

Quantitative Spectrum Analysis, Part III and IV

By

Arata Iwamura

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Part III. Quantitative Emission-Spectrum Analysis of Cadmium contained in Zinc Oxide

1. Sample electrodes and standard electrodes.

For the purpose of estimating cadmium contained in zinc oxide by means of the emission-spectrum, the oxide was first transformed into tablets which were used as the electrode in the same manner as was described in the case of determining lead contained in zinc oxide¹. The standard electrodes containing varying amounts of cadmium were prepared by mixing known amounts of cadmium carbonate and zinc oxide and transforming the mixture into tablets.

2. The apparatus used and the method of experiment.

The experiment was conducted in a manner analogous to that in the determination of lead in zinc oxide, with the apparatus described in the previous reports.¹

3. Sensitiveness of spectrographic analysis.

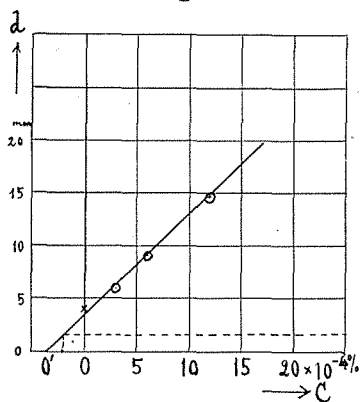
The determination of the sensitiveness of the quantitative spectrum analysis of cadmium contained in zinc oxide was also conducted in the same manner as in the analysis of lead contained in zinc oxide. The relation between the concentration of cadmium contained in zinc oxide and the photographic densities of the Cd line at $\lambda=2288\text{\AA}$ is shown in the following table, figure and the corresponding microphotometer records.

1. These Memoirs, **14**, 49 (1931).

d_{mm}	Conc. of Cd
4.2	x %
6.0	0.0003
9.2	0.0006
14.7	0.0012
11.6	0.0024
15.5	0.0090

(See PL. I. 1)

Fig. 1



The point at which the elongation of this curve and the horizontal dotted line (which shows the density of the back ground of the plate) parallel to the abscissa intersect, corresponds to the concentration of cadmium in zinc oxide, which gives the limit of density of the cadmium line observable by the microphotometer, that is to say, the minimum limit of detectable amount. The value thus found was $1.5 \times 10^{-4} \%$ under the conditions of the experiment. The value may, however, vary within certain limits depending upon the condition of the photographic plate, and the method of developing etc.

The intersection of the elongation of the density-concentration curve and the abscissa denotes the true zero-point, that is to say, the zero-point of the coordinates should be displaced by $00'$, $00'$ denoting the initial concentration of cadmium contained in zinc oxide. The initial concentration of cadmium was thus found graphically to be $3.6 \times 10^{-4} \%$.

4. Influence of acids used for cementing zinc oxide.

The influence of hydrochloric, sulphuric and nitric acids used in cementing the zinc oxide at the concentration of 0.050 % of Cd was determined by using the cadmium line $\lambda = 2288 \text{ \AA}$, and the densities given by the microphotometer were found as follows:

	chloride (a)	sulphate (b)	nitrate (c)
d_{mm}	15.3	9.3	9.1

It will be seen that though the densities are of the same order of magnitude, hydrochloric acid gives the most sensitive result. (See PL. I. 2 & 3).

5. Influence of cations.

Those elements which have some spectral lines in the vicinity of the cadmium line at $\lambda=2288\text{\AA}$ are as follows :

λ	Origin	F (intensity)	λ	Origin	F (intensity)
2298.2	Fe	1	2289.0	Fe	—
2297.8	Fe	—	2288.1	As	3
2294.7	Cd	4	2287.6}	Fe	—
2293.85}	Cu	5	2287.3}		
2294.30}					2286.7
2292.5	Fe	—	2280.2}	Fe	—
2291.1	Fe	—	2279.9}		
2290.6	Fe	—	2279.6	Ni	—
2290.0	Ni	—	2276.6	Bi	2

Now, each of the above mentioned elements was added in small varying amounts, to a definite quantity of a zinc oxide sample containing a definite amount of cadmium till the concentration of the added element became 3 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked and spectrographed as usual. The abovementioned elements were observed to give no detectable lines interfering with the cadmium line, $\lambda=2288\text{\AA}$, and therefore it became evident that the addition of these elements in the concentration mentioned above would influence neither the back-ground nor the cadmium line.

6. Examples of analysis.

The experiments for determining cadmium in zinc oxide ranging from 0.001 to 0.02 % were performed with the results described below, and one of the spectrograms and its microphotometer records are shown in the plate. (PL. I. 4 & 5)

Purely chemical analysis of cadmium contained in zinc oxide in a very small quantity would probably be a painstaking work and the results could not be trustworthy, as the tediousness of the process might introduce many sources of error.

The spectrographic method will be a more convenient and sensitive substitute for that method.

Ex. 1

The content of cadmium in the sample to be analysed is denoted by S, the mean value of which was found to be 0.00136 %.

The content of cadmium initially contained in zinc oxide used in

the present experiment was found to be $3.6 \times 10^{-4} \%$ as was stated in 3. Hence, the total content of cadmium was calculated by adding this amount to that of cadmium which was added for the purpose of preparing sample electrodes with varying cadmium concentrations.

Ex. 1.

$$S = 0.00136 \%$$

% Cd	$d_{\text{mm}} \lambda = 2288 \text{Å}$
0.00066	—
S	—
0.00096	5.8
S	9.4 > 3.6
0.00156	11.0 > 1.6
S	—
0.00276	—
S	—
0.00516	—

(See PL. I. 4 & 5)

$$\text{by proportion we get, } 60 \times \frac{1.6}{5.2} = 18.5 \approx 19$$

$$\therefore S = 0.00156 - 0.00019 = 0.00137$$

$$\Delta = 100 \times \frac{1}{136} = +0.7\%$$

Ex. 2.

$$S = 0.01536 \%$$

% Cd	$d_{\text{mm}} \lambda = 2288 \text{Å}$
0.03746	—
S	—
0.01896	24.2
S	19.8 > 4.4
0.00966	8.2 > 11.6
S	—
0.00496	—
S	—
0.00266	—

(See PL. I. 6)

$$\text{by proportion we get, } 930 \times \frac{4.4}{16.0} = 256$$

$$\therefore S = 0.01896 - 0.00266 = 0.01640$$

$$\Delta = 100 \times \frac{1640 - 1536}{1536} = +6.8\%$$

Two more experiments were performed, and the microphotometer records shown in PL. I. 7 and 8, and the values of S described below were obtained.

Ex. 3. S 0.02012%, for the theoretical value, 0.01921%

Ex. 4. S 0.01135% „ „ „ 0.01082%

7. Comparison of the results of spectrographic analysis with the theoretical.

Let S denote the value of cadmium spectrographically obtained, T, the theoretical value and Δ the percentage deviation from the theoretical values.

No.	S	T	Δ %
I	0.00137	0.00136	+0.7+
II	0.01640	0.01536	+6.8-
III	0.02012	0.01921	+4.7+
IV	0.01135	0.01082	+4.9-

As is shown in the above table, the spectrographic results coincide with the theoretical value fairly well, the percentage error lying between +0.7⁺ and +6.8.

Summary

1. Solid conducting electrodes consisting of a zinc oxide sample containing cadmium were prepared for the purpose of the quantitative emission-spectrum analysis.

2. The sensitiveness of the method for estimating cadmium contained in zinc oxide was determined to be $1.5 \times 10^{-4}\%$ under the conditions used in the experiments.

By elongation of the density-concentration curve, the initial concentration of cadmium contained in zinc oxide was found to be $3.6 \times 10^{-4}\%$.

3. The spectrographic values obtained in the analysis were found nearly coincident with the theoretical values, the divergency being always within the limit of permissible error.

Part IV. Quantitative Emission-Spectrum Analysis of Copper contained in Lead

1. With the object of ascertaining how far the determination of a minute quantity of copper existing in an organic compound may be performed spectro-graphically the writer tried to change the copper combining with an organic radical into the form of an alloy with lead, in the manner described below, and to use it as the electrode in the quantitative emission-spectrum analysis.

2. Preparation of sample electrodes.

As the organic copper compound, copper benzoinoxime $C_{14}H_{10}O_2NCu$ was taken. Now 10.0 grams of pure lead sheet cut in small pieces were melted in a porcelain crucible in the presence of a reducing agent such as cane-sugar and 4.5 mg. of copper benzoinoxime were added to it and well mixed, when the organic compound was decomposed leaving copper as an alloy. Another 10.0 grams of lead were then added and stirred well with a porcelain rod. It was cast quickly, hammered and cut in pieces so as to form cubes of 3mm. \times 1mm. \times 20mm. The lead cubes containing 0.005% copper thus obtained were used as electrodes. In the same way, lead electrodes containing varying amounts of copper were prepared. Other metals such as cadmium or zinc may also be used instead of lead for the same purpose.

3. Reproducibility of the spectrograms.

The spectrograms of lead containing copper were found to be quite reproducible as is shown in PL. II. 1.

4. Sensitiveness.

The sensitiveness of the copper analysis was experimentally determined as in the analysis of lead contained in zinc oxide¹. (PL. II. 2)

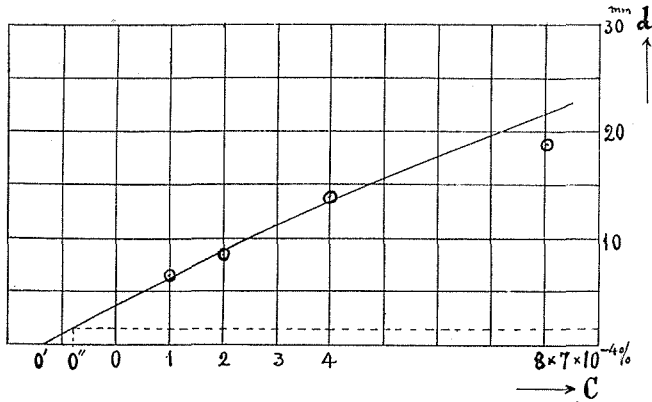
The densities of the copper lines at $\lambda=3248\text{\AA}$ and 3274\AA were photometrically determined by Moll's microphotometer and the sensibility of the line at $\lambda=3274\text{\AA}$ was determined as is shown in the accompanying figure and the table. Microphotometrical records are also shown reproduced in PL. II. 3.

The determination of the initial concentration of copper contained in the sample was carried out in the same way as was mentioned in Part III.

1. These Memoirs, 14, 51, (1931).

% Cu in Pb	d	
	$\lambda=3247.5\text{\AA}$	$=3274.0\text{\AA}$
0.0007	—	6.7 ^{mm}
0.00146	7.9	8.1
0.0029	13.2	13.9
0.00586	—	18.7
0.01172	22.3	—
0.02344	23.5	18.7
0.0469	32.3	20.6
0.0938	33.1	21.0

Fig. 2.



Initial conc. of Cu in Pb = $9.1 \times 10^{-4}\%$ (denoted by 00' in the above figure). Sensitiveness = $3.5 \times 10^{-4}\%$ (denoted by 0'o'' in the above figure).

5. Examples.

Ex. 1.

$$S = 0.01641\%$$

Cu %	$d_{\min}\lambda = 3274\text{\AA}$
S	—
0.02431	10.4
S	5.8 > 4.6
0.01261	4.1 > 1.7

(See PL. II. 4)

by proportion we get

$$S = 0.01261 + 0.00316 = 0.01577$$

$$\Delta = 100 \times \frac{1641 - 1577}{1641} = 100 \times \frac{64}{1641}$$

$$\Delta = -3.9\%$$

Ex. 2.

$$S=0.07091\%$$

Cu %	$d_{\text{min}} \lambda = 3274\text{\AA}$
S	—
0.09466	18.2
S	15.0 > 3.2
0.04779	10.5 > 4.5

(See PL. II. 5)

by proportion we get

$$S=0.04779+0.02739=0.07518$$

$$\Delta=100 \times \frac{427}{7091}$$

$$\Delta=+6.0\%$$

Ex. 3.

$$S=0.15721\%$$

Cu %	$d_{\text{min}} \lambda = 3274\text{\AA}$
S	—
0.18841	39.6
S	37.1 > 2.5
0.09466	33.1 > 4.0

(See PL. II. 6)

by proportion we get

$$S=0.09466+0.05825=0.15291$$

$$\Delta=100 \times \frac{430}{15721}=2.7$$

$$\Delta=-2.7\%$$

6. Comparison of the results of spectrographical analysis with the theoretical value.

Let S denote the value of copper obtained spectrographically, T the theoretical value, and Δ the percentage deviation from T.

No.	S	T	Δ %
I	0.01577	0.01641	-3.9+
II	0.07518	0.07091	+6.0+
III	0.15291	0.15721	-2.7+

As is shown in the above table, the spectrographical values coincide tolerably well with the theoretical value, the percentage deviation ranging between -2.7 and +6.0%.

Summary

1. Copper contained in lead was spectrographically analysed with fairly good results.

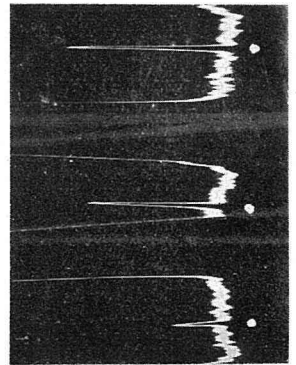
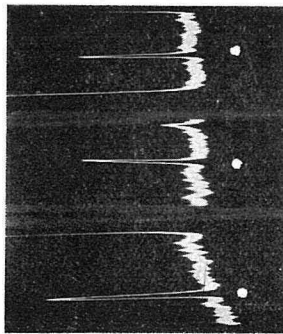
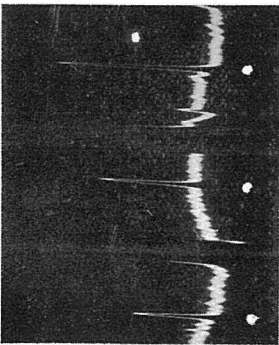
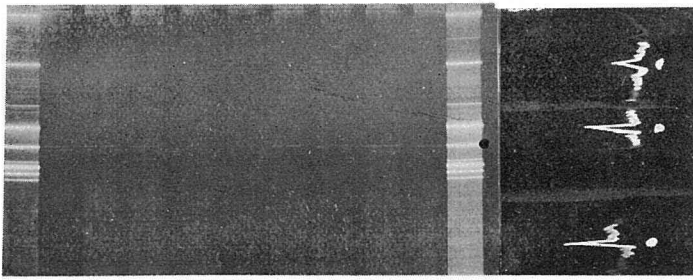
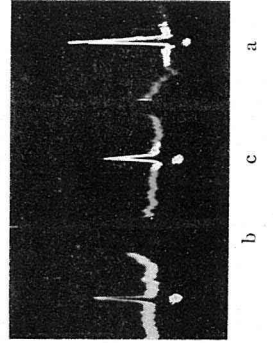
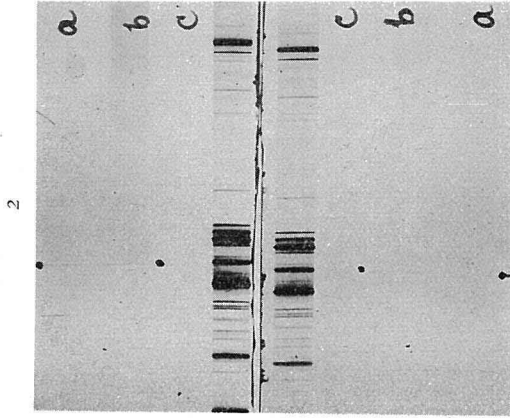
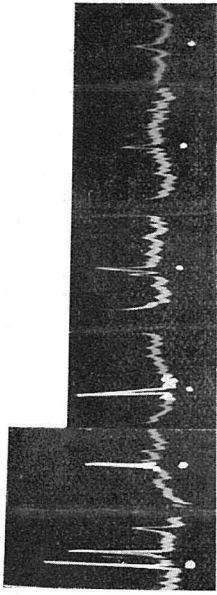
2. The sensitiveness of the method was found to be $3.5 \times 10^{-4}\%$.

The initial concentration of copper contained in the so-called pure lead sheet was found to be $9.1 \times 10^{-4}\%$.

3. It was experimentally confirmed that minute quantities of copper combining with an organic radical might be directly transformed into an alloy with pure lead, cadmium or zinc and the resulting alloys might serve as the electrode for the quantitative spectrographic analysis of the metal.

In conclusion, the writer wishes to express his sincere thanks to Prof. M. Matsui, and Prof. M. Kimura, of the Faculty of Science, K. I. U. for their valuable advice and encouragement.

Plate I



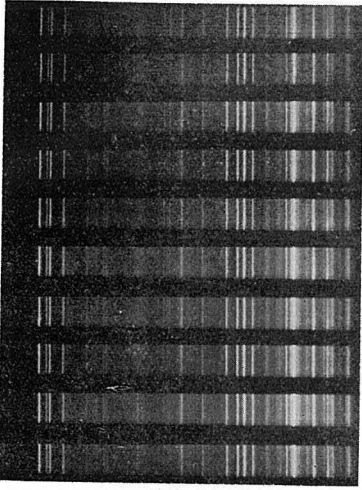
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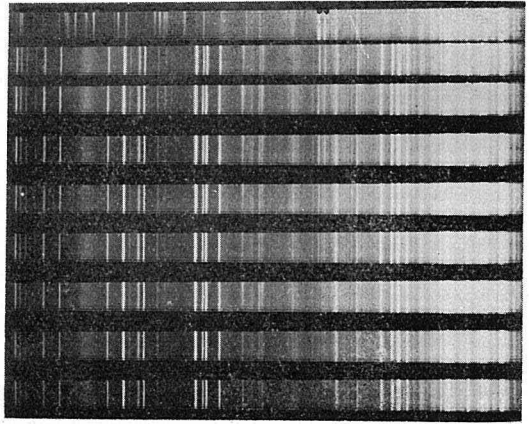
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Plate II

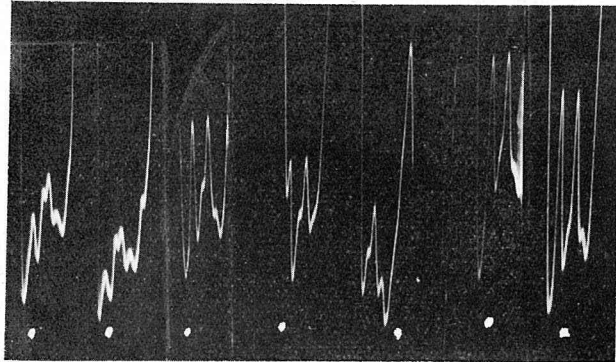
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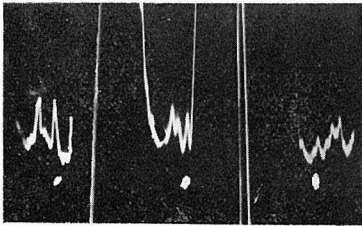
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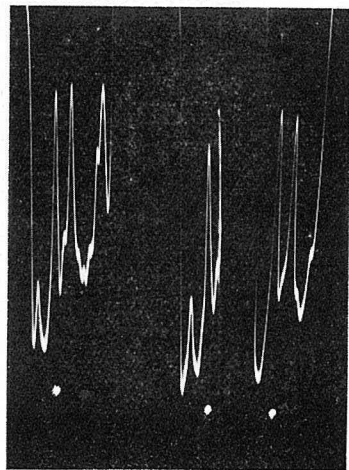
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