

## **Contribution to a study of organic solvent addition on trace determination by FAAS\***

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The influence of the presence of an organic solvent on the determination of trace elements by flame atomic absorption spectrophotometry (FAAS) was investigated under different experimental conditions. The obtained results show that the effect of organic solvents on the signal intensities depends not only on the physical properties of the solution but on the analyte properties too. The extent of the effect is also very dependent on the construction of the nebulization system as well as on the stoichiometric flame composition. These facts indicate the very complex mechanism of the effect and demonstrate the essential importance of taking care strictly of the experimental parameters and conditions when using organic solvents in analytical practice.

*Keywords:* solvent addition, trace determination, FAAS.

When determining trace elements by FAAS, it is often necessary to introduce into the flame samples containing various quantities of some organic matter. This is most frequently the case when analyzing samples with organic components or when organic solvents are applied during separation or/and preconcentration procedures. For these reasons it is of importance to know the nature and mechanism of the influence of organic components on trace element determination by FAAS.

It is known that the presence of an organic solvent in the solution to be analyzed considerably influences the analytical signal. However, literature data on the quantitative evaluation of this influence are quite different, sometimes completely controversial.<sup>1-8</sup> At the same time, there are large differences in the explanation of the mechanism of this influence and different authors point out various factors that predominantly determine the nature and extent of the organic solvent effect. For example, some authors found that the organic solvent effect exclusively causes an increase in the analytical signal which is of the same value for all elements.<sup>1</sup> On the other hand, others point out that this effect can also be depressive and depends on the nature of the element.<sup>2-4</sup> Consideration of the literature data is

\* Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday.

additionally complicated by the fact that the influence of organic solvents was investigated under very different experimental conditions, such as type of flame, fuel/oxidant ratio, aspiration rate, nebulization type, *etc.*

For these reasons, an attempt is made to explain the possible reasons of these disagreements and to contribute to a better understanding of the insufficiently explained mechanism of the influence of organic solvents on the determination of trace elements by FAAS.

#### EXPERIMENTAL

Elements of different physical parameters in the presence of various quantities of ethanol and acetone (as frequently used solvents in analytical practice) were applied in the experiments. The most important physical parameters of the analyte elements and the operating conditions are given in Table I.

TABLE I. Physical properties of the investigated elements and operating conditions

Element	$\lambda$ nm	Ionization potential eV	Strength of the M-O bond kJ/mol	Concentration mg/L	Fuel flow rate L/min	Oxidant flow rate L/min
Cu	324.8	7.72	$269.0 \pm 20.9$	2.0	2.0	10.0
Fe	248.3	7.87	$390.4 \pm 17.2$	2.0	1.5	10.0
Ca	422.7	6.11	$402.1 \pm 16.7$	2.0	3.8	10.0
Cd	228.8	8.99	$235.6 \pm 83.7$	1.0	2.0	10.0
Mg	285.2	7.64	$363.2 \pm 12.6$	0.2	2.0	10.0
Zn	213.9	9.39	$>270.7 \pm 41.8$	1.0	2.0	10.0
Ni	232.0	7.63	$382.0 \pm 16.7$	5.0	2.0	10.0
Cr	357.9	6.76	$429.3 \pm 29.3$	5.0	3.8	10.0
Na	589.0	5.14	$61.2 \pm 4.0$	0.5	2.0	10.0
Li	670.8	5.39	78.0	2.0	2.0	10.0

All the measurements were performed using a Perkin Elmer Model 3300 atomic absorption spectrophotometer (AAS). The ratio of signal intensity in the presence of organic solvent,  $A_o$ , and without it,  $A_w$ , *i.e.* factor  $F = A_o/A_w$ , was measured. In order to investigate the influence of the type of nebulization system on  $F$ , some experiments were also performed using a Perkin Elmer Model 373 AAS.

The influence of the physical parameters of the solution on  $F$  was also investigated. Therefore, the density, viscosity and surface tension of the solutions were determined by standard methods (Table II). All the solutions contained hydrochloric acid at a concentration of 3 % (w/v), while the Na and Li solutions additionally contained potassium at a concentration of 0.2 % (w/w) as KCl.

#### RESULTS AND DISCUSSION

The influence of the concentration of ethanol and acetone on the factor  $F$  of the determined elements is presented in Figs. 1 and 2, respectively. In the case of all the investigated elements except Ca, the addition of organic solvent caused an increase of signal intensity, *i.e.*, the factor  $F$ . The influence of the organic solvent depends not only on the kind of and concentration of the solvent but also on the nature of the analyte.

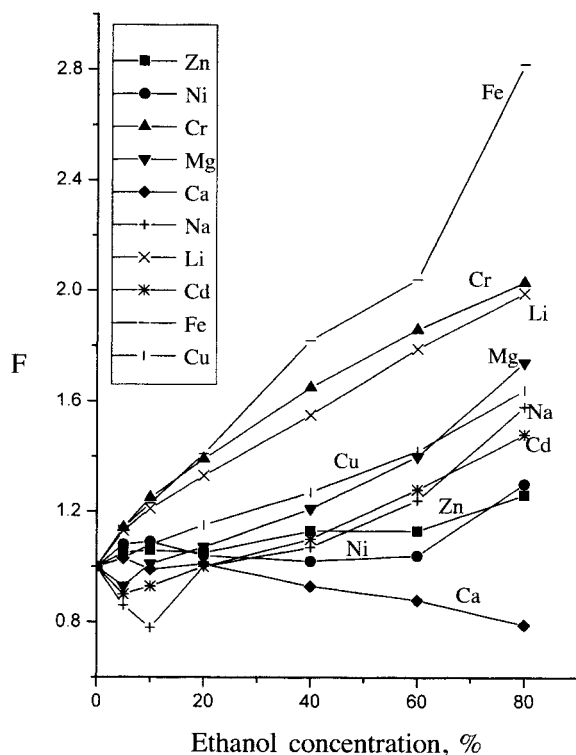


Fig. 1. The influence of the ethanol concentration on the factor  $F$  of the investigated elements.

It is shown that influence of organic solvent increases with increasing concentration in the solution which can be partly explained as a consequence of changes in the physical parameters of the solution (Table II). So, for example, the solutions with 60 % (v/v) of ethanol and acetone have about 150 % and 70 % higher viscosity, respectively, compared to pure water solution. The same solutions show about a 50 % (4.2 ml/min) and 30 % (5.9 ml/min) lower aspiration rate compared to water solution (8.7 ml/min). This is in complete accordance with the known fact that this rate depends only on the viscosity and on no other physical properties of the solution.<sup>5</sup> In spite of this, the presence of organic solvents generally causes an increase of AA signals. The increase of the analyte signal can probably be ascribed to the improved efficiency of the nebulization process into the plasma. It has been shown that the solution surface tension primarily determines the drop size of the so called primary aerosol.<sup>9,10</sup> Thus, in the case of an 80 % (v/v) aqueous solution of both solvents, the surface tension is approximately more than 40 % less than for pure water. Solutions with lower surface tension should generate more surface area. This is accomplished<sup>10</sup> through the production of a finer primary aerosol. However, while passing the spray chamber, as well as along the hole path to the flame, the primary aerosol is further changed, forming secondary and tertiary aerosol. These changes are mainly caused by the elimination of larger drops by gravitation, centrifugal forces, flow spoiler, *etc.* The result of all these processes is the formation

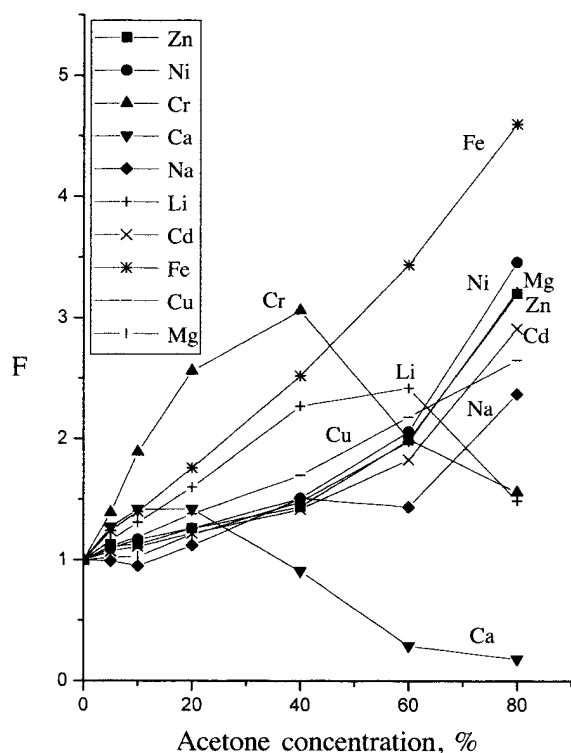


Fig. 2. The influence of the acetone concentration on the factor  $F$  of the investigated elements.

of aerosol enriched in smaller drops, which are transported faster to the plasma where they are evaporated and atomized more efficiently and more completely.

TABLE II. Physical parameters of various aqueous-organic solvent mixtures

Solvent concentration %, v/v	Density/g cm <sup>-3</sup>		Surface tension/mNm <sup>-1</sup>		Viscosity/μPa s	
	Ethanol	Acetone	Ethanol	Acetone	Ethanol	Acetone
0	1.0152	1.0150	72.69	72.71	1010	1010
5	1.0084	1.0075	59.63	60.80	1150	930
10	1.0022	1.0012	51.54	52.21	1310	1010
20	0.9904	0.9880	47.41	48.29	1670	1240
40	0.9648	0.9602	43.61	44.01	2450	1490
60	0.9277	0.9372	42.23	43.49	2600	1720
80	0.8822	0.9183	41.21	42.01	2590	1910

The results also show that the influence of acetone on the factor  $F$  is for all elements higher than that of ethanol. This can be explained primarily by the higher evaporation rate of acetone. Its relative evaporation is almost five times higher than in the case of ethanol.<sup>11</sup> The difference in the evaporation of solvents also shifts the maximum of the drop size distribution towards smaller values, which causes faster analyte transport and atomization.<sup>10,12</sup>

It is obvious that the physical parameters of the solution have a considerable influence on the effect of the organic solvent. Many authors have been trying to correlate the effect of an organic solvent on the AA signal with the physical parameters of the solution.<sup>3,5,13</sup> However, the only quantitative estimation of the effect on the basis of the physical properties of the solution (surface tension, viscosity and density) is given by Greenfield's empirical equation.<sup>14</sup> In order to check the validity of this equation, we have calculated the values of factor  $F$  for solutions with different concentrations of ethanol and acetone (Table III). Comparing the calculated and experimental values, it is found that the Greenfield's equation gives the same  $F$  values for the same solvent concentration, irrespective of the properties of the element. Besides this, the equation predicts that the addition of ethanol should have a greater influence than acetone, giving much lower values of  $F$  for acetone than obtained by experiment. This is primarily the consequence of the fact that the equation does not take into account the influence of the properties of the element and solvent evaporation, which is of considerable importance.

TABLE III. Values of factor  $F$  calculated according to the Greenfield equation

Organic solvent	Organic solvent concentration/%						
	0	5	10	20	40	60	80
Ethanol	0.97	1.09	1.21	1.33	1.56	1.64	1.71
Acetone	0.97	1.05	1.15	1.25	1.37	1.44	1.52

An additional possible source of discrepancies between the literature data is related to the different conditions (such as flame composition, *i.e.*, different flow rate ratio of fuel and oxidant gases) under which the effect of the organic solvent was investigated.

The comparison of the influence of the type of nebulization system on factor  $F$  for different elements is given in Table IV. It is obvious that the effect of organic solvents is dependent to some extent on the complete nebulization system.

The results of the investigation of the influence of the fuel/oxidant ratio on factor  $F$  (Table V) show that a change in the redox conditions in the flame plasma has a different influence on the signal intensities of Cu and Fe for the same concentration of organic solvent. This effect is slightly expressed for Cu, a representative of the elements that are considered to be completely atomized in flame. A quite different picture is obtained for Fe where an increasing participation of fuel in the gas mixture decreases the influence of the organic solvent and that the opposite effect is the more pronounced if the concentration of solvent is higher. The leveling effect is higher for acetone, as the quantity of solvent introduced into the flame is higher. In this case, it is obvious that the atomization efficiency of Cu and Fe is of prime importance for the effect.

TABLE IV. The influence of the type of nebulization system on the factor  $F$  for the investigated elements

Spectrometer	Organic solvent concentration %	Ethanol-aqueous solutions				Acetone-aqueous solutions			
		Cu	Fe	Ca	Cd	Cu	Fe	Ca	Cd
Model 373	5	1.20	1.20	1.08	1.14	1.15	1.19	1.08	1.03
	10	1.32	1.28	1.12	1.23	1.24	1.27	1.18	1.09
	20	1.56	1.38	1.14	1.35	1.42	1.33	1.12	1.19
	40	1.85	1.49	0.69	1.54	1.53	1.53	0.63	1.28
Model 3300	5	1.03	1.14	1.04	0.90	1.11	1.24	1.27	1.07
	10	1.08	1.23	0.99	0.93	1.19	1.40	1.42	1.11
	20	1.15	1.41	1.01	1.00	1.38	1.76	1.42	1.22
	40	1.27	1.82	0.93	1.10	1.70	2.52	0.91	1.42

TABLE V. The influence of the fuel/oxidant ration on the factor  $F$  of Cu and Fe in the presence of organic solvents

Element	Fuel/oxidant flow rates	F			
		40 % of ethanol	80 % of ethanol	40 % of acetone	80 % of acetone
Cu	1.5/10	1.48	1.94	1.76	2.87
	2/10	1.48	1.94	1.70	2.65
	2.5/10	1.52	1.95	1.73	2.64
Fe	1.5/10	1.84	2.84	2.52	4.60
	2/10	1.50	2.18	1.84	2.76
	2.5/10	1.38	1.85	1.45	2.28

The literature data on the possible effect on an organic solvent on the flame temperature are different too.<sup>1,5,15–17</sup> In order to clarify this point, the flame temperature was measured in the presence of organic solvent, by the two-line absorption method, based on the Sn and Pb spectral lines.<sup>18</sup> The results (Table VI) show that the flame temperature is not changed considerably by the addition of ethanol, while the presence of 60 % acetone in the solution decreases the temperature by 240 do 360 K. This fact can explain the decreases of the signal with increasing concentration of acetone noticed in the case of elements which form refractory compounds (Ca, Cr).

TABLE VI. The air-acetylene flame temperature measured during the aspiration of pure aqueous and organic-aqueous solutions

Line pair used	Fuel/oxidant ratio	Flame temperature/K		
		Aqueous solution	60 % of ethanol	60 % of acetone
Pb 368.3 nm 280.2 nm	2/10	2600	2600	2360
Sn 286.3 nm 284.0 nm	3.8/10	2330	2310	1970

## CONCLUSIONS

On the basis of the presented results, it can be concluded that the influence of an organic solvent on the signal intensities in FAAS depends not only on the physical properties of the solution but on the properties of the analyte too. The physical parameters viscosity, surface tension and evaporation rate of the solvent have the greatest influence but the influence of these parameters depends on the analyte atomization characteristics. The extent of the effect is also very dependent on the construction of the nebulization system, as well as on the stoichiometric flame composition, *i.e.*, fuel/oxidant ratio. In order to attain comparable results and having in mind the very complex mechanism of the effect, which includes opposing effects, it is of essential importance to strictly pay attention to the experimental parameters and conditions when using organic solvents in analytical practice.

## ИЗВОД

## ДОПРИНОС ПРОУЧАВАЊУ УТИЦАЈА ОРГАНСКИХ РАСТВОРАЧА НА ОДРЕЂИВАЊЕ ТРАГОВА ЕЛЕМЕНАТА ПОМОЋУ ПААС

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Испитан је утицај органских растварача на одређивање трагова елемената помоћу пламене атомске апсорпционе спектрофотометрије (ПААС) под различитим експерименталним условима. Добијени резултати показују да утицај органских растварача на интензитете сигнала зависи не само од физичких особина раствора, већ и од особина анализата. Величина ефекта у великој мери зависи и од конструкције система за распршивање, као и од стехиометријског састава пламена. Ове чињенице указују на веома сложен механизам утицаја и наглашавају важност строгог контролисања експерименталних параметара и услова при коришћењу органских растварача у аналитичкој пракси.

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