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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	17/18
page range	340-347
year	1965
URL	<a href="http://hdl.handle.net/10097/27266">http://hdl.handle.net/10097/27266</a>

# Increased Sensitivity of Atomic Absorption Analysis\*

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(Received November 30, 1965)

## Synopsis

In order to increase the sensitivity in atomic absorption spectrometry, many improvements, for example, those of light source, detector, flame and atomizer, were investigated. In addition to these improvements, it is asserted that the increased sensitivity of this kind of spectrometry by the addition of or the extraction with an organic solvent is one of the most interesting ideas from the point of analytical chemistry.

## I. Introduction

Since the establishment of atomic absorption analysis by Walsh<sup>(1)</sup> in 1955, this method of analysis has been applied chiefly to medical and agricultural fields such as for the determination of sodium, potassium, calcium, and magnesium in living organisms and in serum<sup>(2,3,4)</sup> and for the determination of sodium, potassium, calcium, and magnesium in soil and fertilizers<sup>(5,6)</sup>. In recent years, the application of this method to industrial fields has increased such as for the analysis of cement, slag, and metals. Many works have been reported regarding the determination of trace components in iron, steel, metals, and alloys, for example, the determination of magnesium in electrolytic nickel<sup>(7)</sup>, and in cast iron<sup>(8,9,10)</sup>. The determination of a microquantity of components in metals by the atomic absorption analysis shows comparatively good sensitivity with magnesium and zinc but satisfactory sensitivity has not yet been obtained in the case of other metals. For this reason, to increase the sensitivity in atomic absorption analysis examinations have been carried out in various fields, both on apparatus and on the method of introduction of the sample, such as examinations of (1) light source, (2) flame and atomizer, and (3) detector. The most notable of such studies is (4) the

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\* The 1221st report of the Research Institute for Iron, Steel and Other Metals. Reported at the Forum of the Analytical Chemistry Society of Japan, 1964.

- (1) A. Walsh, *Spectrochim. Acta*, **7** (1955), 108.
- (2) J.B. Wills, *ibid.*, **16** (1960), 259.
- (3) J.B. Wills, *ibid.*, **16** (1960) 273.
- (4) J.B. Wills, *ibid.*, **16** (1960) 551.
- (5) D.J. David, *Analyst*, **85** (1960), 495.
- (6) J.B. Wills, *Anal. Chem.*, **33** (1961), 556.
- (7) T.R. Andrew and P.N.R. Nichols, *Analyst*, **81** (1962), 25.
- (8) C.B. Belchel and H.M. Bray, *Anal. Chim. Acta*, **26** (1962), 322.
- (9) M. Suzuki and T. Takeuchi, *Kogyo Kagaku Zasshi*, **66** (1963), 690.
- (10) H. Gotô, S. Ikeda and I. Atsuya, *Bunseki Kagaku*, **13** (1964), 111.
- (11) H. Gotô and I. Atsuya, Reported at the 17th Annual Meeting of the Chemical Society of Japan, 1964.

increased sensitivity by the addition of or the extraction with organic solvent, which can be carried out simply during analytical procedures. The present work was especially on the organic solvent, which can be carried out simply during analytical procedures.

## II. Light source

The most important point in atomic absorption analysis is to select light source. Conditions necessary for this selection are (1) narrow resonance absorption lines, (2) strong intensity of spectral lines, (3) absence of other lines in the neighborhood of resonance absorption lines, and (4) no self-inversion. For these reasons, a discharge tube is used for sodium and potassium, and a hollow cathode lamp for other elements. The line width and the intensity of the hollow cathode lamp are determined by the working current. In general, the absorbance becomes greater, the lower the current value of the lamp. For example, as shown in Fig. 1 for the case of magnesium, the absorbance becomes higher as the current

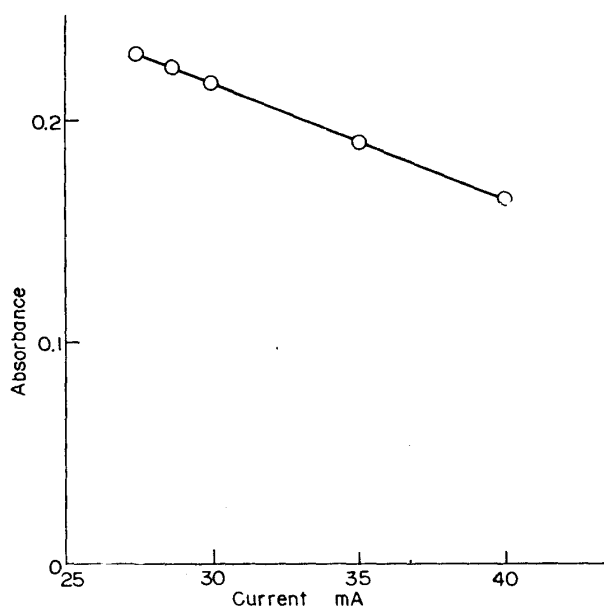


Fig. 1. Effect of lamp current measuring condition.  
Mg: 5 ppm Wavelength: 2852 Å  
Air pressure: 1.1 kg/cm<sup>2</sup>  
Acetylene pressure: 0.48 kg/cm<sup>2</sup>  
Entrance slit width: 0.02 mm

drops<sup>(10)</sup>. This tendency is also observed similarly with iron, copper, and lead, as far as the present observations are concerned. The reason for higher sensitivity obtained by keeping the working current lower has been studied in detail by Yasuda and others<sup>(12)</sup>. In their opinion, higher current results in increased sputtering

(12) K. Yasuda, S. Matsudaira, S. Sato, M. Sugawara and H. Takeuchi, *Hitachi Hyoron*, **44** (1962), 1180.

effect and, consequently, the density of the atoms in ground state inside the lamp increases, which in turn increases self absorption and decreases analytical sensitivity. Higher current also raises the temperature of electrodes and increases the Doppler effect, which results in widening of the absorption lines and decreases analytical sensitivity.

In respect to the presence of proximity lines near the resonance absorption lines, there are two instances: one is the case where the elements themselves have the proximity lines, as markedly observed in manganese, iron, and nickel; the other is the decreased analytical sensitivity due to the proximity or overlapping of the spectral lines of the gas sealed in the lamp and the resonance absorption lines of the testing element. In the former case, increasing of the sensitivity has been tried by making the slit width as narrow as possible to take out only the resonance

Table 1. Effect of spectral slit width on the sensitivity of Ni 3414Å<sup>(14)</sup>

Inlet slit (mm)	Spectral slit width (measured) at 1/2 wave height (Å)	Limit of detection ( $I_0 - I = 2\text{divs}$ ) (ppm)
0.03	3.2	5
0.05	3.2	5
0.075	3.9	6
0.1	4.7	6
0.2	7.7	6
0.3	11.8	7
0.4	16.1	7
0.6	24.7	10
1.0	No resolution	50
1.5	No resolution	100

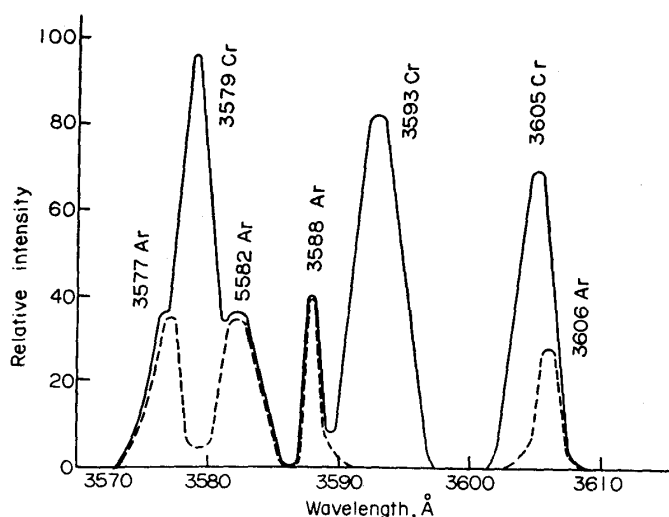


Fig. 2. Relative intensities of significant chromium and argon lines in the wavelength range 3570~3600 Å<sup>(15)</sup>  
 Lamp current: 20 mA  
 Spectrograph dispersion: 10 Å/mm  
 Entrance slit: 0.10 mm  
 — Chromium + Argon spectrum  
 ---- Argon spectrum

absorption lines and to increase the ratio S/N. For example, manganese has three lines at 2795, 2798, and 2801 Å. The line at 2795 Å has the greatest absorbability and other two lines are very weak. In such a case, the slit width is made so narrow as to take out only the line at 2795 Å<sup>(13)</sup>. In the determination of nickel<sup>(14)</sup>, as shown in Table 1, an examination has been made of the relationship between the slit width and the detection limit by using the line at 3414 Å. As an example of the latter case, the use of argon gas for sealing in the hollow cathode lamp for chromium, as shown in Fig. 2, lowers analytical sensitivity because of the overlapping of three resonance absorption lines of chromium and argon lines. In such a case, the use of helium or other inert gases in place of argon would increase the sensitivity.

### III. Flame and atomizer

In atomic absorption analysis, the flame must be stable. In general, the length of gas emission tube of a burner is around 7~10cm. Since the absorbance (sensitivity) of atomic absorption analysis is dependent on the concentration (atomic density) and the thickness of the layer (flame length), and the Beer's law can be followed. Fuwa and others<sup>(16)</sup> reported that the sensitivity was increased by

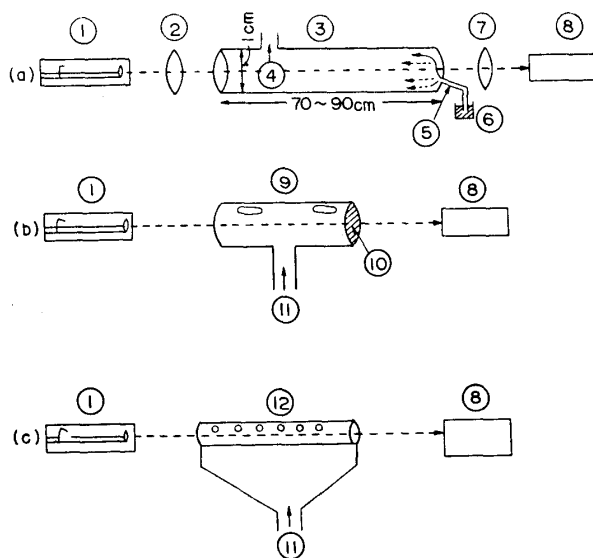


Fig. 3. Some examples of atomic absorption cell

- (a) Absorption cell assembly, by K. Fuwa<sup>(16)</sup>  
 (b) Flame adapter assembly by J. W. Robinson<sup>(14)</sup>  
 (c) Flame adapter assembly by S. Ikeda, I. Atsuya  
 ① Hollow cathode lamp ② Collimating lens ③ Vycor absorption cell ④ Exhaust ⑤ Burner ⑥ Sample  
 ⑦ Focusing lens ⑧ Detector ⑨ Flame adapter  
 ⑩ Quartz window ⑪ Burner sample ⑫ Quartz flame adapter

(13) S. Musha and S. Munemori, Reported at the 17th Annual Meeting of the Chemical Society of Japan, 1964.

(14) J.W. Robinson, *Anal. Chim. Acta*, **27** (1962), 465.

(15) C.B. Belchel, K. Kinison and R.J. Hodges, *Anal. Chim. Acta*, **29** (1963), 134.

(16) K. Fuwa and B.L. Vallee, *Anal. Chem.*, **35** (1963), 942.

several hundred fold in the analysis of cadmium by making the flame portion (thickness of the layer) a Vycor burner of about 70~90 cm and by improving the apparatus as shown in (a) in Fig. 3. J.W. Robinson<sup>(4)</sup> used a flame adopter shown in (b) in Fig. 3, examined this analysis with alkali metals, transition metals, and platinum, and reported that no increased sensitivity was observed with alkali metals and transition metals, but that about 10-fold increase in sensitivity was obtained with platinum<sup>(10)</sup>. In the present series of work, examinations were made with the quartz flame adopter shown in (c) in Fig. 3 and about 10% increase in sensitivity was obtained in the case of iron.

#### IV. Detector

When the intensity of resonance absorption lines of the testing elements in flame is very strong and the sensitivity falls due to this intensity, as in the case of sodium, potassium, and calcium, several measures have been reported to overcome this defect. One is the insertion of a light chopper between the light source and flame, the chopper synchronizing with the detector so as to leave the light inside the flame undetected<sup>(17)</sup>. The other is the use of a compensator. These devices are used in the commercial apparatus for atomic absorption spectrometer. David<sup>(18)</sup> devised a scale expansion apparatus and attempted a 5-fold increase in sensitivity by expanding the meter scale readings.

These examinations on increased sensitivity were made mainly for the improvement of the apparatus and are important for making the atomic absorption spectrometer function better. Increased sensitivity of this kind of spectrometry by the addition of or the extraction with an organic solvent is one of the most interesting ideas from the point of analytical chemistry. Of the effects of organic solvent, the extraction with a solvent is one of the factors in increasing the sensitivity because of separation and concentration. In the present series of work, however, examinations were made of the effects of organic solvents solely as a solvent, such as the addition of an organic solvent or the replacement of aqueous solution by an organic solvent.

#### V. Effect of organic solvent

In flame photometry, examinations have been made by many workers, including J.A. Dean<sup>(19)</sup>, of increased sensitivity by the addition of or the extraction with an organic solvent. In atomic absorption spectrometry, examinations were made of the addition of an organic solvent by J.W. Robinson, J.E. Allan, and R. Rockyer soon after its establishment by A. Walsh. J.W. Robinson<sup>(20)</sup> examined the effect of organic solvents, in comparison with flame analysis, and indicated the mechanism by which the analysis elements attain atomic state when introduced

(17) J.W. Robinson, *Anal. Chim. Acta*, **23** (1960), 458.

(18) D.J. David, *Analyst*, **87** (1962), 576.

(19) J.A. Dean and J.H. Lady, *Anal. Chem.*, **27** (1955), 1533.

(20) J.W. Robinson, *Anal. Chim. Acta*, **23** (1960), 479.

into the flame by spraying, both in the cases of aqueous solution and an organic solvent solution. In the case of aqueous solution, the test element is first hydriized and then becomes semi-crystalline particle so that its dissociation into atomic state is mainly endothermic, and requires a certain time and a fair amount of energy. In the case of organic solvent, the solvent is not only easily evaporated but also the solvent itself undergoes combustion, and the test element easily turns into atomic state effectively.

J.E. Allan<sup>(21)</sup> divided organic solvents into those miscible and immiscible with water, and examined their effect on copper, obtaining the results shown in Tables 2 and 3. In order to elucidate the mechanisms of the organic solvent effect, he

Table 2. Solvents miscible with water.<sup>(21)</sup>

Solvent	Concentration (%)	Sensitivity
0.1 <i>N</i> HCl	—	1.0
Methyl alcohol	40	1.7
Ethyl alcohol	"	1.8
Isopropyl alcohol	"	1.0
Acetic acid	"	1.5
Dioxane	"	2.0
Acetone	"	2.0
Acetone	80	3.5
Acetone	20	2.35
+ Isobutyl alcohol	20	

Table 3. Solvents immiscible with water<sup>(21)</sup>

Solvent	Hundegardh		
	A	B	C
0.1 <i>N</i> HCl	4.0	1.0	1.0
Ethyl amyl ketone	4.7	0.36	2.8
Butyl acetate	5.2	0.32	3.1
Amyl acetate	4.6	0.32	3.1
Propyl acetate	5.4	0.26	3.8
Methyl isobutyl ketone	5.6	0.26	3.9
Ethyl acetate	5.8	0.20	5.1

Column A: Uptake in ml/min

Column B: Concentration of copper for 10 percent absorption (ppm)

Column C: Relative sensitivity

measured the amount of sample introduced into the burner and the amount of the sample aspirated per unit time into atomizer chamber. From his results listed in Table 4, he concluded that the increased sensitivity due to the organic solvent effect resulted neither from the increased amount of the sample aspirated nor from the temperature change but from the increase in the absolute amount of the test element introduced into the flame per unit time because the organic solvent turned into a micro-particle. Allan showed this increase in sensitivity by the determination of copper using methyl isobutyl ketone.

(21) J.E. Allan, *Spectrochim. Acta*, **17** (1961), 467.

Table 4. Collection of copper from burner.

	Solution	
	0.1N HCl	MIBK
Time required to spray 50 ml	10.45 min	7.5 min
Copper collected	128 $\mu\text{g}$	30.5 $\mu\text{g}$
Copper collected for minute for a 10 ppm solution	1.22 $\mu\text{g}$	4.07 $\mu\text{g}$
Relative amount of Cu collected per minute for ppm solution	1	3.35
Sensitivity: ppm copper for 10% absorption	1.4	0.40
Relative sensitivity	1	3.50

MIBK: Methyl isobutyl ketone

From these facts, J.E. Allan stated that organic solvents with low viscosity, small surface tension, and high vapor pressure were the best. However, this cannot be said for all the organic solvents. R. Lockyer<sup>(22)</sup> examined the effect of surface-active agents on the sensitivity by the addition of a surfactant in sample solution of nickel, zinc, and several other elements, and reported that no effect of surfactants was found.

In the present series of work, examinations were made of organic solvents miscible with water. Methanol, ethanol, propanol, acetone, or methyl acetate was added to an iron sample, and changes in the sensitivity, and amount of the sample aspirated by the atomizer, and the amount of the sample vaporized were measured. As shown in Table 5, the amount of the vapor from the atomizer may be considered

Table 5. Effect of organic solvent.

Solvent	Relative sensitivity		Uptake in (ml/min)		Fe introduced in the flame ( $\mu\text{g}/\text{min}$ )	
	30%	60%	30%	60%	30%	60%
Aqueous solution	1.0		2.34		25.0	
Methyl alcohol	1.7	2.7	1.44	1.41	18.1	19.3
Ethyl alcohol	2.0	2.8	1.06	0.94	21.3	20.6
<i>n</i> -Propyl alcohol	2.4	2.9	1.00	0.85	20.6	20.3
<i>iso</i> -Propyl alcohol	2.4	2.8	0.87	0.70	18.8	19.1
Acetone	2.4	3.5	1.60	1.68	24.6	26.9
Methyl acetate	2.1	3.6	1.73	1.76	23.8	28.8
Methyl isobutyl ketone	4.8		3.05		33.5	

to be proportional to the amount of particles reaching the flame through the burner. Consequently, the increased sensitivity by the effect of an organic solvent does not seem to follow the mechanism suggested by J.E. Allan that 'the increased amount of the particles reaching the flame is in the same proportion as the increase in the sensitivity'.

In order to explain the increased sensitivity by the addition of an organic solvent, the ratio of the amount of the sample aspirated per unit time to the amount

(22) R. Lockyer, J.E. Scott and S. Slade, *Nature*, **189** (1961), 830.



of the vapor spouting from the atomizer was named the atomizing efficiency, the atomization of an aqueous solution was taken as 1.0, and the ratio of organic solution to aqueous solution was calculated, designating this as the specific atomizing efficiency. When this value was large, the degree of atomization has increased relative to that of aqueous solution, and the number of particles in the vapor per unit time has increased, with attendant increase in the rate of solvent evaporation, more facile dissociation of the vapor particles into free atoms, and increase in sensitivity. In other words, this would be one of the factors that shows the proportion of increased sensitivity by the addition of an organic solvent. It is seen that the addition of an organic solvent results in the reduction of droplets to very minute particles, but the important point of organic solvent effect is not that this increases the amount of the test element introduced into the flame per unit time but that this increases the rate of dissociation of droplets into the ground state of the atom inside the flame. In such a respect, this view is somewhat different from the opinion held by J.E. Allan. In short, the increased sensitivity due to the effect of an organic solvent is considered to be mainly the effect of reducing droplets to a very minute particle, represented by the specific atomization efficiency, and the effective dissociation of droplets by the combustion of the solvent itself, as was pointed out by J.W. Robinson.

Table 6. Relative coefficient of spray.

Solvent	30%	60%
Aqueous solution		1.0 (Standard)
Methyl alcohol	1.2	1.3
Ethyl alcohol	1.9	2.1
<i>n</i> -Propyl alcohol	2.0	2.3
<i>iso</i> -Propyl alcohol	2.0	2.6
Acetone	1.4	1.6
Methyl acetate	1.3	1.6
Methyl isobutyl ketone		1.1 (extracted)

## VI. Increased sensitivity and coexisting elements

Finally, a mention will be made of the effect of coexisting elements. In general, the atomic absorption analysis is said to be less affected by the presence of other elements but the concentration of acid and the presence of other elements affect its sensitivity. For example, the presence of iron, aluminium, titanium, sulfuric acid, and silicate ion with calcium lower the sensitivity but this interference can be removed by the addition of a large quantity of strontium. The increase or the decrease of sensitivity by the addition of a third element is still unsolved and should be clarified in the near future, as in the case of flame photometry.

### Acknowledgement

The present authors wish to express their hearty thanks to Prof. H. Gotô for his helpful suggestions in the course of the present work.