EFFECT OF VARIOUS SHEATH GASES ON ABSORPTION VS. TIME
PROFILES IN FLAMELESS ATOMIC ABSORPTION

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This experiment explains the absorption vs. time profile and effects of the kinds and flow rates of various sheath gases in graphite furnace atomic absorption spectrometry. The sheath gases in this experiment were helium, nitrogen and argon, as well as each of them mixed with hydrogen. Aluminum, calcium and copper were selected as the elements of measurement. The atomizing time is determined by the absorption vs. time profile. The atomizing time of aluminum, calcium and copper each is the constant value of flow rates of sheath gases at 2,500 °C of graphite tube temperature. The increasing order of the atomizing time (T) is as given below.

Al (T=1.4 sec) < Cu (T=1.9 sec) < Ca (T=3.0 sec) The atomizing time of calcium under nitrogen sheath gas is similar to that of copper.

The use of various sheath gases is important for a flameless atomic absorption spectrometer equipped with a graphite furnace atomizer. Many results¹⁾⁻⁸⁾ have recently been reported on the effects of the kinds and flow rates of sheath gases on atomic absorption.

This paper compares variations in the shapes of atomic absorption signals caused by the different kinds and varying flow rates of sheath gases. The effects of furnace temperatures on the absorption signals are also investigated.

The sheath gases in this experiment were helium, nitrogen and argon as well as each of them mixed with hydrogen. Aluminum, calcium and copper were selected as the elements of measurement. Aluminum was used because it reacts with hydrogen and nitrogen at high temperature, while copper reacts with hydrogen, and calcium with nitrogen.

Experiment

A Hitachi atomic absorption spectrophotometer, Model 308, a Perkin Elmer graphite furnace atomizer HGA-2100, a sampling memory TM-706 and a digital integrator RD-202 S both developed by Tokyo Kagaku, and a Hitachi recorder Model 056 were used. An Omega mixing apparatus was used for mixing the gases. Test solutions prepared prior to use by diluting with 0.01 N HCl containing 0.1 µg/ml

of aluminum, 0.1 $\mu\text{g/ml}$ of calcium and 0.05 $\mu\text{g/ml}$ of copper, respectively.

Argon, nitrogen, helium and hydrogen of more than 99.9% purity were used as sheath gases. The operating parameters for flameless atomic absorption spectrometry and the flow rates of the sheath gases are given in Table 1.

Table 1 Operating parameters for flameless atomic absorption spectrometry

Element	Wave length	Slit, mm		H.C.Lamp current	Gas flow rate	Drying		Ashing		Atomizing	
	nm	EN	EX	mA	ml/min	°C	sec	°C	sec	°C	sec
Al	309.2	0.18	0.5	10	20,40	100	10	1000	20	2500	10
Ca	422.7	0.5	1.0	15	40,60	100	10	650	10	2500	10
Cu	324.8	0.18	0.5	10	40,20	100	10	1000	20	2500	7

Fig. 1. Block diagram of the atomic absorption spectrometry system used for the absorption vs. time profile

The procedure for the experiment is as follows. Each of the test solutions was introduced into the graphite tube by micro pipette. About 10 mg of tantalum powder was weighed into a tantalum boat and carefully transferred to the graphite tube so that the powder in the tube might contain the same amount of the element as that in the test solution. Each sample, i.e., the test solution or the tantalum powder, was uniformly placed into the middle section of the graphite tube. An apparatus was used at the start of the atomizing stage to interrupt the flow of gases for about 10 seconds.

Table 2 Operating parameters for sampling memory and digital integrator

Element	Digital integrator		Sampling memory				Recorder	
	Pre-time (sec)	Integrator-time (sec)	Input range (mV)	Output range (mV)	Reading time (m.sec)	Writing time (m.sec)	Chart speed (min/mm)	Range (mV)
Al	17.1	9.0	10	10	10	50	240	10
Ca	17.1	9.0	20	20	10	50	240	20
Cu	17.1	7.0	20	50	10	50	240	20

Fig. 1 shows a block diagram of the atomic absorption spectrometry system. The atomic absorption signal was transmitted from the atomic absorption spectrophotometer to the digital integrator to record integrated values and peak height of a prefixed time. The time was set progressively at every 0.1 second. The time of the pre-start of atomizing is in the range of from 0.1 to 99.9 seconds. The sampling memory apparatus records at every 0.001 second the signals transmitted from the atomic absorption spectrophotometer. The memorized signals are printed over the range of time from 10 milliseconds to 10 seconds, and recorded. The operating parameters of the sampling memory and the digital integrator are given in Table 2. All experiments were carried out under the conditions of Tables 1 and 2. The sheath gases used were helium, nitrogen and argon as well as each of them mixed with hydrogen up to 10% (wt). The relationships between the heating temperatures of the graphite tube and atomic absorption signal were also studied.

Results and discussions

Aluminum

Fig. 2 shows the typical absorption profile of 2 ng aluminum. The area and the peak height of absorption signal and the atomizing time were determined by these absorption profiles. The atomizing time is defined as the time required to reach maximum absorbance from the appearance of the absorbance signal. The atomic absorption signal of aluminum was transmitted to the sampling memory apparatus and was recorded. The recorder shows the atomizing time [T], and the peak area [S] and the peak height [H] of the signal. Table 3 shows the effects of the sheath gases on the absorption vs. time profile. Fig. 3 shows the effects of graphite tube temperatures on the absorption profile.

The results can be summarized as follows. Aluminum reacts with hydrogen and nitrogen in the heated graphite furnace tube at 2,500 °C. The signal decreases obviously under the sheath gases of nitrogen and its mixture with hydrogen, but

the atomizing time is always constant (1.4 sec). Atomizing time in tantalum powder (about 0.07 ~ 0.15 mm ϕ) by the direct method is the same (1.4 sec).

Fig. 2 Absorption profile of aluminum

[A]: Recorded by a conventional recorder.

[B]: Recorded by the sampling memory. Sheath gas: Ar, 40 cm³/min.
Test solution: 20 μ l

It is described in the previous paper⁸⁾ that the common logarithm of atomic absorbance [S: Peak area (cm^2)] of the aluminum [1 ng] can be expressed by a linear function of flow rates [cm^3/min] of hydrogen concentrations [H]. Also in this experiment, absorbance was quantitatively influenced by addition of hydrogen.

Table 3 Effects of sheath gases on absorption vs. time profile of aluminum*

Sheath gas flow rate	40 cm^3/min			Interruption		
Profile Kind of gas	Peak area	Peak height	Atomizing time	Peak area	Peak height	Atomizing time
	count/sec	mm	sec	count/sec	mm	sec
He	101	13	1.4	619	55	1.4
He+H ₂ (10%)	27	3	1.4	287	10	1.4
N ₂	79	10	1.4	465	49	1.4
N ₂ +H ₂ (10%)	54	9	1.4	376	35	1.4
Ar	280	63	1.4	1363	129	1.4
Ar+H ₂ (10%)	78	6	1.4	451	41	1.4
Ar	-	-	-	-	-	1.4**

* Test solution: 20 μl (2.0 ng Al)

** Determined by the direct method in Ta powder (about 10 mg)

Fig. 3 Effects of graphite tube temperature on absorption profile of aluminum

Ar flow: Regulated at 40 cm^3/min . Twenty microliters of test solution (Al 0.1 ppm) was used.

Calcium

A figure similar to Fig. 2 was obtained as the typical absorption profile of 1 ng calcium. Table 4 shows the effects of the sheath gases on the absorption vs. time profile. Fig. 4 shows the effects of graphite tube temperatures on the absorption profile. The absorption (peak area and peak height) and the atomizing time were determined by the absorption profile. The results can be summarized as follows. The absorption signal of calcium obtained with argon as the sheath gas is equal to that obtained with nitrogen containing 10% hydrogen (Table 4). Table 4 clearly shows that the atomizing times obtained with helium, argon and their respective mixtures with hydrogen are all about 3 seconds, but the atomizing times obtained with nitrogen and its mixture with hydrogen are about 2 seconds, i.e. shorter by about 1 second, than those obtained with the gases described just above.

Table 4 Effects of sheath gases on absorption vs. time profile of calcium*

Profile Kind of gas	40 cm ³ /min			Interruption		
	Peak area	Peak height	Atomizing time	Peak area	Peak height	Atomizing time
	count/sec	mm	sec	count/sec	mm	sec
He	1.8×10^3	47	3.1	1.9×10^3	48	3.2
He+H ₂ (10%)	$1.5 \times "$	49	3.0	$1.5 \times "$	52	3.0
N ₂	7.0×10^2	37	1.8	$4.1 \times "$	105	2.1
N ₂ +H ₂ (10%)	2.7×10^3	111	1.9	$3.9 \times "$	160	2.1
Ar	$2.5 \times "$	110	2.9	$4.2 \times "$	170	3.0
Ar+H ₂ (10%)	$2.7 \times "$	110	2.9	$3.9 \times "$	171	2.9
Ar	-	-	-	-	-	3.2**

* Test solution: 10 μ l (1.0 ng Ca)

** Determined by the direct method in Ta powder (about 10 mg)

Fig. 4 Effects of graphite tube temperature on absorption profile of calcium
Ar flow: Regulated at 40 cm³/min. Ten microliters of test solution (0.1 ppm Ca) was used.

Copper

A figure similar to Fig. 2 was obtained as the typical absorption profile of 1.5 ng copper. Table 5 shows the results of this experiment. Fig. 5 shows the effects of graphite tube temperatures on the absorption profile.

Table 5 Effects of sheath gases on absorption
vs. time profile of copper*

Sheath gas flow rate	40 cm ³ /min			Interruption		
Profile Kind of gas	Peak area	Peak height	Atomizing time	Peak area	Peak height	Atomizing time
	count/sec	mm	sec	count/sec	mm	sec
He	283	55	1.9	403	72	1.9
He+H ₂ (10%)	169	34	1.9	262	45	1.9
N ₂	328	59	1.9	658	100	1.9
N ₂ +H ₂ (10%)	164	29	1.9	325	36	1.9
Ar	372	63	1.6	714	106	1.8
Ar+H ₂ (10%)	178	28	1.6	638	90	1.7
Ar	-	-	-	-	-	1.9**

* Test solution: 30 μ l (1.5 ng Cu)

** Determined by the direct method in Ta powder (about 10 mg)

Fig. 5 Effects of graphite tube temperature on absorption profile of copper

Ar flow: Regulated at 40 cm³/min. Thirty microliters of test solution (Cu 0.05 ppm) was used.

The results of copper can be summarized as follows. When the sheath gases containing 10% hydrogen are used, copper reacts with hydrogen at high temperature. As a result, the absorbance of copper decreases as the number of copper atoms decreases. The absorbance of copper in helium is lower than in argon and nitrogen. This shows that the diffusion of the mass of atomic copper at the time of atomizing is very fast in helium gas. The peak height is proportional to the heating temperature of the graphite furnace. The peak areas of the atomic absorption of copper become a plateau above 2,300°C of heating temperature. The atomizing time is inversely proportional to the heating temperature of the graphite furnace. The atomizing time is inversely proportional to the rate of temperature increase in the furnace. The atomizing time of copper in tantalum powder (about 0.07~0.15 mm ϕ) by the direct method is the same as that in the copper test solution.

The results of all the experiments can be summarized as follows.

(1) Aluminum and calcium react with nitrogen in the heated graphite furnace tube at 2,500°C. The atomic absorption signals of aluminum and calcium decrease more obviously in the sheath gas of nitrogen than in argon gas. But the absorption signal of calcium obtained with argon used as the sheath gas is equal to that obtained with nitrogen containing 10% hydrogen.

Aluminum and copper react with hydrogen in the sheath gases under the condition where 10% hydrogen gas is added to other gas in the heated graphite furnace tube at 2,500°C. The atomic absorbances of aluminum and copper decrease more under the sheath gas of hydrogen than under argon gas.

(2) The increasing order of atomizing time (T) at 2,500°C is as given below.

Al (T=1.4 sec) < Cu (T=1.9 sec) < Ca (T=3.0 sec)

But, the atomizing time of calcium under nitrogen sheath gas is similar to that of copper. The atomizing time decreases with increases in the atomizing temperatures.

(3) The peak heights of the absorption profiles of calcium, aluminum and copper increase with rises in the temperatures of the graphite tube. But the peak areas of the absorption profiles of aluminum and copper are almost constant above 2,300°C. The peak area of the absorption profile of calcium does not become constant. None of the peak areas can be measured within 10 seconds of the heating time of the furnace. Thus, the atomizing time of calcium is long, and calcium in the graphite tube remains for a longer time than do aluminum and copper.

(4) The atomic absorbance of aluminum, calcium and copper in the sheath gas of helium is less than in the sheath gas of argon. This difference seems due to the diffusion coefficient of sheath gases.

(5) The atomizing time of aluminum, calcium and copper in tantalum powder as measured by the direct method is the same as that in the test solution.

References

- 1) K. Ohta, M. Suzuki: *Talanta*, 23, 560 (1975)
- 2) T. Maruta, K. Minegishi, G. Sudoh: *Anal. Chim. Acta*, 81, 313 (1976)
- 3) W. French, A. Cedergren: *Anal. Chim. Acta*, 82, 93 (1976)
- 4) R. E. Sturgeon, C. L. Chakrabarti, P. C. Bertels: *Spectrochimica Acta*, 32B, 257 (1977)
- 5) E. J. Czobik, J. P. Matousek: *Talanta*, 24, 573 (1977)
- 6) J. Persson, W. French, A. Cedergren: *Anal. Chim. Acta*, 92, 95 (1977)
- 7) W. Ishibashi, R. Kikuchi: *Bunseki Kagaku*, 29, 165 (1980)
- 8) R. E. Sturgeon, S. S. Berman: *Anal. Chem.*, 53, 632 (1981)

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