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The Determination of Beryllium in Several Alloys by Means of Atomic Absorption Spectrophotometry

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The atomic absorption spectrophotometric determination of beryllium in aqueous solutions and the effect of some water-miscible organic solvents were studied in a nitrous oxide-acetylene flame, using a Perkin-Elmer Model 303 atomic absorption spectrophotometer. The beryllium atomic absorptions were measured at the 234.9-nm resonance line of beryllium. The sensitivity for beryllium was 0.03 ppm for a 1% absorption. With the exception of palladium and silicon, none of the elements interfered with the determination of beryllium. Phosphoric acid caused an enhancement, while hydrochloric and nitric acids had a slight depressing effect. Furthermore, there seems to be a tendency for organic solvents with a higher ratio of the number of carbon atoms to that of oxygen atoms to cause greater enhancements in beryllium absorption, though there are a good number of exceptions. The atomic absorption method was applied to the determination of beryllium in several aluminum-, copper-, and magnesium-base alloys, with satisfactory results.

Since beryllium is one of the elements capable of forming highly refractory compounds, it cannot be atomized efficiently to give a measurable atomic absorption in low-temperature flames such as in air-acetylene flame, in which a sensitivity of 300 ppm for a 1% absorption has been reported.[1] Slavin and Manning[2] used a fuel-rich oxygen-acetylene flame in conjunction with an ethanolic solution of beryllium to obtain a sensitivity of 0.2 ppm for a 1% absorption. The introduction of a high-temperature and highly-reducing nitrous oxide-acetylene flame enabled Amos and Willis[3] to determine trace levels of beryllium (a sensitivity of 0.02 ppm for a 1% absorption) by means of atomic absorption spectrophotometry. Later Ramakrishna *et al.*[4] described that the nitrous oxide-acetylene flame was useful as well as an oxygen-acetylene flame at a 1 ppm level of beryllium and that the sensitivity was improved when an aqueous solution of 10% in diethylene glycol diethyl ether was used.

In this paper, the enhancement of depressant effects on the atomic absorption of beryllium in a nitrous oxide-acetylene flame will be described. Furthermore, the method was applied to the determination of beryllium in several aluminum-, copper-, and magnesium-base alloys with satisfactory results.

Experimental

Apparatus. All the atomic absorption signals were obtained by using a Perkin-Elmer Model 303 atomic absorption spectrophotometer, fitted with a 5-cm slot burner head for a premixed nitrous oxide-acetylene flame. A beryllium hollow-cathode lamp (Atomic Spectral Lamps Pty., Australia) was used as the source of radiation. A Yanagimoto GCG-252 chart recorder was used after modification so as to adapt it to the Perkin-Elmer instrument.

Reagents. The stock solution of beryllium, 1000 ppm, was prepared by dissolving 9.83 g of analytical-reagent grade beryllium sulfate tetrahydrate in distilled water and by then diluting it to 500 ml. Various concentrations were made by the appropriate dilution of the stock solution.

Results and Discussion

Operating Conditions. The optimum operating conditions listed in Table 1 were established with a 2.0-ppm solution of beryllium. The atomic absorptions for beryllium were measured at different flame heights under various flame conditions in an attempt to find the optimum flame conditions for beryllium. The results are shown in Fig. 1. Under these flame conditions, about 3-cm-long "red feather" zone was produced above the burner head, and the sample aspiration rate was about 13 ml/min.

TABLE 1. OPERATING CONDITIONS FOR THE MEASUREMENT OF BERYLLIUM ATOMIC ABSORPTION

Wavelength	234.9 nm
Slit width	0.3 mm
Spectral bandpass	0.2 nm
Lamp current	20 mA
Scale expansion	×1
Acetylene flow rate	8.1 l/min
Acetylene pressure	0.6 kg/cm^2
Nitrous oxide flow rate	18.0 l/min
Nitrous oxide pressure	1.5 kg/cm^2
Flame height	3—4 mm above the top of the burner head
Burner slot	0.48 mm×50 mm

Calibration Graph and Sensitivity for Beryllium. Under the optimum operating conditions described above, a straight calibration graph passing through the point of origin was obtained over the concentration range of 0—5 ppm for beryllium aqueous solutions. A good linearity held to the relatively high absorbance of about 0.6. The sensitivity for beryllium was 0.03 ppm for a 1% absorption. In this range, beryllium absorbances were measured with a precision of a relative standard deviation of 2.1%.

Effects of Other Elements. It has already been presented that a number of foreign elements have no

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1) J. E. Allan, *Spectrochim. Acta*, **18**, 259 (1962).

2) W. Slavin and D. C. Manning, *Anal. Chem.*, **35**, 253 (1963).

3) M. D. Amos and J. B. Willis, *Spectrochim. Acta*, **22**, 1325 (1966).

4) T. V. Ramakrishna, P. W. West, and J. W. Robinson, *Anal. Chim. Acta*, **39**, 81 (1967).

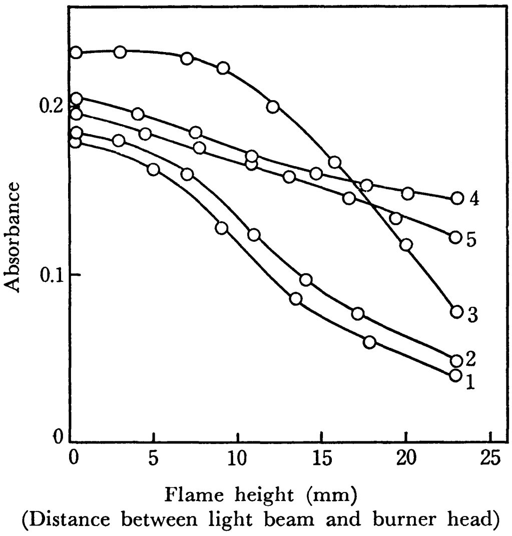

Fig. 1. Effect of flame composition and flame height on beryllium atomic absorption. Concentration of beryllium: 2 ppm. Nitrous oxide flow rate: 18.0 l/min.
Acetylene flow rate: (1) 7.5 l/min; (2) 7.8 l/min; (3) 8.1 l/min; (4) 8.5 l/min; (5) 9.0 l/min.

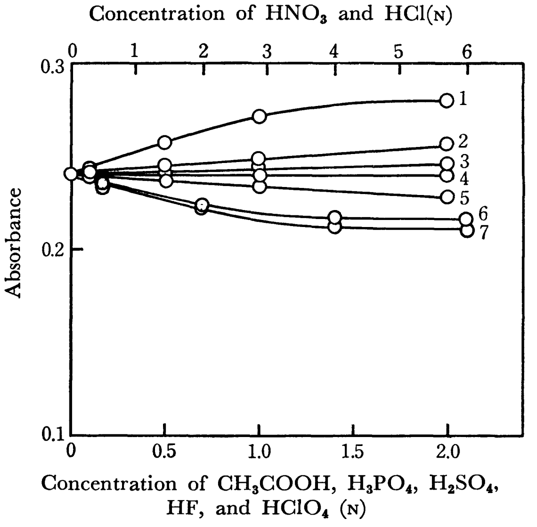

Fig. 2. Effect of acids on beryllium atomic absorption. Concentration of beryllium: 2 ppm.
1: Acetic acid, 2: phosphoric acid, 3: sulfuric acid, 4: hydrofluoric acid, 5: perchloric acid, 6: nitric acid, 7: hydrochloric acid.

effect on the beryllium atomic absorption.[3—5] In the present investigation, the effects of various elements were also examined. The concentration of beryllium was 2 ppm, and that of the element, 200 ppm. The elements examined were Al, As, Au, Ba, Bi, Ca, Cd, Co, Cr(III), Cs, Cu, Fe(III), Hg(II), In, La, Mg, Mn(II), Mo, Na, Ni, Pb, Pd, Sb, Se, Si, Sn(II), Sr, Te, Th, Ti, V, Zn, and Zr. These elements were added as chloride, nitrate, or sulfate in most instances. An element was considered to interfere with the beryllium atomic absorption when it produced a variation in the absorbance of more than twice the relative standard deviation for beryllium alone.

With the exception of palladium and silicon, none of the elements interfered with the determination of beryllium at this concentration level. Palladium and silicon depressed the beryllium absorbance by about 29 and 8% respectively. A large amount of aluminum, however, depressed the beryllium atomic absorption, as will be described later.

Effects of Acids. Amos and Willis[3] have reported no interference from 2.5 N sulfuric acid with, and a slight enhancement by phosphoric acid of the beryllium absorption. On the other hand, Fleet *et al.*[5] have described that no interference occurred from hydrochloric, hydrofluoric, nitric, and phosphoric acids at the 10000 ppm level with respect to Cl, F, N, and P respectively.

In this study, the effect of hydrochloric, hydrofluoric, nitric, perchloric, phosphoric, sulfuric, and acetic acids in the concentration range of 0—2.0 N or 0—6.0 N on the beryllium atomic absorption was studied for 2-ppm solutions of beryllium. The results are shown in Fig. 2. Phosphoric acid caused an enhancement, as has been reported by Amos and Willis.[3] Sulfuric acid caused, but in a somewhat different way and in a higher concentration, an enhancement such as has been described by Fleet *et al.*[5] Hydrochloric and nitric acids in the 0—6.0 N range had, contrary to expectations, a slight depressing interference. Acetic acid caused an enhancement. A similar effect has been observed on the atomic absorption of vanadium in a nitrous oxide-acetylene flame.[6] The enhancement by acetic acid may be considered to be a kind of organic-solvent effect, such as has been described by Ramakrishna *et al.*[4] and by Fleet *et al.*[5]

As has been mentioned above, somewhat different results for the interference effects have been observed in the several investigations in this field, including this study. This may be ascribable to the difference in the efficiency of the nebulizers employed in those investigations.

Effect of Water-miscible Organic Solvents. Ramakrishna *et al.*[4] have described that the addition of glycols considerably enhanced the beryllium atomic absorption and that the sensitivity for beryllium was increased by 25% in the presence of 5% of diethylene glycol diethyl ether, which was the most effective on the glycols. Fleet *et al.*[5] have reported that the presence of methanol, ethanol, and isopropyl alcohol in the concentration of 20 vol% enhanced by 11—20% the beryllium atomic absorption, while glycol had a depressing effect of 17%.

In this study, the effect of water-miscible organic solvents, *e.g.*, alcohols, ketones, and glycols, on the beryllium absorption was studied. Solutions of 1 ppm in beryllium and 5- or 10-% in commonly-available alcohols, ketones, or glycols were prepared. These solutions were nebulized into the flame, and the beryllium absorptions were measured. At the same time, sample aspiration rates were measured. The results are shown in Table 2. It can be seen from Table 2 that the enhancement in the presence of organic

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[5] B. Fleet, K. V. Liberty, and T. S. West, *Talanta*, **17**, 203 (1970).

[6] T. Nakahara, M. Munemori, and S. Musha, *Nippon Kagaku Zasshi*, **90**, 697 (1969).

TABLE 2. EFFECT OF SOME WATER-MISCIBLE ORGANIC SOLVENTS ON THE ATOMIC ABSORPTION OF BERYLLIUM

Organic solvent	Molecular weight	Boiling point (°C)	5%-Addition		10%-Addition		C/O ratio
			Sample aspiration rate (ml/min)	Absorbance	Sample aspiration rate (ml/min)	Absorbance	
None	—	—	13.0	0.120	13.0	0.120	—
Ethylene glycol	62.07	197.7	12.4	0.122	11.4	0.124	1.0
1,4-Dioxane	72.11	79.6	12.3	0.128	11.9	0.146	2.0
Methanol	32.04	64.65	12.5	0.137	12.1	0.150	1.0
Acetone	58.08	56.3	12.3	0.146	11.6	0.161	3.0
Ethanol	46.07	78.3	12.0	0.153	11.4	0.165	2.0
Diethylene glycol diethyl ether	162.23	186.0	11.5	0.154	10.8	0.166	2.6
Isopropyl alcohol	60.10	82.4	11.5	0.163	11.1	0.185	3.0
Propyl alcohol	60.10	97.15	11.6	0.164	10.8	0.186	3.0
Diethylene glycol monobutyl ether	162.23	230.4	11.4	0.174	10.8	0.196	2.6
Isobutyl alcohol	74.12	108.0	10.9	0.210	10.4	0.252	4.0
Butyl alcohol	74.12	117.5	10.9	0.213	10.3	0.254	4.0

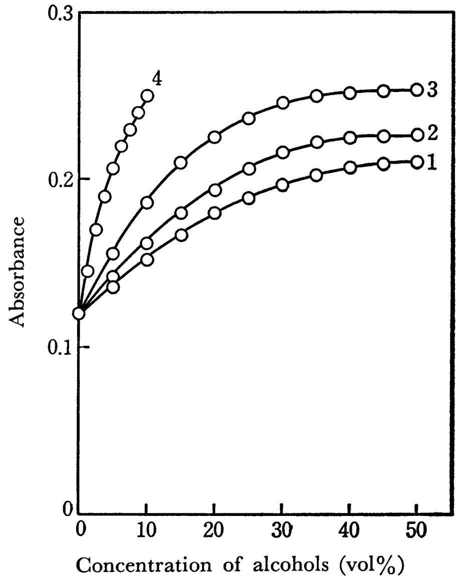

Fig. 3. Effect of alcohols on beryllium atomic absorption. Concentration of beryllium: 1 ppm.
1: Methanol, 2: ethanol, 3: propyl and isopropyl alcohols, 4: butyl and isobutyl alcohols.

solvents has no relation to their molecular weights and boiling points. As for alcohols alone, however, the beryllium absorbance was increased in the order of the molecular weights and the boiling points. With an increase in the concentration of alcohols, the absorbance was increased as is shown in Fig. 3. Butyl alcohol was the most effective for the enhancement of the beryllium absorption, though its concentration was limited below 10% because of its solubility. Table 2 shows also that the absorbance was increased in the reverse order of the increase in the sample aspiration rate. If it can be assumed that the increase in the sample aspiration rate signifies an increase in the amount of the solution reaching the flame, the enhancement must be explained in terms of an increase in the efficiency of atomization. Perhaps a hotter or more reducing condition was created in the flame, with the result that the vaporization and dissociation of the metal compounds were increased.

The ratio of the number of carbon atoms to that of oxygen atoms (C/O ratio) in the flame is taken into account in determining the reducing properties of the flame.[7] L'vov[8] calculated the variation in the flame composition with a variation in the fuel-to-oxidant flow ratio for a total-consumption nebulizer-burner using an oxygen-acetylene flame and nebulizing aqueous or ethanolic solutions. According to L'vov's conclusions, optimum reducing properties of the flame are achieved when the composition of the flame, including the solvent, have a C/O ratio equal to unity. Solvents with a higher ratio of C/O increase the reducing properties of the flames more efficiently than ethanol. It should be remembered also that, when using organic solvents, the cooling effect due to an aspirated solution is decreased and a temperature rise takes place.[9] The C/O ratios of the organic solvents used are shown in Table 2. There seems to be a tendency for solvents with higher C/O ratios to cause greater enhancements, though there are a good number of exceptions. It may be concluded that the organic solvent provides a more reducing property for the flame, resulting in an increased production of beryllium atoms in the flame.

Application to the Determination of Beryllium in Several Aluminum-, Copper-, and Magnesium-base Alloys. The use of small amounts (0.01 to 0.5%) of beryllium as an additive to aluminum-, copper-, and magnesium-base alloys to improve their yield strength has created the need for a rapid and simple method for the determination of beryllium. For such a determination, atomic absorption spectrophotometry is the most

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[7] I. Rubeska in "Flame Emission and Atomic Absorption Spectrometry," Vol. 1, J. A. Dean and T. C. Rains, eds., Marcel Dekker, New York, N. Y. (1969), p. 325.

[8] B. V. L'vov, "Atomic Absorption Spectroscopy" (Trans-. lated from the Russian), Israel Program for Scientific Translations, Jerusalem, Israel (1969), p. 133.

[9] M. R. Baker and B. L. Vallee, *Anal. Chem.*, **31**, 2036 (1959)

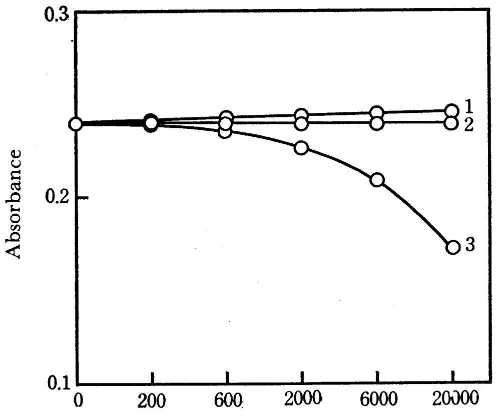

Fig. 4. Effect of a large amount of aluminum, copper, and magnesium on beryllium atomic absorption. Concentration of beryllium: 2 ppm.
1: Magnesium, 2: copper, 3: aluminum.

useful. In this investigation the determination of beryllium in several aluminum-, copper-, and magnesium-base alloys was studied.

The effect of a great amount of aluminum, copper, and magnesium, which are matrix elements in the sample alloys, on the beryllium atomic absorption was studied first. The effects observed in the actual concentration levels (200—20000 ppm) of these elements for 2 ppm of beryllium are shown in Fig. 4. Copper and magnesium showed no interference, but a great amount of aluminum (above 600 ppm of aluminum) had a depressing interference. At the 2000- and 20000-ppm aluminum levels, depressions of 6 and 28% respectively were observed. This depression must be taken into consideration in the case of the determination of trace beryllium in aluminum-base alloys; otherwise, serious errors will obviously result.

It has been already reported by Fleet *et al.*[5] that the depressing effect by aluminum can be overcome by the addition of oxine (8-hydroxyquinoline) to a solution containing beryllium and aluminum. The "masking" of aluminum by oxine, however, falls off steadily if the concentration of aluminum is increased to above 4000 ppm, and a corresponding increase in the oxine concentration to, say, 5% can not offset this.

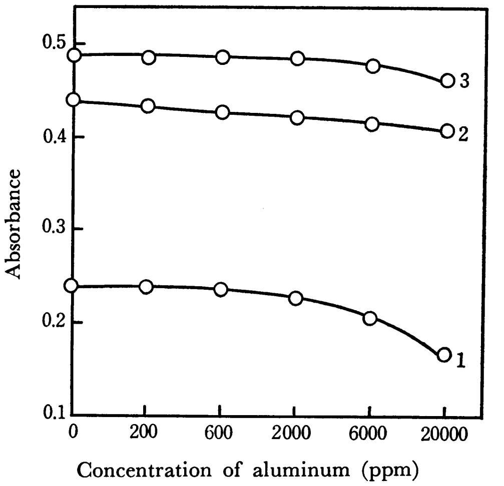

Fig. 5. Effect of aluminum in the presence of diethylene glycol monobutyl ether or butyl alcohol on beryllium atomic absorption. Concentration of beryllium: 2 ppm.
1: With no addition, 2: with the addition of diethylene glycol monobutyl ether(20 vol%), 3: with the addition of butyl alcohol(10 vol%).

In this study, another method for eliminating the interference from aluminum was examined; that is, beryllium absorptions were measured upon the addition of 20% of diethylene glycol monobutyl ether or 10% of butyl alcohol; such additions caused a relatively great enhancement, as is shown in Table 2, to 2-ppm beryllium solutions containing aluminum in the 200—20000 ppm range. The results are shown in Fig. 5. It can be seen that the addition of diethylene glycol monobutyl ether or butyl alcohol was effective not only in enhancing the beryllium absorption, but also in eliminating the depressing interference of aluminum. This fact also suggests that the organic solvents play an important role in the process of beryllium atom-production. However, the interference-suppressing effect of diethylene glycol monobutyl ether and butyl alcohol falls off slightly in the presence of a a greater amount (6000 ppm) of aluminum (as is is shown in Fig. 5); therefore, a standard addition technique in the presence of diethylene glycol monobutyl ether was employed in the determination of beryllium in aluminum-, copper-, and magnesium-base alloys.

The methods of preparing the sample solutions were as follows. Aluminum-base alloy: A 1-g sample was weighed precisely and dissolved in 25 ml of 6 N hydrochloric acid by gentle heating on a hot plate. After cooling, the resultant solution was transferred to a 100-ml volumetric flask and diluted to volume with distilled water. Copper-base alloy: A 1-g sample containing less than 0.1% of beryllium was weighed and dissolved in 10 ml of 6 N nitric acid, or a 0.1-g sample containing more than 0.1% of beryllium was weighed and dissolved in 4 ml of 2 N nitric acid by gentle heating on a hot plate. After cooling, the resultant solutions were transferred to 100-ml volumetric flasks and diluted to volume with distilled water. Magnesium-base alloy: A 1-g sample was weighed

Table 3. Results of the determination of beryllium in aluminum-, copper-, and magnesium-base alloys

Sample	Beryllium content (%)			
	Colorimetric method	Atomic absorption method		
Aluminum-base alloy				
No. 1	0.06	0.06_5	0.06_2	0.06_3
No. 2	0.18	0.18_2	0.18_7	0.18_4
No. 3	0.43	0.43_5	0.43_3	0.43_6
Copper-base alloy				
No. 1	0.11	0.11_1	0.10_8	0.11_5
No. 2	0.24	0.23_8	0.24_5	0.24_0
Magnesium-base alloy				
No. 1	0.02	0.01_3	0.01_3	0.01_2

and dissolved in 25 ml of 6 N hydrochloric acid by gentle heating on a hot plate. After cooling, the resultant solution was transferred to a 100-ml volumetric flask and diluted to volume with distilled water.

Five 10-ml portions of the sample solutions and 5 ml of diethylene glycol monobutyl ether were taken into 25-ml volumetric flasks, 0-, 1-, 2-, 3-, and 4-ml portions of the 12.5 ppm standard solution of beryllium were added, and the mixtures were diluted to volume with distilled water. The solutions were sprayed into the nitrous oxide-acetylene flame, and the beryllium atomic absorption signals were measured under the optimum operating conditions. The determinations were performed three times on each aliquot of aluminum-, copper-, and magnesium-base alloys.

The beryllium contents in the samples were determined by using a standard addition method. The results are shown in Table 3. Table 3 shows the results of the colorimetric determination of beryllium with Arsenazo I[10] on the alloy samples. Atomic absorption spectrophotometry and colorimetry with Arsenazo I gave consistent results on the aluminum-, and copper-base alloys, but inconsistent results on the magnesium-base alloy. The latter results were possibly caused by the irrelevance of the application of the colorimetric method to such a sample, but, at any rate, they may be tolerable in view of the smallness of the beryllium content in the sample.

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10) T. Hattori, I. Tsukahara, and T. Yamamoto, *Bunseki Kagaku*, **15**, 41 (1966).