ARSENIOUS OXIDE AS AN ALKALIMETRIC STANDARD.

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The fact that arsenic acid can be estimated volumetrically with an exceedingly sharp end point[1] suggested the possibility of the employment of this acid for purposes of standardization in alkalimetry. It is well known that arsenious oxide is a most desirable starting material in oxidimetry, and that the arsenious acid-iodine titration is one of the most accurate of the processes of volumetric analysis.[2] It will be shown below that arsenious oxide can be converted quantitatively into arsenic acid with comparative ease. This makes it possible to employ the same substance as a primary standard both in alkalimetry and in oxidimetry. A suitable procedure has been worked out for the standardization of an alkali solution starting from arsenious oxide, and the titer so found has been compared with that found for the same solution using three other methods of standardization of known accuracy.

Some Characteristics of Arsenious Oxide Desirable in a Primary Standard.—Arsenious oxide may be purchased commercially at a low price already in a high state of purity. It may readily be purified further both by recrystallization, if necessary, and by sublimation. The material used in our work was merely sublimed once, involving an astonishingly small amount of labor in view of the accuracy of the results obtained. White arsenic is not a hydrated substance, and can readily be dried by heating—the vapor pressure of the octahedral variety being at 200° and 240°, respectively, 0.6 and 6.0 mm. of mercury, while its melting point is 251°.[3] The arsenic acid into which it is converted by oxidation is quickly and largely soluble[4] in water, and yields a colorless solution.

Synthesis of a Decinormal Solution of Arsenic Acid.—The manipulation is simple and does not require, for example, the transference of a precipitate; but close attention to details is well repaid in saving of time.

In our work, a good commercial quality[5] of arsenious oxide was purified by subliming once. To do this, a 6 × 1 in. test tube was drawn down to one-fourth of its bore at a point a couple of inches from the closed end, and the end pocket so formed was charged with white arsenic. The tube was clamped horizontally, suitably protected by asbestos paper above and set aside to heat over, but not in contact with, two lowered Bunsen flames. The sublimate was removed by cutting the tube at the constriction, dried by heating and bottled hot.

To prepare 500 cc. of 0.1 N solution, a quantity of about 2.47 g. of the

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[1] Menzies and Potter, This Journal, 34, 1452 (1912).

[2] Cf. Washburn, *Ibid.*, 30, 31 (1908).

[3] Welch and Duschak, Bur. Mines, *Tech. Paper*, 81 (1915).

[4] Menzies and Potter, *loc. cit.*

[5] This was the "Arsenious Acid of Tested Purity" of Eimer and Amend.

powder is weighed out accurately in a 75 cc. conical flask. This is then treated with 5 cc. of chloride-free concentrated nitric acid, followed by 5 cc. of water[1] and warmed, at first gently, then more boldly, loss by spattering being prevented by a truncated calcium chloride tube.[2] When solution is complete, the further addition from a pipet of 5 cc. of concentrated nitric acid serves to wash the calcium chloride tube, which is now removed, and is necessary, also, to ensure complete oxidation. The solution is then taken to dryness to expel nitric acid. This part of the treatment is vastly expedited by blowing cotton-filtered, ammonia-free, air from a small glass jet obliquely on the surface of the liquid so as to cause rotation of the flask contents. The blower jet is clamped so that its twisted nozzle is close to the liquid surface, while the flask itself is clamped a couple of inches above a heated concave empty sandbath tray and screened from draughts by a glass cylinder consisting of a bottomless beaker. It was found that a thermometer whose bulb was placed alongside the bottom of the flask could register a temperature of 180–200° without any symptoms of ebullition appearing in the flask.

The dry white residue obtained in this manner still contains nitric acid that is not removable by heating at 230° for many hours. This nitric acid, possibly in solid solution,[3] makes its presence evident not only by causing too high acidity but also by responding to the nitron test.[4] The application of this test showed that the nitric acid can be removed, for analytical purposes, by redissolving the residue in water and taking to dryness again twice. For this purpose, after the first evaporation to dryness with nitric acid, the flask is allowed to cool, the residue is covered with distilled water and the flask then reheated as before. The residue soon dissolves, and the air-current evaporates the water again in a few minutes. This treatment with water is repeated, and it only remains to dissolve the residue and to dilute to the required weight or volume of solution.

The Process of Titration.—This has been described and discussed elsewhere,[5] but may be again outlined for convenience. To a measured quantity of perhaps 30 or 40 cc. of the 0.1 N acid solution are added the phenolphthalein indicator and 3 or 4 cc. of saturated barium chloride solution —a quantity which is largely in excess of that required to form the permanent precipitate mentioned below. The alkali is then run in until the amorphous white precipitate formed locally becomes rather slow in redissolving, which occurs when about one-half of the required alkali has been added. At this stage the titration is interrupted and the vessel

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[1] The nitric acid is added first as it wets the powder more effectively than does water.

[2] Cf. Gooch and Browning, *Am. J. Sci.*, [3] **29**, 197.

[3] Cf. Menzies and Potter, *loc. cit.*

[4] Busch, *Ber.*, **38**, 861 (1905).

[5] See Menzies and Potter, *loc. cit.*

scratched beneath the surface of the clear liquid, if necessary, to induce the formation of the very characteristic lustrous silky crystalline precipitate of $BaHAsO_4$, with respect to which the solution is supersaturated. After stirring for a minute to remove this supersaturation, the titration is completed in the usual manner. Should the vessel in which the titration is performed have been used for this type of titration already and merely rinsed with water, then the minute crystals of $BaHAsO_4$ remaining on the walls serve to inoculate their supersaturated solution and thus obviate any necessity for scratching. The entire proceeding is perfectly simple if only it be understood by the operator.

Comparison of Titre of Alkali as Standardized by this and by Other Methods.—The analytical details are tedious, as is their narration, which may, therefore, be curtailed. Weight burets were employed throughout, and quantities of 30–40 g. of solution were used in the analyses. As indicator 1 cc. of 0.1% phenolphthalein was employed, and a 7% transformation aimed at.[1] In making the corrections to vacuum, the densities of arsenious oxide and of benzoic acid were taken as 3.6 and 1.1, respectively. Carbonate-free sodium hydroxide containing barium hydroxide was employed as alkali, and the solutions were kept free from carbonic acid.

(I) The titre of the alkali was determined against suitably dried[2] benzoic acid[3] by the method described by Morey.[4] The 0.1 *N* factor for the alkali found in five determinations was, 1.0037, 1.0037, 1.0040, 1.0045, 1.0041; average, 1.0040.

(II) Hydrochloric acid of known concentration was prepared by the distillation method of Hulett and Bonner.[5] The 0.1 *N* factor of this acid was thus, synthetically, 1.0028.

(III) The chloride in this acid was estimated gravimetrically, following as closely as possible the procedure of Morey[6] in order to obtain results comparable with his. The 0.1 *N* factor of the acid obtained in four estimations was, 1.0028, 1.0030, 1.0034, 0.0020; average, 1.0026.

The titre of the alkali was now determined against this acid. Using 1.0026 as factor for the acid, six titrations gave, as 0.1 *N* factor for the alkali, —1.0042, 1.0035, 1.0038, 1.0039, 1.0036, 1.0035; average, 1.0037. Using an acid factor of 1.0028, this average would become 1.0039.

(IV) Five different solutions of arsenic acid were synthesized by the method described, and of each of these two titrations were made against

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[1] Cf. A. A. Noyes, THIS JOURNAL, **32**, 857 (1910).

[2] This drying requires care. Cf. Weaver, *Ibid.*, **35**, 1309 (1913).

[3] Purchased from the Bureau of Standards.

[4] Morey, THIS JOURNAL, **34**, 1027 (1912). To obtain a satisfactory color change of the indicator, it was found necessary to distill the laboratory alcohol over lime.

[5] THIS JOURNAL, **31**, 390 (1909).

[6] *Loc. cit.*

the alkali, yielding the following figures for its 0.1 *N* factor: (1) 1.0039, 1.0045; (2) 1.0031, 1.0030; (3) 1.0037, 1.0033; (4) 1.0039, 1.0037; (5) 1.0035, 1.0033; average, 1.0036.

The results of standardizing the alkali by these various methods may be exhibited most clearly in tabular form:

Method.	0.1 *N* alkali factor.
I. Benzoic acid	1.0040
II. Hydrochloric acid, factor from constant boiling pressure	1.0039
III. Hydrochloric acid, factor from AgCl determination	1.0037
IV. Arsenic acid	1.0036

Summary.

It has been pointed out that arsenious oxide is a desirable substance for use as a primary standard in volumetric analysis; and it has been shown that it may be employed, without too complicated manipulation, for this purpose in alkalimetry.

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COAGULATION OF ARSENIOUS SULFIDE SOL BY ELECTROLYTES.

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The coagulation of arsenious sulphide sol by electrolytes has been studied by a number of investigators,[1] who observed certain peculiarities which led the present writer to undertake a study of the coagulation phenomenon in detail.

The sols examined were prepared in the way given by Linder and Picton; the water used was obtained by the method described by Jones and Mackay.[2] Two sols were prepared, one containing 32.9 (No. I), the other (No. IV) a very fine one containing 3.54 millimols As_2S_3 per liter; Nos. II and III were made by diluting No. I four times and twenty times, respectively. Series of parallel experiments were made, in which equal depths of liquid contained in similar test tubes were observed and compared; very slight changes in the sol can be detected if comparison is made between the sample under observation and a blank with water added in place of the electrolyte solution.

Influence of the Quality of the Sol.—The changes observed on addition of an electrolyte are that after a certain time, depending on the concentration of the electrolyte, an increased turbidity is perceptible; this turbidity increases until the sol becomes almost, or even completely, opaque. The maximum opacity depends upon the quality of the original

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[1] Schulze, *J. prakt. Chem.*, 25, 431; Linder and Picton, *J. Chem. Soc.*, 61, 114, 172 (1892); 67, 63 (1895); Freundlich, *Z. physik. Chem.*, 44, 129 (1903); 73, 385 (1910); 83, 97 (1913); 86, 458 (1914).

[2] *Z. physik. Chem.*, 14, 317 (1894).