[Contribution from the Chemical Laboratory of the College of Liberal Arts,
Northwestern University]

# A METHOD OF DETERMINING THE ARSENIC CONTENT OF ORGANIC ARSENICALS

By F. E. Cislak[1] and Cliff S. Hamilton

Received March 7, 1929 Published February 6, 1930

Numerous methods have been proposed for the estimation of the arsenic content of organic compounds containing arsenic. Bunsen[2] estimated the arsenic content by difference; Dumas[3] determined the increase in weight of the combustion tube after the elementary analysis of the organic arsenical and ascribed this increase to the presence of arsenious oxide. In other procedures[4] the compound was oxidized by fusion and the arsenic weighed as magnesium pyroarsenate. Monthulé[5] destroyed the organic matter present by nitric acid. The work of F. A. Norton and A. E. Koch[6] gave rise to numerous volumetric methods. Among the most widely known of these methods may be mentioned those of Lehmann,[7] Ewins[8] and Robertson.[9]

In all the above volumetric methods a standard iodine solution is used as the titrating solution with starch as an indicator. Rather exacting conditions are required in order to get reliable and reproducible results by these methods.[10]

A means of determining arsenic in inorganic compounds by the potentiometric method has been proposed by Zintl and Wattenberg.[11] The authors adapted this method to the determination of the arsenic content of organic compounds. The method is described below.

## Details of Method

A saturated calomel electrode was used as the cathode, and a piece of platinum

---

[1] Research Fellow under a grant from Parke, Davis and Company. This article is an abstract of a portion of a thesis submitted to the Graduate School of Northwestern University by F. E. Cislak in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bunsen, *Ann.*, **24**, 278 (1837).

[3] Dumas, *ibid.*, **27**, 149 (1838).

[4] La Coste and Michaelis, *ibid.*, **201**, 224 (1889); Pringsheim, *Am. Chem. J.*, **31**, 386 (1904).

[5] Monthulé, *Ann. chim. anal.*, **9**, 308 (1904).

[6] Norton and Koch, This Journal, **27**, 1249 (1905).

[7] Lehmann, *Apoth. Ztg.*, **27**, 545 (1912).

[8] Ewins, *J. Chem. Soc.*, **109**, 1355 (1916).

[9] Robertson, This Journal, **43**, 182 (1921).

[10] Since the completion of the work described in this article a method of estimating the arsenic content of organic compounds with the aid of a standard bromate solution and the use of suitable indicators has been published by Schulek and Villecz, *Z. anal. Chem.*, **76**, 81 (1929).

[11] Zintl and Wattenberg, *Ber.*, **56**, 472 (1923).

wire sealed into a T-tube served as the anode; these electrodes were connected directly to a Leeds and Northrup portable potentiometer. A slow stream of carbon dioxide was passed through the anode above (not into) the solution. A mechanical stirrer was provided. An approximately 0.05 *N* solution of potassium bromate was used as the titrating solution.

Procedure.—Between fifteen hundredths and two-tenths of a gram of the substance was weighed out and introduced into a Kjeldahl flask of 300-cc. capacity. Twenty grams of potassium sulfate, 0.2 to 0.3 g. of starch, and 20 cc. of concentrated sulfuric acid were then added to the sample in the flask and the mixture was warmed gently over a small flame for about thirty minutes; then the size of the flame was increased very slightly and the heating continued for another thirty minutes, when the flame was increased to a fairly good size and the digestion continued until the solution became clear and colorless.[12] The flask was removed as soon as the solution became colorless, allowed to cool to about 80° and diluted with approximately 70 cc. of distilled water. The solution was transferred quantitatively into a beaker of 600-cc. capacity and to this solution 30 cc. of concentrated sulfuric acid was added and sufficient water to make the total volume of the solution about 400 cc. The solution was then ready for titration.

The arm of the calomel half-cell was rinsed with distilled water and then about 10 cc. of the potassium chloride solution from the reservoir was run through the cell. The platinum wire was also rinsed with water. The two electrodes were then immersed in the solution which was to be titrated and connected to the potentiometer. A slow stream of carbon dioxide was turned on and the stirrer started.

The resistance of the potentiometer was adjusted so that there was no deflection of the galvanometer when this instrument was thrown into the circuit. The bromate solution was then added slowly from a buret. At this stage of the titration the solution was added at the rate of about 4 cc. per minute.[13] After the addition of each cubic centimeter of the standard solution the galvanometer was thrown into the circuit and the deflection of the galvanometer needle observed. The deflection, at this point, was so slight that by merely increasing the resistance a very small amount, corresponding to one to two hundredths of a volt, the null point was again reached. When the end-point was only about 2 cc. away,[14] the rate of addition was slowed down to such an extent that it was possible to observe the deflection of the galvanometer needle after the addition of each drop. When the end-point was reached, one drop of the bromate solution caused a rather complete deflection of the galvanometer needle. This single drop threw the needle to one side so strongly that resistance

---

[12] The heating should not be prolonged after the solution has cleared as there is a tendency for the hot sulfuric acid, in the absence of any other reducing matter, to oxidize the trivalent arsenic.

[13] The addition of the bromate solution should not be too rapid as the reaction is not extremely fast in reaching equilibrium even in the presence of so high an acid concentration.

[14] In this method of determining the end-point of the reaction, there is no indication of an approach to it. Hence, in order not to go past the end-point, one must either add the reagent very slowly during the entire course of the titration or else have an idea as to the amount of reagent the given sample will require.

corresponding to at least 0.200–0.400 volt was necessary to balance the circuit.[15]

## Experimental

A large number of organic arsenicals was analyzed by the method herein described; the results of a few of these analyses are given in Table I.

TABLE I

TESTS OF THE METHOD

| Compound | Arsenic trioxide | | Arsanilic acid | | *n*-Butylarsonic acid | | Diphenylamine-*o*-arsonic acid | |
|---|---|---|---|---|---|---|---|---|
| Sample, g. | 0.1002 | 0.1013 | 0.2022 | 0.2009 | 0.1986 | 0.1987 | 0.2095 | 0.2199 |
| As found, % | 75.76 | 75.78 | 34.59 | 34.58 | 41.26 | 41.24 | 25.62 | 25.54 |
| As calcd., % | 75.75 | 75.75 | 34.56 | 34.56 | 41.21 | 41.21 | 25.57 | 25.57 |
| Deviation, % | +0.01 | +0.03 | +0.03 | +0.02 | +0.05 | +0.03 | +0.05 | −0.03 |

## Summary

The arsenic content of organic compounds can be determined readily and accurately by digesting the compound with hot sulfuric acid in the presence of potassium acid sulfate, diluting the solution thus obtained and titrating electrometrically with potassium bromate.

EVANSTON, ILLINOIS

---

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

# THE CATALYTIC "COUPLING" OF MANGANESE DIOXIDE WITH PHOSPHORIC OR SULFURIC ACID AS AN OXIDIZING AGENT. THE EFFECT OF ACIDITY ON THE OXIDATION OF BUTYRIC ACID WITH HYDROGEN PEROXIDE

BY EDGAR J. WITZEMANN

RECEIVED MAY 13, 1929 PUBLISHED FEBRUARY 6, 1930

The results given in this paper constitute a part of a study of the influence of a few chemical variables upon the oxidation of butyric acid.[1] This report concerns the influence of the amount and nature of the acids present on the oxidation of butyric acid by hydrogen peroxide.

**The Influence of Phosphoric Acid.**—Since previous work had brought out the catalytic properties of dialkali phosphate in the oxidation of butyric acid, attention was first given to phosphoric acid, in studying the effect of acidity upon this oxidation, especially in view of the fact that it is possible that the catalytic effects of dialkali phosphates may be due to the intermediate formation of a perphosphate.

---

[15] When this 0.200–0.400 volt increase in e.m.f. caused by a single drop of the bromate solution is compared to the increase of 0.01–0.03 volt caused by one cubic centimeter of the solution, it is obvious that the end-point is extremely easy to recognize.

[1] (a) Witzemann, *J. Biol. Chem.*, **35**, 83 (1918); **49**, 123 (1921); (b) THIS JOURNAL, **48**, 202, 208, 211 (1926); **49**, 987 (1927).