Optimization of the Atomic Absorption Spectrometric Methods
I. Matrix Effects in Flame Atomization Analysis of Waters

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Optimization of atomic absorption spectrometric determination of elements requires, first of all, the study of spectrochemical matrix effects which, in case of insufficient elimination, may cause remarkable systematic errors in evaluation of analytical concentrations. The mentioned matrix effects were studied using experimentally determined analytical calibration lines or curves of trace element lines in the presence of varying addition of main elements Ca, Fe, K, Mg, Na, and their mixtures to the individual calibration solutions of analytical elements.

According to their origin, waters are natural and waste; the natural and purified waters are: drinking water, technical water, and industrial water with various degree of contamination. The natural waters are of surface or subsurface character. The following standards CSN 75 7221 [1] and CSN 75 7111 [2] concerned with specific requirements on the quality of drinking waters decide about the degree of water contamination. According to *Wood* [3] classification toxic elements in waters can be divided as follows:

- highly toxic inorganic elemental pollutants: Ag, Au, As, Be, Bi, Cd, Co, Cu, Hg, Ni, Pb, Pd, Pt, Sb, Se, Sn, Te, and Zn;
- toxic, low-soluble pollutants, usually occurring in low or extremely low concentrations: Ba, Cr, Ga, Hf, Ir, La, Mn, Pr, Zr, Mo, Nb, Os, Re, Ru, Ta, Ti, W, and Rh.

Observing the chemical quality of waters, mainly that of surface waters from the industrial and economical agglomerations it is purposeful to notice the variation of concentrations of the following elements: Ag, Ca, Cd, Co, Cu, Fe, Hg, K, Mg, Mo, Na, Ni, Pb, Sn, Ti, V, and Zn. From these elements, Hg was determined by classical flameless technique with matrix effects elimination by standard addition method without optimization. Ca and Mg, or K and Na which are the macroelements in waters, were determined only for typical localities. The testing of Ag, Ni, Pb, Sn, Ti, V, and Zn levels confirmed that their concentrations were below those permitted by CSN 75 7221 [1]; therefore their determination was not necessary and they were not included in the set of trace elements chosen for the optimization of the AAS method. The optimization itself was, in addition to experimental parameters, directed mainly towards the study of matrix effects which may cause unwanted systematic errors when using fixed calibration lines.

EXPERIMENTAL

The experimental conditions used in flame atomization with AAS 1N (Zeiss, Jena) apparatus and with Perkin—Elmer instrument, model 2380, are summarized in Tables 1 and 2, respectively. The use of two different apparatuses was justified by the idea of comparing the influence of performance parameters of the apparatuses upon the

Table 1. Experimental Conditions for AAS Determination on the AAS 1N Apparatus Using Flame Atomization

Type of flame			acetylene + air				acetylene + N_2O	
Character of flame			oxidation				stoichiometric	
Flow-rate of acetylene/(dm^3 h^{-1})			120; 132 for Cr				180	
Flow-rate of air/(dm^3 h^{-1})			530; 520 for Cr				–	
Flow-rate of N_2O/(dm^3 h^{-1})			–				190	
Elements	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Mo
Wavelength/nm	422.7	228.8	357.9	324.7	248.4	285.2	279.5	313.3
Slit/μm	30	30	20	30	40	40	40	40
Concentration range of calibration/(mg dm^{-3})	1—10	1—10	1—15	1—10	1—10	1—10	1—10	10—100

Table 2. Experimental Conditions for AAS Determination on the Perkin—Elmer Apparatus, Model 2380 Using Flame Atomization

Element	Cd	Mo
Wavelength/nm	228.8	313.3
Concentration range of calibration/(mg dm^{-3})	1—10	1—10
Slit/mm	0.7	0.7
Flow-rate of air/ (dm^3 h^{-1})	1050	-
Flow-rate of N_2O/ (dm^3 h^{-1})	-	270
Flow-rate of acetylene/ (dm^3 h^{-1})	120	650

matrix effects and other evaluating parameters of the analytical methods.

The study of matrix effects was based not only on the linear part of the calibration line as in previous works [4—6], but also on wider concentration range including the nonlinear part as well [7] due to the fact that matrix effect differentiation in flame atomization is usually more remarkably observed from the middle of the concentration range ($\rho(X) > 5$ mg dm^{-3}).

The choice of matrix elements Ca, Fe, K, Mg, and Na was verified by the analysis of typical samples of surface and drinking waters. Two concentrations were chosen: the concentration corresponding to pure, partly and highly contaminated water - the degree of pollution A, and the concentration corresponding only to highly contaminated water according to CSN 75 7221 [1] definition - the degree of pollution B. The concentration data can be seen in the appropriate figures showing the analytical calibration lines.

In addition to the matrix effects study the evaluating parameters of the analytical methods were determined, *i.e.* the relative precision of concentration determination $s(\rho_{X,\,r})$, the limit of detection $\rho(X_L)$ and guaranteed limit of purity $\rho(X_G)$ values, the values of sensitivity $B(X)$, the slope of analytical calibration lines in accordance with IUPAC recommendation [8]. The observations from the emission atomic spectrochemistry [9] were applied in determination of the detection limits, namely the repeated blank experiments variant.

Table 3. Experimental Determination of Sensitivity Values $B(X)$ and Further Standard Deviation Values

Parameter	Elements(X)					
	Cd	Cu	Cr	Fe	Mn	Mo
$B(X)$	*ca.* 1.0	0.71	0.47	0.70	0.66	*ca.* 1.0
$s(A_X)$	0.006	0.006	0.004	0.005	0.005	0.002
$s(A_{X,\,r})$/%	± 1.0	± 2.0	± 1.2	± 3.2	± 1.6	± 1.3
$s(\rho_{X,\,r})$/%	± 0.6	± 0.85	± 0.85	± 0.72	± 0.76	± 0.25

The corresponding values of the relative precision of absorbance measurement $s(A_{X,\,r})$ and relative precision of concentration determination $s(\rho_{X,\,r})$ were calculated by help of experimental determination of sensitivity $B(X)$ and standard deviation of absorbance measurement $s(A_X)$ values.

DISCUSSION

Experimental conditions were chosen in accordance with the AAS devices manufacturers data and then varied in order to reach maximum precision of absorbance measurement. This optimization condition was given by the requirement of maximum possible precision in matrix effects testing. The results are summarized in Table 3. It is obvious that the value of mean of the relative precision of absorbance measurements is less than ± 2 %, consequently, the mean value of the relative precision of concentration determination is ± 0.7 %. Such precision guarantees the differentiation of individual calibration points of several matrices.

Different matrix effect is defined as follows: the course of the analytical calibration lines for one element (X) in various matrices is significantly different, *i.e.* in case of straight lines the sensitivities $B(X)$ and in case of curves the curvatures are different in comparable concentration ranges.

Analytical calibration curves for Cd show evidently different and nonlinear course in case of addition of none single, and of all matrix elements (Fig. 1). As quasilinear may the course be considered in

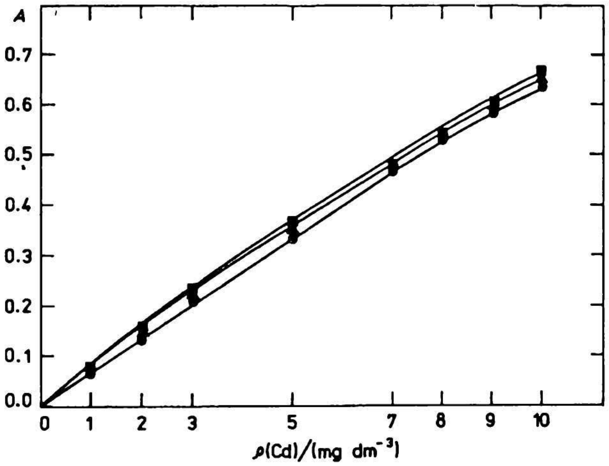

Fig. 1. Analytical calibration lines for Cd obtained on the AAS 1N apparatus for aqueous Cd solution: ● without matrix elements addition; with added matrix elements: ■ 50 mg dm^{-3} of Ca, 10 mg dm^{-3} of Mg, 0.5 mg dm^{-3} of Fe, 100 mg dm^{-3} of Na, and 10 mg dm^{-3} of K - degree of pollution A, ▲ 500 mg dm^{-3} of Ca, 100 mg dm^{-3} of Mg, 5 mg dm^{-3} of Fe, 1000 mg dm^{-3} of Na, and 100 mg dm^{-3} of K - degree of pollution B.

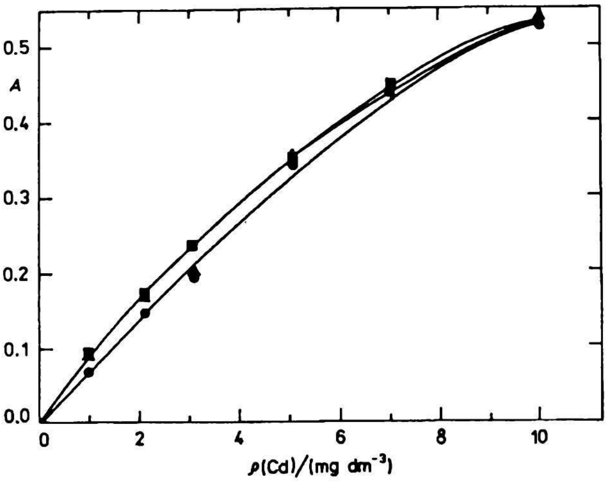

Fig. 2. Analytical calibration lines for Cd obtained on the Perkin—Elmer apparatus for the same three different types of solutions as in Fig. 1.

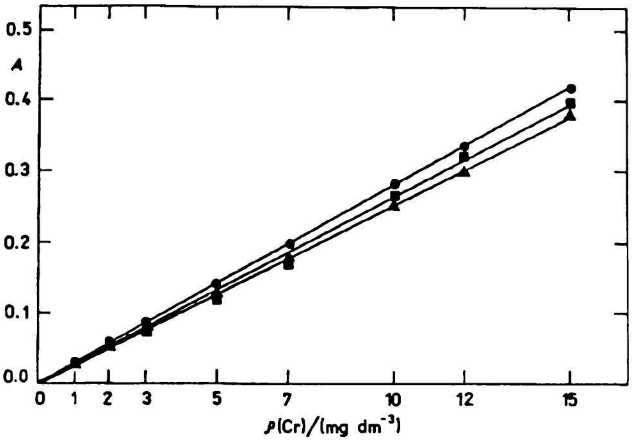

Fig. 4. Analytical calibration lines for Cr obtained on the AAS 1N apparatus for aqueous Cr solution: ● without matrix elements addition; with added ■ 50 mg dm^{-3} of Ca, ▲ 500 mg dm^{-3} of Ca.

a short range of concentrations from 1 to 3 mg dm^{-3}, sometimes to 5 mg dm^{-3}. The absorbance values for all concentrations of Cd in the presence of matrix elements are always higher than for pure Cd aqueous solution. It is worth noticing that neither K nor Na in the applied concentrations caused the assumed reduction and elimination influence upon the matrix effect [7]. The matrix effects studied using Perkin—Elmer apparatus are different and in general lower (Fig. 2). As to the influence of individual matrix elements, K and Na up to 5 mg dm^{-3} have not disturbed the linear character of the studied function, as it can be seen in Fig. 3. It may be concluded from this fact that such matrix effects should be taken into account independently of the measuring technique used. Only solutions with actual concentrations of all matrix elements should be used for calibration and concentration evaluation of Cd.

Matrix effects in case of analytical curves of Cr were quite different. The matrix element Ca only changed the sensitivity value in the direction of its lowering, *i.e.* with increasing concentration of Ca the sensitivity values were lower (Fig. 4). Mg and Fe, similarly as K, showed only slight matrix effects without disturbing the linearity. Na partially changed the linear character of the analytical curves of Cr. The most remarkable matrix effects were reached when applying the mixture of all matrix elements as it is shown in Fig. 5. These analytical curves of Cr unambiguously prove that increase in the concentration of the mixture of Ca,

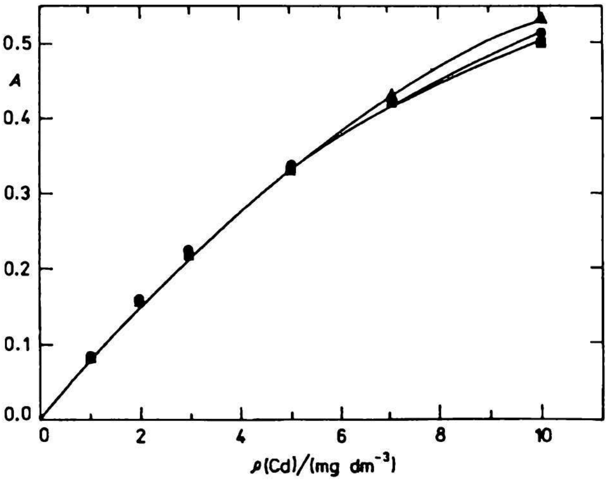

Fig. 3. Analytical calibration lines for Cd obtained on the Perkin—Elmer apparatus for aqueous Cd solution: ● without matrix elements addition; with added ■ 10 mg dm^{-3} of matrix element K, ▲ 100 mg dm^{-3} of K.

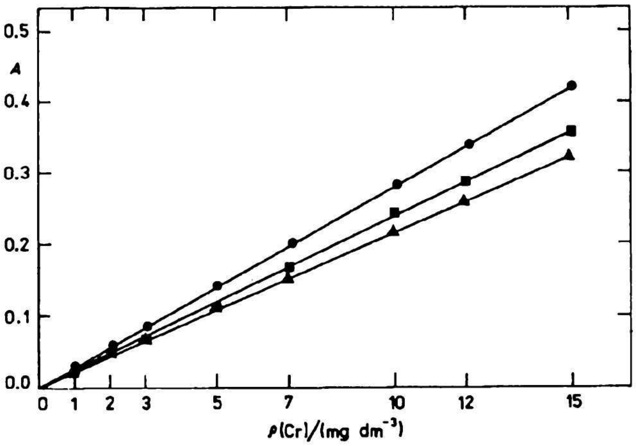

Fig. 5. Analytical calibration lines for Cr obtained on the AAS 1N apparatus for aqueous Cr solution: ● without matrix elements addition; ■, ▲ with added matrix elements in various degrees of pollution A, B as in Fig. 1.

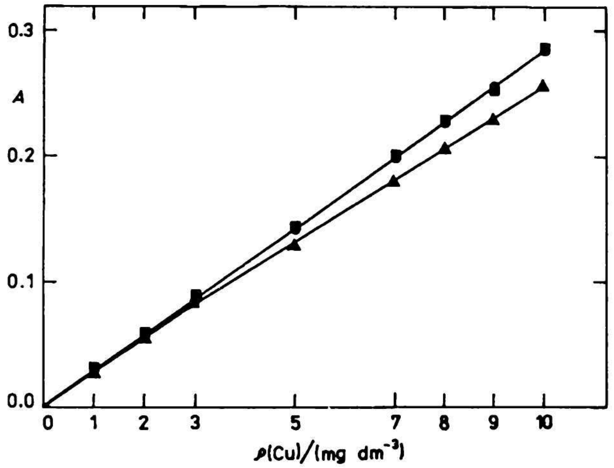

Fig. 6. Analytical calibration lines for Cu obtained on the AAS 1N apparatus for aqueous Cu solution: ● without matrix elements addition; with added ■ 10 mg dm^{-3} of matrix element Mg, ▲ 100 mg dm^{-3} of Mg.

Mg, Na, K, and Fe matrix elements causes remarkable reduction in sensitivity of the analytical determination of Cr.

Matrix effects on the analytical calibration lines of Cu are the least remarkable of all studied analytical elements. In Fig. 6 it may be seen that Mg causes the already observed depressive effect. The mixture of all matrix elements mutually compensates the depressive or synergic effect upon the absorbance of Cu (Fig. 7).

In case of analytical element Mn the linearity is disturbed only by addition of Ca (Fig. 8), and partially Mg as matrix elements. The addition of the mixture of matrix elements up to the degree of pollution A causes no observable effects whereas the addition of the mixture up to the degree of

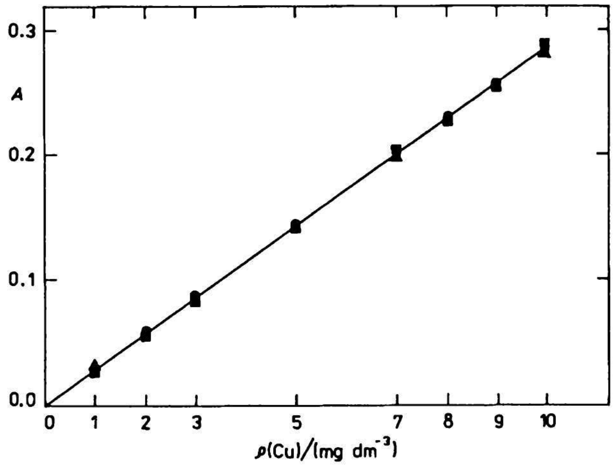

Fig. 7. Analytical calibration lines for Cu obtained on the AAS 1N apparatus for aqueous Cu solution: ● without matrix elements addition; ■, ▲ with added matrix elements in various degrees of pollution as in Fig. 1.

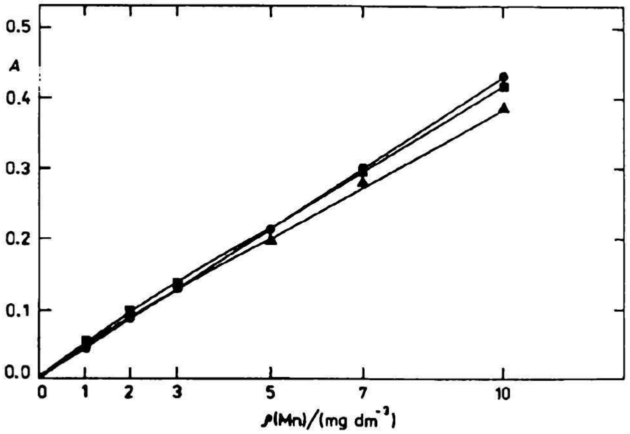

Fig. 8. Analytical calibration lines for Mn obtained on the AAS 1N apparatus for aqueous Mn solution: ● without matrix elements addition; with added ■ 50 mg dm^{-3} of Ca, ▲ 500 mg dm^{-3} of Ca.

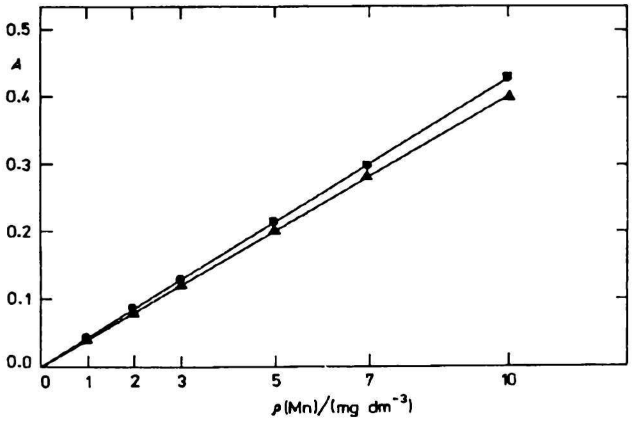

Fig. 9. Analytical calibration lines for Mn obtained on the AAS 1N-apparatus for aqueous Mn solution: ● without matrix elements addition, ■, ▲ with added matrix elements in various degrees of pollution as in Fig. 1.

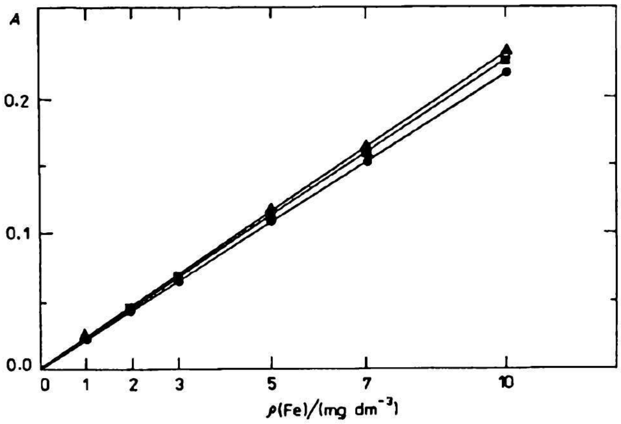

Fig. 10. Analytical calibration lines for Fe obtained on the AAS 1N apparatus for aqueous Fe solution: ● without matrix elements addition; with added matrix elements: ■ 50 mg dm^{-3} of Ca, 10 mg dm^{-3} of Mg, 100 mg dm^{-3} of Na, and 10 mg dm^{-3} of K, ▲ 500 mg dm^{-3} of Ca, 100 mg dm^{-3} of Mg, 1000 mg dm^{-3} of Na, and 100 mg dm^{-3} of K.

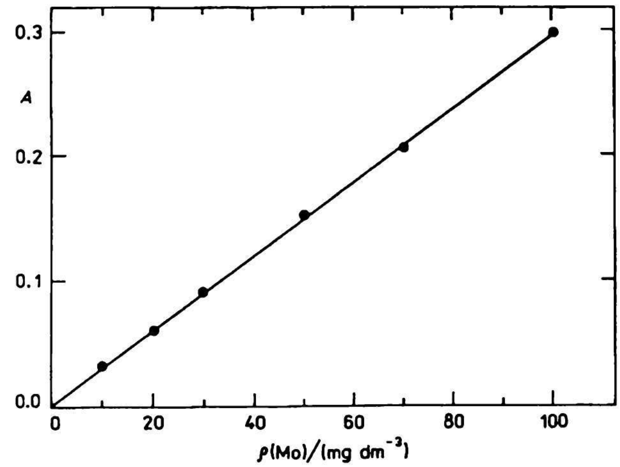

Fig. 11. Analytical calibration line for Mo without addition of matrix elements obtained on the AAS 1N apparatus.

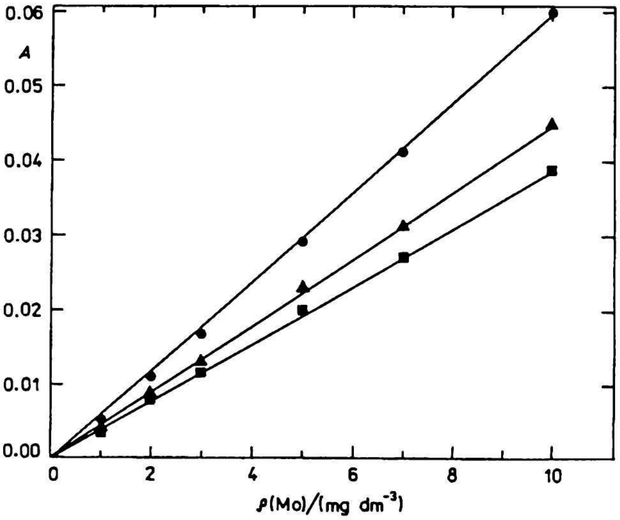

Fig. 12. Analytical calibration lines for Mo obtained on the Perkin—Elmer apparatus for aqueous Mo solution: ● without matrix elements addition; with added ■ 10 mg dm^{-3} of Mg, ▲ 100 mg dm^{-3} of Mg.

pollution B results in slight decrease in the sensitivity of Mn determination (Fig. 9) without disturbing the linearity. The same is true for the analytical calibration lines of Fe as it is shown in Fig. 10, although this element does not belong to the trace elements of surface waters.

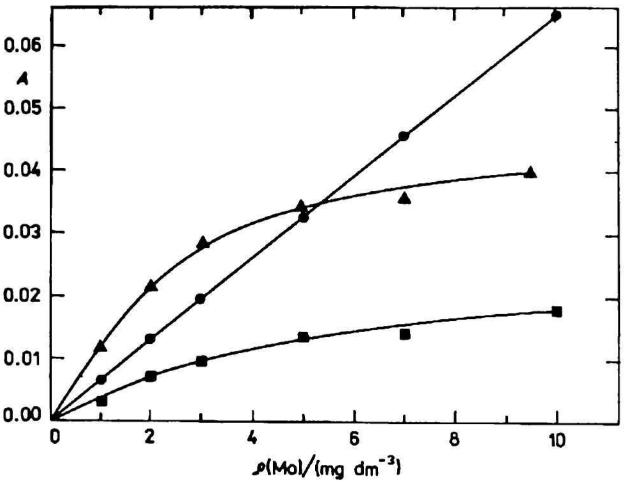

Fig. 13. Analytical calibration lines for Mo obtained on the Perkin—Elmer apparatus for aqueous Mo solution: ● without matrix elements addition; ■, ▲ with added matrix elements in various degrees of pollution as in Fig. 1.

The analytical calibration line for Mo could be constructed on the AAS 1N only for the concentration range from 10 to 100 mg dm^{-3} which is not relevant for the waters considered (Fig. 11). Therefore, the matrix effects were not tested and the further study was carried out on the Perkin—Elmer apparatus. A detectable matrix effect was observed with 100 mg dm^{-3} of K, on the other hand 50 mg dm^{-3} of Ca, 10 mg dm^{-3} of Mg, and 0.5 mg dm^{-3} of Fe as matrix elements caused remarkable matrix effects (Fig. 12). The addition of matrix element mixtures to the Mo solution in two different concentrations caused enormous matrix effect (Fig. 13).

It may be concluded from the above facts that detectability in case of flame atomization may be influenced by matrix effects (Table 4). As basic values should be regarded those obtained for individual elements in pure aqueous solution without matrix elements. The "limiting" values were measured again after addition of the mixture of the following matrix elements: 50 mg dm^{-3} of Ca, 10 mg dm^{-3} of Mg and K, 0.5 mg dm^{-3} of Fe, and 100 mg dm^{-3} of Na. Remarkable decrease towards worsening of the detectability was observed in case of Fe which confirmed that matrix elements affected only slightly the atomization and recombination processes. The absorbance signal in this concentration range was less remarkably changed with respect to the signals obtained for element in aqueous solution.

Finally, the measured limit of detection $\rho(X_L)$ and guaranteed limit of detection $\rho(X_G)$ values were compared for both tested spectrometric methods (Table 5). It is evident from the data presented that by the use of the Perkin—Elmer apparatus even by two orders more advantageous values

Table 4. Matrix Elements Effect upon the Limit of Detection $\rho(X_L)$ and Guaranteed Limit of Detection $\rho(X_G)$ Values

Parameter	Solution	Elements(X)					
		Cd	Cu	Cr	Fe	Mn	Mo
$\rho(X_L)$/	aqueous	0.14	0.42	0.32	0.34	0.21	2.0
(mg dm^{-3})	with matrix	0.11	0.42	0.37	0.64	0.21	–
$\rho(X_G)$/	aqueous	0.27	0.84	0.64	0.70	0.41	4.0
(mg dm^{-3})	with matrix	0.22	0.84	0.71	1.28	0.41	–

Table 5. Limit of Detection and Guaranteed Limit of Detection Values for Different Apparatus Techniques

Parameter	Cd		Mo	
	AAS 1N	Perkin—Elmer	AAS 1N	Perkin—Elmer
$\rho(X_L)$/ (mg dm^{-3})	0.2	0.002	2.0	0.001
$\rho(X_Q)$/ (mg dm^{-3})	0.3	0.005	4.0	0.003

were obtained. This fact is most probably due to the optical properties of the mentioned apparatus, as well as to the performance of the complex atomization process including preparation of aerosol.

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Application of Solid-Phase Extraction to HPLC Determination of Carbamate Pesticides in Water

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A simple device for the preconcentration of carbamate pesticides from water samples was used for their determination. Solid-phase extraction was carried out on sorbents Separcol SI C18 T and/or Porapak Q. The whole preconcentration procedure was optimized. Extracts were analyzed by RP-HPLC with UV detector on a column packed with Separon SGX-C18 in mobile phase methanol—water.

The quantitative determination of pesticides in water is important for the protection of environment. The analysis of pesticides in natural samples cannot be carried out, as a rule, without the appropriate concentration and clean-up process. The reviews of principles and applications of individual procedures can be found in many papers [1—5].

The application of multiresidual procedures in the analysis of pesticides is reported by *Ambrus* and *Thier* [6]. This paper is devoted to the sample preparation, extraction process, clean-up process of extract, and conditions for chromatographic determination. *Ambrus et al.* [7] describe the common method of the determination of pesticide residues, too.

The choice of concentration methods depends on the nature of compounds analyzed, concentration factor required, and the method of sample analysis.

The liquid-phase extraction used earlier has been recently replaced by the solid-phase extraction. The organic porous sorbents based on styrene—divinylbenzene, styrene—methacrylate or ethylene glycol—methacrylate copolymers or fluorinated polymers are used for the preconcentration of pesticides. The possibilities of the porous organic polymers application to the trace amount extraction of organic compounds from water are reviewed by *Dressler* [8]. Sorbents prepared by the chemical modification of silica gel by introduction of alkyl, cycloalkyl or aryl substituents are used frequently, octadecylsilica gel is used most frequently. *Tatar* and *Popl* [9] studied possibilities of preconcentration of triazine, phenoxycarboxylic acid pesticides, chlorpropham and triallate on sorbents Separon SE, Tenax GC, Porapak Q and Separon SI C18.