Optimization of the Atomic Absorption Spectrometric Methods II.* Matrix Effects in Electrothermal Atomization of Waters in W-Tube**

[a]G. HOLÉCZYOVÁ, [b]M. MATHERNY, and [b]N. PLIEŠOVSKÁ

[a]*Institute of Hygiene, Faculty of Medicine, P. J. Šafárik University, SK-041 80 Košice*

[b]*Department of Chemistry, Faculty of Metallurgy, Technical University of Košice, SK-042 00 Košice*

Received 9 June 1996

The formation of the signal of the blank as well as of the analytical signal for the atomic absorption spectrometry with the electrothermal atomization is along with the electronic properties of the detection and registration equipment of the spectrometer, similarly conditioned by the purity of the used chemicals as well as by the spectrochemical matrix effects. Each signal is the complex one, and it is composed of the element-specific component and the component conditioned by the background. The detailed study of such complex signals is necessary as these conditions influence the evaluation parameters of the method, especially the detectability and the analytical calibration. The analytical calibration for the determination of the trace elements in water matrixes itself is significantly conditioned by the presence of the major and minor element components in the analyzed waters.

Detectability of atomic absorption spectrometric determination by the flame atomization of the actual trace elements in the waters such as Cd, Cr, Cu, Fe, Mn, and Mo was valuated [1] in the concentration values range from 0.1 to 1.3 mg dm^{-3} Such limits of the detection $\rho(X_L)$ are still useable from the viewpoint of the classification of the extent of pollution of surface waters [2], however they are not satisfactory from the standpoint of the river and especially drinking waters classification of the extent of pollution [3]. Application of the combination of the AAS method with the electrothermal atomization (ETA) in W-tube [4, 5] represents significantly more advantageous conditions from the standpoint of the detectability of the actual trace elements. The principal optimization condition for the AAS-ETA application was the shift of the above defined concentration range up to the area from 1 to 10 μg dm^{-3} and attainment of the values of the limits of detection in the range from 1 to 0.1 μg dm^{-3}

At the same time is was necessary to verify experimentally the matrix effects nature which is caused by the main components of the waters, namely the salts of Ca and Mg and by some minor cationic components as Na^+ and K^+, or even Fe^{3+} As the above element components with the cationic nature are bound on the anions, it was necessary to pay attention also to the anions effects, as those of Cl^-, NO_3^- and partially SO_4^{2-} on the matrix effects formation, as well as on the signals formation of the blanks. The influence of the carbonate and hydrogencarbonate anions is negligible for the low thermal stability of those anions. The present study is rather complex from the standpoint of experiments as the signals of the blanks are conditioned even by the degree of purity of all chemicals applied in the given problem modelling. Thus the problem represents a synergism of the matrix effects impact and influence of the undesirable pollutants.

The part of the complex optimization of the AAS-ETA method is the selection and application of the spectrochemically active modifiers as well [6]. It is of interest that just the presence of Mg salts, most frequently of magnesium nitrate [7, 9, 10], and phosphate [7, 8, 11] induces the positive stabilization effect in the atomization process. Such a fact is welcome for the analysis of the trace elements in the drinking waters, while these waters contain relatively constant, with time slightly alternating amount of Mg salts. Such a fact enables the autostabilization of the atomization complex process when analyzing the samples of the drinking waters.

* For Part I see Ref. [1].

**Presented at the 2nd European Furnace Symposium, St. Petersburg, May 1996, Russia.

Table 1. Experimental Conditions of AAS-ETA Determinations of Elements

Parameter/Unit	Cd	Cr	Cu	Pb
Wavelength/nm	228.8	357.9	324.7	217.0
Width of slit/mm	0.03	0.04	0.03	0.02
Time of resolution/ms		6		
Conc. range of the calibration/(μg dm^{-3})		1—10		
H_2 flow rate/(dm^3 min^{-1})		8.2		
Ar flow rate/(dm^3 min^{-1})		2.0		
Volume of analyte/dm^3		10^{-5}		
I. Drying temperature/ °C	110	130	130	130
I. Time of drying/s	25	25	25	5
II. Drying temperature/ °C	180	230	195	220
II. Time of drying/s	25	25	25	5
I. Time of pyrolysis/s		10		
II. Pyrolysis temperature/ °C	470	490	490	340
Temperature of atomization/ °C	2020	2300	2200	1800
Time of atomization/s	2	1	2	1
Gradient/(°C ms^{-1})		20		
Temperature of cleaning/ °C	2280	2420	2320	2080

EXPERIMENTAL

The entire analytical process was realized by a combination of AAS 1N (Zeiss, Jena) instrument and atomizer WETA 82 [12]. The registration of the output analytical signal as well as its time resolution was controlled by the A/D transducer, linked with the PC: PP06 and recorder [4]. In such a manner the time resolution of the analytical signal with 6 ms is obtained. The final experimental conditions are given in Table 1. For all experiments the high purity laboratory chemicals from Merck, Darmstadt were exclusively used.

RESULTS AND DISCUSSION

The optimization of AAS-ETA determination of trace elements in drinking water is preferentially oriented on the elements as Cd, Cr, and Cu [13]. Next, analyzed were the possibilities of the determination of Sb and Pb. The determinations of As and Hg were eliminated from this project while their determination by the flameless methods meets the requested detectability and precision under the conditions of high element selectivity [14].

The experiments confirmed [13] that it is of significance to apply two separate phases of the analyte drying with two temperature regimes, and at the same time two phases of the thermal destruction with different temperatures and time characteristics, thus from the standpoint of the determination of concentration precision $s(\rho_X)$, as well as from the standpoint of values of limits of detection $\rho(X_L)$. The proposed experimental conditions show obviously the element-specific nature. The special attention was paid to the experimental conditions optimization for Cd determination. In this case the increase of the thermal destruction temperature above 500 °C gives the significant reduction in detectability with the simultaneous increase in the precision of the concentration determination. Similarly, even the prolongation of the time of the thermal destruction over 10 s worsened the entire set of the analytical determining parameters. Finally, in accordance with the Cd thermal properties the temperature of the atomization was adjusted to 2020 °C. As a result of the above adjustments of the experimental conditions it was sufficient to apply the temperature of 2250 °C to 2300 °C when cleaning the W-tube, and this fact influences positively their lifetime. The Sb determination was carried out according to the operational conditions for Cd. The experimental conditions for Cr meet the conditions for the determination of elements such as Co, Ni, and V

The assumed matrix effects were simulated with the modelling solutions. First of all the chlorides of Ca, Mg, Fe, Na, and K were added to the deionized water. Along with the chlorides the influence of the nitrates and sulfates was observed. Waters can be potentially contaminated by the industrial waste water having a higher nitrates content and the rain waters are always contaminated with "acid rains" in which the anionic part is preferentially formed by sulfates ions. The concentration of the individual cationic components was chosen on two levels, the lower, ρ/(mg dm^{-3}): Ca 50, Mg 10, Na 100, K 10, Fe 0.5 (set A), which modelled the state in the drinking waters composition and ten times higher (set B), which modelled contamined river waters; in both cases anionic components of concentration Cl 285, NO_3 500, SO_4 389 were used. The occurrence of the so-called false analytical signals was observed in the model solutions, mainly for Cd and Pb. The false signals of other analytical elements were studied earlier [13].

However, the false signals were observed when Cd and Pb hollow cathodes were used in solutions containing major and minor cationic and anionic components. In case of dosing the deionized water into the

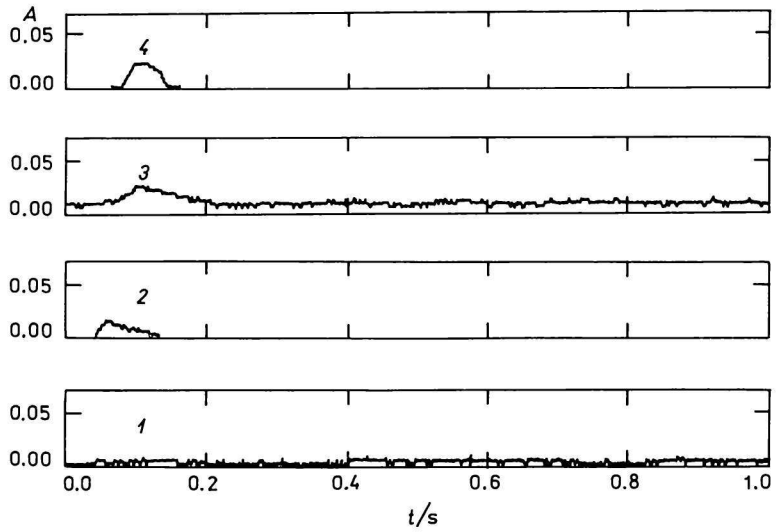

Fig. 1. The time-resolved analytical signals of the Cd hollow cathode discharge lamp with *1.* deionized water in the W-tube, *2.* addition of HCl, *3.* HNO_3, *4.* H_2SO_4.

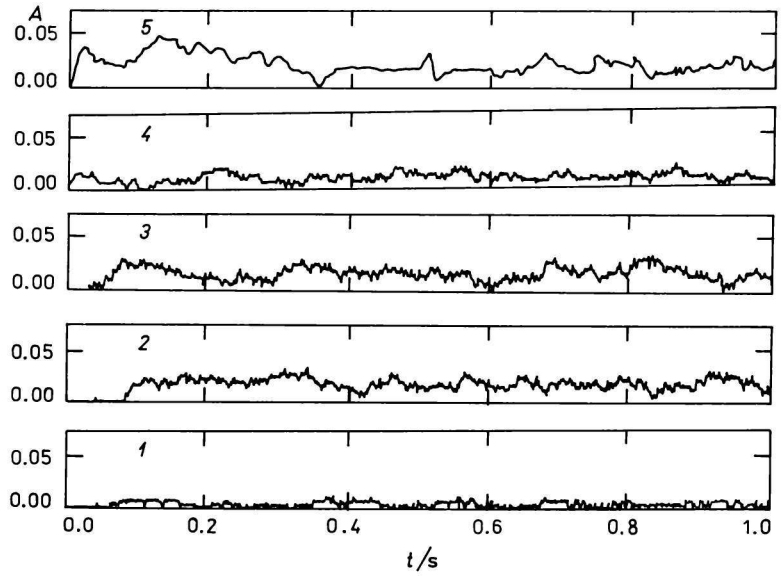

Fig. 2. The time-resolved analytical signals of the Pb hollow cathode discharge lamp with *1.* deionized water in the W-tube, *2.* addition of HCl, *3.* HNO_3, *4.* H_2SO_4, *5.* deionized water and KCl added into the W-tube.

W-tube exclusively, even in the case of Cd (Fig. 1) and Pb (Fig. 2) hollow cathode application no disturbing signals occurred. It is a proof of the fact that the W-tube was prepared with no disturbing memory effects.

The time dependence of the analytical signal when HCl was added to the deionized water (Fig. 1) confirms that when Cd hollow cathode was used, an inexpressive broadened maximum was present (0.02 *A*). When HNO_3 was added, the above maximum was more expressive (0.03 *A*) and finally when H_2SO_4 was added the compact significant maximum having the value of 0.045 *A* was gained. When the thermodynamic data [15] are taken into consideration, it is obvious that the value of ΔG°_{298} (kJ mol^{-1}) for the ion Cd^{2+} is −78, for the ion $(CdCl)^+$ −220, $(CdNO_3)^+$ −187, and finally for $CdSO_4$ even −835. That is why the minimum concentration of Cd^{2+} was already manifested by the most expressive compact maximum when H_2SO_4 was added.

Completely different was the structure of the time-resolved analytical signals in the case of the blanks observation (false analytical signals) when the Pb hollow cathode was used. When HCl was added to the deionized water, the significantly developed time dependence of the analytical signal with high fluctuations was observed (Fig. 2). The structured, highly fluctuating analytical signal was formed even in the case when HNO_3 or H_2SO_4 were added. The similar structured and time-decomposed signals were observed in the case of Cr and Sb hollow cathodes application [13].

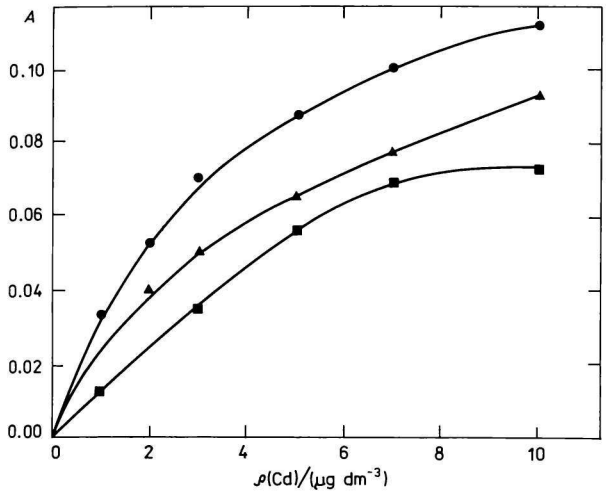

Fig. 3. Calibration curves of the Cd spectral line with addition of Ca in mg dm^{-3}: ● 0, ■ 50, ▲ 500.

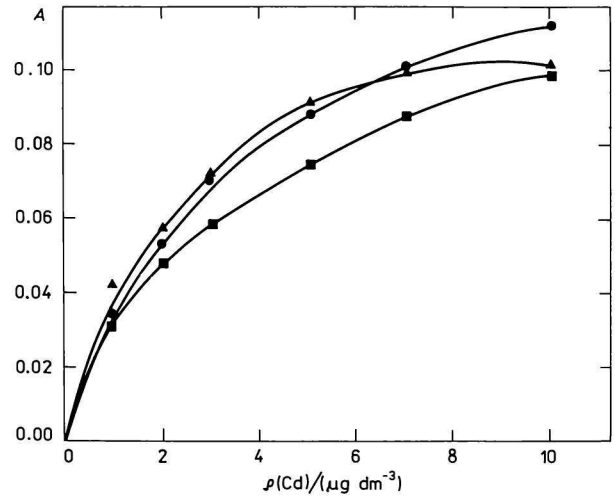

Fig. 4. Calibration curves of the Cd spectral line with addition of Mg in mg dm^{-3}: ● 0, ■ 10, ▲ 100.

The common feature of these fluctuated and time-resolved signals is that their maximum value does not excess the value of 0.03 *A*. This enables to apply the correction for the background or for the blank also in the case of the analytical calibration.

The addition of the inorganic cationic components either does not cause the formation of the structured time-resolved spectrum or if so, this is slightly significant only (Fig. 2). The significant contaminations of the compounds applied for the matrix modelling of the major and minor elements of the river and drinking waters form an exception. These should be examined in advance by the blanks for their contamination [13].

The matrixes were observed when the individual major and minor cationic components were added. These components were added in the form of the chlorides. The chlorides of the matrix cationic components were selected in accordance with the above experiments for the anions impact on the analytical signals. The matrix elements were added in two significantly different concentrations for the matrix effect study on the model mixture of the drinking water as well as highly polluted river water.

The most expressive cationic matrix effects were obtained in case of the analytical element Cd, and in this case the concentration range from 1 to 10 μg dm^{-3} was observed. When the major matrix element Ca (Fig. 3) was added, the corresponding calibration curves curvatures were different, however, their trajectories were always under the level of the calibration curve for Cd aqueous solution. In the case of the addition of the minor matrix element Mg (Fig. 4) in the framework of the standard deviation of the individual experimental points, the course of the calibration curve for Cd aqueous solution was practically identical with the course of the Cd curve when 10 mg dm^{-3} of the element were added. The course of this curve

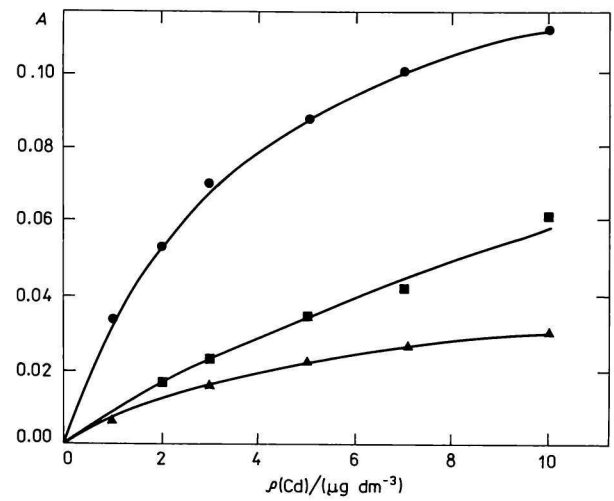

Fig. 5. Calibration curves of the Cd spectral line with addition of Na in mg dm^{-3}: ● 0, ■ 100, ▲ 1000.

when 100 mg dm^{-3} of Mg were added was significantly different. Addition of the minor matrix element Na induced the most significant matrix effects. The courses of all three calibration curves were significantly different (Fig. 5). On the contrary, the addition of a minor matrix element such as K (Fig. 6) practically does not cause any matrix effects for the calibration curves in the range of the standard deviations of the individual experimental points identical from the viewpoint of statistics. Addition of the minor matrix element Fe gives rise again to the significant and rather nonuniform matrix effects (Fig. 7). Finally, the simultaneous addition of the matrix elements such as Ca, Mg, Na, K, and Fe showed (Fig. 8) that their complex matrix effect is similarly identical for the set of the matrix elements A and B. However, this means that it is not

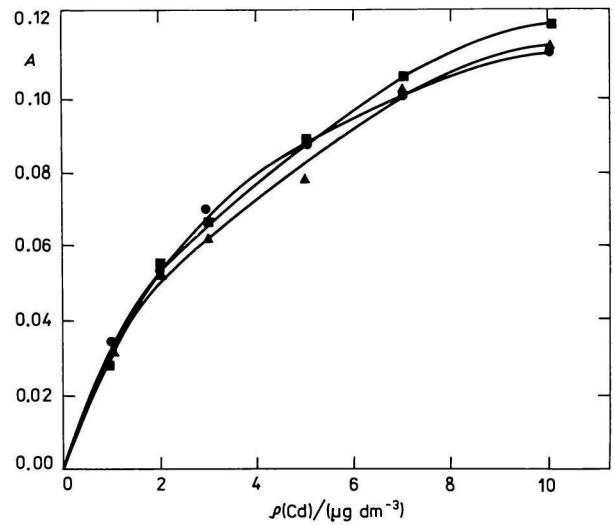

Fig. 6. Calibration curves of the Cd spectral line with addition of K in mg dm^{-3}: ● 0, ■ 10, ▲ 100.

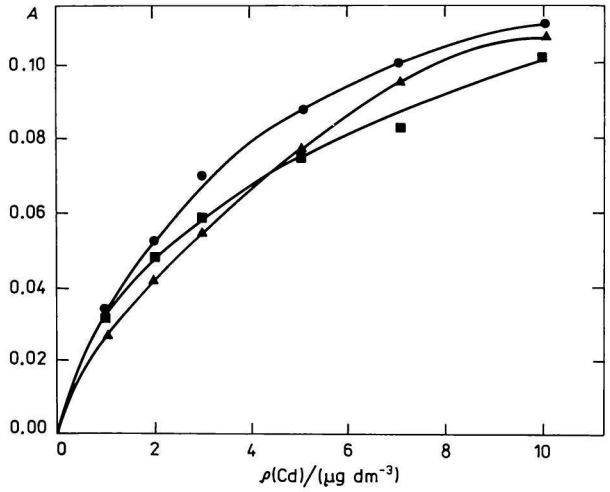

Fig. 7. Calibration curves of the Cd spectral line with addition of Fe in mg dm^{-3}: ● 0, ■ 0.5, ▲ 5.

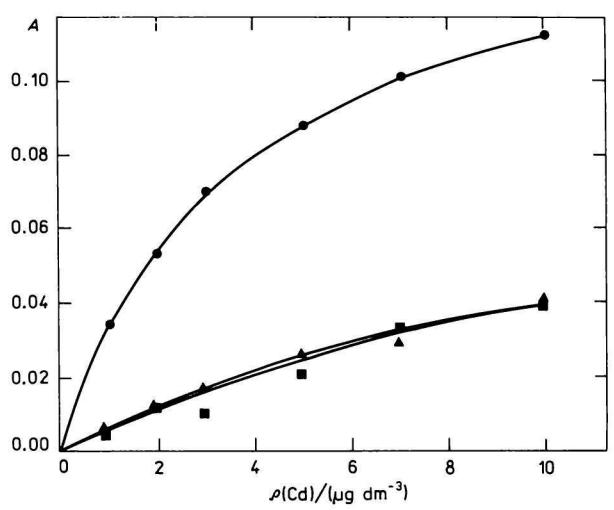

Fig. 8. Calibration curves of the Cd spectral line with addition of matrix elements. ● No addition, ■ A set, ▲ B set.

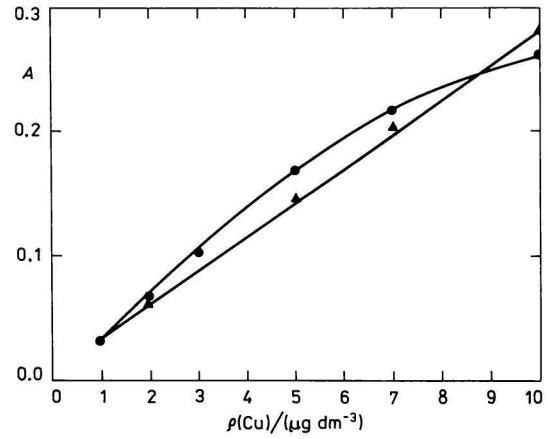

Fig. 9. Calibration curves of the Cu spectral line with addition of matrix elements. ● No addition, ▲ A set.

necessary to operate with two matrix mixtures different in concentration from the standpoint of the analytical calibration. When the A set of the matrix elements was used, the risk of the false disturbing signals occurrence is lower.

The matrix effects of other analytical elements as Cr, Cu, Sb, and Pb were significantly less important and it was confirmed that it is sufficient to model the matrix A by the set of the matrix elements and that Mg is also a spectrochemically active additive [7, 10]. In the case of the analytical element Cr (Fig. 10) the linear graphs were obtained and with the analytical element Cu (Fig. 9) the linear graph was obtained in the case of A set of the matrix elements addition only. The analytical calibration of Sb and especially Pb represented significant complications. The area under the peak, in compliance with the results of *Krakovská* and *Puliš* [16], was shown to be as absolutely inconvenient metrologic parameter. At the same time, the shift of the maxima on the time-resolved Pb signals was observed (Fig. 11). Especially maxima, obtained under the lower concentration values than 20 $\mu g\ dm^{-3}$, were gradually shifted to the value of 0.12 s and on the contrary, the maxima for the concentration values higher than 20 $\mu g\ dm^{-3}$ were shifted to the lower values than 0.09 s. In all cases, the values of the absorbance maxima were used in the final calibrations exclusively.

After the matrix effects tests and after the analytical calibration, the values of the relative precision of the concentration determination $s(\rho_{X,r})$, as well as the values of the detection limits $\rho(X_L)$ were determined. The formulations canonized by IUPAC were applied [17] as well as the proposal given in [18], which respect the measurements in the repeated spectra. Therefore

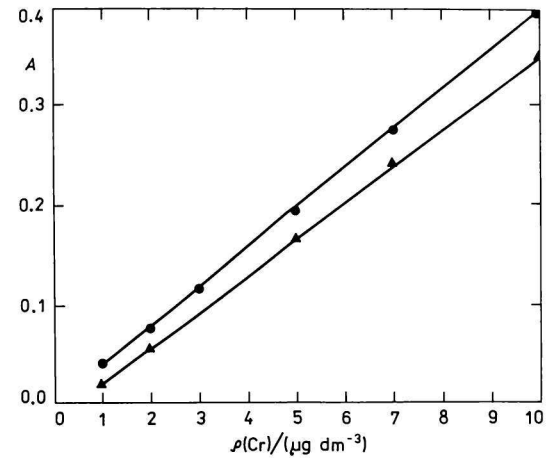

Fig. 10. Calibration curves of the Cr spectral line with addition of matrix elements. ● No addition, ▲ A set.

it was possible to apply the results of the repeated blanks for the determination of the values of the detection limits. Relative precision of concentration determinations and limits of detection of Cd, Cr, Cu, and Pb was $s(\rho_{X,r})/\%$ 1.7, 1.8, 8.1, 5.7 and $\rho(X_L)/(\mu g\ dm^{-3})$ 0.1, 0.6, 0.3, 0.9, respectively.

CONCLUSION

The set of the experimental results can be finally characterized in the following manner. The anion components added to the analytes in the form of HCl, HNO_3, H_2SO_4 when the Cr, Cd, Cu, Sb, and Pb hollow cathode discharge lamps are used show for the blanks the significantly different behaviour of the time-resolved analytical signals. The relationships $A = f(t)$ for the radiation of the Cr and Pb hollow cathode discharge lamps when the analyte is present in the form of the deionized water exclusively, show the absorption fluctuations related to the time dependences of the signal and of the background as well. On the contrary, the relationships $A = f(t)$ show the false analytical signals only rarely for Cd and Cu hollow cathode discharge lamps and all the time with no significant absorption fluctuation nature.

The correction for the background for the analytical calibrations in both cases was needed, moreover sufficiently efficient. The analytical calibration was carried out for the first time for the aqueous solutions of the analytical elements and then even after the gradual addition of the individual major and minor matrix elements of the drinking and river waters.

The forms of the graphical description for Cd as analytical element were always of nonlinear nature. The addition of the matrix elements shifted the analytical calibration curves for Cd always under the level of the curves for the aqueous solutions. When the solutions contained Cr, Cu, and Pb and matrix elements, the linear relations were obtained, however, only in the case of the correction with respect to the blanks. When Pb was considered, the maximum of the time-resolved analytical signals, in relation to its analytical concentration, was gradually shifted to the lower time values.

Also the relative precision of the concentration determinations and the limits of detections were derived from the analytical calibrations. These parameters as a whole, confirmed the suitability of the ETA-AAS method application when WETA was used for the analysis of highly pure river water and drinking water.

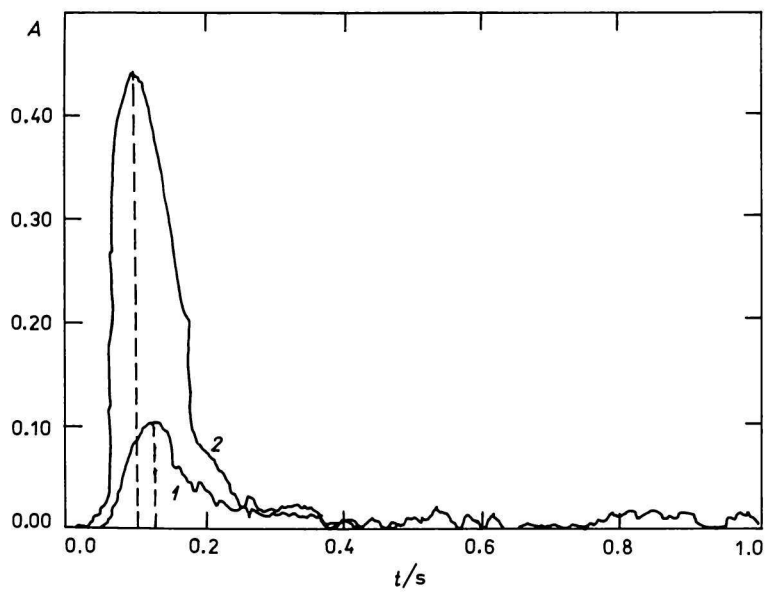

Fig. 11. The time-resolved analytical signals of the element Pb. *1.* ρ(Pb) 10 $\mu g\ dm^{-3}$; *2.* ρ(Pb) 25 $\mu g\ dm^{-3}$

REFERENCES

1. Holéczyová, G. and Matherny, M., *Chem. Papers 46*, 385 (1992).
2. CSN 75 7221 Klasifikace jakosti povrchových vod. (Classification of the Quality of Surface Waters.) Prague, 1990.
3. CSN 75 7111 Pitná voda. (Drinking Water.) Prague, 1989.
4. Krakovská, E. and Sučik, G., *Chem. Listy 85*, 312 (1991).
5. Krakovská, E., *Chem. Listy 86*, 556 (1992).
6. Krakovská, E. and Puliš, P., Sonderband CANAS '93, 357 (1993), Univ. Leipzig.
7. Schindler, E., *Dtsch. Lebensm. Rundsch. 81*, 1 (1985).
8. Manning, D. C. and Slavin, W., *Appl. Spectrosc. 37*, 1 (1983).
9. Fischman, M. J., Perryman, G. R., Schroder, L. J., and Mathews, E. W., *J. Assoc. Off. Anal. Chem. 69*, 704 (1986).
10. Welz, B., Schlemmer, G., and Mudakavi, J. R., *JAAS 3*, 695 (1988).
11. Frech, W., *Fresenius Z. Anal. Chem. 275*, 353 (1975).
12. Vyskočilová, O., Sychra, V., and Kolihová, D., *Anal. Chim. Acta 105*, 271 (1979).
13. Holéczyová, G. and Matherny, M., Sammelband CANAS '95, 115 (1996), Bodenseewerk Perkin—Elmer, Bodensee.
14. Pinta, M., *Atomic Absorption Spectrometry*. A. Hilger, London, 1975.
15. Lidin, R. A. Andreeva, L. L., and Molochko, V A., *Spravochnik po neorganicheskoi khimii. Konstanty neorganicheskikh veshchestv*. Khimiya, Moscow, 1987
16. Krakovská, E. and Puliš, P., *Spectrochim. Acta, B 51*, 1271 (1996).
17. Irving, H. M. H., Freiser, H., and West, T. S., *Compendium of Analytical Nomenclature IUPAC*. Pergamon Press, Oxford, 1978.
18. Matherny, M., *Fresenius Z. Anal. Chem. 271*, 101 (1974).

Translated by M. Repášová