

## A SIMPLE AND RAPID ELECTROMETRIC DETERMINATION OF ALKALOIDS WITHOUT THE USE OF HYDROGEN ELECTRODE.

BY STEPHEN POPOFF AND M. J. MCHENRY.

The quantitative determination of alkaloids has been accomplished by using physico-chemical methods with varying degree of success. McGill<sup>1,2</sup> and his co-workers have used the hydrogen electrode, Kolthoff,<sup>3</sup> Treadwell and Janett,<sup>4</sup> Dutoit and Meyer-Levy<sup>5</sup> and others have used conductometric methods, Wagner and McGill<sup>6</sup> employ the quinhydrone electrode while Krantz, Jr.<sup>7</sup> makes use of the potentiometer in the quantitative analysis of alkaloidal solutions. Colorimetric methods have been used but, as pointed out by McGill, the end-point, at least in some cases, is not sharp and definite.

Recent advances along the use of physico-chemical methods in analytical chemistry have shown the enormous and very useful applications of the electrometric methods. In connection with the analysis of alkaloids, McGill<sup>1</sup> states: "Electrometric methods afford opportunity of avoiding the long drawn out purification and the necessity of choosing the proper indicator as well as the correct shade of color for the end-point." Kolthoff is quoted in the abstract of discussion of Krantz's<sup>7</sup> paper as saying that the hydrogen electrode reduces the alkaloids and that there could not be equilibrium where there is reduction. This may account for the difference of results obtained by McGill, comparing the electrometric with the U. S. P. method. It is very difficult to prepare most alkaloids of 100% purity, and it is still more difficult to draw any conclusion as to whether or not the colorimetric or the electrometric methods give more nearly correct results.

In order to avoid the use of the hydrogen electrode in reactions in which reduction takes place, various electrodes have been devised. Haber and Klemenslowics<sup>8</sup> and, recently, A. L. Steiger<sup>9</sup> have used glass electrode in place of the hydrogen electrode while the quinhydrone has been employed for the determination of  $p_H$  in acid solution (the quinhydrone method being useless in alkaline solution). The theory of the above electrodes has been well developed but their use is limited and in case of the glass electrode, equilibrium is obtained with difficulty. Recently P. van der Meulen and Wilcoxon<sup>10</sup> used a plain platinum wire in place of the hydrogen electrode in titration of acidimetry and alkalimetry. Heretofore, the hydrogen electrode has been used only in titrations involving acids, bases and salts, while the platinum wire is used only in reactions involving oxidation and reduction. In this connection, it is well to state the use of the oxygen electrode

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<sup>1</sup> McGill and Faulkner, *Jour. A. Ph. A.*, 11, 1003-7 (1922).

<sup>2</sup> McGill and Wagener, *Ibid.*, 12, 855-6 (1923).

<sup>3</sup> Kolthoff, *Z. anorg. allgem. Chem.*, 112, 196-208 (1920).

<sup>4</sup> Treadwell and Janett, *Helv. Chim. Acta*, 6, 734-43 (1923).

<sup>5</sup> Dutoit and Meyer-Levy, *Jour. Chim. Phys.*, 14, 355-60 (1916).

<sup>6</sup> Wagner and McGill, *Jour. A. Ph. A.*, 14, 288-94 (1925).

<sup>7</sup> Krantz, *Ibid.*, 14, 294-99 (1925).

<sup>8</sup> Haber and Klemenslowics, *Z. Physik. Chem.*, Vol. 56, p. 385.

<sup>9</sup> A. L. Steiger, *Z. Elektrochem.*, 30, 259-63 (1924).

<sup>10</sup> P. van der Meulen and Wilcoxon, *Ind. Eng. Chem.*, 15, 62-3 (1923).

by Furman<sup>1</sup> and others, especially in the presence of oxidizing agents which will be reduced by the hydrogen electrode. However, the oxygen electrode comes to equilibrium rather slowly and of necessity its use is limited.

This method of van der Meulen has been studied extensively and in another article we shall point out its numerous applications in some important theoretical and practical problems. We shall make no attempt at this time to develop the theory of the use of plain platinum wire in titrations involving acidimetry and alkalimetry; neither shall we claim that voltage readings were obtained after complete equilibrium had been reached, as this is hardly necessary. Numerous titrations involving acids and bases have shown that it is not necessary to wait more than one-half minute before taking voltage readings. The end-point is determined by a process of interpolation, using potential readings and cubic centimeters of solutions obtained immediately preceding and following the end-point. The following data will illustrate the method used:

Cc. of reagent.	E.	dE.
39.86	0.295	
39.89	0.283	0.012
39.92	0.246	0.037
39.95	0.204	0.042
39.98	0.194	0.010

The end-point is between 39.92 and 39.95 but since dE at 39.92 is 0.037, while at 39.98 it is 0.010, the end-point is nearer 39.92 than 39.95 and 39.93 is taken at the true end-point. If dE at 39.92 and 39.98 were reversed, the end-point would have been taken at 39.94. It is possible to obtain results which check to 0.05% by this method and the end-point, when titrating 0.1N HCl and NaOH coincides with that with phenolphthalein.

#### EXPERIMENTAL PROCEDURE.

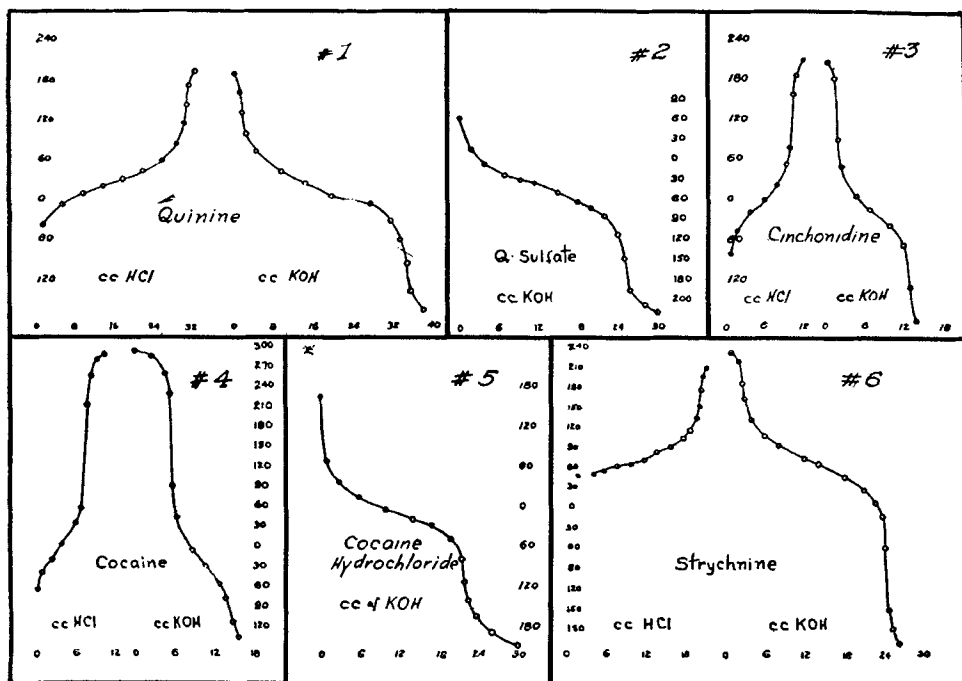
*Apparatus.*—Student potentiometer, lamp and scale galvanometer, Weston standard cell, two dry cells, and three-dial resistance box were set up in the usual way.<sup>2</sup> The saturated type of calomel and a plain platinum wire served as the electrodes. The latter was cleaned after every titration by dipping it into cleaning mixture (dichromate) for a few minutes and washing it thoroughly. The titration flask consisted of a 300-cc. tall beaker which was ground to fit tightly against a glass plate. The latter had six openings, one for the stirrer (electrically driven), the second for the calomel capillary tubing, the third for a T tube into which the platinum wire was fastened and which was used for passing CO<sub>2</sub> free air, the fourth and fifth openings were for two burettes, while the sixth opening was for washing down the sides of the beaker.

*Preparation of Material.*—Potassium hydroxide solution free from carbonates was prepared by determining the carbonate content, adding slight excess of barium hydroxide and then removing the excess barium by potassium sulphate. The potassium hydroxide was standardized against benzoic acid obtained from the Bureau of Standards. The hydrochloric acid was standardized against

<sup>1</sup> Furman, *J. Amer. Chem. Soc.*, 44, 2685-97 (1922); *Trans. Am. Electrochem. Soc.*, 43, 79-88 (1923).

<sup>2</sup> Popoff, *Quantitative Analysis*, P. Blakiston's & Son, 1924, p. 300.

the potassium hydroxide, using phenolphthalein as the indicator. The ordinary distilled water was redistilled from alkaline permanganate and kept in a paraffined bottle suitably protected from the CO<sub>2</sub> of the air. A good grade of alcohol was used and its acidity was previously determined by using phenolphthalein and standard KOH solution. The alkaloid, or the alkaloidal salt, was dissolved either in alcohol or in a mixture of alcohol and water, according to their solubilities. Carbon dioxide was expelled from the beaker and the alkaloids titrated either with 0.1 N HCl solution or with KOH solution, depending on whether alkaloids or alkaloidal salts were titrated. In case of the alkaloids, excess of acid was first added, then potassium hydroxide, until two breaks were obtained. Altogether there were three breaks, the first representing the conversion of alkaloid



The electrometric titration curves of alkaloids and their salts, using plain platinum wire in place of hydrogen electrode.

to the hydrochloride, the second representing the excess of acid added, and the third, the conversion of the salt into the free alkaloid.

*Results and Their Interpretation.*—Comparatively large breaks were obtained in titrating the alkaloids or their hydrochlorides or sulphates. At this time no special attempt has been made to obtain quantitative results except in some cases. In these cases, values obtained checked very closely with the theoretical, if the latter can be ascertained with any degree of certainty. In general, the results checked against themselves.

Alkaloid.	Cc. calculated.	Cc. found.
Strychnine	20.37	20.42
Cocaine HCl	21.82	21.72

Alkaloid.	Cc. calculated.	Cc. found.
Quinine Sulphate*	21.82	25.05
Quinine Sulphate*	21.82	24.99
Cinchonidine	10.18	10.10

\* The calculations were made on the hydrated form. Upon heating to 115° the material lost in weight only about 3%, showing that we were not dealing with the hydrated form.

Curves are given for the following: Quinine, quinine sulphate, cocaine, cocaine hydrochloride, cinchonidine and strychnine. The curves were plotted by using cc. of acid or base as abscissae and millivolts as ordinates. Potential readings were taken about one-half minute after the addition of either acid or base.

This work is being continued using purer materials.

#### SUMMARY.

It is possible to titrate electrometrically alkaloids or their salts using a plain platinum wire. Two breaks are obtained when an excess of acid is added to the alkaloid, the first representing the excess of acid, the second the conversion of the salt to the alkaloid. The method is simpler and more rapid than that using either the hydrogen electrode or the quinhydrone electrode.

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## THE ACTION OF RED PHOSPHORUS ON IODINE IN ORGANIC SOLVENTS.

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Gordon and Krantz in a paper entitled, "Adsorption of Iodine from Organic Solvents by Red Phosphorus and Charcoal"<sup>1</sup> set forth experimental results obtained by them for the adsorption of iodine from various organic solvents, using charcoal and red phosphorus as adsorbing agents. They have drawn various deductions from their own work and the work of others among which we note "when adsorption of iodine by red phosphorus is considered the absence of moisture is essential for correct results."

Adsorption isotherms are given by the authors using iodine and red phosphorus in carbon bisulphide and xylene at 30° C. and 45° C., and 30° C. and 50° C., respectively. Numerical data are given for the removal of iodine from solution by red phosphorus using 0.3, 0.2 and 0.1 Gm. of iodine and 1 Gm. dried red phosphorus in 50 cc. of toluene, xylene, chloroform, benzene, carbon tetrachloride and carbon bisulphide. The amount of adsorption is found to be quite high in all of the cases.

The present writers have investigated the action which takes place when red phosphorus is brought into contact with iodine dissolved in carbon bisulphide. The results obtained from these investigations lead to the conclusion that adsorption has little or nothing to do with the removal of the free iodine from that solvent when the solid substance used is red phosphorus.

When dry red phosphorus (as used by Gordon and Krantz) is added to a solution of iodine in purified carbon bisulphide at 22° C. under conditions which exclude

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<sup>1</sup> Gordon and Krantz, *THIS JOURNAL*, Vol. 13, No. 7, p. 609-12.