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Quantitative Spectrum Analysis

By

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Part I. On the electrodes used in quantitative emission-spectrum analysis

There are several methods of carrying out quantitative emission-spectrum analysis, such as A. de Gramont's "test method", Gerlach and Schweitzer's "absolute method", or the "internal standard method" and so forth. Of these, the one first mentioned is widely used.

In these methods of analysis, it is necessary to prepare a large number of electrodes composed of standard samples the main constituent (or constituents) of which contains varying amounts of the element in question, and also electrodes of the sample to be analysed, which are taken to be nearly the same as those of the standard samples.

We shall now consider various forms of electrodes when the sample to be analysed is given in the form of (1) a solution, or (2) a soluble or insoluble non-conducting solid or powder.

1. The sample to be analysed is given in the form of a solution

Such a sample may be employed either

- a. in the form of the solution itself, or
- b. in the form of a solid electrode prepared from zinc oxide, calcium oxide or magnesium oxide mixed with the solution.

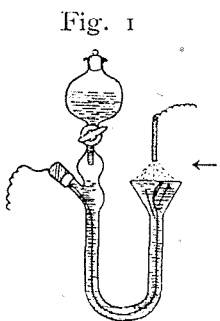
1. a. In this case Delachanel and Mermot's electrodes¹ are convenient, but they have the defect that a glass capillary is easily broken,

1. Baly-Spectroscopy II Fig. 43. a. p. 120.

and the solution soon evaporates and is easily dispersed. E. Becquerel's electrodes¹ are simple and convenient when excited with small sparks, but a defect similar to the above results when the sparks are large. In this case it is better to use the electrodes employed by Hartley,² but it is somewhat difficult to keep the electrodes wet with the solution uniformly, so as not to interrupt the spark during the time of exposure.

The gold electrodes of Pollok and Leonard are also used for a sample in the form of solution, but if the solution is very dilute, a large volume of solution and long time of sparking are required in order to obtain a good spectrogram. As the evaporation and dispersion of the solution are greater at the beginning than at the end of sparking, the intensities of the required spectrum lines are not kept constant.

Such are the most detrimental phenomena in the practical procedure of the quantitative emission-spectrum analysis of a solution. The present writer found that by using the apparatus shown in Fig. 1. constancy in the spectra of the solution is attained. The figure is one half the actual size and is self-explanatory.



During the sparking, the surface of the solution should be kept at a definite height by regulating the speed at which the solution is dropped.

If the lower electrode is wet with the solution, a definite noise of sparks is constantly heard, but if the lower electrode gets dry, the noise changes and sounds destructive.

The radius of the funnel containing the lower gold electrode is made a little larger than the distance between the electrodes, otherwise sparks pass between the edge of the funnel and the upper electrode. The glass or quartz capillary through which the solution ascends is often broken by condensed sparks, so that two or three thin gold plates, $2 \times 10 \times 0.3 \text{ mm}^3$, are substituted for it. The upper gold electrode consists of gold wire of 2 mm. dia. The paths of the discharges are shown by the dotted lines in Fig. 1 and the spark is viewed and spectrographed in the direction of the arrow.

1. Baly-Spectroscopy II Fig. 43. b. p. 120.

2. " " Fig. 44. "

Another metal may be substituted for the gold, if necessary.

1. b. To convert a liquid sample into a conducting solid. It is often convenient to convert a given sample of solution into a conducting solid. According to Baly (Vol. II, p. 119) "the dry cones (purified carbon cones) are boiled in an aqueous solution of the required metallic salt. If available, the nitrate is the most suitable salt to use, since metallic oxide is formed simply by heating the cones at a red heat. In this case, the treatment with the solution and the subsequent heating may be repeated several times." This method is suitable for the purpose of qualitative spectrum analysis, but not for quantitative spectrum analysis, because the homogeneous adsorption of a definite amount of a salt of known concentration by carbon can not be expected. The adsorption of some metallic salt on wood charcoal is irreversible. Some metallic ion loses its charge and is deposited on the pores of the charcoal and is not removed by simply washing it with water, the remaining solution becoming strongly acidic. This is a marked phenomena when charcoal is used as adsorbent. The same phenomenon will take place in a less degree when a less porous carbon such as gas carbon or artificial graphite is used, and homogeneity of the sample electrode thus prepared is highly improbable. Even though it is assumed to be really homogeneous, the amount of salt adsorbed is not proportional to the concentration of the solution.

According to colloidal chemistry, the relation

$$\frac{x}{m} = aC^{\frac{1}{n}} \quad \text{holds at constant temperature,}$$

where

x = the amount of salt adsorbed on adsorbent (carbon)

m = mass of adsorbent (carbon)

C = concentration of the salt solution and n = constant.

If m is taken to be constant, say $m = 1$. gm. or 10 gms. in each case, then

$$x = A.C^{\frac{1}{n}}, \quad \text{where } A = am.$$

Thus we see x is proportional to $C^{\frac{1}{n}}$, and not to C , showing that the amount of salt adsorbed by carbon from a solution of known concentration at constant temperature is not proportional to the concentration of the salt solution. If n is known, it may be adequate to use such electrodes in quantitative emission spectrum analysis, provided the other conditions are quite satisfactory.

An electrode of a uniform sample may be obtained according to the methods described below :

(a) 10 gms. of pure carbon or powdered carbon made from molasses are put into a mortar, and a definite quantity of sample solution, (for standard electrodes, definite quantities of known concentrations of an element) is added to it and well mixed. Then 9.5 gms. of cane sugar molasses are added to give proper consistency, and the mixed mass thus produced is formed into a circular disc or rectangular stick by means of an aluminium mould and heated gently over a Bunsen burner,—heating in an electric furnace under diminished pressure will produce better results more quickly. All this process takes about an hour. Spectrograms taken with such electrodes are shown in PL. I. a, b & c.

(b) To the solution mixed with concentrated hydrochloric acid in such a proportion that the concentration of the acid becomes 6 *N*, pure zinc oxide, pure magnesium oxide, or pure calcium oxide is added and after thorough mixing the mixture is moulded into electrodes and dried.

2. Soluble or insoluble non-conducting solid or powder

In the case of determining very small quantities of lead contained in zinc oxide, the usual method is to dissolve the oxide in hydrochloric or sulphuric acid, and to examine the solution by means of spark spectra, using pure gold or pure zinc electrodes.

But in that method the concentration of lead in the zinc solution is naturally smaller than that in zinc oxide in the solid state, which makes the quantitative estimation of the lead in the original zinc oxide very difficult.

In Sawyer and Becker's¹ method zinc oxide is made to adhere to asbestos threads which are moistened with a zinc chloride or sulphate solution to render them conductive. But the zinc oxide is soon dispersed as the high-tension alternating current passes through the thread and consequently this method can not be used to prepare good long-lasting electrodes.

According to Baly's² A. de Gramont's method of converting a non-conductor into a conductor is stated as follows :

“ If the mineral is a non-conductor, it may be fused with Na_2CO_3

1. Baly-Spectroscopy II, p. 88.

2. „ II, p. 149.

in a small platinum-capsule, and the spark spectra of the melted material examined. By the use of known weight of mineral and alkali, an estimate of the relative proportion of the metallic constituents present in the mineral can be made." This method is generally recommended for the quantitative emission-spectrum analysis of a non-conducting insoluble solid mass or powder. But from the practical point of view, the above method is found still inconvenient in the following points: (1) The sample becomes diluted, (2) The fused mass is hygroscopic, (3) The spectrum is complicated by the presence of platinum lines, and (4) The process of fusing the sample with an alkali requires rather a long time.

After several trials the present writer succeeded in procuring suitable electrodes which have no such defects as those mentioned above. The manner of preparation is as follows:

The sample of zinc oxide and some pure carbon (activated carbon) are kneaded in a mortar together with some cane-sugar molasses, moulded in an aluminium tube, and heated on a Bunsen-burner. After cooling, the aluminium is removed, and the resulting mass is used as electrodes. This process has, however, the demerit that it causes some of the lead to be lost, as it is reduced in the presence of reducing substances at the temperature of a Bunsen-burner.

The method of cementing zinc oxide with a zinc chloride solution may also be used. In using this method it must be borne in mind that a trace of lead is frequently detected even in carefully purified zinc chloride. Instead of using a zinc chloride solution, if some zinc oxide is added little by little to 3N-HCl solution contained in a mortar and is stirred, it gradually dissolves, leaving some zinc oxide in suspension. By further addition of zinc oxide, it is transformed into a pasty mass which solidifies rapidly and conducts electricity.

This paste, when properly moulded and set, is suitable for use as the sparking electrodes. For the purpose of increasing the conductivity, some electrolyte such as KNO_3 , K_2SO_4 etc. or a metal powder such as aluminium may be added at the time of kneading. The solidity of the mass depends on the proportions of the components and the method of mixing them, as is seen in the case of forming a magnesia cement from magnesium oxide and magnesium chloride.

The following was found to give a good result: 30 grammes of zinc oxide is gradually added to 35 c.c. of 6N-HCl in a porcelain mortar, kneaded and moulded before it sets; it is then dried in an

air-oven and used. Zinc oxide containing some carbonate behaves similarly. This procedure is applicable for the preparation of conducting solid electrodes from carbonates and basic carbonates of other metals, mixing them with pure zinc oxide, magnesium oxide or calcium oxide for cementing purpose.

Oxides and carbonates of metals are generally bad conductors of electricity, but they are soluble in mineral acids, giving homogeneous solutions. Quantitative spectrum analysis is usually performed with such a solution. But it is more convenient to transform them into solid masses conducting electricity in the way described above and to use them directly as sparking electrodes for the determination of minute quantities of elements contained in such substances.

Insoluble, non-conducting powders may also be transformed into conducting solid electrodes by similar treatment. Spectrograms taken with such electrodes by means of a small Hilger quartz spectrograph are shown in PL. II; *a* showing the one obtained with electrodes containing powdered natural silver ore and prepared in the above mentioned way. Silver lines at $\lambda=2934, 2902, 2897, 2661, 2535, 2507$ and $2481-71 \text{ \AA}$ are seen in *a*.

Silica sand, talc, siliceous ores of gold and silver and such like are insoluble in chemicals and also non-conductors of electricity. All such substances in a finely powdered state can be transformed into a conducting solid electrode when mixed with zinc oxide and zinc chloride or zinc oxide and hydrochloric acid, or magnesium oxide and HCl, or calcium oxide and HCl.

Photo *b* in PL II. shows a spectrogram of talc + ZnO + HCl
 „ *c* „ „ that of ZnO + HCl.

Summary :

- (1) A modification of the gold electrodes of Pollok and Leonard so as to keep their sparking conditions constant for a longer period of time with very dilute solutions is described.
- (2) A method of converting a liquid sample into a conducting solid electrode is described.
- (3) A method of converting samples of soluble or insoluble non-conducting materials into conductive solid electrodes to be used in quantitative emission-spectrum analysis is given.

Part II. Quantitative emission-spectrum analysis of lead contained in zinc oxide

1. Sample Electrodes.

For the purpose of spectrographically determining very small quantities of lead 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 :

20 grams of zinc oxide were gradually added to 23.3 c.c. of 6 N-HCl in a porcelain mortar and this 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 cms. in diameter and 3 mm. thick, a round hole being made at its centre. Two such tablets containing zinc oxide having no foreign impurities were employed as the electrodes; the hydrochloric acid also contained no foreign impurities, as a very pure hydrochloric acid is easily obtained.

2. The apparatus used and the method of experiment.

To excite sparks between a pair of such electrodes, a transformer giving 10 K.V. in the secondary was used. Self inductance of a magnitude of about 62,000 cms. 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, the lead lines at $\lambda = 4058$, and 3684 \AA are always detected on the plate.

The photographic density of a line was recorded by means of a 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.

3. Reproducibility of the spectrograms of zinc oxide electrodes containing lead.

In spectrographical quantitative analysis of metals and alloys, it is generally assumed that the result is always reproducible, within a range of permissible error under certain definite conditions of experiment.

With the present electrodes it is necessary to show experimentally that the electrodes always give a reproducible result.

This was proved to be the case as is shown in the following spectrograms and the corresponding microphotometry curves given in plates I and II.

From curves I. a.

$d(\lambda=4058)$	Δ	$\Delta\%$	$d(\lambda=3684)$	Δ	$\Delta\%$	$d(\lambda=3640)$	Δ	$\Delta\%$
(13.4)	—	—	15.5	$-\frac{7}{1557}$	-0.5-	6.8	$-\frac{5}{685}$	-0.8-
18.1	$-\frac{5}{1815}$	-0.3-	15.6	$-\frac{3}{1557}$	+0.2-	6.9	$+\frac{5}{685}$	+0.8-
mean: $\frac{18.2}{18.15}$	$+\frac{5}{1815}$	+0.3-	$\frac{15.6}{15.57}$	$+\frac{3}{1557}$	+0.2-	$\frac{(9.6)}{6.85}$	—	—

From curves I. b.

$d(\lambda=4058)$	Δ	$\Delta\%$	$d(\lambda=3684)$	Δ	$\Delta\%$	$d(\lambda=3640)$	Δ	$\Delta\%$
34.4	$+\frac{210}{3230}$	+6.5+	30.3	$+\frac{167}{2803}$	+5.8+	16.6	$+\frac{93}{1567}$	+5.9+
30.0	$-\frac{230}{3230}$	-6.1+	27.5	$-\frac{113}{2803}$	-3.9+	15.4	$-\frac{27}{1567}$	-1.7+
M: $\frac{32.5}{32.30}$	$+\frac{20}{3230}$	+0.6+	$\frac{28.1}{28.63}$	$-\frac{53}{2803}$	-1.9-	$\frac{15.0}{15.67}$	$-\frac{67}{1567}$	-4.3-

From curves II. A.

$d(\lambda=4058)$	Δ	$\Delta\%$	$d(\lambda=3684)$	Δ	$\Delta\%$	$d(\lambda=3640)$	Δ	$\Delta\%$
74.4	$+\frac{137}{7303}$	+1.9-	66.7	$-\frac{37}{6707}$	-0.6-	48.9	$-\frac{3}{4893}$	-0.1-
73.2	$+\frac{17}{7303}$	+0.2+	68.5	$+\frac{143}{6707}$	+2.1+	51.3	$+\frac{243}{4893}$	+5.0-
M: $\frac{71.5}{73.03}$	$\frac{153}{7303}$	-2.1-	$\frac{66.0}{67.07}$	$-\frac{107}{6707}$	-1.6-	$\frac{46.6}{48.93}$	$-\frac{233}{4893}$	-4.8-

Δ ≡deviation from the arithmetical mean.

d ≡photographic density in mm.

From the above figures we see that the result is always reproduced within 6.5% to -6.1%.

The sensibility of the recording microphotometer was tested by placing a plate in the plate holder of the apparatus, and the photometric records were taken twice as shown in plate II. B.

The height of the curve corresponding to a line was measured to a fraction of a mm. and this is given in the following tables.

From PL. III.

No.	λ_{Pb}	Intensity Measure								
		d 4058			d 3684			d 3640		
		mm	Δ	$\Delta\%$	mm	Δ	$\Delta\%$	mm	Δ	$\Delta\%$
1		30.2	$-\frac{30}{3050}$	-0.98+	26.7	$-\frac{15}{2685}$	-0.56+	15.8	$-\frac{15}{1595}$	-0.94+
2		$\frac{30.8}{30.50}$	$+\frac{30}{3050}$	+0.98+	$\frac{27.0}{26.85}$	$+\frac{15}{2685}$	+0.56+	$\frac{16.1}{15.95}$	$+\frac{15}{1595}$	+0.94+
mean										

From PL. II c & d.

No.	λ_{Pb}	Intensity Measure								
		d 4058			d 3684			d 3640		
		mm	Δ	$\Delta\%$	mm	Δ	$\Delta\%$	mm	Δ	$\Delta\%$
1		71.5	$+\frac{5}{7145}$	+0.06+	66.0	$+\frac{5}{6595}$	+0.08-	46.6	$+\frac{15}{4645}$	+0.35-
2		$\frac{71.4}{71.45}$	$-\frac{5}{7145}$	-0.06+	$\frac{65.9}{65.95}$	$-\frac{5}{6595}$	-0.08-	$\frac{46.3}{46.45}$	$+\frac{15}{4645}$	-0.35-
mean										

The recording photometer is sensitive within a range of $\pm 1\%$ of error.

4. Sensibility of the spectrographic analysis of Pb contained in ZnO.

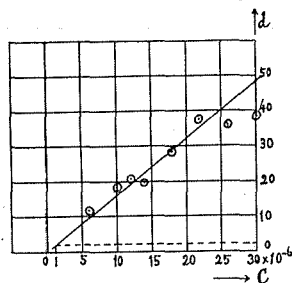
The sensibility is usually expressed by the smallest detectable amount of an element contained in a main constituent. In the present case, this corresponds to the smallest detectable height of the Pb line $\lambda=4058 \text{ \AA}$ on the microphotometer curve and this is extrapolated in the following way. A series of spectrograms were taken of sparks emitted from electrodes containing a varying amount of lead, and the practical intensities of the line were measured on microphotometer curves for various contents of lead, and a curve connecting intensity of the line and the corresponding amount of lead was drawn as shown in the accompanying figure and table (see also PL. II. C).

The extrapolation of this curve gives the minimum detectable limit in the present method, i. e. the sensitivity of the method.

C %Pb	$d(\lambda=4058 \text{ \AA})$
0.0030	38.6
0.0026	36.0
0.0022	37.8
0.0018	28.4
0.0014	19.6
0.0012	20.5
0.0010	18.5
0.0006	11.9

See PL. II. C.

Fig. 2



The dotted line in Fig. 2 denotes the density of the back ground of the plate

The sensibility is therefore found to be 1×10^{-6} under the conditions of the present experiment. This value may vary within certain limits depending upon the conditions of the photographic plates and the method of developing.

5. Examples.

For practical purposes, the present experiment was confined to the determination of the quantity of lead contained in zinc oxide, ranging from 6×10^{-6} to 3×10^{-5} and the method gave the following result:

One of the spectrograms and photometer records are shown in PL. III—1.2.3.

Examples. (S denotes the % of Pb in the sample taken)

(I)		(II)		(III)	
% Pb	d	% Pb	d	% Pb	d
0.0090	—	0.0070	—	0.0070	—
S	—	S	—	S	—
0.0050	—	0.0030	—	0.0050	—
S	—	S	—	S	—
0.0025	—	0.0020	18.4	0.0040	—
S	—	S	13.4	S	—
0.0012	9.0	0.0006 ^a	7.5	0.0030	27.5
S	5.4			S	27.2
0.0004	3.2			0.0020	25.0

by proportionality

$$8 \times \frac{2.2}{5.8} = 3$$

by proportionality

$$13.7 \times \frac{5}{10.9} = 6.3$$

by proportionality

$$10 \times \frac{0.3}{2.8} = 1.1$$

$$S = 0.0004 + 0.0003 = 0.0007 \quad S = 0.0020 - 0.00063 = 0.00137 \quad S = 0.0030 - 0.00011 = 0.00289$$

6. Chemical Analysis.

It will be not without interest to compare the above method with the ordinary method of chemical analysis to determine a minute trace of lead. This was done in the following way :

100 grams of the zinc oxide sample to be analysed were dissolved in concentrated hydrochloric acid and the solution was saturated with hydrogen sulphide gas.

After standing overnight, the precipitate that settled was filtered, washed with water containing hydrogen sulphide, dissolved in hot dilute nitric acid, and the nitric acid solution was evaporated in a water bath nearly to dryness. Some hot water was then added to the residue and the basic bismuth nitrate thus separated was separated by filtration and washed (when estimation of bismuth is not required, evaporation to only a small bulk of solution is sufficient).

The filtrate and the wash water were united, acidified with concentrated nitric acid and electrolysed according to the usual method. The deposit on platinum anode was washed, dried, heated at 180°C for 1 hr. and the lead peroxide thus obtained was iodometrically determined. The results are shown in the following table :

No. of Sample.	I	II	III
Pb found (%)	0.0006	0.00133	0.0027

7. Comparison of the results of spectrographical analysis with those of chemical.

Let *S* denote the value of lead spectrographically obtained and *C* that chemically found.

Sample.	I	II	III
S	0.0007	0.00137	0.00289
C	0.0006	0.00133	0.0027
Δ	0.0001	0.00004	0.00019
Δ%	$(\frac{100 \times 1}{7})14.+$	$(\frac{100 \times 4}{133})=)3.-$	$(\frac{100 \times 19}{289})=)7.-$

As is shown in the above table the spectrographical results are generally somewhat higher than the chemical ones, but they are of the same order of magnitude.

It will be noticed that the spectrographic method of analysis has advantage over the chemical in the following points : (1) its rapidity, (2) its simplicity, (3) no loss of a sample during analysis, (4) quantity of a sample required for analysis is comparatively very small, (5) the

result of the experiment is recorded almost free from any personal errors and (5) the method is especially suitable for microanalysis.

It must, however, be remembered that this method often introduces comparatively large errors which may perhaps be due to unavoidable fluctuation of sparks.

8. Summary.

1. Electrodes consisting of a zinc oxide sample containing lead, 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 sensibility of this method for estimating lead contained in zinc oxide was determined to be 1×10^{-6} under the conditions used in the experiment.

4. The values obtained by emission-spectrum analysis were compared with those found by chemical analysis.

Both were found to be in the same order of magnitude, though the spectrographic values were always somewhat higher than the chemical ones.

In conclusion, the writer expresses 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

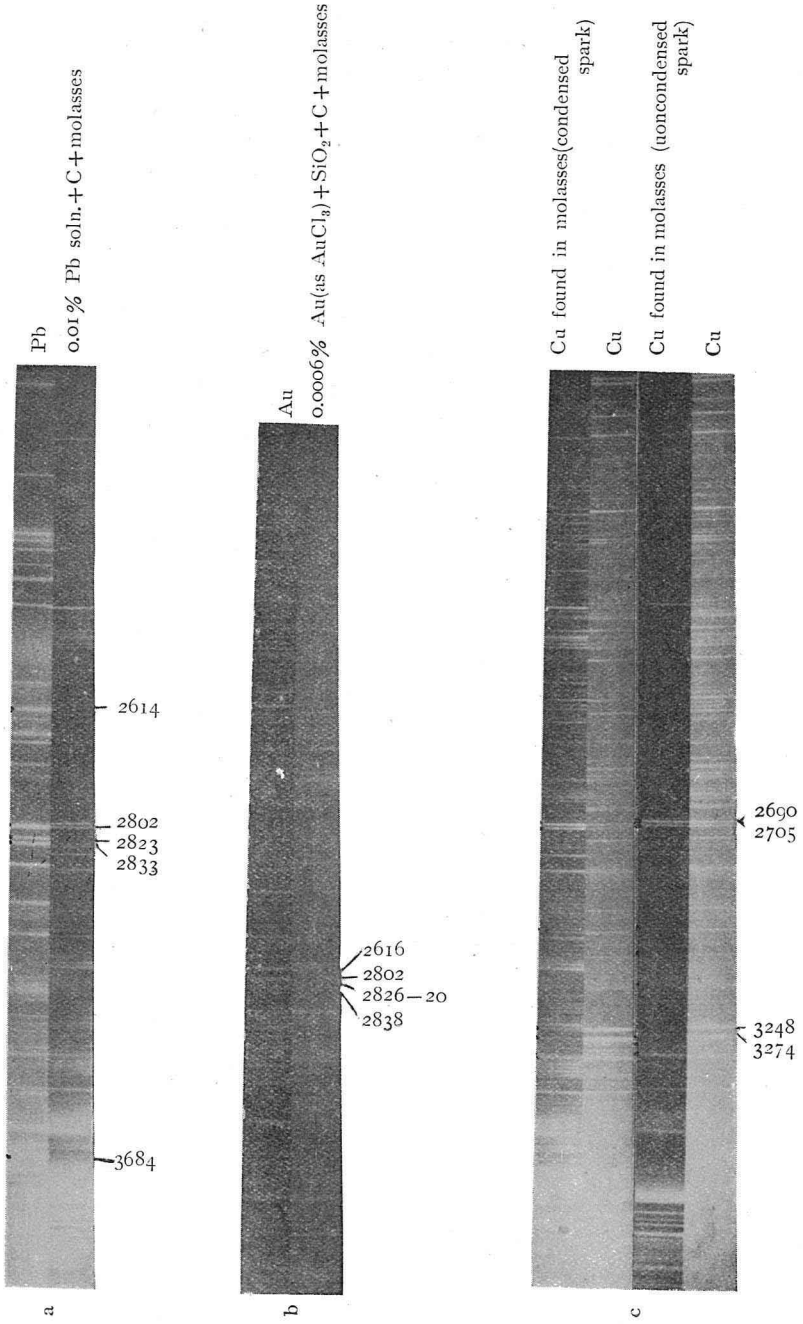


Plate II

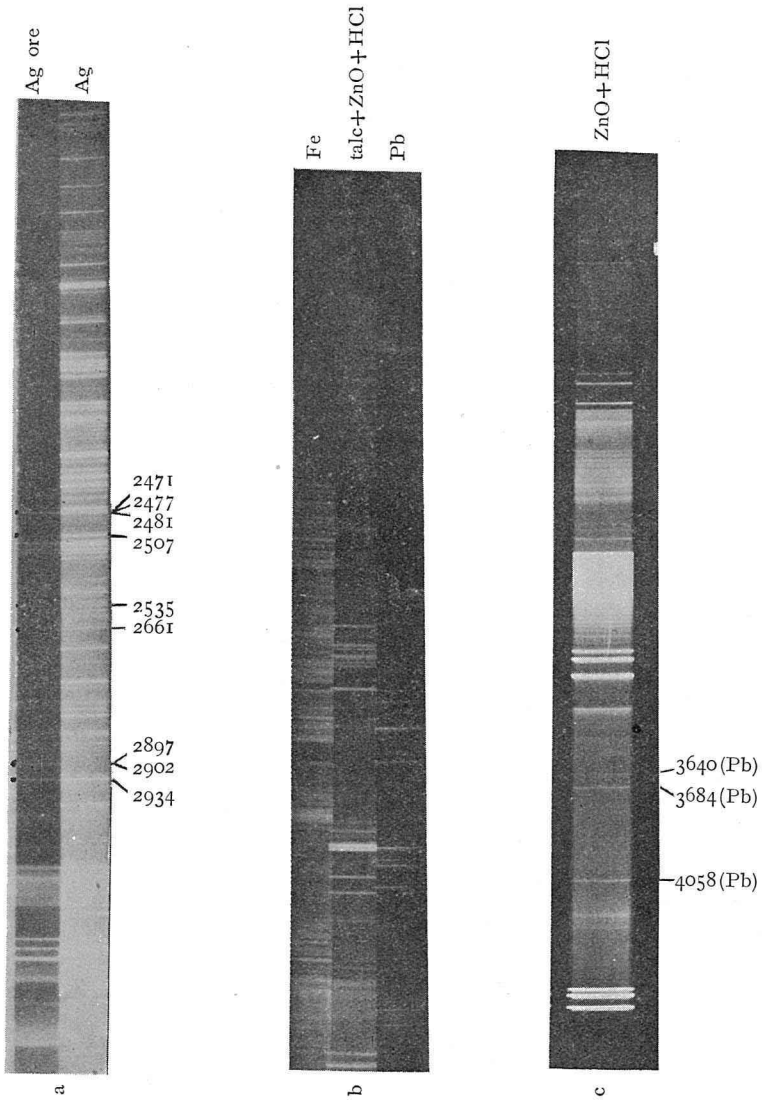
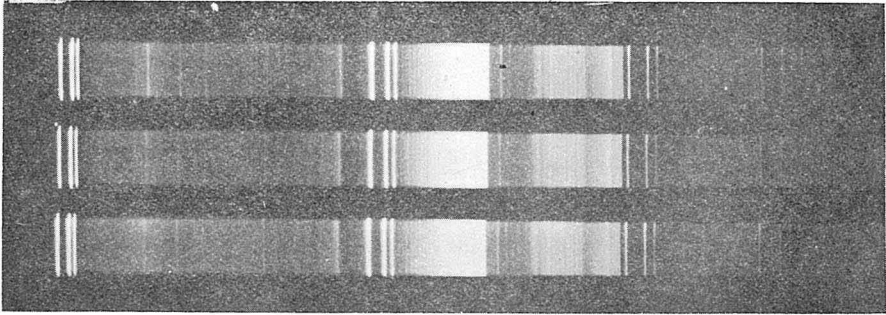
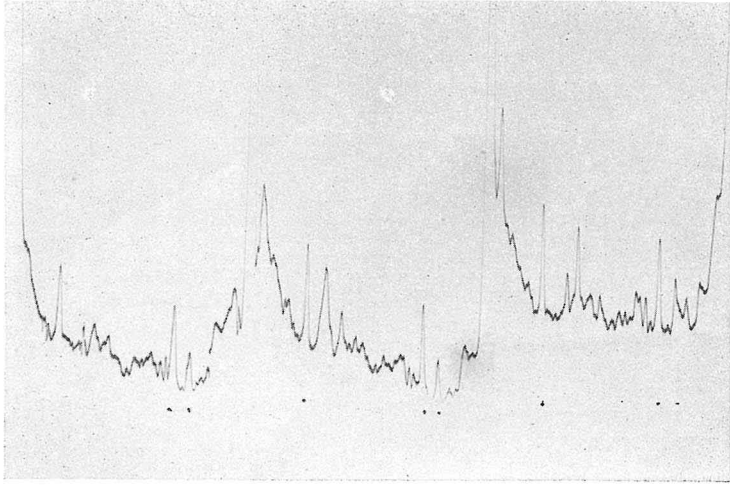
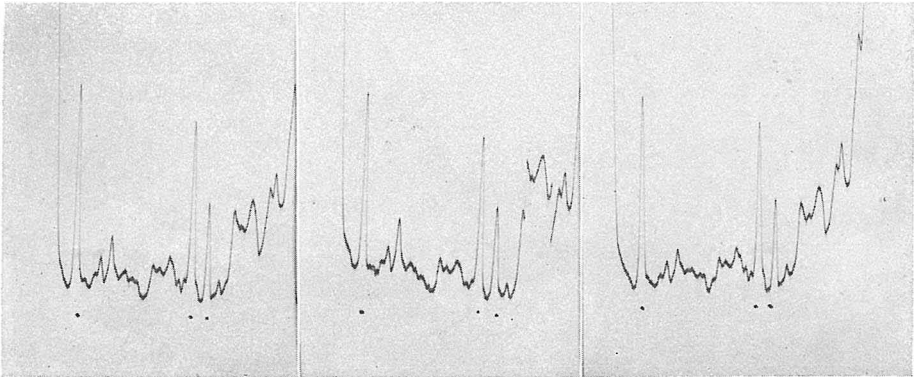


Plate I



b



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Plate II

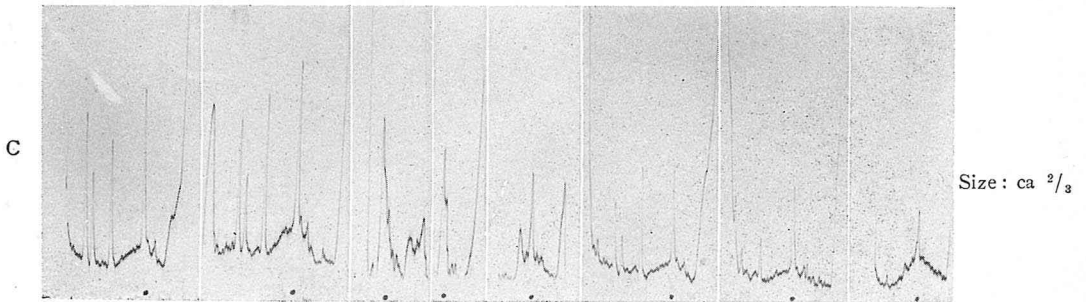
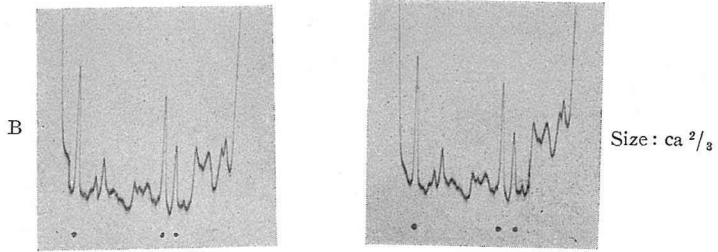
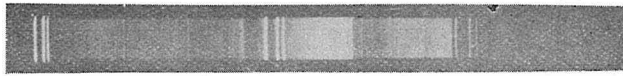
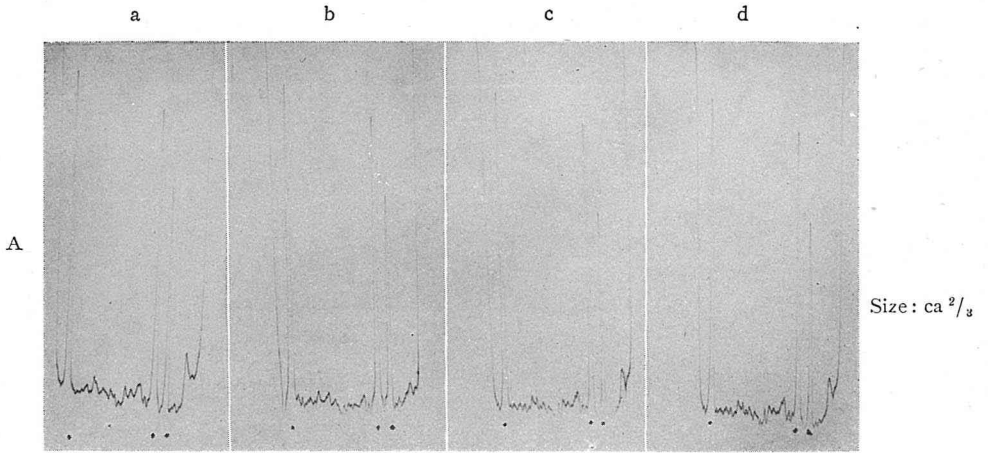
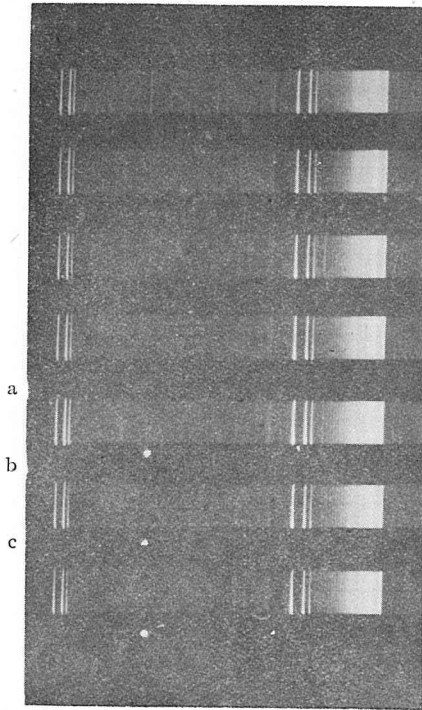
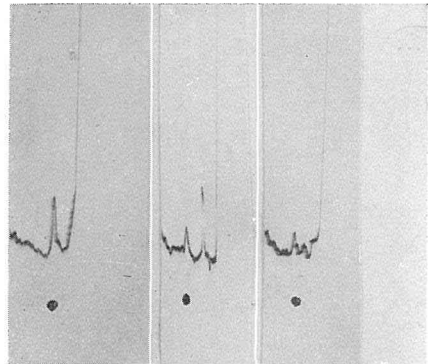


Plate III

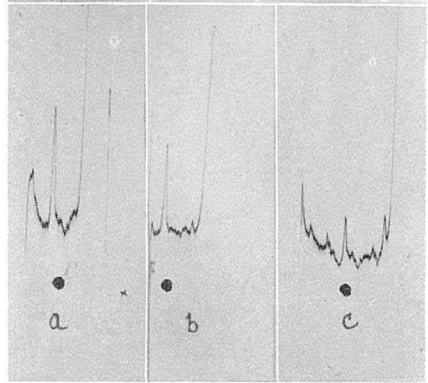
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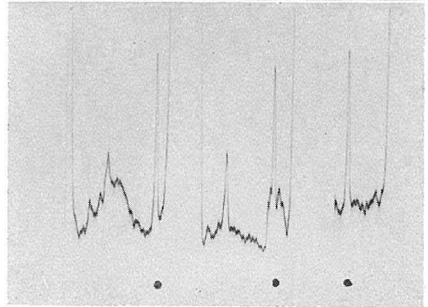
Ex. I.



Ex. II.



Ex. III.



Size: $\frac{9}{10}$