QUANTITATIVE EMISSION SPECTRUM ANALYSIS OF LEAD AND CADMIUM CONTAINED IN ZINC OXIDE.

By Arata IWAMURA.

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(1) **Sample Electrodes.** For the purpose of spectrographically determining very small quantities of lead and cadmium contained in zinc oxide, the oxide was first transformed into a solid conducting mass by treating merely with hydrochloric acid and then dried. A most suitable electrode was prepared in the following way:

Zinc oxide (30 g.) was gradually added to 35 c.c. of 6N HCl in a porcelain mortar and the mixture was constantly agitated, kneaded, and then moulded in a wooden mould before it was quite set, and the product was dried in an air-oven. The solid mass thus prepared was a round tablet, 3 cm. in diameter and 3 mm. thick, a round hole being made at its centre. Two such tablets containing zinc oxide with no foreign impurities except lead and cadmium were employed as the electrodes; the hydrochloric acid also contained no foreign impurities.

(2) **The Apparatus Used and the Method of Experiment.** To excite sparks between a pair of such electrodes, a transformer giving 10 kilovolts in the secondary was used. Self-inductance of a magnitude of about 62,000 cm. was always inserted in the secondary circuit. The light from an uncondensed spark between the electrodes was focused by means of a quartz lens on the slit of a small Hilger quartz spectrograph and spectrograms were thus obtained. When the sample contains a trace of lead and cadmium, the lead lines at λ4058, 3684 Å and the cadmium line at λ2288 Å were always detected on the plate. The photographic density of a line was recorded by means of Moll's recording microphotometer and for practical purposes the maximum heights of the curve for these lines measured from the neighbouring background were taken as a measure of the practical intensities of these lines.

The so-called "comparison method" was tried in analysing lead or cadmium in zinc oxide. Another method of analysing cadmium was to draw a density concentration curve in connection with the line at λ4201.8 Å and to determine graphically the content of cadmium from the density of the cadmium line in the spectrum of the sample of unknown cadmium content.

(3) **Reproducibility of the Spectrograms of Zinc Oxide Containing Lead and Cadmium and the Sensitivity of the Analysis.** Reproducibility of the spectrograms of zinc oxide electrodes containing lead was studied and it was observed that the result was reproducible within a range of $+6.5$—-6.1%. The microphotometer record proved to be sensitive within a range of $\pm 1\%$ of error. Sensitivity of the spectrographic analysis of lead or cadmium in zinc oxide was graphically determined from the density concentration relation in the following way: A series of spectrograms were taken of sparks emitted from electrodes containing varying amounts of lead or cadmium, and the practical intensities of the line were measured on microphotometer curves for various contents of lead or cadmium, and a curve connecting intensity of the line and the corresponding amount of lead or cadmium was drawn. The extrapolation of this curve gave the minimum detectable limit in the present method, i.e. the sensitivity of the method. The sensitivity of the analysis of lead in zinc oxide was thus found to be 1×10^{-6} under the conditions of the present experiment. In the case of cadmium in zinc oxide, the sensitivity was found to be 1.5×10^{-6} under the conditions of the experiment.

(4) **Influence of Acids Used for Cementing Zinc Oxide.** The influence of hydrochloric, sulphuric, and nitric acids used in cementing the zinc oxide containing 0.010% of lead or 0.050% of cadmium was determined by using the lead line at λ 4058 Å, or the cadmium line at λ 2288 A, and the densities (d_{mm}) given by the microphotometer were found as shown in Table 1.

Table 1.

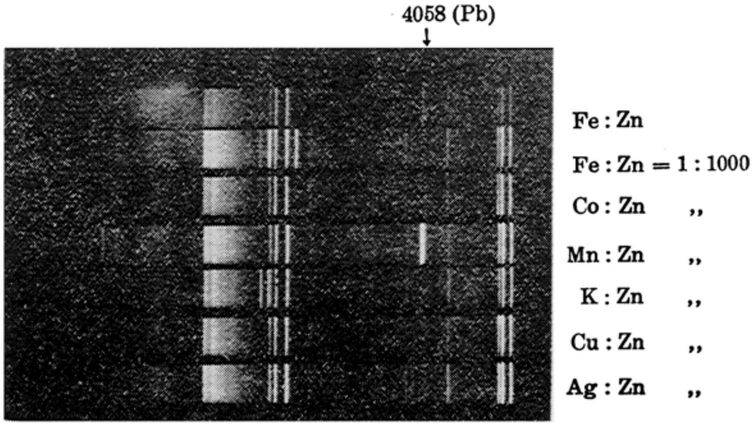
Acids / d_{mm}	Hydrochloric acid	Sulphuric acid	Nitric acid
d_{mm} $\lambda = 4058$ Å	23.2	22.3	$17.5+\alpha$
d_{mm} $\lambda = 2288$ Å	15.3	9.3	9.1

It will be seen that though the densities are of the same order of magnitude, hydrochloric acid gave the most sensitive result. The sample of zinc oxide containing much carbonate was not suitable to be cemented into the electrodes for the purpose of analysing lead, because the lead lines at λ 4058 Å and 3683 Å were masked by the cyanogen bands. Such a sample containing carbonate should be heated in a porcelain dish for the purpose of decomposing carbonate and then be prepared into electrodes as described above.

(5) **Influence of Cations.** Those elements which have some spectral lines in the vicinity of the lead line at λ 4058 Å are shown in Table 2.

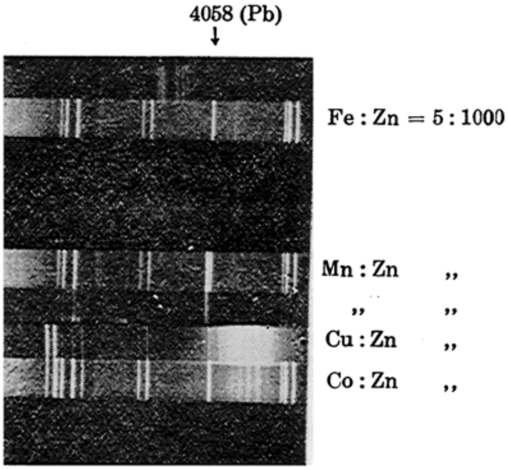
Table 2.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
4077.7	Sr II	10 R	4045.8	Fe I	8 R
4066.4	Co I	7 R	4045.4	Co I	8 R
4063.6	Fe I	8 R	4044.2	K I	10 R
4056.6	Cu	2 R	4041.4	Mn I	8 R
4055.3	Ag I	8 R	4035.7	Mn I	5 R
4047.2	K I	10 R	4034.5	Mn I	8 R



a

c Fe+Pb



b

d Mn+Pb

Plate I.

Now, each of the above-mentioned elements was added in small varying amounts to a definite quantity of zinc oxide sample containing a definite amount of lead till the concentration of the added element became 0.5 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked, and spectrographed as usual. It was observed that the elements iron and manganese had marked influence upon the densities of the line at λ 4058 Å (Plate I, a and b, and the corresponding microphotometer records c and d). Hence these two elements should be avoided in preparing the electrodes for a given sample of zinc oxide. If such elements are unavoidably present, then observe the lead line at λ 3684 Å.

Now, the common elements which have some spectral lines in the vicinity of the lead line at λ 3684 Å are shown in Table 3.

Table 3.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
3705.6	Fe I	6 R	3682.2	Fe	6
3700.3	Co	7	3679.9	Fe I	5
3687.5	Fe I	6 R	3677.6	Fe	6
3685.2	Ti II	10 R	3676.6	Co	8
3683.5	Pb	3 R	3674.2	Ni I	6
3683.1	Co	8	3669.5	Fe	6
			3669.0	Ti I	6

Iron and cobalt lines will practically coincide with the lead line at λ 3684 Å. But, it is practically very rare that cobalt occurs in zinc oxide, but iron does frequently as one of the impurities. If iron is present in zinc oxide in an appreciable quantity, then the spectrograph of higher dispersion should be employed.

With regard to the estimation of cadmium in zinc oxide, similar attention was paid. Those elements which have some spectral lines in the vicinity of the cadmium line at λ 2288 Å are shown in Table 4.

Table 4.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
2298.2	Fe	I	2293.85 2294.30	Cu	5
2297.8	Fe	—	2292.5	Fe	—
2294.7	Cd	4	2291.1	Fe	—

Table 4. (*Concluded*)

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
2290.6	Fe	—	2286.7	Sn	3
2290.0	Ni	—	2280.2	Fe	—
2289.0	Fe	—	2279.9		
2288.1	As	3	2279.6	Ni	—
2287.6 2287.3	Fe	—	2276.6	Bi	2

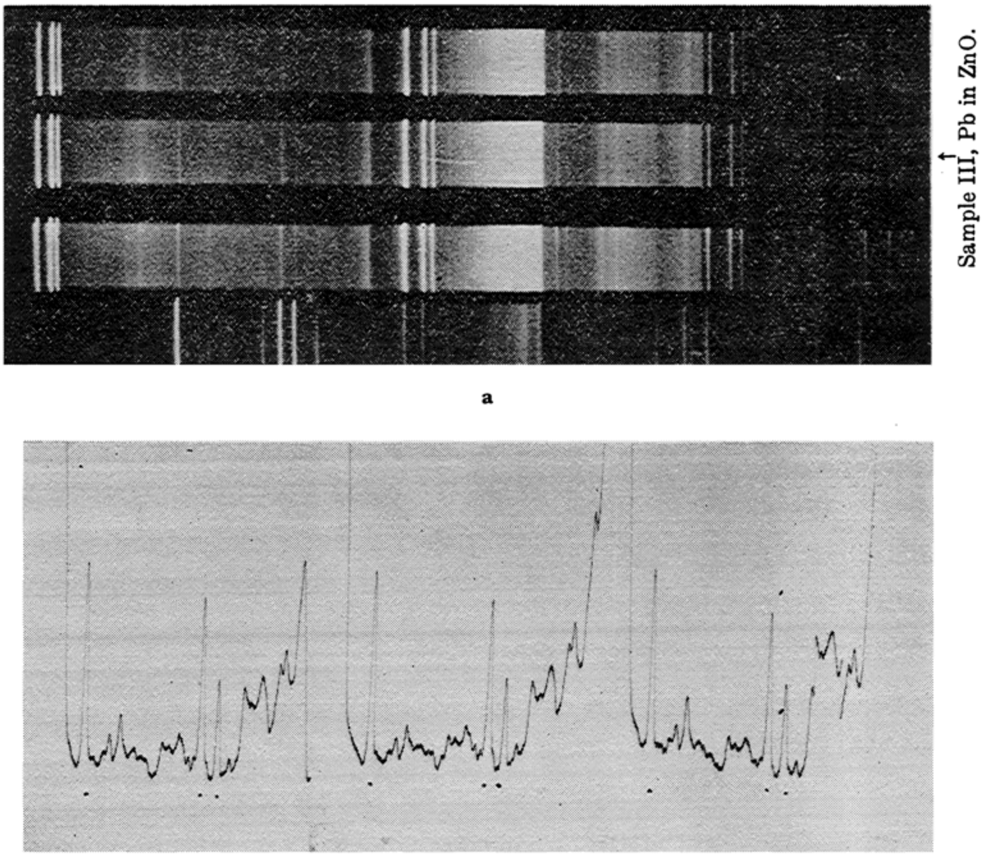
Now, each of the above-mentioned elements was added in small varying amounts, to a definite quantity of a zinc oxide sample containing a definite amount of cadmium till the concentration of the added element became 3 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked, and spectrographed as usual. The above-mentioned elements were observed to give no detectable lines interfering with the cadmium line, λ2288 Å, and, therefore, it became evident that the addition of these elements in the concentration mentioned above would influence neither the background nor the cadmium line.

(6) **Influence of Capacity and the Self-inductance.** When condensed discharge was effected between the electrodes consisting of zinc oxide, they were easily broken and no desirable exposure could be made. The present writer was forced to use uncondensed spark discharge throughout the experiment and was unable to study the influence of capacity systematically. The introduction of capacity into the secondary circuit of the transformer was possible after the uncondensed spark discharge was continued for a few minutes, but then, there appeared air-lines which masked the lead lines in question.

The introduction and increase of self-inductance in the secondary circuit of the transformer cleared up those air-lines and gave a clear back ground in the spectrogram. In analysing cadmium by uncondensed spark discharge nothing particular was observed.

(7) **Influence of Developers upon the Fogging of the Background of the Plate.** During the course of the experiment, the present writer has found that the hydroquinone developer which gives a strong contrast is one of the most satisfactory developers in order to make the background clear in contrast to the blackening of the lines. The use of pyrogallol developer or metol hydroquinone developer seems to be less satisfactory.

(8) Comparison of the Results of Spectrographical Analysis of Lead or Cadmium with those of Chemical Analysis or with Theoretical Values. Let *S* denote the value of lead or cadmium spectrographically obtained, *C* that chemically found, *T* the theoretical value, and Δ the divergency from the chemical or theoretical values. (See Plate II, **a** and **b**.)



a

b

Plate II.

As is shown in Table 5 the spectrographical results are generally somewhat higher than the chemical or theoretical ones, but they are of the same order of magnitude in case of lead and cadmium, the divergency being always within the limit of the permissible error.

Table 5.

	Pb %			Cd %			
	I	II	III	I	II	III	IV
S	0.0007	0.00137	0.00289	0.00137	0.01640	0.02012	0.01135
C	0.0006	0.00133	0.00270	—	—	—	—
T	—	—	—	0.00136	0.01536	0.01921	0.01082
$\varDelta$	0.0001	0.00004	0.00019	0.00001	0.00104	0.00091	0.00053
$\varDelta\%$	$+14^{+}$	$+3^{-}$	$+7^{-}$	$+0.7^{-}$	$+6.8^{-}$	$+4.7^{-}$	4.9^{-}

Summary.

(1) Electrodes consisting of a zinc oxide sample containing lead or cadmium, were prepared for the purpose of quantitative emission-spectrum analysis.

(2) The reproducibility of the spectrograms of the electrodes was tested, and was shown to be within -4.8 to $+6.5\%$, under the conditions of the experiment.

(3) The sensitivity of this method for estimating lead and cadmium contained in zinc oxide was determined to be 1×10^{-6} and 1.5×10^{-6} respectively under the conditions of the experiment.

(4) Influence of acids used for cementing zinc oxide, influence of the presence of carbonate and that of some metallic salts added to zinc oxide were tested. Some remarks on capacity and on the developing of the plate were described.

(5) The values obtained by emission-spectrum analysis were compared with those found by chemical analysis or with theoretical values.

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Faculty of Science,
Imperial University of Kyoto.