It was found that removal of the sulfate ion as barium sulfate or calcium sulfate probably does not increase the velocity, although the effect of adding barium ion to the reacting mixture seems to be somewhat greater than it should if it is to be explained merely as a specific salt effect. Finally, the main conclusion of the first article, that is, that the observed reaction velocity is the sum of the velocities of the iodide and of the tri-iodide ions reacting with persulfate ion, was confirmed by measurements at considerably greater velocities.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STUDIES ON SILICODUODECITUNGSTIC ACID.
I. THE PREPARATION OF SILICOTUNGSTIC ACID[1]

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Silicotungstic acid originally prepared and described by Marignac[3] in 1863, has lately become an important analytical reagent on account of its ability to precipitate alkaloids. The present official method for the determination of nicotine is based on this property.

Drechsel[4] improved the original method of separating the acid by isolating it in the form of a complex which it formed with ether in the presence of a mineral acid. This procedure was only slightly modified by North and Beal,[5] who in 1925 extended the usefulness of this reagent by producing it in the form of a dry powder, stable in air and readily handled without decomposition. They also introduced a volumetric method, in which silicotungstic acid was used for the quantitative determination of alkaloids without previous isolation and purification. More recently Salzberg[6] has questioned the purity of the acid when prepared according to North's directions, and also North's assumptions with regard to the end-products obtained following decomposition of the acid by means of excess of alkali.

Because of the lack of agreement in the literature and the unsatisfactory status of the knowledge concerning silicotungstic acid, the researches of the present writer were undertaken with the following objectives: (a)

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[1] Throughout this paper the term silicotungstic acid will be understood to refer to silicoduodecitungstic acid.

[2] This communication is an abstract of a portion of a thesis submitted by Arthur G. Scroggie in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Marignac, *Ann. chim. phys.*, [3] **69**, 5 (1863).

[4] Drechsel, *Ber.*, **20**, 1452 (1887).

[5] North and Beal, *J. Am. Pharm. Assoc.*, **13**, 889, 1001 (1924).

[6] Salzberg, Master's "Thesis," University of Illinois, **1925**; unpublished report, University of Illinois, **1925**.

to investigate the possibility of forming the complex with new reagents and to determine the optimum concentrations for a maximum yield of acid, (b) to follow up the work of Salzberg and investigate quantitatively the methods of purification and dehydration of the acid, (c) to examine the methods of analysis of the acid and (d) to identify the end-products obtained by decomposing the acid with an excess of alkali.

1. **Complex Formation.**—Originally Drechsel had used ether and sulfuric acid to isolate the silicotungstic acid, but North had substituted hydrochloric acid for sulfuric, since an excess could be removed by heating. Rosenheim[7] has suggested that the compound concerned is of the oxonium salt type, but no records were found in the literature of investigations to establish this point or to find substitutes for the ether and acids previously used.

The method of extraction by a complex consists in adding ether to an aqueous solution of silicotungstic acid which contains a large excess of free mineral acid and then agitating the mixture. The complex sinks to the bottom as a heavy oily liquid and the excess of solvent floats on the surface of the aqueous layer.

To be suitable for the formation of a complex then, a solvent must be immiscible with and lighter than water, as well as a solvent for silicotungstic acid. If the oxonium salt theory is correct the solvent must also contain an oxygen atom.

A large number of solvents were tried in a qualitative way and the following facts established. Of the solvents containing oxygen, a number of esters, ketones and aldehydes could be substituted for ether, but ethyl acetate was the only one that seemed to merit quantitative investigation; a number of other solvents, including the lower alcohols, ketones, etc., were miscible with water and could not be used; acetic acid in addition to miscibility with water did not dissolve silicotungstic acid. Of the solvents which do not contain oxygen none was found to be satisfactory since they did not dissolve silicotungstic acid. These included petroleum ether, benzene, toluene, chloroform, carbon tetrachloride and carbon disulfide.

These results are in agreement with the work of Baeyer and Villiger[8] on oxonium compounds and are a general confirmation of this theory of the nature of the complex, but it was not found possible to isolate the pure compound for analysis.

Experiments demonstrated that nitric acid could be substituted for the usual precipitating agents, hydrochloric acid or sulfuric acid, but owing to its effect on the specific gravity of the solution it was not as efficient an agent as the ones previously used. Acetic acid would not

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[7] Rosenheim and Jaenicke, *Z. anorg. Chem.*, **100**, 319 (1917).

[8] Baeyer and Villiger, *Ber.*, **34**, 2679 (1901).

cause the separation of the complex and was distinguished by its ability to prevent this action by the stronger acids. Sodium chloride in a concentration of 20% was found to be quite effective, particularly with ethyl acetate. Lithium chloride, nitrate and sulfate were all effective, but sodium sulfate, perchlorate and the salts of other metals could not be used. Just why the Li^+ is so much better than the Na^+ is not understood.

The presence of salt in a solution lowered the amount of mineral acid necessary to cause the separation of the complex, and a yield of 85–90% based on the weight of tungstate taken could be obtained using salt and ethyl acetate without any mineral acid. This method in fact is the most efficient for the extraction of the original process mixture which already contains 10 to 15% of salt. The combination ether and sodium chloride is not satisfactory, however, since the yield is only 50–60% of the theoretical. For purification of the acid by re-extraction from a solution which does not contain salt, ether and hydrochloric acid is the most efficient combination, and a yield of 98% can be obtained by adding an amount of hydrochloric acid equal to one-third of the original volume of the solution.

2. **Methods of Analysis of the Acid.**—As a preliminary step toward establishing the purity of the acid when prepared according to North's directions, methods of analysis were carefully examined. North dried the acid in an oven at 70° and then analyzed it in two ways: (1) by igniting the acid in a muffle furnace at a dull red heat, considering the loss in weight as water and the residue as anhydride; (2) by titrating the acid with standard alkali, using methyl orange as an indicator, which gave an end-point after the addition of four equivalents of base.

In the present investigation, the best temperature for ignition of the acid was found to be between 400 and 500°, since a sample of anhydride heated above this temperature underwent a progressive loss in weight depending, for any one sample, on the time and temperature of ignition. Method II was improved by using very dilute alkali solutions, which gave sharper end-points, and the use of chlorophenol red as an indicator (P_H range 5.0 to 6.0) because silicotungstic acid had been shown to give precipitates with methyl orange and most compounds containing basic nitrogen.

Salzberg used a third method of analysis which consisted in precipitating the silicotungstic acid with an excess of cinchonine solution, filtering the precipitate and igniting it to obtain the anhydride as a residue. In the hands of the writer this method gave results which varied slightly with different conditions and were uniformly higher than the value for the anhydride given by the first method mentioned. This method was not considered as reliable as the previous ones.

3. **Purification of the Acid.**—North dried the acid at 70° and obtained the following values for the percentage of anhydride: 94.58% (Method I),

and 94.94% (Method II). He concluded that the acid had retained 5 molecules of water of hydration and had the formula $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 5H_2O$ (anhydride, 94.64%).

In the present investigation three samples of acid were prepared: (A) according to North's directions, (B) by re-extracting the above acid with ether (Salzberg's directions) and (C) by reforming the complex with ether twice. All samples were dried at 70° and analyzed, with the following results.

Percentage of Anhydride

Sample	Method I, %	Method II, %	Mean, %
A	95.62	83.50	89.56
B	95.30	95.34	95.32
C	95.21	95.41	95.31

These results indicated an impurity in Sample A, the crude product, which was confirmed by precipitation of samples of the acid with cinchonine, filtering the precipitate and taking the filtrate to dryness in the presence of perchloric acid. The residue from Sample A, after adjusting for a blank on the reagents, was 1.2% of the sample weight, while the analyses of Samples B and C showed that within the limits of experimental error the impurity had been completely removed. These results confirmed the work of Salzberg and showed that a pure acid could be obtained only by following purification by reformation of the complex by means of ether and mineral acid, and also showed that a second reformation was not necessary.

4. **Dehydration of the Acid.**—In drying in an oven at 70° the acid, after a large initial loss, underwent a very gradual loss in weight which extended over several days and varied with the humidity of the atmosphere. Salzberg reported finding more moisture in a series of samples dried at 100° than he obtained from a series of samples dried at 70°. To solve these difficulties drying agents were tried as substitutes for the oven method and found to be far superior. Anhydrone or dehydrite under reduced pressure would dry small samples of the acid to constant weight in less than twenty-four hours. Hempel type desiccators were used and were evacuated by means of a Hyvac pump to a pressure of approximately 7 mm. Analysis of the acid as dried with different reagents gave the following percentages of anhydride as determined by ignition.

Drying agent	Dehydrite	H_2SO_4	$CaCl_2$	KOH or NaOH
Anhydride, %	95.40	95.50	95.31	95.25

All of these results correspond to an acid with somewhat less than the four molecules of water of crystallization expressed in the formula $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 4H_2O$, and would indicate that the last four molecules of water of hydration are retained quite persistently.

5. Decomposition of the Acid by Means of Excess of Alkali.—North assumed that the acid would be decomposed by a reversal of the process of preparation, which would require 26 equivalents of base per molecule of acid, according to the following

$$4H_2O{\cdot}SiO_2{\cdot}12WO_3 + 26NaOH \longrightarrow Na_2SiO_3 + 12Na_2WO_4 + 17H_2O$$

He carried out the determination by adding an excess of alkali, boiling the solution and back-titrating the excess with a standard acid, using phenolphthalein as indicator. His experimental values were 26 and 25.5 equivalents.

Salzberg, repeating the work with a purer acid, got values ranging from 23.5 to 24.5 equivalents and concluded that the theoretical value was 24 equivalents, which he explained by assuming that the silicic acid formed in the decomposition was not neutralized under the conditions of the experiment.

The writer by carrying out the decomposition in a system free from atmospheric carbon dioxide was able to get results that verified the latter theory. The experimental values obtained were 24.06 and 24.09 equivalents (assuming the acid to retain 4 molecules of water of hydration). The decomposition may therefore be represented by the following

$$4H_2O{\cdot}SiO_2{\cdot}12WO_3{\cdot}4H_2O + 24NaOH \longrightarrow H_2SiO_3 + 12Na_2WO_4 + 19H_2O$$

This decomposition is analogous to the decomposition of the yellow ammonium phosphate precipitate by alkali when the third hydrogen of phosphoric acid is not replaced by the alkaline metal. Assuming the theoretical ratio of 24 equivalents of base per molecule of acid, the reaction was used to analyze the acid, and it might be possible to work out a volumetric method for the analysis of the alkaloidal salts of silicotungstic acid as well, but this work was not undertaken.

6. A Modification of the Method of Isolation and Dehydration of Silicotungstic Acid.—As a result of these investigations, the writer would amend North's directions for the preparation of the acid as follows. Extract the original process mixture by adding an excess of ethyl acetate and 10–15% of common salt; dissolve the complex obtained in this operation in a liter of dilute hydrochloric acid (1 vol. of HCl to 3 vols. H_2O) and extract with an excess of ether which has been washed with 10% sodium hydroxide solution; take the complex to dryness on the water-bath, add water and take to dryness again; repeat this procedure till the residue no longer smells of volatile acid.

A very pure product can be obtained by recrystallizing this first yield from water; if the crystals are washed with an alcohol–chloroform mixture the loss by solution is not great. A current of air passed over the crystals for a few hours will dehydrate them sufficiently to permit of coarse powdering, after which they may be dried to constant weight by exposure to a good drying agent.

The acid produced in this way will absorb a small amount of moisture if exposed to the air.

The mother liquors, which are occasionally dark colored, may be readily clarified by heating with norite for a few minutes and filtering off the suspended matter.

The writer wishes to take this opportunity of thanking Dr. George D. Beal for suggesting this problem, and of expressing his regret that circumstances forced the latter's withdrawal from active participation in the work at such an early date.

Summary

1. The comparative value of different reagents for the formation of a complex with silicotungstic acid has been established and the probability that the compound formed is an oxonium salt has been indirectly confirmed.

2. Salzberg's conclusion with regard to the purity of the acid when prepared according to North's directions has been verified.

3. The truth of the assumption that the acid is decomposed by twenty-four molecules of base has been established experimentally.

4. The methods of analysis have been improved.

5. A new method of isolating the acid, depending on the formation of a complex with ethyl acetate, and a new method of dehydrating it have been proposed.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. III. INFLUENCE OF LITHIUM, RUBIDIUM, CESIUM AND MAGNESIUM UPON THE DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE[1]

BY RUFUS D. REED AND JAMES R. WITHROW

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We have shown the availability of zirconium sulfate as a reagent for potassium in the presence of sodium[2] and ammonium.[3] The less frequently occurring members of the fifth group, rubidium and cesium, both interfere with the detection of potassium by sodium cobaltic nitrite, perchloric acid or chloroplatinic acid. Lithium can be separated from ions of these elements by perchloric acid or chloroplatinic acid. Tread-

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[1] The authors are indebted to the Chemical Department of this University in that Professor Marion Hollingsworth of the Analytical Chemical Division of that Department furnished the rubidium and cesium chlorides used as the basis of part of this work.

[2] Reed and Withrow, THIS JOURNAL, **50**, 1519 (1928).

[3] Reed and Withrow, *ibid.*, **50**, 2985 (1928).