[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. No. 9.]

THE ELECTROLYTIC ESTIMATION OF MERCURY.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

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THE precipitation of this metal from a cyanide solution[1] has given quantitative results, which render the electrolytic procedure decidedly more advantageous to the analyst than the usual gravimetric course. However, conditions sometimes occur when even the preceding rapid method is made time-consuming. Thus in the working with mercury sulphide it would be necessary to first dissolve the substance in acids and remove the excess of the latter before advancing to the electrolytic decomposition of the resulting salt. Conscious of this fact and that mercury sulphide, as cinnabar, is a natural product, which is quite often offered for analysis, we took occasion to review the method first proposed by Smith,[2] and subsequently confirmed by Vortmann,[3] *viz.*, the electrolytic deposition of mercury from its solution in an alkaline sulphide. The chief point to be ascertained was whether the time factor could be reduced. This had been accomplished with the cyanide solution by simply applying a gentle heat, thereby precipitating two-tenths gram of metal in about two hours. Another point which we wished to definitely establish was the exact current density for a given electrode surface. To this end several determinations were made, using a mercuric chloride solution of known mercury content:

Mercury present as chloride. gram.	Mercury found. gram.	N. D. of current in amperes for 100 sq. cm. surface.	Dilution of solution. cc.	Time.	Temp.
0.1913	0.1917	0.13	125	3 hrs.	65°
"	0.1916	"	"	"	"
"	0.1908	"	"	"	"

In each case twenty cc. of sodium sulphide of specific gravity 1.22 were present.

These results indicate that mercury can be determined as rapidly and as accurately in this way as when working with a cyanide solution.

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[1] This Journal, 17, 612.

[2] *J. Franklin Inst.*, 1891, and *J. Anal. Chem.*, 5, 202.

[3] *Ber. d. chem. Ges.*, 24, 2749.

We next determined the mercury in a sample of cinnabar by distilling the latter with lime, collecting and weighing the metal as directed in Fresenius' Quantitative Analysis, Am. Ed., p. 306.

1. 0.9590 gram of mineral gave 0.8194 gram of metal, or 85.44 per cent.

2. 0.8586 gram of mineral gave 0.7325 gram of mercury, or 85.31 per cent.

Portions of the same mineral were weighed out in platinum dishes and after solution in twenty to twenty-five cc. of sodium sulphide of specific gravity previously mentioned, were diluted with water to 125 cc. and electrolyzed at a temperature of 70°, with a current of $N.D_{100} = 0.12$ ampere. The period of time allowed for the precipitations never exceeded three hours. The results were :

	Cinnabar. gram.	Mercury. gram.	Percentage.
1	0.2167	0.1850	85.37
2	0.2074	0.1769	85.29
3	0.2432	0.2077	85.40

We would observe that during the electrolytic decomposition the platinum dishes should be carefully covered to prevent evaporation, thereby exposing a rim of metal, which if not in part volatilized, would yet be changed to mercury sulphide. The latter is indicated by a dark-colored film. With a little attention there should be no question as to the final outcome of any determination made in this way. We regard the method as entirely satisfactory. The short time required for a determination, as outlined above, will recommend it in our judgment to analysts generally.

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THE PRECIPITATION OF PHOSPHOMOLYBDATE IN STEEL ANALYSIS.

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IN a recent paper[1] Messrs. Blair and Whitfield give a new formula for the preparation of molybdate solution, which is a great improvement on the old one, as by its use the separation of

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[1] This Journal, 17, 747.