLE V The recovery of Pb added to solution after sample digestion

Sample	*Mean detected concentration of Pb* µg/l*	*Standard deviation of the mean µg/l*	*Recovery %*	*Significance of differences** %*
unspiked	239.5	3.7	-	-
spiked 99,2 µg/l	349.6	4.7	111.0	no
spiked 198,4 µg/l	455.5	5.5	106.8	no

*4 replicates were taken for each sample.
**The Student's t test at $\alpha = 0.05$ was used.

TABLE VI Contents of cadmium and lead in the grass sample

Element	*Mean concentration mg/kg*	*Standard deviation of the mean mg/kg*	*Relative standard deviation %*
cadmium	0.31	0.03	9.0
lead	13.8	0.8	5.6

The method developed with the use of 0.4 M oxalic acid and 0.06 M thiourea was successfully applied (without clogging effect) to the determination of cadmium and lead in various plant materials of different matrix composition, e.g., leaves of leek (*Allium porrum*), leaves of parsley (*Petroselinum sativum*), leaves of kale (*Brassica var. sabellica*), leaves of red beet (*Beta vulgaris var. Esculenta*), leaves of strawberry (*Fragaria grandiflora*), needles of Siberian fir (*Picea obovata*) and grass (*Poa annua*). The method was thoroughly checked using Polish Certified Reference Material; Oriental Tobacco Leaves (CTA-OTL-1). No precipitation was observed and following results 4.8 ±

0.1 mg/kg for lead and 1.09 ± 0.03 mg/kg for cadmium were obtained. Certified values are respectively: 4.91 ± 0.80 mg/kg and 1.12 ± 0.12 mg/kg.

CONCLUSIONS

During determination of cadmium and lead in plant materials by the FI-FAAS method with C_{18}-DDPA preconcentration, masking agents for iron and copper are required. Such complexing reagents as citric, oxalic, tartaric acids or thiourea used with DDTC[16–18] can be also used with DDPA. It seems that thiourea could be sufficient for masking both iron and copper in digested sample solutions, but the combination with oxalic acid increases the masking efficiency.

Thiourea and oxalic acid in defined concentrations have no significant influence on the sensitivity of cadmium and lead determination. Enrichment factors of about 38 for lead and 42 for cadmium were determined at 30 s period of preconcentration. When there is no constraint in quantity of a sample and its solution volume, an increase in preconcentration time could provide further improvement of the EF.

The recovery examination of the analytes added to the sample solution after digestion shows that there are no matrix effects caused by either original matrix components or by reagents introduced into the sample. The recovery of analytes spiked into the sample before digestion is proof that there are no significant analyte losses in the applied digestion method either.

For the determination of cadmium and lead in trace contents in various plant materials, the FI-FAAS method with C_{18}-DDPA preconcentration can be used but only with addition of the reagent which complexes iron and copper. Oxalic acid and thiourea concentrations at 0.3 M and 0.06 M respectively are recommended. No clogging effect and good accuracy were observed for tested certified reference material, as well. Before the method can be applied to other kinds of biological samples it must be tested at least, and/or masking agents must be optimized in terms of composition and concentration.

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