e. m. f. obtained with different specimens of lead cast in sticks, with electrolytically deposited lead and with amalgams, were practically identical.

(2) The normal electrode potential of lead was calculated to be *0.4121* volt referred to the normal calomel electrode and *0.1293* against the normal hydrogen electrode.

(3) The values of the e. m. f. of cells containing electrodes which had been immersed for varying periods of time in Heller's solution were found to be uniformly higher than the values obtained with cells containing electrodes which had not been subjected to this treatment.

(4) The heat of the reaction

$$Pb + Hg_2Cl_2 = PbCl_2 + 2Hg,$$

was calculated and found to be 21840 cal., whence the heat of formation of lead chloride was computed to be 84440 cal.

(5) The heat of reaction U_o, and the maximum work $A_{234°}$ were calculated by means of the Nernst-Lindemann equation and the computed value of the e. m. f. at 234° A. was found to be in close agreement with the observed value.

STAMFORD, CONN.

NOTES.

The Oxidation of Sulfides with Potassium Iodate.—In a previous article[1] it was shown that in the oxidation of sulfides with potassium iodate, the amount of sulfur oxidized to sulfuric acid depended on the concentration of hydrochloric acid, and that with an amount of iodate nearly equivalent to the sulfide, the greatest amount of oxidation obtainable with any strength of acid was represented by the equation

$$3MS + 3KIO_3 + 12HCl \rightleftarrows 3MCl_2 + 2S + 3ICl + 5H_2O.$$

We find that if a *large excess* of iodate be used the sulfur may be completely oxidized, whatever the strength of hydrochloric acid provided it be strong enough to prevent the hydrolysis of ICl. This is evidenced by the following analyses:

Freshly prepared hydrogen sulfide water was measured with a 25 cc. pipet into flasks kept at 0°. Some of the samples were titrated with $N/10$ iodine solution and found to contain 0.00154 g. hydrogen sulfide per cc. 100 cc. of 0.05 molar potassium iodate and the desired amount of hydrochloric acid were added to the other flasks and the excess of iodate was titrated with an equivalent iodide solution. The results were as follows

Normality hydrochloric acid.....	6.40		4.00		3.00	
Iodate used.....	45.32	45.30	45.31	45.28	45.30	45.32

Theory for complete oxidation according to the equation

$$H_2S + 2KIO_3 + 4HCl \rightleftarrows 2ICl + H_2SO_4 + 2H_2O + 2KCl$$

is 45.30 cc.

[1] THIS JOURNAL, 37, 1134 (1915).

A similar scheme was tried with lead sulfide precipitated from 25 cc. of 0.05 molar lead sulfate in ammonium acetate. 100 cc. of iodate were used as before and the lead sulfide after filtering on asbestos and washing was introduced into the reaction mixture. Theory for complete oxidation of the sulfur requires 50 cc. iodate.

The results were as follows:

Normality HCl	6.50		3.00	
Iodate used	50.02	50.05	50.03	50.05

My thanks are due to Prof. G. S. Forbes for suggestions during the course of this work.

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An Accurate Method for Taking "Aliquots" in Volumetric Analysis.—A method for accurately taking "aliquot" portions of a pure substance for use in the standardization of certain volumetric solutions has been recently proposed by C. F. Miller.[1] About five times as much of the standard substance as is required for each titration is weighed out accurately and dissolved in a volume of water slightly exceeding five times the capacity of the pipet to be used. Five equal portions of the solution are then withdrawn, each portion being delivered from the pipet in exactly the same manner. The remainder of the solution together with the rinsings from the pipet, is evaporated in a tared platinum dish, dried, and weighed. The weight of material used for each titration can then be calculated. The method is applicable only with substances which are soluble and which separate again in weighable form on evaporation of the solution. If proper precautions in regard to drying the residue to constant weight are observed, as many weighings and more time are required than with the usual procedure of weighing out separate samples—with no increase in accuracy.

As a matter of fact, occasions where an advantage is to be gained in the standardization of volumetric solutions by a procedure of dividing the initial samples of the pure substances, are infrequent. There are, however, numerous instances in volumetric procedure in which it is desirable to weigh out more of a sample for analysis than is convenient for a single titration. The usual procedure in such a case is to take aliquot portions of the solution of the sample, or of a filtrate or precipitate obtained therefrom, with the use of graduated flasks and pipets. Even if these have been carefully calibrated, this method is not entirely satisfactory because of temperature fluctuations and unavoidable errors in manipulation.

The present writer proposes a procedure, suggested by the one described above, which, in addition to being simpler, more rapid, and more accurate

[1] THIS JOURNAL, 39, 2388 (1917).

than Miller's method, can be used in either standardization or analysis, with substances which are soluble in any manner and which do not necessarily separate in weighable form from the solution on evaporation. The sample is weighed out, dissolved in water or suitable reagent, and equal portions of the solution are withdrawn in the manner outlined above; the equal portions and also the remainder, including the rinsings from the pipet, are then titrated. The result may be calculated as follows: If W is the weight of the original sample, n the number of equal portions taken,[1] w the weight of sample in each of these portions, a the average number of cc. required for the titration of each portion, and r the number of cc. required for the remainder, then

$$nw + rw/a = W, \text{ or } w = aW/(an + r).$$

In standardization procedure, letting s represent the weight of the standard substance required for 1 cc. of N solution, we have for the normality factor of the solution

$$N.\,F. = w/sa = W/s(an + r);$$

or in analysis, if x is the weight of the substance X required for 1 cc. of N solution, we should have

$$\% X = 100\ (N.\,F.)\ xa/w = 100\ (N.\,F.)\ (an + r)\ x/W.$$

It is evident that the result in either standardization or analysis is the average of the titrations used in computing a, but since it depends entirely on the one initial weight W of substance taken, we have in reality only one carefully obtained value. To insure the discovery of a possible error in weighing or recording of weights, or variation in the sample, a duplicate series of titrations should be made with another weighed portion of the substance.

The use of the procedure described to replace in general the usual standardization or analytical procedure of weighing out separate samples, is by no means desirable. In instances of standardization, however, in which the weight required for a single titration is small and consequently the error in weighing may be relatively large, an increase in accuracy is obtained. In analysis when it is desired to take a larger sample of the material than is required for a single titration, the method makes possible the same or an even greater degree of accuracy without the use of calibrated flasks and pipets than is obtained with the usual procedure when carefully calibrated instruments are employed. Even when these are at hand, the extra titration involved in the procedure described (to determine r) is no more

[1] It is obvious that the weight of material and the volume of the solution can be varied to give any desired number of equal portions; also that the titration of only such a number of these portions need be completed as are required to determine a within the limits of error.

time-consuming than that of allowing the solution to come to a definite temperature and carefully diluting to an exact volume.

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Detection of Carbon Dioxide in the Analysis of Carbonates or Oxalates.—In testing for carbon dioxide in the qualitative analysis of carbonates or oxalates a convenient method of making use of the calcium or barium hydroxide reagent is indicated in Fig. 1. The novel feature of the method is the tube with a capillary point for containing the reagent. This capillary point must be fine enough to permit a small quantity of the reagent to remain in the tube without dripping, but not too fine to prevent the passage of gas bubbles upward through the liquid when gentle suction is applied to the open end of the tube. The introduction of the point of the capillary into any space where carbon dioxide may be and the simultaneous aspiration of a few bubbles of the gas in that space into the reagent in the tube will produce the familiar carbonate precipitate with great certainty and delicacy.

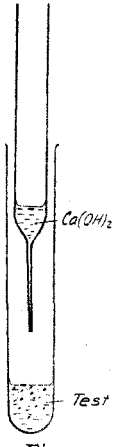

Fig. 1.

The device may be made roughly quantitative for minute quantities of carbonates or oxalates by a slight modification in which the reagent tube containing the lime or baryta water is sealed by means of "de Khotinsky" cement into another similar tube containing the test material as in Fig. 2. By careful aspiration, a drop of 30% sulfuric acid is drawn up into contact with the solid or solution to be tested, after which the aspiration may be continued until the generated carbon dioxide is absorbed by the reagent above. Where oxalates are in question the acid used must carry the necessary amount of permanganate. Parallel tests with similar tubes in which known amounts of a carbonate or oxalate have produced a graduated turbidity standard will, by comparison, give approximately correct quantitative readings with even very minute samples of materials.

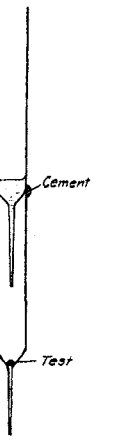

Fig. 2.

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The Extrapolation of Conductivity Data to Zero Concentration.—In a recent issue, Washburn[1] claims to have devised a *new* method for the evaluation of Λ_0, the equivalent conductivity of an electrolyte at zero concentration. Washburn starts with the assumption that "those in-

[1] THIS JOURNAL, 40, 128 (1918).

fluences which cause a strong electrolyte to deviate from the Mass-Action law at high concentrations *gradually and steadily* become smaller and smaller and finally disappear at infinite dilution." The new method then "consists simply in plotting values of K_E, the Mass-Action expression, against corresponding values of the concentration, employing different assumed values of Λ_0, and rejecting those values which cause the curve in dilute solutions to exhibit radical changes in direction."

Reference to the literature will show that this identical method, founded upon precisely the same assumption, was employed by the present writer six years ago,[1] in the determination of the velocity of the hydrogen ion.

Further and extended comment upon Washburn's articles must be postponed until the writer is free to return to pure scientific work.

JAMES KENDALL.

[CONTRIBUTION FROM THE HAHNEMANN MEDICAL COLLEGE AND HOSPITAL OF CHICAGO.]

ON THE DIGESTIBILITY OF BREAD.

III. ERYTHRODEXTRIN IN STARCH HYDROLYSIS.

BY J. C. BLAKE.

Received December 22, 1917.

It was shown in the second paper of this series[2] that amylolytic activity may be followed quantitatively with great facility by the digestion of erythrodextrin to the achromic point. Efforts made to obtain pure erythrodextrin, partly for the purpose of standardizing amylolytic agents and partly for clinical use in this connection, led to some new discontinuous hydrolyses of starch and to some new methods of estimating the relative concentrations of some of its decomposition products. It is believed that as a consequence of this work pure erythrodextrin will soon be prepared.

New Methods of Analysis.

The relative concentrations of 4 of the decomposition products present in boiled starch partially hydrolyzed with dil. hydrochloric acid were estimated by reading the colorations given with iodine water of different concentrations against Lovibond color glasses by means of a Duboscq colorimeter. The smallest amount of iodine gives a yellow color, thought to be due to protein.[3] Further addition of iodine gives an orange color, then a red or purple, the red color being due to erythramylum.[4] Further

[1] *J. Chem. Soc.*, **101**, 1279 and 1291 (1912).

[2] THIS JOURNAL, **39**, 315 (1917).

[3] Blake, THIS JOURNAL, **38**, 1247 (1916). It is well known that protein gives a yellow color with iodine, especially well seen with the gluten of bread.

[4] This name, given to this substance by Brücke at the time he named the dextrins (*Ber. Wien. Akad.*, **65**, 126 (1872)), from which he clearly distinguished it, has preference over the name rose-amylose proposed by Day ("Digestibility of Starch," etc., University of Chicago Press, 1908, pp. 37, 41). The name cellulose originally given to it by C. Nägeli ("Die Stärkekörner," Zurich, **1858**; *Ber. Akad. München*, **1862**, p. 281) is, of