A Tracer Study on the Penetration of a Sample Solution into Carbon Electrode of Spectrographic Analysis

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Quantitative spectrographic analysis of non-ferrous metals is carried out by means of spark spectra. This method is normally satisfactory to obtain accurate results, but is less desirable when applied to samples of a high purity, since its sensitivity is rather low. Non-ferrous metals of a high purity are analysed through the solution-arc method, which consists in dissolving the sample in acid, making the solution up to a definite volume, impregnating it into a porous carbon electrode and using this in an arc discharge. This method is certainly very sensitive; it requires however, a very careful procedure in accordance with precise directions.

The present authors are of the opinion that the need for precision could be, at least partly, ascribed to the different nature of the carbon electrode. They intended therefore to examine the penetration process into a carbon electrode with the aid of tracer technique[1].

Radioactive Isotope. — Radioactive zinc-65 was used as indicator. Its β-activity (electron capture 97.5%, β^+ 2.5%) of a half life of 245 days is satisfactory for the present purpose; since its decay product is not radioactive, the measurement of activity directly indicates the relative amount of zinc. A solution was prepared from a solution of radioactive zinc chloride and pure lead nitrate, which contained 0.24 g. of lead nitrate and 0.11 mg. of zinc (carrier) in one cc., corresponding to 0.07% of zinc in lead. This content is slightly greater than the practical content of zinc in lead ingot, but a less concentrated solution could not maintain radioactivity strong enough to be measured. This solution was used throughout this work.

Procedure.—Several sorts of carbon electrode were examined as shown in Table I. Each capital letter A, B etc. corresponds to a product of a different manufacturer. The preliminary treatment of an electrode may affect the penetration of the sample solution; the various treatments are also shown in Table I. After the preliminary discharge, carbon electrodes were cooled to about 60°C and the sample solution was dripped from a measuring pipette so slowly that the second drop was not added until the first one had already been absorbed. Then they were dried in an air-bath and sections cut with a saw so that several fractions of carbon powder containing salt were obtained corresponding to the definite distance from the top of the elctrode. They were weighed in a steel dish and their radioactivity measured with a counter. Some of the electrodes are of so close a texture that it takes a long time for the solution to penetrate into them, whilst that of others is less so. About 30 mg. of the powder were used for each activity measurement. The influence of geometrical distribution of the sample powder in the dish was examined and not found to be significant.

Table I shows the results. Each frame corresponds to a fraction of the carbon powder, each figure showing the average count per 10 mg. of the powder. The count should be directly proportional for any one elctrode to the amount of zinc in the sample. The error of measurement was of the order of 10%.

Autoradiograph. — A carbon electrode, after being submitted to impregnation of the solution, is vertically divided into two pieces and put on to a piece of photographic film. Non-screen Eastman Kodak X-ray film was used, since it is quite sensitive, though coarse grained. They were set aside for six days and developed. The results coincide well with those in Table I.

Measurement of Density.—The apparent density (d) of the carbon electrodes was found from their size and weight. The real density (d_0) was measured with a pyknometer and benzene. The porosity (p) can be calculated from the following formula. $p=(d_0-d)/d_0$. They were measured at 15 ± 0.02°C and the results are tabulated in Table II. When an electrode is heated at a high temperature for a long time, the apparent density decreases and the real density increases, resulting in a higher porosity. (Electrodes of maker B do not do this, but the quality is not uniform even in one packet so that no account was taken of these results.)

Discussion

From Table I it can be seen that the zinc ion penetrates farther into a carbon electrode than expected, showing a marked maximum at a distance several millimeters from the top. The apparent hardness of carbon appears to bear little relation to the extent of penetration, presumably because the apparent hardness depends

1) The authors could not find any reference about such a consideration nor any such kind of application of radioactive tracers.

TABLE I

Carbon	A	B	B	C	C	A	B	C	D	A	A
Diameter	5.2	5.4	5.4	8.1	8.1	5.3	5.7	8.3	7.9	5.3	5.3
Preliminary Discharge (sec.)	55 V 6 A 40	55 V 5 A 30	55 V 8 A 60	55 V 6 A 50	55 V 6 A 50	none	none	none	none	55 V 6 A 30	55 V 6 A 30
Solution Added, ml.	0.2	0.2	0.2	0.5	0.2	ca. 0.02	ca. 0.02	ca. 0.01	ca. 0.01	0.15	0.15
Distance from the top of the electrode, mm. 2	377	277	252	620	357	168	125	276	120	58	68
				190	314	118		0	8		
4	205	172	243	152				0	0		113
				166	220		74			70	
6	187	153	231	231		52			0		
				558	167						127
8	505		184	405		6				69	
				148	200		14				
10	228	185	118	90							220
				132	128					123	
12	87	201	128								172
				290	6					138	
14		175	187								
										89	198
16		211									
											120
18				125						44	
		143									
20											
			156								
22											
		5									
24											
26											
Note						Without preliminary discharge, the solution soaks very slowly and with difficulty.				Kerosene, 0.07 ml.	

mainly on the nature of the binding material and not on the nature of carbon itself. The penetration should, on the contrary, be dependent on the nature of carbon, the conditions of preliminary discharge and the way the solution is put on to the electrode. Since the zinc ion extends in front of the lead ion in a chromatographic series, the formation of a maximum point of zinc content can be correlated to the chromatographic effect of capillary texture of the carbon, although the way of addition of the solution is certainly too complicated for the comparison to be made. As a matter of fact, the heterogeneous distribution of the zinc ion should be considered in connection with the relative ratio of zinc to lead, nevertheless this fact ought to be taken into account in the practice of spectrographic analysis.

Another line of argument may be introduced from the data of porosity. It should be noticed that the values of d, d_0 and p are independent of the apparent hardness

TABLE II

MEASUREMENT OF DENSITY AND POROSITY

Manufacturer	Preliminary Discharge	d	d_0	p
A	Without	1.65	2.20	0.25
A	6A, 40 sec.	1.47	2.26	0.35
B	Without	1.43	1.89	0.24
B	5A, 30 sec.	1.51	1.65	0.08
B	6A, 40 sec.	1.42	1.70	0.16
B	8A, 60 sec.	1.40	1.84	0.24
C	Without	1.28	1.55	0.17
C	6A, 50 sec.	1.27	2.01	0.37
D	Without	1.38	1.64	0.16
D	6A, 50 sec.	1.29	1.89	0.32

of the carbon, and so is the extent of penetration. This fact can be easily seen from the comparison of Tables I and II. The depth of penetration appears to increase with porosity, at least for the electrode of the same manufacturer, whilst the time taken for penetration depends on the apparent hardness of the carbon.

The authors also examined the effects of some liquids on the penetration, including liquid paraffine and other organic solvents, which may affect the surface state of carbon, only to find that these have very little effect. These liquids were dripped on to the electrode prior to the addition of the sample solution.

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