Optimization of Cadmium Determination by Vapour Generation AAS*

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The vapour generation of cadmium by the reaction with sodium tetrahydroborate ($NaBH_4$) was performed using a continuous flow reactor. The effects of thiourea and cobalt(II) ions on the sensitivity of the determination were tested. Depressive effect of chelating compounds (EDTA) on the Cd signal was investigated. The method was applied to the determination of Cd in soil extracts and the results were compared with the results of ETAAS and FAAS. The detection limit (3σ) was 0.03 ng cm^{-3} and the precision for 2 ng cm^{-3} was up to 10 %. A certified reference material CRM 483 (BCR) was extracted and analyzed for cadmium content, the results were in good agreement with certified values.

The determination of cadmium in the environmental samples, often at the trace levels, is a commonly required analytical task. Atomic absorption spectrometry (AAS) is certainly the most widely employed method, especially flame AAS (FAAS) and electrothermal AAS (ETAAS). However, in recent years an increased attention has been paid to application of vapour generation AAS (VGAAS) for the determination of Cd [1]. In comparison with FAAS it reaches lower detection limit and in comparison with ETAAS it is more tolerant to higher content of salts in solutions (*e.g.* extracts of soils in various extractants). Although VGAAS has significant advantages over the techniques mentioned above, there are some problems which limit the common employment of this technique in the analytical practice [2].

The present paper describes a sensitive method for the determination of cadmium using the vapour generation technique. The applicability of the developed method for the determination of Cd in different soil extracts is demonstrated.

EXPERIMENTAL

Soil samples were taken from industrially polluted and unpolluted areas of Slovakia. Extraction of soil samples with calcium chloride solution was carried out as follows: 5.00 g of soil were shaken in 100 cm^3 PE bottles with 50 cm^3 of 0.01 mol dm^{-3} $CaCl_2$ for 3 h and afterwards the mixture was centrifuged for 10 min at 3000 *g* [3]. Extraction with 0.43 mol dm^{-3} acetic acid was performed according to the procedure described in the certificate of CRM 483 [4].

All chemicals were of anal. grade or better.

A Perkin—Elmer Model 1100 (USA) atomic absorption spectrometer equipped with hydride generator HG-2 (Labtech, Czech Republic) and electrically heated quartz cell was used for VGAAS, and a Perkin—Elmer Model 5000 (USA) atomic absorption spectrometer with graphite furnace Perkin—Elmer HGA-500 (USA) was used for ETAAS.

RESULTS AND DISCUSSION

At the Cd determination by VGAAS the generation of cadmium volatile species is sensitive to experimental conditions, therefore the following parameters were optimized: HNO_3 concentration in the sample, $NaBH_4$ and NaOH concentration in the reducing agent. The results are presented in Fig. 1. The concentration of HNO_3 in the sample solution strongly affects the efficiency of CdH_2 formation. The maximal absorbance was achieved with solution containing 0.30 mol dm^{-3} HNO_3 at the flow rate of 5.4 cm^3 min^{-1}. This concentration is in agreement with [2] and we used it in further experiments. For reduction, the solution concentration 30 g dm^{-3} $NaBH_4$ in 15 g dm^{-3} NaOH at the flow rate 1.8 cm^3 min^{-1} was used. The argon flow rate was 0.1 dm^3 min^{-1}.

At the interference study the effect of 13 coexisting cations and 3 anions at three concentration levels on the generation of cadmium volatile species was tested (Mg, Ca, Al, Mn, Fe, Zn, Cu, Ni, Pb, Se, Sb, As, Hg, NO_3^-, SO_4^{2-}, PO_4^{3-}). It was found that the presence of

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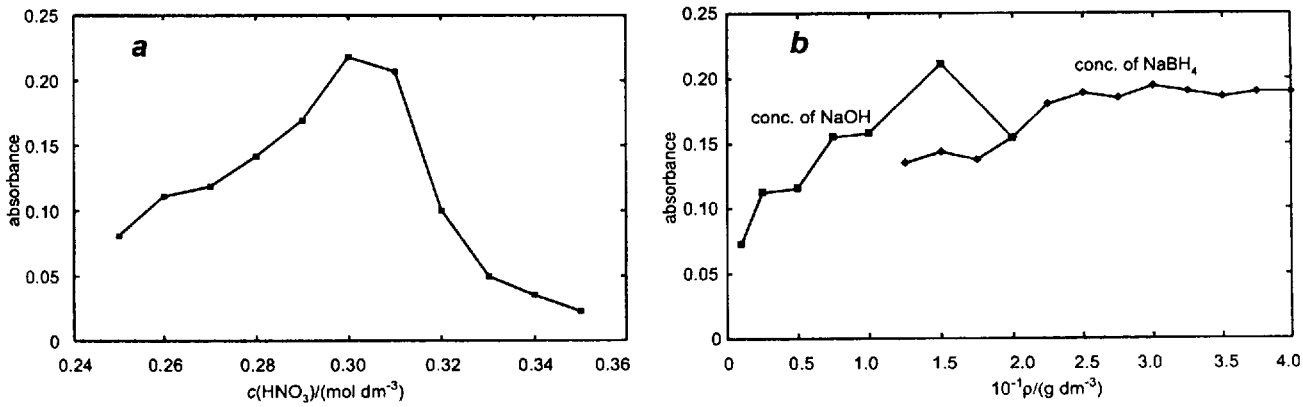

Fig. 1. Effect of HNO_3 (*a*), NaOH and $NaBH_4$ (*b*) concentration on the signal of 2 ng cm^{-3} Cd sample solution: *a*) Reductant: 30 g dm^{-3} $NaBH_4$ in 15 g dm^{-3} NaOH; *b*) sample contains 0.30 mol dm^{-3} HNO_3.

Table 1. Comparison of Results of Cadmium Determination (mg kg^{-1}) from Three Methods (Mean ± Standard Deviation, n = 5)

Soil sample	Extract in 0.43 mol dm^{-3} acetic acid			Extract in 0.01 mol dm^{-3} $CaCl_2$		
	VGAAS	ETAAS	FAAS	VGAAS	ETAAS	FAAS
ICSK-2	0.112 ± 0.09	0.125 ± 0.010	0.128 ± 0.016	N.D.	0.006 ± 0.001	N.D.
ICSK-11	8.62 ± 0.32	8.76 ± 0.35	9.00 ± 0.21	1.02 ± 0.08	1.16 ± 0.09	1.10 ± 0.07
ICSK-12	12.7 ± 0.9	13.4 ± 1.1	13.2 ± 0.26	3.82 ± 0.14	4.04 ± 0.45	4.10 ± 0.32
ICSK-13	0.316 ± 0.075	0.332 ± 0.033	0.320 ± 0.018	0.019 ± 0.03	0.022 ± 0.002	N.D.
ICSK-15	0.880 ± 0.081	0.896 ± 0.066	1.00 ± 0.04	0.015 ± 0.001	0.021 ± 0.002	N.D.
C-1	8.54 ± 0.21	9.20 ± 0.51	8.76 ± 0.17	0.830 ± 0.038	0.842 ± 0.026	0.893 ± 0.011
C-5	2.32 ± 0.12	2.48 ± 0.14	2.52 ± 0.08	0.038 ± 0.002	0.045 ± 0.007	N.D.
CRM 483	17.4 ± 0.4	17.3 ± 1.0	17.6 ± 0.2	0.364 ± 0.022	0.372 ± 0.041	0.393 ± 0.012
	Certified value: (18.3 ± 0.6 mg kg^{-1}) Cd				No certified value	

N.D. – not determined.

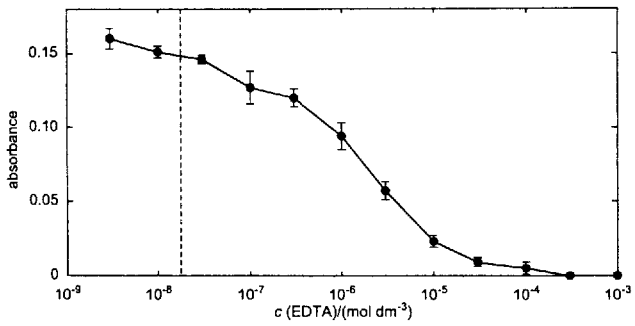

Fig. 2. Effect of EDTA in samples on Cd absorbance signal (vertical dashed line shows the equimolar ratio of EDTA and Cd); sample solution: 2 ng cm^{-3} Cd in 0.30 mol dm^{-3} HNO_3, reductant: 30 g dm^{-3} $NaBH_4$ in 15 g dm^{-3} NaOH.

Fe, Zn, Cu, Ni, and Pb at mg dm^{-3} concentration level causes serious signal reduction, while the presence of tested anions at g dm^{-3} levels had no effect. We tested also the influence of EDTA. It reduces cadmium signal by 20 % at concentration higher than 10^{-8} mol dm^{-3} and it suppresses the signal completely at concentration of 10^{-4} mol dm^{-3}. The effect of EDTA is documented in Fig. 2.

It has been reported [5] that the presence of thiourea and cobalt(II) ions in the sample solutions increases the absorbance of cadmium and eliminates some interferences. We also examined their effect. The presence of thiourea in concentration of 5 g dm^{-3} in samples increased the absorbance of Cd by 40 %, therefore in further experiments we used it in all the solutions in this concentration. Cobalt has suppressive effect on Cd vapour formation (by 10 % at concentration of 0.5 mg dm^{-3}) and therefore we did not use it in further experiments.

We compared the developed method of determination of cadmium using vapour generation AAS with conventional ETAAS and FAAS as independent techniques, when it was possible due to the low concentration of Cd. The results are summarized in Table 1.

CONCLUSION

The optimization of cadmium determination by VGAAS was performed in terms of concentration of sample solution, $NaBH_4$ solution, and the gas flow

rate. An extensive interference study was performed and the suppressive effect of EDTA on the cadmium volatile species generation was documented. Efficiency of two often recommended additives, thiourea and cobalt(II) ions, on generation of Cd vapour was evaluated. The results of Cd determination using VGAAS in soil extracts and waters corresponded to the results of two independent methods. The detection limit (3σ) was 0.03 ng cm^{-3} and the precision (RSD of 10 replicate analyses) was up to 10 % at 2 ng cm^{-3} cadmium concentration level.

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