TABLE II

Vacuum weight of material, g.	Corrected weight of NaOH, g.	Normality	
	HCl 20.240%	Mol. wt. 36.468	
0.9125$_7$	45.296	0.11181	
.8997$_2$	44.679	.11176	Average 0.11179
.9018$_6$	44.780	.11178	Av. dev. 2.2 parts per
.9332$_1$	46.320	.11182	10,000
	Acid potassium phthalate 99.97%	Mol. wt. 204.180	
1.3388$_4$	58.563	0.11193	
1.1865$_2$	51.978	.11177	Average 0.11186
1.4629$_5$	64.024	.11188	Av. dev. 4.2 parts per
1.4835$_2$	64.928	.11187	10,000
	Benzoic acid 99.98%	Mol. wt. 122.083	
0.4460$_1$	32.642	0.11190	
.8561$_0$	62.717	.11179	Average 0.11183
.4924$_2$	36.081	.11177	Av. dev. 4.2 parts per
.7644$_5$	55.973	.11185	10,000

Mean value for twelve titrations 0.11183

chloric acid, which in turn is dependent on the gravimetric analysis by silver chloride, the use of cadmium sulfate provides an independent standard of acidimetry comparable with the hydrochloric acid.

We have carried out some preliminary experiments to determine the suitability of the pentahydrate of copper sulfate for determinations of the kind just described. Although the efficiency with which copper can be removed from the electrolyte is greater than in the case of cadmium, the color of the crystals makes the selection of the flawless ones difficult, and the low solubility of copper in mercury is a distinct disadvantage over the cadmium.

Hart and Croasdale[7] have removed the copper from dilute copper sulfate solutions by electrolysis and then determined the amount of acid produced, by weighing the copper; but the work has not been done with a degree of precision that would enable one to draw any conclusions regarding the possible usefulness of this method.

Summary

A new and independent method for preparing standard solutions of sulfuric acid by the electrolysis of cadmium sulfate in aqueous solution has been described.

The method has been compared with three established standards in acidimetry and shown to yield quite as precise results.

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(7) Hart and Croasdale, *J. Anal. Appl. Chem.*, **4**, 424 (1890).

PRINCETON, NEW JERSEY RECEIVED FEBRUARY 20, 1934

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Para-normal-butylphenylarsonic Acid as a Reagent for the Determination of Iron

BY K. A. CRAIG AND G. C. CHANDLEE

In a recent investigation of phenylarsonic acid as a reagent for the determination of tin,[1] it was observed that iron showed some tendency to precipitate. A large number of substituted phenylarsonic acids were investigated but *p*-*n*-butylphenylarsonic[2] was the only one found that would precipitate iron quantitatively in the presence of mineral acids.

Procedure.—The unknown sample containing not over 70 mg. of iron is dissolved in nitric acid or aqua regia, if necessary, the solution diluted to 200 cc. and carefully neutralized with ammonium hydroxide until a barely permanent precipitate is formed. Hydrochloric, nitric or sulfuric acid is then added in sufficient quantity so that the solution after addition of the reagent is approximately but not over 0.4 *N*. The solution is then heated nearly to boiling and 0.75 g. of reagent dissolved in 100 cc. of water at 80–90°,[3] is added slowly with stirring, whereupon a white flocculent precipitate is obtained. The mixture is then digested for twenty to thirty minutes, allowed to stand until completely cold, usually overnight, and the precipitate washed first by decantation and then on the filter paper with warm 0.02 *N* hydrochloric acid and finally with warm water until free from chloride.

The precipitate is ignited in a porcelain crucible over a low flame until the filter paper has been burned off. It is then heated for half-hour intervals over a strong Bunsen flame to constant weight. Usually one heating suffices. It is not possible to expel all the arsenic by heating in an open crucible, but by employing a propped lid this can be accomplished. The residues, tested by the Gutzeit method, never show more than 0.05 mg. and in many cases are entirely free of arsenic.

Thirteen determinations of pure solutions of iron salts whose iron content had been established by well-known methods, using samples containing approximately 0.05

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(1) Knapper, Craig and Chandlee, THIS JOURNAL, **55**, 3945 (1933).

(2) The *p*-*n*-butylphenylarsonic acid used in this work was prepared by Mr. D. M. Jones of this Laboratory according to a method developed by Dr. W. L. Evers (M.S. Thesis, Northwestern University) and as yet unpublished.

(3) This compound is only slightly soluble in cold water and in all determinations the excess reagent was recovered by evaporating the filtrate.

g. of ferric oxide, gave results with an average deviation of 4.5 parts per thousand.

Similar analyses of solutions containing simultaneously 0.1 to 0.2 g. of nickel, zinc, cobalt, manganese, copper and cadmium oxides and of solutions containing simultaneously 0.05 to 0.1 g. of potassium, aluminum, magnesium, calcium, beryllium, lanthanum, erbium and neodymium oxides were also conducted with a similar degree of concordance.

Chromium.—Complete separation of iron from chromium as dichromate was obtained by one reprecipitation. The precipitate was washed only with the dilute hydrochloric acid, then dissolved in the original beaker in 20 cc. of 1:1 hydrochloric acid. After preparing the solution as described, the iron was precipitated by adding 0.60 g. of reagent dissolved in 100 cc. of hot water.

Employing 0.0509 g. of ferric oxide and approximately equal amounts of chromic oxide, three determinations gave 0.0508, 0.0510, and 0.0508 g. of ferric oxide.

Thallium.—The strong tendency for thallic salts to hydrolyze necessitated as a first wash solution a saturated solution of the reagent in 1% hydrochloric acid. This was followed by the usual one with warm water to remove chloride.

Five determinations involving 0.0509 g. of ferric oxide and amounts of thallic oxide from 0.04–0.20 g. gave an average value of 0.0510 g.

Vanadium.—Separations of iron from vanadium when in the vanadate state gave no difficulty. With approximately 0.05 g. of ferric oxide in the presence of 0.01–0.02 g. of vanadium pentoxide, nine determinations gave results with an average deviation of 2.5 parts per thousand.

Determination of Iron in Monel Metal and German Silver.—A monel metal containing 35.48% copper, 57.36% nickel, 0.10% manganese, 0.71% insoluble, and 6.28% iron was analyzed as already described. Employing one-gram samples, four determinations gave an average value of 6.32% iron. A German silver containing 55.99% copper, 20.15% nickel, 23.38% zinc, small % insoluble, and 0.11% iron was analyzed in a like manner. Three determinations, employing two-gram samples, gave an average value of 0.11% iron.

Interfering Elements and Radicals.—The precipitation of iron is prevented by the presence of radicals with which it forms complexes such as fluoride, phosphate, tartrate, and citrate.

Iron cannot be determined in the presence of the following ions of the fourth periodic group: zirconium, tin, titanium and thorium nor in the presence of uranium and cerium. Since the precipitation is made in hot solution, hydrogen peroxide could not be used satisfactorily to hold up titanium. Iron failed to precipitate completely in cold solutions.

Further investigation of the separation of these elements with this reagent and with other substituted phenylarsonic acids is in progress.

Summary

1. A new gravimetric method has been described for the determination of iron in which it is precipitated with *p*-*n*-butylphenylarsonic acid.

2. By this method the direct determination of iron is possible in the presence of a large number of elements with which it is commonly associated.

3. Iron cannot be determined by this method in the presence of zirconium, tin, titanium, thorium, uranium and cerium or in the presence of radicals with which it forms complexes such as fluoride, phosphate, tartrate and citrate.

STATE COLLEGE, PA. RECEIVED FEBRUARY 26, 1934

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Calculation of Heterogeneous Reaction Rates

BY ROBERT E. BURK

Attempts to correlate catalytic reaction rates on surfaces with kinetic estimates of what they should be, have long been frustrated[1] because an adequate knowledge of the number of molecules adsorbed in the particular way required for reaction could not be arrived at.

However, J. B. Taylor and I. Langmuir[2] through a study of cesium films adsorbed on tungsten have developed a remarkable knowledge of a tungsten surface which has been etched by heating to a high temperature in a high vacuum. Langmuir had found in earlier work[3] that a tungsten surface which had been heated to such high temperature that some evaporation had occurred, consisted exclusively of dodecahedral faces, and that the extent of the total developed surface does not increase as the size of the faces increases.

Taylor and Langmuir were then able to show that with respect to cesium adsorption this surface may be divided into two portions, one portion A representing 0.5% of the surface is able to hold cesium far more strongly than the rest. This

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[1] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 3d ed., Oxford, 1933, p. 357.

[2] J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44**, 423 (1933).

[3] Langmuir, *ibid.*, **22**, 374 (1923).