Studies on Quantitative Emission Spectrum Analysis. II : Determination of Berylium by Liquid-Condensed-Sparking Method

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Determination of Berylium by Liquid-Condensed-Sparking Method*

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I. Introduction

Micro-quantitative emission spectral analysis of Be in large quantities of Al or Cu was studied, in order to employ it for the quantitative analysis of Be in Al or Be-bronze. A cover of Pt crucible and an iron salver were newly deviced and used as an electrode for liquid samples. Liquid was acidified with nitric acid and also all salts were nitrates. Cd was used as a coupling electrode and Ca as an internal standard. Be 3131.1; 3130.4 (II)/Ca 3158.9(II) was chosen as a line pair and analysis was performed by the comparing method. It was also ascertained that analysis could be done with the line pair of Be 3131.1/Cd 3250.2(III) without any internal standard, and the analytical accuracy was from ±4.45% to ±7.32% in both procedures.

II. Experimental apparatus and sample

Apparatus used is almost same as in the last paper(1). Water resistance: a dilute aquous solution of Na_2CO_3 and two parallel iron electrodes (7×15cm) dipped in it.

Electrode for liquid: a distilled water was poured in an iron salver which was a cylinder (5cm in diameter and 2.4 cm in height) with a conical concave on the top and had a large heat capacity. A cover of Pt crucible was placed on it closely and a few ml of the sample was taken on it as shown in Fig. 1. So, it was not needed to cool the electrode with an ice. The coupling electrode was a Cd rod with a conical end, which was 5 mm in diameter and 7 cm in length.

Dry-plate: Fuji Process Hard. Developed with the designated reagents of FD No. 31 at 19°C for 3 minutes.

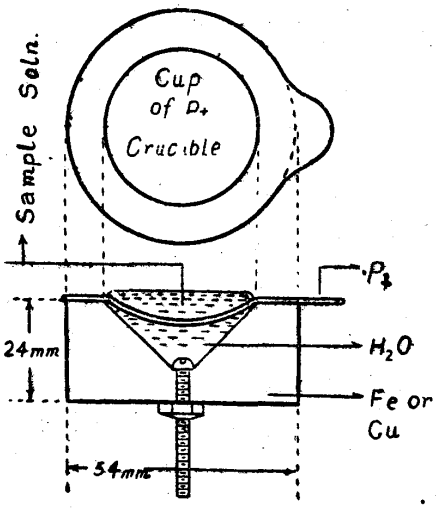

Fig. 1.

* The 552nd report of the Research Institute for Iron, Steel and Other Metals; this is abstracted from the auther's paper published in the Journal of the Japan Institute of Metals, **12** (1948), 47.

(1) S. Musha, Journal of the Japan institute of Metals, **12** (1948), 37.

Sample: the concentration of $Be(NO_3)_2$ solution was 1.354 mg per ml as Be in in which Fe and Al could not be detected by the spectral analysis. $Al(No_3)_3$ and $Ca(NO_3)_2$ were the extra pure Japanese reagents but $Cu(NO_3)_2$ was a "Kahlbaum" guaranteed reagent. The concentration of Al was 1.011 mg per ml (determined by the oxine method) and Cu was 3.064 mg per ml (determined by the internal electrolysis) but $Ca(NO_3)_2$ was 5/4 mol solution.

Sparking condition: a water resistance was connected with secondary circuit in series, and the motor switch and the potential stabilizer (by reason of the electric capacity of the stabilizer) did not be used. Other conditions were same as in the last report[1].

III. Experiments and results

(A) Effects of the concentration of HNO_3 and the secondary resistance. A solution containing Be only was analysed so as a preliminary experiment in order to find the suitable concentration range of Be and the effects of the water resistance (R) and of the concentration of nitric acid. That is, R was changed from 0 to 150, 400 and 7500 Ω, the concentration of nitric acid was varied from 0 to 0.6 N, the electrode-distance was 2.5 mm and each exposing time was 60 sec. The results obtained were illustrated in Fig. 2.

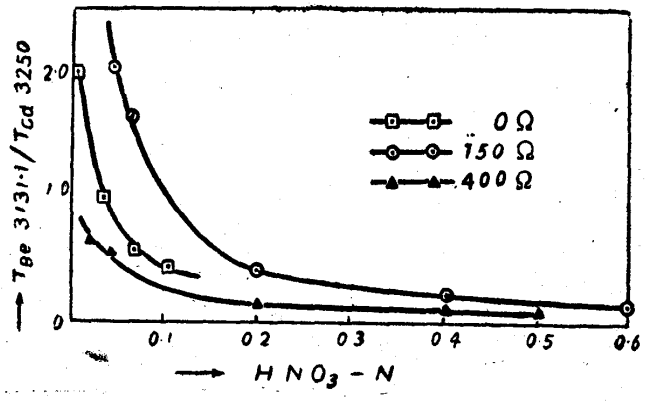

Fig. 2.

In this experiment, the concentration of Be was kept at 0.01083%. From results in Fig. 2, the following conditions are decided:—R=150 Ω, and nitric acid=0.2 N. 0.25% Ca was added in a form of $Ca(NO_3)_2$ as the internal standard and the concentration range was decided, in which Be could be analysed quantitatively by the spectrum method. From these results, the suitable range of Be concentration from 0.02979% (0.03) to 0.00134% (0.001) was found. On the other hand, quantitative sesults were obtained by the line pair of Be and Cd 3250.2(II), which was used as the coupling electrode. It is almost parallel to the former obtained from the line pair of Be and Ca, and the fact is ascertained that the quantitative analysis can be performed without the internal standard.

(B) The analytical procedure. A few ml of 0.2N nitric acid is put into the electrode for the liquid analysis and the preliminary discharge is performed for 2 or 3 min. Then, the Pt plate is taken out at once and washed. About 5 ml of the sample solution is poured into it and discharge is performed without the preliminary, and the exposure for 60 sec is taken. This electrode for the liquid analysis is distinctive in the easy exchange of sample and the rapid washing. When sample is replaced, the coupling

electrode Cd needs not to be removed from the holder, but it is merely rotated around the insulated rod. So, it is very simple to adjust the electrode distance. Therefore, the procedure by this electrode is far easier than by the U type or other electrodes for liquid.

(C) Experimental result. Five dry-plates are exposed respectively for the each experiments and two curves on a log $C-\Delta S$ diagram are drawn, which are obtained in two cases when the line pair of Be 3131.1: 3130.4(II)Å or Be 3131.1: 3130.4(II)Å/Cd 3250.2(II)Å is adopted. These two curves are almost parallel and any distinct difference in the inclination is not recognized. The results of both analysis only for Be bronze are illustrated in Table 1.

Table 1

Analysis line pair	Plate No.	Be in berylium bronze			
		Be Taken (%)	Be Found (%)	Erorr (%)	Mean erorr
Be 3131.1(II)/3130.4 Ca 3158.9(II)	72	0.02166	0.02214	+ 6.83	±5.19%
		0.005416	0.005416	± 0.00	
		0.002031	0.001778	−12.45	
	73	0.02166	0.02243	+ 3.55	
		0.005416	0.005217	− 3.68	
		0.002031	0.001903	− 6.31	
	74	0.02166	0.02184	+ 0.85	
		0.005416	0.005699	+ 5.23	
		0.002031	0.002284	+12.44	
	75	0.20166	0.02086	− 3.68	
		0.005416	0.005400	− 0,30	
		0.002031	0.002169	+ 6.97	
Be 3131.1(II)/3130.4 Cd 3250.2(II)	72	0.02166	0.02331	+ 7.90	±4.45%
		0.005416	0.005821	+ 7.47	
		0.002031	0.002013	− 0.87	
	73	0.02166	0.02002	− 7.59	
		0.005416	0.005441	+ 0.46	
		0.002031	0.001907	− 6.09	
	74	0.02166	—	—	
		0.005416	0.005416	± 0.00	
		0.002031	0.002094	+ 3.09	
	75	0.02166	0.02140	− 0.98	
		0.005416	0.005584	+ 3.10	
		0.002031	0.002263	+11.43	

(i) Be 3131.06Å, which is used as the line pair, is a doublet and coupled with 3130.4Å. There is no objection to analyse by the blackness of the superposed part, because both line have the same properties and are emitted from $2P_2$—1S; $2P_1$—1S[2]. But the doublet is superposed each other in about 70% on the dry-plate under the above conditions with this apparatus. So, the photometer must be used with a great attention.

(ii) The analysis can be performed without the internal standard, by the line pair of Cd which is used as the coupling electrode.

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(2) W. Grotrian, *Spectren von Atomen und Ionen, II* (1928). 17, (Berlin).