Graphite Furnace Atomic Absorption Spectrometry with a Tantalum Boat for the Determination of Yttrium, Samarium, and Dysprodium in a Mish Metal

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The determination of yttrium, samarium, and dysprodium by means of graphite-furnace atomic absorption spectrometry (AAS) was studied by a tantalum boat inserted into a graphite tube atomizer. These elements could not be determined by the use of a commercial graphite tube. In the atomization from a tantalum boat, better analytical sensitivities and negligible memory effects for these rare earths are obtained. The analytical sensitivities of yttrium, samarium, and dysprodium with the tantalum boat were 0.60 ng, 0.86 ng, and 0.17 ng respectively. This method was applied for the determination of yttrium, samarium, and dysprodium in a mish metal. The measurements were performed with slightly acidified solutions (0.01 mol dm^{-3} HCl or HNO_3). The sensitivities and the precisions for these elements decreased with increasing acid concentration. An enhancement in the sensitivities of yttrium and dysprodium upon the addition of a large excess of lanthanum, neodymium, and praseodymium salts were observed. The yttrium, samarium, and dysprodium in a mish metal were determined with both analytical curves of standard solutions containing an excess of lanthanum, cerium, and neodymium ions and of the standard addition. The precisions for this work were in the 3—9.3% range.

Atomic absorption analysis in an electrically heated graphite atomizer has a number of disadvantages. The graphite itself has been improved to overcome these problems. Particularly, a graphite-tube atomizer pyrocoated with a hydrocarbon such as methane has recently been used. Attempts have also been made to use a pre-coated graphite tube with salts of tantalum,[1,2,6] zirconium,[3,4] tungsten,[5] or lanthanum.[3,6] Other attempts have been to use a tantalum or tungsten liner, collar or wire inserted inside the graphite furnace.[7–15] Enhancements in the sensitivity of many elements were obtained with a metal liner, collar, or wire, because metal carbide formation in these causes is impossible. There have been few studies for the determination of rare earths by means of graphite-furnace atomic absorption spectrometry (AAS). Dittrich[16] determined traces of rare earths by means of electrothermal atomization with a carbon rod, a graphite furnace, and a tantalum ribbon. Kuga[17] and Grobenski[18] measured rare earth by the use of a pyrolitic graphite-coated tube. Sastry[6] repoated the determination of rare earth in uranium by the use of a pyrolitic carbon-coated tube pre-coates with lanthanum, tantalum, or yttrium. Moreover, Wahab[14,15] studied the atomization of yttrium using a pyrocoated graphite tube, a carbidized graphite tube, and tantalum or tungsten foil.

In this work, we determined yttrium, samarium, and dysprodium in a mish metal by the use of a laboratory-made tantalum boat inserted inside a graphite tube.

Experimental

Instrumentation. A Nippon Jarrel-Ash atomic absorption spectrophotometer, AA-1E, fitted with a flameless atomizer, FLA 100, A Hamamatsu TV deuterium Arc lamp, and hollow cathode lamps, was used.

Reagents. Stock solutions of 1000 or 2000 μg ml^{-1} of yttrium, samarium, dysprodium, praseodymium, neodymium, and lanthanum were prepared from oxides of these elements dissolved in hydrochloric acid and nitric acid respectively. Stock solutions of 1000 μg ml^{-1} aluminum and iron were prepared from high-purity metals dissolved in hydrochloric acid and nitric acid respectively. A stock solution of 5000 μg ml^{-1} cerium was prepared from cerium nitrate dissolved in distilled water. The acidities of these solutions were 0.1—0.5 mol dm^{-3}. Analytical solutions were prepared from stock solutions by dilution with distilled water. Distilled water was prepared by the distillation of Milli-Q water.

Tantalum Boat. The tantalum boat was made by cutting pure tantalum foil (99.95%) 0.1 mm thick and exerting pressure on it. This boat was then fitted in a commercial graphite tube with an inner diameter of 3.2 mm, as is shown in Fig. 1.

Procedure. A comparison of the situation with and without the tantalum boat was achieved by the injection of volumes (10 μl) of standard solutions and by the subsequent measurement of the peak absorbance. The hollow cathode lamps were used at 14 mA for yttrium, at 10 mA for samarium, and at 12 mA for dysprodium. The argon flow rate through the graphite furnace was 2.0 l min^{-1}.

Results and Discussion

The ashing and atomizing conditions in the use of the tantalum boat for yttrium, dysprodium, and samarium are shown in Figs. 2—4. The dotted lines in each figure show the relationship between the absorbances (as the peak height) and the ashing temperature. The full lines show the relationship between the absorbances and the atomizing temperature. The operating conditions selected from these results are shown in Table 1. When yttrium, samarium, and dysprodium are determined under these operating conditions, the absolute sensitivities are obtained as 0.60 ng for yttrium, 0.86 ng for samarium, and 0.17 ng for dysprodium. These sensitivities are similar to the values in previous reports.[6,13,17,18] The sensitivity of samarium by the use of a commercial graphite tube is obtained as 20 ng. In this determination, a strong memory effect of carbide formation is observed. The determinations of yttrium and dysprodium by the use

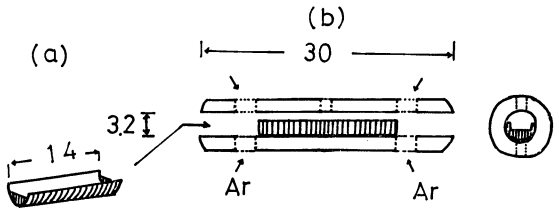

Fig. 1. Design of tantalum boat (a) and commercial graphite tube (b) used in this study.

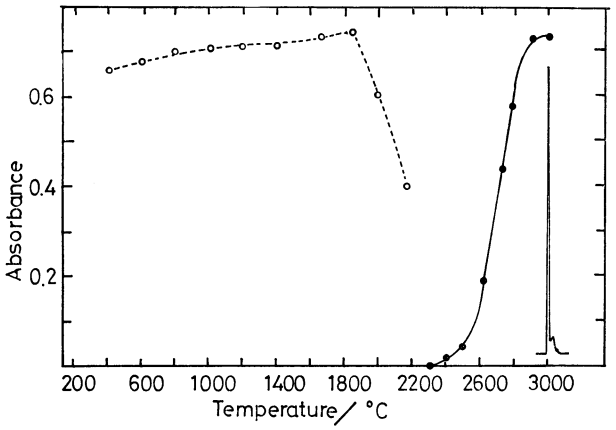

Fig. 2. Ashing and atomizing conditions for yttrium of 100 ng at 410.2 nm.
Dry: 120 °C, --○-- ashing: 40 s, atomizing-3000 °C-7 s, —●— atomizing: ashing-1600 °C-40 s.

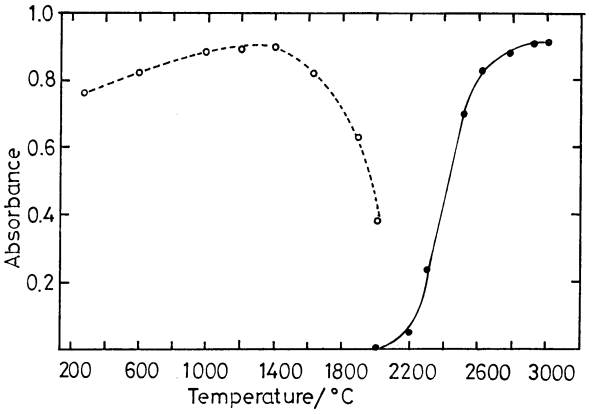

Fig. 3. Ashing and atomising conditions for dysprodium of 43 ng at 421.1 nm.
Dry: 120 °C, --○-- ashing: 40 s, atomizing-2900 °C-7 s, —●— atomizing: ashing-1400 °C-40 s.

of the graphite tube were impossible, because the memory effects by the formation of the refractory carbides of these elements are too great.

Wavelength and Sensitivity. Tables 2—4 show several atom lines of yttrium, dysprodium, and samarium, the relative intensities emitted by the hollow cathode lamps, the *gf* values,[21] and the absorbances of 50 ng of yttrium, 43 ng of dysprodium, and 100 ng of samarium by the use of the tantalum boat. Wahab[13,14] and Manning[19] used 407.7 nm in the determination of yttrium. In this work, the atom line at 410.2 nm shows the highest intensity and the maximum absorption of all the atom lines of yttrium. For dysprodium,

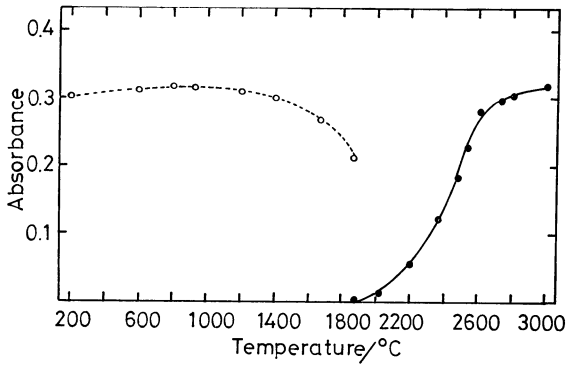

Fig. 4. Ashing and atomizing conditions for samarium of 100 ng at 429.7 nm.
--○-- Ashing: 40 s, atomizing-2900 °C, —●— atomizing: 10 s, ashing-900 °C.

Table 1. Operating conditions for the determination of Y, Dy, and Sm with a tantalum boat inserted inside a graphite tube

Wavelength nm		Temperature/°C (Time/s) Drying	Ashing	Atomizing
Y	410.2	120 (30)	1600 (40)	3000 (10)
Dy	421.1	120 (30)	1400 (40)	2900 (10)
Sm	429.7	120 (30)	900 (40)	2900 (10)

Table 2. Relative intensity and absorbance for yttrium at various wavelengths

Wavelength/nm	Relative intensity	*gf*[a]	Absorbance[b]
410.2	100	1.3	0.375
407.7	78	1.1	0.270
414.3	52	0.8	0.222
412.8	78	1.1	0.155
417.4	22	0.24	0.098
464.3	83	0.12	0.082
416.8	13	0.29	0.045

a) C. H. Corliss and W. R. Bozman, NBS Monograph 53. b) 50 ng of yttrium.

the most sensitive lines are observed at 421.1 nm and 419.4 nm. The sensitivity at 419.4 nm is high in comparison with the results obtained by the use of a nitrous oxide–acetylene flame.[19,20] For samarium, absorbances are obtained at various atom lines.

Effect of Acids and Matrix Elements. The effects of acids for the determined elements are shown in Figs. 5—7. The sensitivities and precisions for these elements decrease with increasing acid concentration. Therefore, the acidity for the determination of these elements is selected as 0.01 mol dm^{-3} HCl for yttrium and dysprodium and as 0.01 mol dm^{-3} HNO_3 for samarium. The effect of acids for samarium differ from those in the previous report using pyrolitic-coated graphite tube.[18]

Graphite-furnace AAS, with the tantalum boat inserted inside the graphite tube, was used for the determination of yttrium, dysprodium, and samarium in a mish metal. The composition of a mish metal con-

TABLE 3. RELATIVE INTENSITY AND ABSORBANCE FOR DYSPRODIUM AT VARIOUS WAVELENGTHS

Wavelength/nm	Relative intensity	Absorbance[a)]
421.1	100	0.910
419.4	52	0.905
418.6	67	0.855
404.6	70	0.820
422.1	15	0.175
416.8	33	0.140
421.5	12	0.110
422.5	7	0.050

a) 43 ng of dysprodium.

TABLE 4. RELATIVE INTENSITY AND ABSORBANCE FOR SAMARIUM AT VARIOUS WAVELENGTHS

Wavelength/nm	Relative intensity	gf[a)]	Absorbance[b)]
429.7	52	5.7	0.310
444.2	50	0.56	0.262
476.0	60	1.1	0.248
472.8	42	1.5	0.248
478.3	51	0.77	0.248
511.7	75	?	0.248
464.9	37	0.42	0.244
458.2	43	0.34	0.236
459.6	27	?	0.230
520.0	100	0.49	0.228
471.7	52	0.35	0.200
436.3	25	0.48	0.200
527.1	56	0.63	0.194
464.5	25	0.28	0.180
484.1	37	3.6	0.174
488.4	100	0.27	0.168
428.2	54	2.0	0.142
468.9	24	0.91	0.142
433.6	38	0.12	0.142
478.5	41	0.54	0.142
440.3	32	1.0	0.138
467.1	44	0.62	0.136
491.8	29	0.73	0.120
484.8	23	0.61	0.088
438.0	12	0.86	0.086
504.4	29	2.2	0.086
497.6	12	0.25	0.080
540.4	100	0.17	0.054
534.1	67	0.15	0.052
551.6	47	0.50	0.050

a) NBS Monograph 53. b) 100 ng of samarium.

sists of 45% cerium, 30% lanthanum, 15% neodymium, 4% praseodymium, and small percentage of iron, aluminum, and silicon. The interferences of these matrix elements with the determinations of yttrium, dysprodium, and samarium are shown in Figs. 8—10. Enhancements in the absorption sensitivity of yttrium are observed with increasing lanthanum, praseodymium, and neodymium concentrations. With increasing samarium concentration, the absorption of yttrium decreases. The sensitivity of dysprodium is

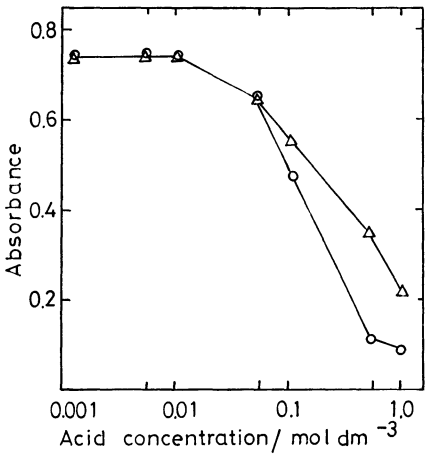

Fig. 5. Effect of acids on absorbance of yttrium of 100 ng.
○: HCl, △: HNO_3.

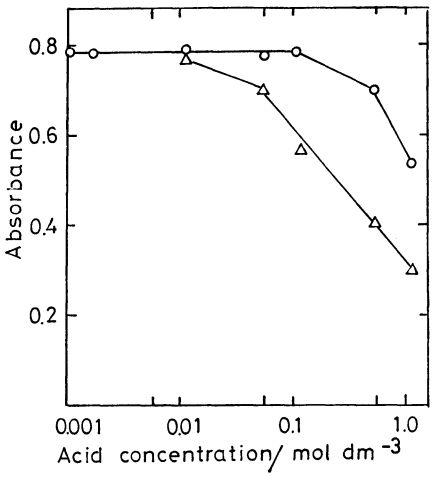

Fig. 6. Effect of acids on absorbance of dysprodium of 43 ng.
○: HCl, △: HNO_3.

enhances by increasing lanthanum, praseodymium, cerium and neodymium concentrations. The effects of other elements are negligible. In the determination of samarium, the effect of iron is important. The existence of 100 μg ml^{-1} of iron causes a remarkable decrease in the absorbance of samarium. However, the effect of iron in this sample is slight, for the concentration of iron in this sample is below 50 μg ml^{-1}. The sensitivity of samarium is slightly decreased by the presence of lanthanum and neodymium. The effects of the other elements on samarium are negligible.

Two samples of about 0.5 g were dissolved in hydrochloric acid and in nitric acid. The sample solution containing hydrochloric acid was used to analyze the yttrium and dysprodium, while the other solution was used to analyze the samarium. The determinations of these elements were done by the following two methods. One method used the analytical curves in the range of 1.0—6.0 μg ml^{-1} of yttrium and in the range of 0.5—3.0 μg ml^{-1} of dysprodium. To these standard solutions of yttrium and dysprodium we added 500 μg ml^{-1} of lanthanum, 600 μg ml^{-1} of cerium,

Table 5. Comparison between determinations of Y, Dy, and Sm by graphite-furnace AAS with a tantalum boat and by flame AAS

	Graphite-furnace AAS				Flame AAS	
	Standard[a]		Standard addition		Standard addition	
	Found(wt%)	RSD(%)	Found(wt%)	RSD(%)	Found(wt%)	RSD(%)
Y	0.70_2	3.1	0.69_4	9.3	0.69	2.5
Dy	0.20_2	5.5	0.19_0	2.6	0.19	1.6
Sm	0.82_4	8.2	0.81_7	3.6	0.80	1.8

a) Standard method (1.0—6.0 μg ml^{-1} of Y+0.5—3.0 μg ml^{-1} of Dy)+500 μg ml^{-1} of La+600 μg ml^{-1} of Ce+300 μg ml^{-1} of Nd, (1.0—6.0 μg ml^{-1} of Sm)+500 μg ml^{-1} of La+600 μg ml^{-1} of Ce+100 μg ml^{-1} of Nd. b) RSD: relative standard deviation, $n=10$.

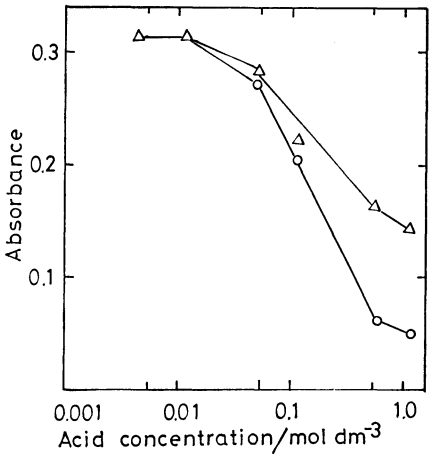

Fig. 7. Effect of acids on absorbance of samarium of 100 ng.
○: HCl, △: HNO_3.

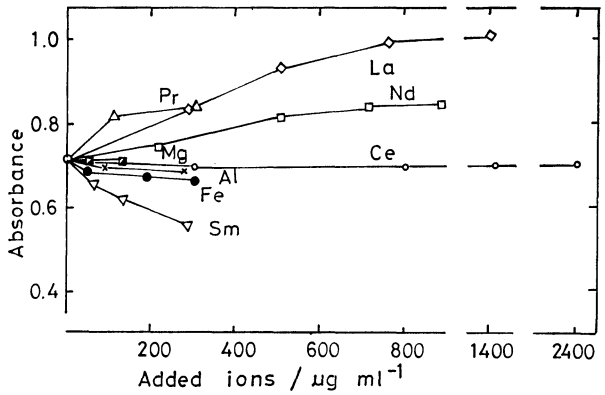

Fig. 8. Effect of matrix elements on absorbance of yttrium of 10 μg ml^{-1}.

and 300 μg ml^{-1} of neodymium. To the other solutions containing 1.0—6.0 μg ml^{-1} of samarium, we added 500 μg ml^{-1} of lanthanum, 600 μg ml^{-1} of cerium, and 100 μg ml^{-1} of neodymium. The other method used the analytical curves obtained by standard addition. Both analytical curves for each element gave identical slopes. These results are shown in Table 5. The precision of these determinations was in the range of 3—9.3%. It was found that the concentrations of these elements in a mish metal was 0.70% for yttrium, 0.20% for dysprodium, and 0.82% for

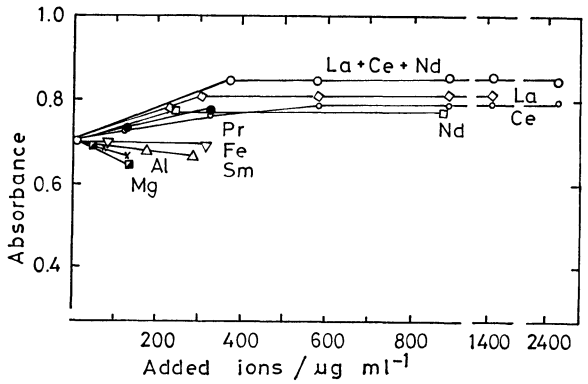

Fig. 9. Effect of matrix elements on absorbance of dysprodium of 4.3 μg ml^{-1}.

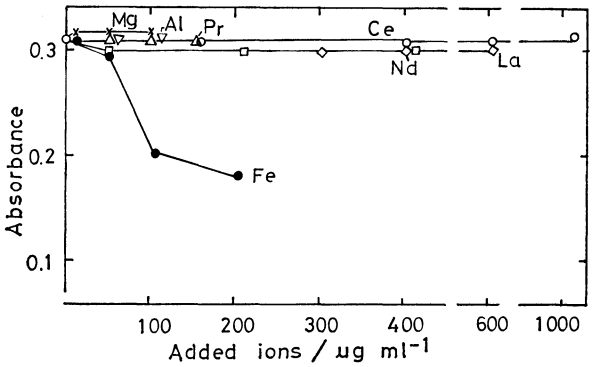

Fig.10. Effect of matrix elements on absorbance of samarium of 10 μg ml^{-1}.

samarium. It was also estimated by flame AAS; these results are shown in Table 5.

Conclusion

Yttrium, dysprodium, and samarium are determined by the means of graphite-furnace AAS with a tantalum boat inserted inside a graphie tube. In this method, the memory effect of carbide formation is negligible and the analytical sensitivities of these elements suffice for the determination of this sample.

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