

THE APPLICATION OF ORGANIC SOLVENTS IN ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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The sensitivity of flame-spectrometric determinations is known to be considerably increased by organic solvents and complex forming agents excepted to certain elements [1—6]. Several, sometimes contradictory explanations have arisen to interpret the mechanism of this effect. Although FINK [3] initially attributed the higher sensitivity to the increase of flame temperature, later the sensitivity was found to be little affected by temperature changes of the flame [6—14].

Other researchers presume that the increase of sensitivity is due to the changing concentration of flame reducing components, a process facilitating atomization. In quite a few publications the effect is ascribed to the greater amount of aerosol getting into the flame due to the formation of smaller drops, but no quantitative correlation has been set up [8—9, 16—21].

Recently, CULP *et al.* [22] as well as LEMONDS and McCLELLAN [23] explained the increased sensitivity by the increased aspiration rate and the improvement of the evaporation coefficient. TAYLOR *et al.* [24] as well as LERNER *et al.* [25] wanted to quantitatively correlate the nebulization efficiency and the increase of absorbance.

The present paper discusses the changes caused by organic solvents in the process of nebulization, within the flame and in the sensitivity of the atomic-absorption determinations. Aspiration rate, nebulization efficiency and the relationship between the dispersion degree of the aerosol and the physical properties (viscosity, surface tension, density) of the solvents were examined. Flame expansion was studied by the Schlieren technique [26], and the flame temperature change by the two-line atomic-absorption method [27, 28]. Concentration changes in the radical OH of the flame were shown by way of the lithium-sodium method introduced by SMYLY and his collaborators [29]. In possession of all experimental data, an explanation was given to the absorbance changes of certain elements, such as lead, iron, tin, chromium-aliphatic alcohols in the presence of ketones and carboxylic acid esters, compared to water. In order to generalize our experiences, the changes in the absorbance

of elements such as silver, aluminium, cobalt, copper, potassium, sodium, nickel upon the effect of certain solvents picked out of random have also been examined.

Experimental

Instruments

Atomic-Absorption apparatus

Measurements were made by means of an atomic-absorption apparatus UNICAM SP 90A. The apparatus has a quartz prism and one light path. The original spray chamber has been adapted to the experiments, by connecting the new spray chamber directly to the burner, minimizing impurity deposits likely to impair the reproducibility of measurements.

Microscope

A ZEISS detecting microscope with a microphotographing part was used to determine the dispersion degree of the aerosol. The microphotos were taken with a PRACTICA-NOVA reflex camera, on 15 DIN film.

Particle size analyser

The adequately enlarged microphotos calibrated by means of a micrometer with eyepiece, were evaluated by means of an OPTON TGZ-3 particle size analyser.

Schlieren-equipment

A ZEISS-80 type Schlieren-equipment was used for examining flame expansion.

Device for determining the nebulization efficiency

A simple device made to determine nebulization efficiency is shown in *Fig. 1*. A glass tube of 35 cm length and of the same diameter as that of the pipe stub for the burner were connected. The glass tube was filled up with alternating layers of cotton and 0.5×0.5 cm size Raschig-rings. The column charge was moistened with methanol and exhausted by suction through a water-pneumatic pump.

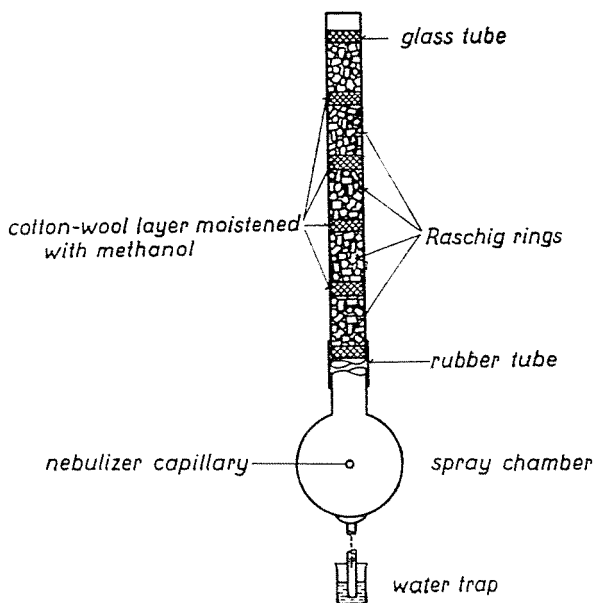


Fig. 1. Device for determining the nebulization efficiency

Table I
Properties of the solvents affecting nebulization

Solvent	Viscosity (dyn/cm ⁻²)	Surface tension (dyn · cm ⁻¹)	Density (g · cm ⁻³)
Methanol	0.0059	22.61	0.790
Ethanol	0.0120	22.75	0.790
N-propanol	0.0225	23.78	0.779
N-butyl alcohol	0.0295	24.60	0.809
N-amyl alcohol	0.0299	—	0.811
Acetone	0.0031	23.70	0.790
Methyl-ethyl-ketone	0.0042	24.60	0.805 (20°)
Methyl-propyl ketone	0.0042	—	0.812 (15°)
Methyl-isobutyl ketone	0.0059	22.70	0.800
Methyl-acetate	0.0038	24.60	0.899
Ethyl-acetate	0.0045	23.90	0.920
N-butyl-acetate	0.0073	—	—
N-amyl acetate	0.0089	24.70	0.880
Water	0.0100	73.05	1.000

Solutions and solvents

Organic solvents

The organic solvents tested, with their physical properties, are listed in *Table 1*.

Phenolphthalein test solutions

3.0 g of phenolphthalein were dissolved in 100.0 ml abs. methanol and stocks of 1.0 ml each were diluted with organic solvents or, instead of water, with 0.01 N sodium-hydroxide free of carbonate and filled in 50.0 ml and 100.0 ml flasks up to gauging notch.

Metallic test solutions with organic solvents

Lead test solutions were made from lead-acetate-trihydrate, solutions of other metals were made of the methanol stock solution of their chloride salts. Test solution concentrations together with experimenting procedures have been compiled in *Table 2*.

Table 2
Tested element and testing data

Element	Concentration of the solution ($\mu\text{g/ml}$)	Wavelength (nm)	Nebulizer
Ag	5	328.0	II
Al	100	309.3	II
Co	5	240.7	II
Cr	10	357.9	II
Cu	10	324.7	II
Fe	5	248.8	I, II
K	2	769.9	II
Na	2	589.0	II
Ni	10	232.0	II
Pb	10	217.0	I
Sn	100	224.6	I

Indium test-solutions

The indium test solutions for determining flame temperature had a concentration of 100 $\mu\text{g In/ml}$. The solutions for examining water, methanol and n-propanol were made of indium chloride, the complex of ammonium pyrroli-

dine-dithio-carbamate of the indium was diluted in the solvents ethyl-acetate n-butyl-acetate and methyl-isobutyl ketone.

Lithium and sodium test solutions

Lithium and sodium test solutions were made of the metal chlorides. To eliminate ionization, they also contained potassium acetate. Concentration values of the lithium and sodium test solutions, differing with each solvent, are given in *Table 3*, together with measurements results.

Table 3

Nebulization characteristics of solvents mean drop sizes, and correlation between relative rate of entry and relative sensitivities

Solvent	Aspiration rate (cm ³ /min)	Nebulization efficiency (%)	Entrance rate (cm ³ per min)	Mean drop size (μm)		Q _{rel}	A _{rel}		
				calculated	measured		Pb	Fe	Sn
Methanol	2.91	12.4	0.360	12.2	11.0	5.2	3.9	5.12	2.0
Ethanol	1.36	15.1	0.205	12.6	10.6	2.9	3.2	3.8	2.0
N-propanol	0.97	16.2	0.157	13.1	11.8	2.2	2.7	—	2.0
N-butanol	0.81	18.0	0.145	12.6	11.2	2.0	1.8	1.9	—
N-amyl-alcohol	0.65	13.2	0.085	—	10.2	1.2	1.3	—	—
Methyl-acetate	3.82	39.9	1.333	—	—	19.0	11.0	—	—
Ethyl-acetate	4.00	20.5	0.820	11.8	11.2	11.7	9.7	—	7.6
N-butyl-acetate	3.34	15.9	0.530	—	13.6	7.6	5.6	6.1	4.8
N-amyl acetate	2.88	11.6	0.334	14.8	15.0	4.8	4.5	4.7	—
Acetone	2.56	35.2	0.902	12.6	8.2	12.8	7.8	—	—
Methyl-ethyl ketone	3.84	18.2	0.698	—	10.0	9.9	8.5	—	—
Methyl-propyl ketone	4.16	11.6	0.483	—	11.8	6.9	5.9	—	—
Methyl-isobutyl ketone	3.21	11.7	0.376	14.9	11.8	5.4	5.9	5.1	5.4
Water	1.95	3.6	0.0702	19.8	17.2	1	1	1	1

Measuring procedures

The nebulizer of the equipment was adjusted by means of a mercury gauge as shown in *Fig. 2*. While the nebulizing gas is passing through the ring-shaped slot between the bore of the nebulizing body and the other wall of the capillary, the pressure at the end of the capillary decreases. This loss of pressure is easy to measure at the capillary inlet and suits checking the reproducible adjustment of the nebulizer. UNICAM nebulizer I and II exhibited inlet pressure values of 275 torr, and 470 torr, respectively. Solution absorbances were measured under instrument parameters actually yielding the highest values for the given element.

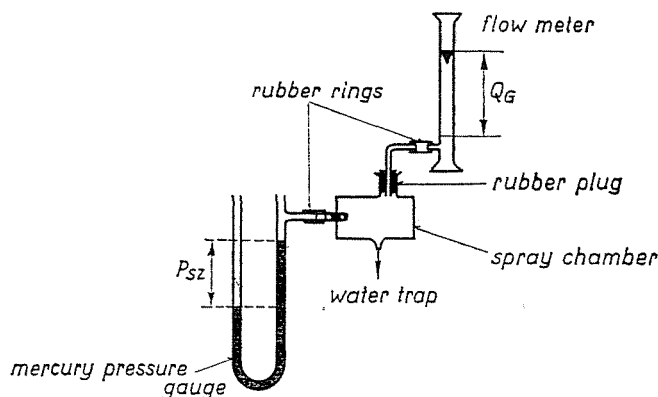


Fig. 2. Measurement of the inlet pressure (P_{sz}) of a sign opposite to that of the pressure loss in the nebulizer, and of air flow rate

Procedures for measuring the flame expansion, flame temperature change and hydroxyl-radical concentration will be described in connection with the particulars.

Determination procedure

Aspiration rate was determined from times required to nebulize 2.0—2.0 ml aliquot stock solutions. Aerosol drops mean diameters have been determined by making them collide on a dark glass plate [30, 31] taking micro-photos of the plate and enlarging them using an OPTON TGZ-3 type particle size analyser. The data obtained were also compared to the mean drop size values obtained from the empirical relationship by Nukiyama—Tanasawa [32] (Table 4).

Table 4

Trends of acetylene-air flame temperatures, and of hydroxyl-radical concentration in presence of certain solvents

Solvent	Flame temperature (K)	Concentration of Li and Na solutions (mol/liter)	$p[\text{OH}] \cdot 10^{-4}$ (atm)
Water	2420	$2 \cdot 10^{-4}$	6.22
Methanol	2780	$2 \cdot 10^{-4}$	7.05
N-propyl-alcohol	2590	$2 \cdot 10^{-4}$	3.51
Ethyl acetate	2840	$5 \cdot 10^{-5}$	23.71
N-butyl acetate	2530	$1.4 \cdot 10^{-2}$	2.65
Methyl-isobutyl ketone	2635	$1.0 \cdot 10^{-4}$	11.77

To state the efficiency of nebulization the absorber columns were connected to the outlet pipe of the spray chamber and phenolphthalein test solutions of 2.0 ml each were nebulized. The phenolphthalein adhering to the column was washed off with 0.01 N sodium hydroxide solution free of carbonate, the volume was added up to 100.0 ml. The concentration was determined by means of a spectrophotometer at a wavelength of 550 nm.

To examine the flame expansion, changes in the Schlieren-picture of an originally stoichiometric flame (1.6 l/min acetylene, 10 l/min air) affected by different solvents were observed.

Flame temperature changes were examined at a flame height of 15 mm, corresponding to thermal equilibrium, as well as in a flame of stoichiometric composition of acetylene and air. Flame temperature was calculated by means of an equation published in [28].

Changes in the concentration of the hydroxyl-radical were calculated according to the conception and by the formulae described in [29] and [33].

Absorbance changes due to organic solvents were always examined at the most sensitive resonance line, by measuring either the absorbance of the test solutions of equal concentration, made with the test solvent or with water.

Results

Knowing the rate and efficiency of the nebulization, the most important value for flame spectrometry: the quantity of aerosol getting into the flame has been calculated. The volume of aerosol leaving the spray chamber in unit time, the so-called entrance is defined as:

$$\frac{\text{Nebulization efficiency } \% \times \text{rate (ml/min)}}{100} = q(\text{ml/min})$$

Thus, the entrance rate is the aerosol quantity leaving the spray chamber in unit time expressed as non-dispersed liquid volume. Aspiration rate, nebulization efficiency, entrance rate and mean drop size values have been compiled in *Table 3*.

The effect of the spray chamber clearly appears from the difference between calculated and measured drop size values. The calculated value is higher than the actually measured value.

All physical properties of the solvent are responsible for changes in the entrance rate during nebulization. When only the nebulization rate changed as a result of a different plastic capillary connected to the nebulizer, aspiration rate and nebulization efficiency were related by a hyperbolic function

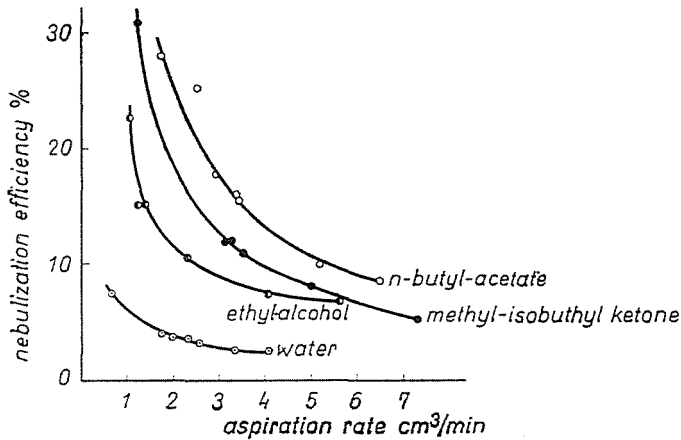


Fig. 3. Aspiration rate vs. nebulization efficiency

(Fig. 3), leading to the important, still unpublished conclusion, that the quantity of solvent getting into the flame, i.e. the entrance rate is unaffected by a change in the aspiration rate because of an eventual exchange or damage of the capillary, or of temperature changes.

The entrance rate and the physical properties of the solvent are empirically related as:

$$q = 0.00647 \cdot \left(\frac{\rho^2 \gamma}{\eta^3} \right)^{0.31} \text{ cm}^3/\text{min}$$

where

- q solvent or solution entrance rate
- η solvent viscosity (cP)
- γ surface tension of the solvent (dyn/cm)
- ρ solvent density (g/cm³)

The computer equation is only valid for the applied spray chamber and nebulizer.

When some aerosol containing a combustible solvent gets into the flame of a given composition, there is a visible change in the colour and shape of the flame. The lower, luminescent, blue zone is expanding and the higher part of the flame is flickering in strong yellow colour. The flame expansion caused by the organic solvent was studied by the Schlieren-technique. Outlines of the Schlieren pictures taken when water and methyl-acetate were nebulized are shown in Fig. 4.

Parts redrawn in continuous line in the figure show the outline of the flame when water was sprayed in, while the dotted lines indicate flame ex-

pansion during spraying in methyl-acetate. The organic solvent was found to little affect the flame cross-section, but the expansion of the inner, blue part to be considerable. The less the aerosol drop size, and the higher the entrance rate of the tested solvent, the greater the expansion.

Changes in the flame-temperature and the hydroxyl-radical concentration are shown in *Table 4*. The flame temperature rises by 200 K under the effect of organic solvents as an average in compliance with data in the litera-

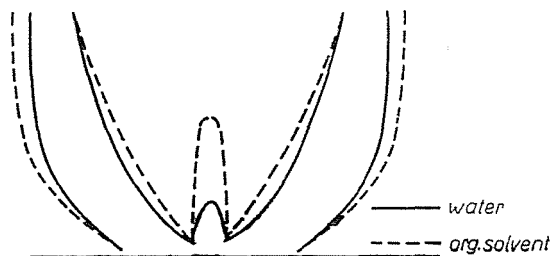


Fig. 4. Scheme of the flame expansion. Solvents: — water, ---- methyl-acetate

ture [36]. The concentration of the hydroxyl-radical is under the complex effect of the varying entrance rates of the different solvents and by the chemical structure of the solvent molecule. With a few exceptions, the concentration of hydroxyl-radicals is higher, when organic solvents are sprayed in, than when water is sprayed in.

Changes in the sensitivity of the tested elements were always investigated at optimum instrument parameters for the solvent and element concerned. The absorbance ratio of water to organic solvent diluted nebulized solutions of equal concentration, will be referred to as relative sensitivity A_{rel} hereinafter. Changes in the relative sensitivity and the entrance rate of the solvent have been compared in *Table 3*. Tabulated data show a rather fair relation between the increases of sensitivity and the entrance rates. With certain solvents like methyl-acetate, ethyl-acetate, acetone and methyl-ethyl-ketone the measured increase in sensitivity falls short of the value expected from the increase of the entrance rate. In case of these solvents, as it has been proved by flame expansion examinations, the borderline of the reaction zone in the flame was shifted upwards. When the widening part of the flame is crossed by the light beam from the hollow cathode lamp, the volume of the introduced solution is distributed over wider cross-section, consequently less of free metal atoms will pass through a given flame cross section in unit time [34].

The absorbance of tin decreased, or even increased below expectation in presence of organic solvents, compared to its aqueous solution. On the other hand, the sensitivity of the atomic absorption determination of chromium

exceeded the value expected from the increase of the entrance rate. The irregular reaction of both elements is due to the change of the chemical properties of the flame. The formation of free tin atoms is strongly affected by the hydroxyl-radical concentration in the flame because the decomposition of the by-product tin hydride is energetically much more advantageous than that of the tin oxide [35].

Organic solvents cause the hydrogen radicals within the flame to be replaced by radicals of carbon and various radicals of hydrocarbon [36, 37] besides, the majority of solvents tested increased the hydroxyl-radical concentration in the flame. Both processes impeded the formation of atomic tin partly by reducing the probability of transient tin hydride formation, and partly, by hampering the dissociation of tin oxide and tin hydroxide as a result of the increased concentration of hydroxyl-radical. Also, a chemiluminescence process may be responsible for the decrease of free tin atoms capable of absorption [38, 39]. The range of chemiluminescence wavelength is about 225–240 nm [40]. To study chemiluminescence radiation the flame emission spectra of tin solutions diluted in water and in n-propanol at equal concentrations have been recorded. Compared to the aqueous solution, there was no new band in the flame spectrum, thus the stimulus of chemiluminescence was unimportant in this case.

The relative sensitivity of the chromium determination increased by more than expected from the entrance rate, attributed to the increased efficiency of chromium oxide reduction.

As concerned other elements, the increase of silver, cobalt, copper, potassium and sodium determination sensitivities was observed to be proportional to the rates of entrance. The behaviour of nickel is similar to that of chromium, in an organic solvent it shows higher sensitivity than expected. Attempts to determine aluminium failed in any solvent certainly due to the high dissociation energy of aluminum oxide.

Conclusions

Knowledge of the aspiration rate is insufficient in the flame spectrometry of solutions, to penetrate into the correlation between nebulization and analytical sensitivity, the entrance rates have to be known. Changes in the sensitivity of determination is in close correlation with the entrance rate for all elements which do not form heat-resisting compounds in the flame. According to flame expansion examinations, minor deviations may be ascribed to the shift of the reaction zone of the flame. For elements, such as chromium and nickel, where the determination sensitivity is considerably affected by the chemical composition of the flame, the reductive ambience adds to the sen-

sitivity of determination. Tin determination sensitivity is lower than expected from the increased rate of entrance: attributed to the reduction in tin-hydride formation and the repressed dissociation of tin oxide and hydroxide.

Summary

Organic solvents, applied in atomic absorption analysis, affect the aspiration rate, nebulization efficiency and the volume of aerosol getting into the flame. For measuring the efficiency of nebulization, a simple device working on the absorption principle has been constructed. The aspiration rate and nebulization efficiency of aliphatic alcohols, ketones and carboxylic acid esters, and the average drop size of the aerosol were examined. Shift of the flame reaction zone was measured by the Schlieren-technique, temperature changes were stated by way of the two-line atomic absorption method and the concentration of hydroxyl-radicals was evaluated by the lithium-sodium method. If the aspiration rate only fluctuates the plastic capillary size, the aspiration rate and the nebulization efficiency are related by a hyperbolic function. An empirical relation has been found between the entrance rate and the physical parameters of the solution.

Flame expansion examinations showed solvents not to affect the spatial location of the flame shell but the inner blue ring of the flame to extend. Flame temperature increased by 200 °K as an average compared to water spray. Concentration of the hydroxyl-radical increased in the presence of most of test solvents.

Relative determination sensitivities of lead, silver, cobalt, copper, sodium and potassium changed with the entrance rate. Tin determination sensitivity decreased as changes of the chemical composition of the flame do not favour the formation of free tin atoms. Chrome and nickel determination sensitivities were higher than expected, because of the increased flame reductivity.

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