[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Preparation of Iron-Free Solutions of Titanic Sulfate and Titanous Sulfate[1]

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Several years ago we used the double oxalate of titanium and potassium, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, for the preparation of standard titanium solutions in colorimetry.[3] It was found subsequently that the technique employed for making these dilute titanic sulfate solutions (0.013 *N*) could be applied to the preparation of solutions as strong as 0.1 *N*. And in both cases the double oxalate possesses certain desirable properties as compared with such other titanium-bearing substances as are available.[3]

It is the purpose of the present paper to describe the preparation of iron-free solutions of titanic sulfate and titanous sulfate of the usual concentrations, the initial material being titanium potassium oxalate.

Purification of Titanium Potassium Oxalate.[4]—A given amount of the commercial salt is dissolved in an equal weight of distilled water by heating, and the resulting solution is filtered while hot through a rapid paper. The receiving vessel is placed in an ice-bath, and the filtrate is stirred vigorously during the crystallization period to prevent caking. The formation of crystals begins in a little while and goes quickly to completion. The residual oxalate is collected on a filter paper in a Büchner funnel and sucked as free from the adhering liquor as possible with the aid of a pump. If no further recrystallizations are contemplated, the material is spread upon filter paper and dried in the air for a day or more. Recoveries of 80 to 90% are not uncommon.

The efficacy of the above process is illustrated by the data of Table I, wherein the amounts of iron found in equal quantities of different samples of titanium potassium oxalate (1.9 g., from which is obtainable somewhat more than 50 cc. of 0.1 *N* titanic sulfate solution) are recorded.[5]

TABLE I

PURITY OF DIFFERENT SAMPLES OF TITANIUM POTASSIUM OXALATE

Sample of $K_2TiO(C_2O_4)_2 \cdot 2H_2O$	Iron in 1.9 g. sample, g.
"Purified Powder" of commerce	0.0003
Recrystallized twice	< .00008
Recrystallized 8 times	Negligible

In general, we have found that if one starts with a salt of only fair quality, two or three recrystallizations from water will give a product containing but a negligibly small amount of iron.

Preparation of Titanic Sulfate Solutions.—To obtain solutions of titanic sulfate from the double oxalate of titanium and potassium, we have made use of the reaction

$$K_2TiO(C_2O_4)_2 \cdot 2H_2O + 3H_2SO_4 = K_2SO_4 + Ti(SO_4)_2 + 2CO + 2CO_2 + 5H_2O$$

ammonium sulfate being used to facilitate it. For the preparation of 1 liter of approximately 0.1 *N* titanic sulfate solution, the following procedure is recommended.

Thirty-eight grams of the purified double oxalate (theory demands 35.4 g.) and 32 g. of pure ammonium sulfate[6] are mixed well and placed in a 750-cc. Kjeldahl flask. Eighty cubic centimeters of pure concentrated sulfuric acid is also added. The flask is heated carefully with a small flame, intermittently, until foaming subsides, and then with a strong flame (thereby causing the solution to boil) for some time, to ensure complete destruction of the oxalate radical. The heating is now discontinued, and, after cooling, the sirupy liquid is poured cautiously into 500 cc. of distilled water while stirring, and this solution is diluted to 1 liter. Thorough agitation results in practically complete disappearance of the curdy precipitate that forms at first. After allowing some time (best overnight or longer) for any insoluble material to settle, the solution is filtered through a quantitative paper (previously washed with boiling-hot water), whereupon it is ready for use. That the treatment with sulfuric acid has been thoroughly effective in destroying the oxalate radical can be shown by adding 1 drop of 0.1 *N* potassium permanganate to 50 cc. of the filtered solution heated to 85°—there should be no decolorization of the permanganate. If this pink solution is now diluted with 50 cc. of water and allowed to come to room temperature, any iron present may be detected readily by adding 15 cc. of a 10% solution of potassium thiocyanate.

By proceeding in the above manner and employing reagents of tested purity, we succeeded in preparing solutions of titanic sulfate which were virtually free from iron.

Electrolytic Preparation of Titanous Sulfate Solutions.[7]—The reduction of titanic sulfate by means of either amalgamated zinc[8a] or liquid zinc amalgam[8b] serves as a very convenient method for the preparation of titanous sulfate. However, partly because additional metals (zinc and per-

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[1] From Ph.D. dissertation of Reuben Roseman, Johns Hopkins University, June, 1933.

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[3] Thornton and Roseman, *Am. J. Sci.*, [5] **20**, 14 (1930); *Chem. News*, **141**, 119 (1930).

[4] *Cf.* Péchard, *Compt. rend.*, **116**, 1513 (1893).

[5] Furthermore, several samples of titanium potassium oxalate obtained from different sources were tested for iron. Among these was a specimen generously donated by the Vanadium Corporation of America through the kind agency of Mr. A. E. Marshall. This salt proved to be of excellent quality—entirely satisfactory, as received, for all ordinary analytical purposes.

[6] Several "C. P." samples were examined and an imported ammonium sulfate was selected as being quite satisfactory; a 10-g. sample gave a scarcely perceptible test for iron with potassium thiocyanate.

[7] *Cf.* Spence, U. S. Patent No. 758,710, May 3, 1904; Evans, *Mem. Proc. Manchester Lit. Phil. Soc.*, **49**, No. 2 (1904); *Chem. News*, **90**, 313 (1904); Diethelm and Foerster, *Z. physik. Chem.*, **62**, 129 (1908).

[8] See (a) Van Brunt, THIS JOURNAL, **36**, 1426 (1914); Bray, Simpson and MacKenzie, *ibid.*, **41**, 1363 (1919); Lundell and Knowles, *ibid.*, **45**, 2620 (1923); (b) Nakazono, *J. Chem. Soc. Japan*, **42**, 526 (1921); Russell, *J. Chem. Soc.*, 497 (1926).

haps mercury) are thereby introduced into the resulting product, and partly because of the difficulty of obtaining really pure granulated zinc, we made a practical study of the electrolytic reduction method for obtaining an uncontaminated solution of titanous sulfate. In this study the two-compartment type of electrolytic cell was used. The catholyte was a solution of titanic sulfate acidified with sulfuric acid, and the anolyte consisted of dilute sulfuric acid alone, diffusion being prevented by means of a porous partition.

The reduction apparatus which was finally adopted as being most satisfactory is shown in Fig. 1. The Jena glass cylinder C (height, 27 cm.; diameter, 14.5 cm.; capacity, 4.5 liters), with a fritted-glass bottom D (thickness, 0.5 cm.), contains the solution to be reduced.[9] The Pyrex jar J holds the sulfuric acid solution which surrounds the cylinder C. The platinum-sheet electrodes E (3.7 × 3.6 cm.) and F (6.4 × 6.2 cm.) are sealed into glass tubes, each of which confines a small amount of mercury to provide contact between the platinum wire of the electrode and the copper wire of the external circuit. The copper bath B serves to keep the liquids cool during an electrolysis. Cooling water enters at I and leaves at either the upper or lower outlet (O′ or O), depending upon the volume of titanium solution with which one is working. The glass stirrer S mixes the cathode liquid throughout a reduction. The watch glass G, which is sealed to S, and the glass cover resting on top of the jar serve the double purpose of preventing acid spray from reaching the metal parts of the pulley and of keeping extraneous matter from falling into the solutions below. A rheostat R, an ammeter A and a knife switch T are included in the electrical circuit.

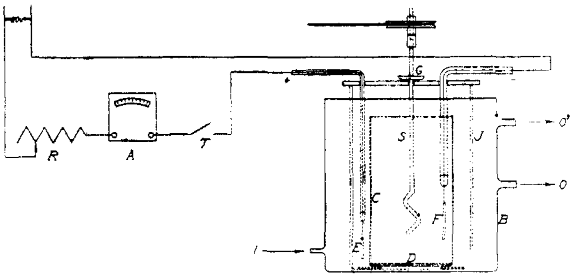

Fig. 1.

In an actual experiment with this apparatus, 2300 cc. of a 0.1 N titanic sulfate solution (prepared as previously outlined, the fifth product of crystallization from the above-named "Purified Powder" being used) was charged into the cup of Jena glass, which in turn was surrounded by 2700 cc. of pure sulfuric acid (1:15). Electrolysis was allowed to proceed for approximately twenty-eight hours, the average current being 7.5 amperes. At the conclusion of the run the liquid in the porous cup was stored in an atmosphere of hydrogen.[10]

The solution resulting from the above experiment was found to be 0.082 N with respect to titanous ion.

A colorimetric test showed that 50 cc. of this titanous sulfate solution contained considerably less than 0.00005 g. of iron.

Summary

The purification of the double oxalate of titanium and potassium and the preparation therefrom of solutions of titanic sulfate and titanous sulfate for use in refined analysis are described.

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[9] In early experiments a Coors cup of unglazed earthenware which was employed as the porous vessel, was found to be a serious source of iron. Accordingly, we looked for a container which would be inert toward all ordinary chemical reagents and which would, in addition, retain liquids poured into it and yet not offer too much resistance to the electric current. It was found that a Jena glass cylinder with a fritted-glass bottom of porosity "G4" fulfilled these requirements. Several cylinders of this type (C, D, *Fig.* 1) were made to order for us by the Jenaer Glaswerk Schott & Gen., Jena (Germany).

[10] The storage apparatus was similar to the one employed by Thornton and Chapman, This Journal, **43**, 91 (1921).

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NOTES

The Preparation of Diphenylbenzidine and its Use as an Oxidation–Reduction Indicator

By L. A. Sarver and J. H. Johnson

The value of diphenylbenzidine as an oxidation–reduction indicator has been pointed out in previous papers.[1] In the present communication a method is reported for the preparation of this substance in quantity.

To a mixture of 1 liter of concentrated sulfuric acid, 2 liters of glacial acetic acid, and 12 liters of water is added, slowly and with stirring, a solution of 50 g. of diphenylamine in 500 cc. of acetic acid. Should any diphenylamine separate during the process, it may be redissolved by warming to not higher than 50°. To the resulting solution at 15–25° is added slowly and with vigorous stirring a solution of 22 g. of potassium dichromate in 500 cc. of water; after five minutes the excess dichromate is reduced with a solution of 10 g. of sodium bisulfite. The colloidal precipitate is collected on the filter with the aid of a filter medium. The greenish-black product is placed, while still wet, in a warm concentrated solution of sodium bisulfite; when light brown, it is filtered off, washed with hot water, thoroughly dried, pulverized, and extracted with 1250 cc. of boiling xylene. The residue is extracted again with the

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[1] I. M. Kolthoff and L. A. Sarver, *Z. Elektrochem.*, **36**, 139 (1930); This Journal, **52**, 4179 (1930); L. A. Sarver and I. M. Kolthoff, *ibid.*, **53**, 2906 (1931).