Effect of Organic Solvents on Atomic Absorption Spectrometry

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Synopsis

The effects of organic solvents on the sensitivity of atomic absorption spectrometry were investigated by using iron and magnesium as examples. The sensitivity increased remarkably when organic solvent was added to the sample solution. To clarify this effect, the feeding rates of sample solution into atomizer chamber and into flame were measured. The former rate was lower in the case of mixed solvent than aqueous solution, but the latter one was almost the same in both cases, because the atomization efficiency was greater when organic solvent was added to the sample solution.

From these observations, the increase in sensitivity can be explained by the fact that the size of spray droplets is smaller when mixed solvent is used, and that species in droplets can be effectively dissociated into atomic state in flame.

I. Introduction

Dean and Lady[1] were the first to use an organic solvent for increasing the sensitivity of flame photometry by a simple means. Later, numerous works have been reported on the examination of the effect of organic solvents in flame photometry, and the sensitivity increase by the addition of or the extraction with organic solvents has been put to practical use. On the other hand, Robinson[2] was the first to report the effect of organic solvents in atomic absorption spectrometry. Allan[3] examined the effect of water-miscible and -immiscible organic solvents, and reported mainly the mechanism of the sensitivity increase by the use of water-immiscible solvents.

In the present series of work, the effect of organic solvents in atomic absorption spectrometry was examined by adding water-miscible solvents of methyl alcohol, ethyl alcohol, propyl alcohol, acetone, and methyl acetate, and also the mechanism of this effect. Water-immiscible solvent tested was methyl isobutyl ketone.

(1) J.A. Dean and J.H. Lady, Anal. Chem., **27** (1955), 1533.
(2) J.W. Robinson, Anal. Chim. Acta, **23** (1960), 479.
(3) J.E. Allan, Spectrochim. Acta, **17** (1961), 469.

II. Reagents and apparatus

1. Reagents

Standard iron solution: Electrolytic iron (99.9%) was dissolved in hydrochloric acid with addition of a small amount of nitric acid and the solution was evaporated to dryness. A small amount of nitric acid was added to the residue and dissolved in distilled water to make a solution of 10 mg/ml. This stock solution was diluted at the time of use.

Standard magnesium solution: Magnesium metal (99.9%) was dissolved in hydrochloric acid, the solution was evaporated to dryness, and the residue was dissolved in distilled water to make a solution containing 1mg of Mg/ml. This stock solution was diluted at the time of use.

Methyl isobutyl ketone: Commercial product of analytical grade was shaken with 7N hydrochloric acid to use the ketone previously saturated with hydrochloric acid.

2. Apparatus

Hitachi spectrophotometer Model EPU-2A and atomic absorption attachment RA-1 were used. Air-acetylene flame was used, and light source was a hollow cathode lamp of iron and magnesium. Water-cooled, fish-tail burner, with gas outlet of 7cm in length, was employed.

III. Experimental and results

1. Increase in sensitivity by the addition of organic solvents

Methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, acetone, or methyl acetate was added to the standard iron solution (Fe $20\,\mu g$/ml) and to the standard magneisum solution (Mg $2\,\mu g$/ml) until the final concentration becomes of 30% and 60% (v/v), respectively, and the absorbance of the solution was measured. Since the solubility of methyl acetate was small (33% at 20°C), acetic acid was added until the concentration becomes of 10% (v/v).

Conditions for the measurement are given in Table 1. Acetylene pressure was varied in the range of $0.3\sim0.5$ kg/cm^2 according to the kind and the concentration of the solvent added, and so chosen that the flame was at the most stable and perfect burning. Results of absorption measurements under these conditions,

Table 1. Working condition.

	Mg	Fe
Wave length	2852 Å	2483 Å
Current of H. C. L.	30 mA	30 mA
Slit width	0.02 mm	0.10 mm
Air pressure	1.5 kg/cm^2	1.5 kg/cm^2
Acetylene pressure	$0.3\sim0.5$ kg/cm^2	$0.3\sim0.5$ kg/cm

Table 2.   Effects of organic solvents.

Organic solvents	Fe (20 μg/ml)		Mg (2 μg/ml)	
	30% (v/v)	60% (v/v)	30% (v/v)	60% (v/v)
Methyl alcohol	0.138	0.222	0.135	0.201
Ethyl alcohol	0.165	0.235	0.155	0.225
n-Propyl alcohol	0.202	0.240	0.165	0.250
iso-Prophyl alcohol	0.198	0.235	0.165	0.255
Acetone	0.195	0.290	0.165	0.320
Methyl acetate	0.175	0.301	0.175	0.013
Methyl isobutyl ketone	0.401		—	
Aqueous solution	0.083		0.080	

with addition of one of these organic solvents, are given in Table 2.   These results show that the sensitivity is increased by methyl alcohol, ethyl alcohol, and propyl alcohol, in that order, at the same concentration.

2.   Changes in the amount of sample solution sucked with addition of various organic solvents

   To examine the reason for the increase in sensitivity by the addition of organic solvents, changes in the amount of the sample solution sucked during addition of organic solvents were measured.   The sample solutions containing 30% and 60% (v/v) of an organic solvent, the same as those prepared for the foregoing experiment, were used to measure the amount of the solution sucked in per minute.   For this measurement, accurately measured 3 ml of the sample solution containing an organic solvent was transferred to a cylinder, 12 mm in internal diameter and 4 mm in length, and the time required for the entire amount to be sucked was measured.   In this case, the time required for 3 ml of distilled water being sprayed was measured and in order to ascertain that the nozzle was free of other samples,

Table 3.   Changes in the amount of sample solution sucked with
addition of various organic solvents

| Organic solvents	The amounts of sample solution sucked (ml/min)	
	30% (v/v)	60% (v/v)
Methyl alcohol	1.44	1.41
Ethyl alcohol	1.06	0.94
n-Propyl alcohol	1.00	0.85
iso-Propyl alcohol	0.87	0.70
Acetone	1.60	1.68
Methyl acetate	1.73	1.76
Methyl isobutyl ketone	3.05	
Aqueous solution	2.34	

and that no variation in the measurement would result, measurement with distilled water was carried out each time before the sample solution was submitted to the measurement. Each sample was measured three times and with the average the amount sucked in per minute was calculated.

Results of these measurements are given in Table 3, from which it is seen that the addition of alcohols, acetone, or methyl acetate results in the decrease of the amount of sample solution sucked in. With alcohols, the decreasing tendency increases in the order of methyl alcohol, ethyl alcohol, and propyl alcohol, while, as seen from Table 2, the sensitivity increases in the inverse order. The addition of acetone and methyl acetate decreased the amount sucked in to about one-third of that of aqueous solution, but the sensitivity was increased markedly.

3. Changes in the amount sprayed by the addition of various organic solvents

Allan examined the mechanism of the effect of organic solvents in increasing the sensitivity by using methyl isobutyl ketone and pointed out the increased amount of the sample solution sprayed. However, the foregoing experiment showed that the addition of water-miscible organic solvent decreased the amount of the sample solution sucked in to 1/3 to 2/3 of the aqueous solution. Consequently, changes in the amount of the vapor from the atomizer were examined.

The shape of the atomizer used is shown in Fig. 1. An atomizer chamber like this signifies that large vapor particles tend to be sedimented and liquefy, whereas small vapor particles are sprayed out of the atomizer chamber in micro-particles to reach the burener, thereby effecting homogenization of sprayed vapor. The sample solution that was liquefied in the atomizer chamber is expelled from the outlet.
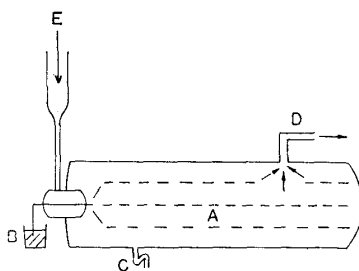
(A) Atomizer chamber   (B) Sample solution   (C) Outlet of drain
(D) Outlet of spray gas   (E) Compressed air
Fig. 1. Schematic diagram of atomizer chamber.

In general, liquids with small surface tension tend to form fine granules in vapor. On the other hand, small particles of vapor are more easily condensed, the smaller the surface tension, and more difficult to be condensed, the larger the surface tension. In the latter case, the amount of the solution expelled as vapor and reaching the burner increases. Therefore, the following experiment was carried out to measure the amount of vapor per unit time.

Sample solutions containing 500 μg/ml of iron with 30% and 60% of an organic solvent were sprayed and the vapor coming out of the atomizer was led through a glass tube, 8 mm in internal diameter and 15 cm in length, into 100 ml of ammonia water (2.5%, v/v) contained in a 200-ml conical beaker, which was tilted at about 45° so that the tip of the glass tube did not touch the wall or bottom of the beaker, in order to collect iron as its hydroxide. The ammonia solution was evaporated to dryness, the residue was dissolved in hydrochloric acid, and the solution was submitted to the photometry by the thiocyanate coloration method[4], from which the amount of spray per minute was calculated.

The result of this measurement, as shown in Table 4, indicated that only about 80% of the solutions mixed with various alcohols reached the flame as vapor, compared with the aqueous solution. The amount of vapor reaching the flame from the solutions containing acetone or methyl acetate was approximately the same as that of the aqueous solution. This amount of vapor may be considered to be proportional to the amount of vapor reaching the flame through the burner when and if the gas pressure is maintained constant.

Table 4. Changes in the amounts of sample solution sprayed by the addition of various organic solvents from atomzier chamber.

Organic solvents	The amounts of sample solution sprayed (μg/min)	
	30% (v/v)	60% (v/v)
Methyl alcohol	18.1	19.3
Ethyl alcohol	21.3	20.6
n-Propyl alcohol	20.6	20.3
iso-Propyl alcohol	18.8	19.1
Acetone	24.6	26.9
Methyl acetate	23.8	28.8
Methyl isobutyl ketone	23.5	
Aqueous solution	25.0	

4. Variation in specific spray efficiency by the addition of various organic solvents

As stated above (III-1), the sensitivity increased with increasing number of carbon atoms when alcohol was added as an organic solvent, at the same concentration of the solvent. When a sample solution containing 30 and 60% (v/v) of alcohol was used, the amount of the sample solution sucked in was 1/2 that of water in the case of methyl alcohol and 1/3 in the case of ethyl alcohol and propyl alcohol, while the amount sprayed from the atomizer was 4/5 that of aqueous solution when a sample solution containing alcohol was used. Although this amount sprayed is about the same in the cases of sample solutions containing acetone and or methyl acetate, the sensitivity increase was 2- to 3-fold in the latter

(4) H. Sawamura, "Series of Chemical Analysis for Steels", 9 (1963), 4.

case. In atomic absorption spectrometry, the vaporization of an element at high temperatures passes through two stages of evaporation (clot formation) and heat dissociation (formation of atomic vapor). Therefore, it was considered that one of the reasons for the increased sensitivity by the addition of an organic solvent might be attributed to a large effect of the size of vapor particles. In order to examine the increase in sensitivity by fine particles of vapor, a factor called 'specific spray efficiency' was introduced.

The spray efficiency is the ratio of the amount of the sample sucked in per unit time to the amount of vapor sprayed from the atomizer chamber. Taking that of spraying water as 1.0, the ratio of that using solutions containing an organic solvent to that of water was calculated.

Considering the nature of the atomizer shown in Fig. 1, the finer the vapor particle will be, the greater the specific spray efficiency, which in turn would increase the number of vapor particles per unit volume, increase the rate of evaporation, and facilitate dissociation into free atoms. This is considered to reflect the proportional increase of sensitivity from the effect of finer particles. The vapor efficiency and the specific spray efficiency of samples containing an organic solvent were calculated from the data given in Sections III-2 and III-3. The result

Table 5. Spray efficiency and specific spray efficiency by the addition of various organic solvents (I).

Organic solvents	Concentration % (v/v)	Spray efficiency (%)	Specific spray efficiency
Methyl alcohol	30	2.5	1.2
Ethyl alcohol	30	4.0	1.9
n-Propyl alcohol	30	4.1	2.0
iso-Propyl alcohol	30	4.3	2.0
Acetone	30	3.0	1.4
Methyl acetate	30	2.7	1.3
Methyl isobutyl ketone		2.2	1.1
Aqueous solution	—	2.1	1.0

Table 6. Spray efficiency and specific spray efficiency by the addition of various organic solvents (II).

Organic solvents	Concentration % (v/v)	Spray efficiency (%)	Specific spray efficiency
Methyl alcohol	60	2.7	1.3
Ethyl alcohol	60	4.4	2.1
n-Propyl alcohol	60	4.8	2.3
iso-Propyl alcohol	60	5.4	2.6
Acetone	60	3.3	1.6
Methyl acetate	60	3.3	1.6
Aqueous solution	—	2.1	1.0

obtained with samples containing 30% (v/v) of an organic solvent is given in Table 5 and that with 60% (v/v) of an organic solvent in Table 6. These tables show that, in the cases of alcohols, the specific spray efficiency increases in the order of increasing sensitivity, but the increase of specific spray efficiency is not proportional to the increase in sensitivity in the cases of acetone and methyl acetate (containing 10% by volume of acetic acid). As will be clear from Tables 3 and 4, the latter values are consistent with the fact that the amount of sample solution sucked in and the amount sprayed are both greater in the cases of acetone and methyl acetate than in the cases of alcohol.

5. Variation in the sensitivity and amount of sample solution sucked by changes in the concentration of organic solvents

The absorbance of a solution containing 20 μg/ml of iron was measured by adding 10～70% (v/v) of methyl alcohol, ethyl alcohol, propyl alcohol acetone, or methyl acetate (containing 10% by volume of acetic acid). These results are given in Fig. 2 for alcohols, and in Fig. 3 for acetone and methyl acetate. These two graphs show that the sensitivity increase, in both cases, with increasing concentration of the organic solvent. Although the result is omitted, the same tendency was seen also in the case of magnesium (2 μg/ml).

In order to examine the relationship between the variation in concentration of organic solvents and the amount of sample solution sucked in, the amount of sample solution sucked in per unit time, i.e. flow rate, was measured. This result obtained with alcohol is given in Fig. 4 and that with acetone and methyl acetate in Fig. 5. These graphs show that the amount of sample solution sucked in decreases with increasing concentration up to 30～40% (v/v), while the amount increases slightly above 40% (v/v) in the cases of alcohol but remains approximately constant in the cases of acetone and methyl acetate.
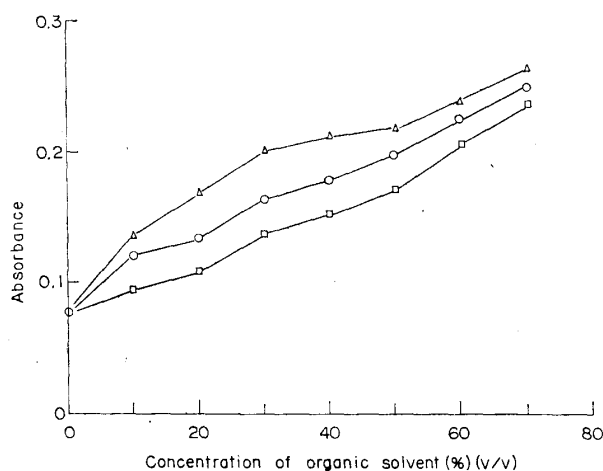
□: Methyl alcohol   ○: Ethyl alcohol   △: n-Propyl alcohol

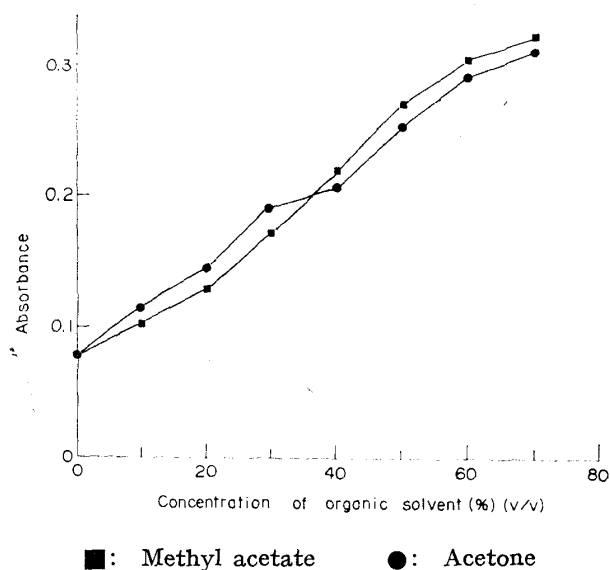Fig. 2. Effect of changes in the concentration of organic solvents (I).

■: Methyl acetate   ●: Acetone

Fig. 3.   Effect of changes in the concentration of organic solvents (II).

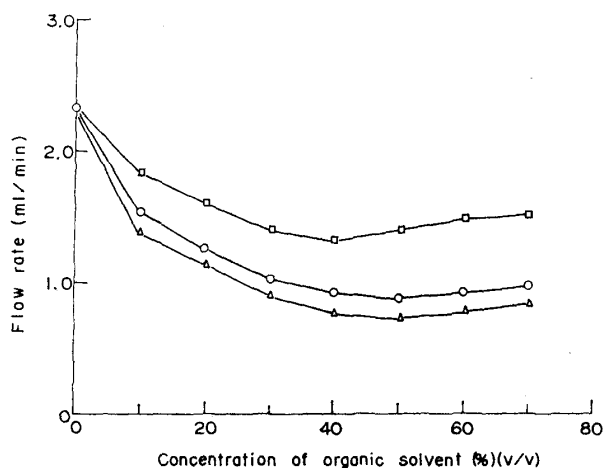□: Methyl alcohol   ○: Ethyl alcohol   △: n-Propyl alcohol

Fig. 4.   Variation in the amounts of sample solution sucked by changes in the
         concentration of organic solvents (I).

6.   Variation in the amount of vapor according to variation in the concentration of organic solvents

The variation in the increased sensitivity and the amount of the sample solution sucked in were respectively similar to one another with various kinds of alcohol and more or less different between acetone and methyl acetate. Therefore, the amount of the sample solution sprayed was measured by varying the concentration of ethyl alcohol and acetone between 10 and 70% (v/v), and the results obtained are shown in Fig. 6. As seen from this graph, the amount of vapor decreased up to 10% (v/v) addition both in the cases of ethyl alcohol and acetone, and the amount remained approximately constant in the concentration range of
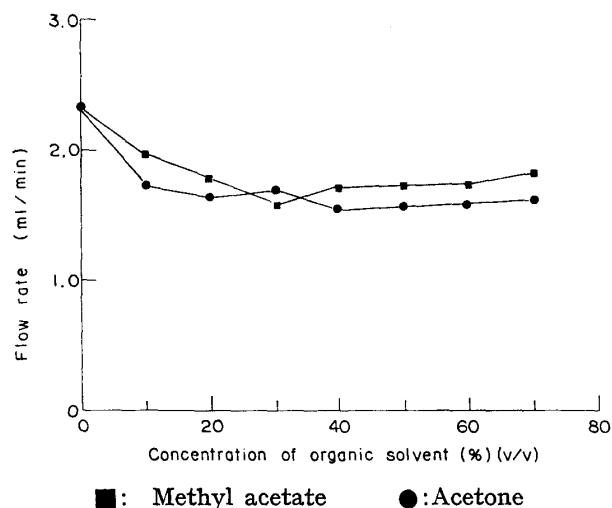
■: Methyl acetate   ●:Acetone

Fig. 5. Variation in the amount of sample solution sucked by changes in the concentration of organic solvents (II).
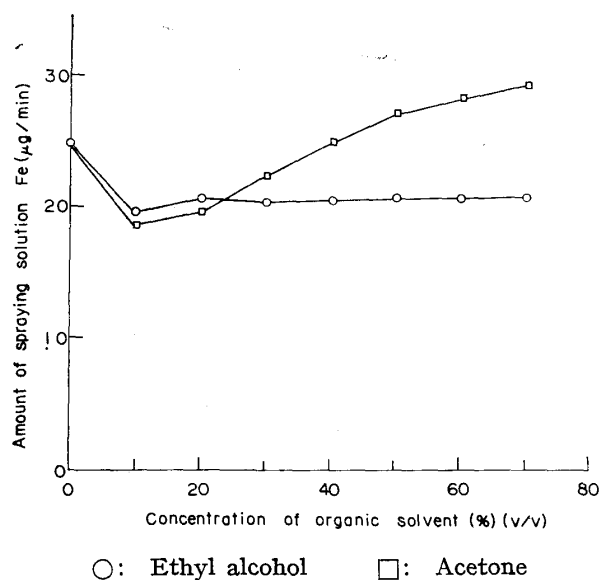

○: Ethyl alcohol   □: Acetone

Fig. 6. Variation in the amount of sample solution sprayed by changes in the concentration of organic solvents.

20~70% (v/v) of ethyl alcohol but increased gradually in the case of acetone in the same range.

7. Changes in specific spray efficiency with variation in the concentration of organic solvent

The vapor efficiency and the specific spray efficiency were calculated in the case of addition of ethyl alcohol and acetone in the concentration range of 10~70% (v/v) from the data given in Sections III-5 and 6. Results given in Table 7 show that the specific spray efficiency hardly changes up to 40% (v/v) of ethyl alcohol and

Table 7. Spray efficiency and specific spray efficiency with variation
in the concentrations of ethyl alcohol and acetone.

Organic solvent	Ethyl alcohol		Acetone	
Concentration %(v/v)	Spray efficiency (%)	Specific spray efficiency	Spray efficiency (%)	Specific spray efficiency
0	2.1	1.0	2.1	1.0
10	2.3	1.1	2.2	1.1
20	3.4	1.6	2.3	1.1
30	4.0	1.9	3.0	1.4
40	4.5	2.1	3.0	1.4
50	4.6	2.2	3.3	1.6
60	4.4	2.1	3.3	1.6
70	4.3	2.0	3.3	1.6

50% (v/v) of acetone, but that the sensitivity increases with increasing concentration of the organic solvent.

IV. Discussion

In order to examine the effect of organic solvents in atomic absorption spectrometry the increase in specific spray efficiency was introduced as a factor indicating the ratio of the increased atomic density in the flame due to finer particles of vapor to the increased rate of evaporation. As can be seen from Table 7, the sensitivity increased with increasing concentration of organic solvents, but the specific spray efficiency did not show any change above 40% (v/v) of ethyl alcohol or above 50% (v/v) of acetone. One of the reasons for this phenomenon might be attributed to the increased atomic density in the flame accompanying changes in the ratio of air pressure to fuel gas (acetylene) pressure. Principles of the atomization part in the atomic absorption spectrometry apparatus used are shown in Fig. 7. There is a correlation between the acetylene pressure and the amount of vapor indroduced into the flame by air pressure when the acetylene pressure is varied. This signifies that, when air pressure is constant, increased pressure on the atomizer chamber increases with increasing acetylene pressure, resulting in a more facile condensation and liquefaction of vapor particles, and that the pressure in atomizer chamber decreases when the acetylene pressure is low, and that condensation and liquefaction of vapor particles become more difficult, resulting

(A) Gas flow meter (a: acetylene pressure, b: air pressure)
(B) Burner
(C) Flame
(D) Sample solution
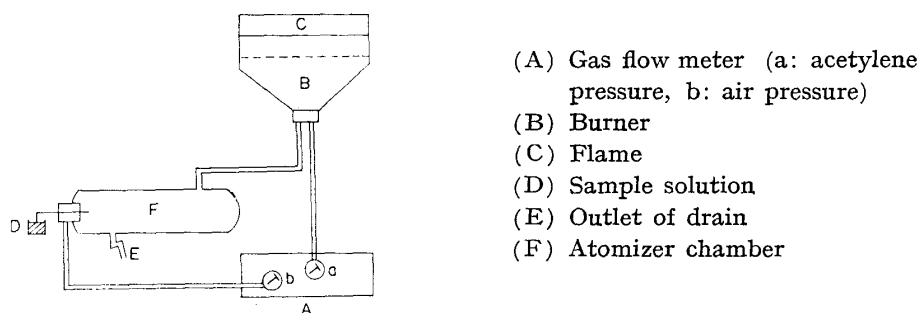(E) Outlet of drain
(F) Atomizer chamber

Fig. 7. Schematic diagram of parts of atomization in the atomic absorption apparatus.

in increased amount of the vapor introduced into the flame. Since the solvent itself is burnt in the flame, it is necessary to lower the acetylene pressure in order to stabilize the flame and to effect complete combustion. In this case, even if the air pressure is kept constant by following gas flow-meter, the ratio of air pressure to acetylene pressure increases near the burner and the sample in finer vapor particles reaching the flame would increase. This is considered to be one of the reasons for the increase in the sensitivity accompanying increasing concentration of an organic solvent.

As a reason for increased sensitivity by the use of methyl isobutyl ketone, a non-miscible solvent, Allan[3] pointed out the increased amount of the vapor reaching the flame since, when compared with that in the case of aqueous solution, the rate of sensitivity increased (3.46 times) in equal to the increased amount of vapor (3.5 times) reaching the flame. According to examinations on iron and copper by the present author[5,6] and to the report by Takeuchi and Suzuki[7] on nickel, the sensitivity increased to around $5 \sim 10$ times that of the aqueous solution but the amount of vapor coming out of the atomizer increased only around 1.5 times, as will be seen from Table 4. Considering the fact that the specific spray efficiency of MIBK solvents is 1.1, the increased ratio of air pressure to fuel gas pressure by the decrease in acetylene pressure and Robinson's statement[2] that effective dissociation of organometallic compounds into atoms is due to combustion of the solvent itself, may both be taken as reasons for increased sensitivity. Finer particles of vapor must be considered as a reason for the effective dissociation in the latter case.

Summary

Increased sensitivity in atomic absorption spectrometry when adding water-miscible organic solvents was examined. The reason for increased sensitivity by the addition of an organic solvent, in spite of decreases in the amount of the sample solution sucked and in the amount of vapor from the atomizer chamber, was examined by introducing a factor termed 'specific spray efficiency'.

When the sample solution is sprayed after the addition of an organic solvent, it becomes necessary to decrease the acetylene pressure, and the effect of increased ratio of air pressure to acetylene pressure due to the decrease in acetylene pressure, and that of increased atomic density in the flame that accompanies it were examined The use of water-immiscible solvent, methyl isobutyl ketone, was also examined and a few observations were made.

Ackowledgement

(5) I. Atsuya, Japan Analyst, **14** (1965), 592.

(6) H. Gotô and I. Atsuya, ibid., **15** (1966), 247.

(7) T. Takeuch, M. Suzuki and H. Doki, Kogyo Kagaku Zasshi, **66** (1963), 1194.