monobasic phosphate solution (*P*H, 4.5) containing the indicator is used for comparison. The end-point is a barely visible pink. The titration can then be continued, using phenolphthalein as indicator.

Using pure potassium dichromate solution containing the indicator for comparison, it was possible to detect 0.2–0.25% of free chromic acid in 1 g. of the salt in 25 cc. of water.

Ammonia and alkaloids may be satisfactorily titrated, using this indicator.

Pentamethoxy red may be used in determining the *P*H of gastric juice.

Summary

1. A number of triphenyl carbinol derivatives containing 5, 6 or 7 methoxy groups have been found to make excellent indicators which are unique in being colorless in alkaline and colored in acid solution.

2. Their constants and properties are given.

3. 2, 4, 6, 2′, 4′, 2″, 4″-Heptamethoxytriphenyl carbinol changes color so slowly as to be useless in titrations, but the others are satisfactory.

UTRECHT, HOLLAND

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

THE PREPARATION AND ANALYSIS OF PURE AURIC OXIDE[1]

BY W. E. ROSEVEARE WITH T. F. BUEHRER

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In connection with the determination of the free energy of auric oxide from electromotive-force measurements, the results of which will be set forth in another paper by the authors,[2] it became necessary to prepare pure auric oxide which could be depended upon to give reproducible potentials. The present paper embodies the results of a critical study of existing methods of preparation as well as of certain analytical procedures which were devised and tested to determine the purity of the product obtained.

The various methods of preparing auric oxide have been summarized and discussed by Mellor[3] and by Abegg.[4] The method of Fremy[5] proved most satisfactory as a starting point in this preparation. It consists of three essential steps: (1) precipitation of the oxide from chloro-auric

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[1] A paper presented by W. E. Roseveare, at the meeting of the Southwestern Division of the American Association for the Advancement of Science, Phoenix, Arizona, February 15–18, 1926.

[2] To be published by Buehrer and Roseveare in THIS JOURNAL.

[3] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., **1923**, vol. 3, p. 580.

[4] Abegg, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, **1908**, vol. 2, pt. 1, p. 819.

[5] Fremy, *Ann. chim. phys.*, [3] **31**, 481 (1851). Ref. 3, p. 580.

acid with potassium hydroxide; (2) conversion of oxide to aurate with an excess of potassium hydroxide; (3) reprecipitation of the oxide with sulfuric acid. The latter two steps are desirable because the occlusion of potassium as chloride or aurate is not likely to occur to a considerable extent in acid solution and because basic auric chloride does not precipitate out under these conditions. Since Fremy's method as published did not yield pure auric oxide, this procedure was studied critically and the experimental details were modified to accomplish adequate purification.

Modified Method of Preparation and Purification

Potassium hydroxide solution is added slowly to a boiling aqua regia solution of gold until the precipitate first formed is just dissolved as aurate. The concentrations of reagents in this precipitation may vary over wide limits, but in general the greater the concentration of gold in the solution, the better the yield, as would be expected from its solubility in solutions containing chloride ion. Sulfuric acid (3 N) is then added until the solution is just acid to litmus, and the mixture is boiled for some time to coagulate the suspension of the hydroxide. This latter step has two advantages: (1) the solubility of the oxide is very slight in sulfuric acid solution, and (2) colloid formation is entirely prevented. It was found to be impossible, however, to remove chlorides entirely either by decantation or filtration. To make certain that every particle of oxide had been thoroughly washed, the precipitate was transferred to a glass-stoppered bottle and vigorously agitated with 0.01 N sulfuric acid, on a shaking machine for about an hour. The suspension was then centrifuged and the entire operation repeated several times.

Even this vigorous treatment failed to remove chlorides entirely, and to accomplish this it became necessary to redissolve and reprecipitate the oxide under conditions such that occlusion of chlorides might be entirely prevented. The observation of Fremy[5] that the oxide dissolves readily in concd. nitric acid was employed with the hope of redissolving and reprecipitating it by hydrolysis on dilution with water. It was found, in fact, that auric oxide does dissolve quite readily in concd. nitric acid when freshly precipitated, but on long-continued boiling it decomposes into its elements. A further complication arises from the facts that it is difficult to test for nitrate ion in the presence of auric oxide[6] by the ordinary tests, because auric oxide reacts similarly, and that nitric acid is likely to contain reducing oxides.

The purification was finally effected by redissolving the oxide in *boiling potassium hydroxide* solution and reprecipitating it with an excess of *sulfuric acid.* On alternately shaking and centrifuging the suspended

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[6] A reviewer of this paper has suggested testing for nitrate by reduction to ammonia. This device had not been tried by the writers.

precipitate, it could be completely freed from chlorides and sulfates, as was evidenced by the ordinary qualitative tests.

Quantitative Analysis of the Oxide

Since the oxide is hydrated to a variable extent and decomposes partially into its elements when dried, the degree of hydration cannot readily be established. The only result which has quantitative significance is the ratio of gold to oxygen, which for auric oxide is 8.22. On account of its instability on being dehydrated, any method of analysis of auric oxide necessitates handling the compound in wet form.

Two types of method might conceivably be employed. 1. Thermal decomposition of the oxide, measurement of the volume of oxygen liberated, and weighing of the gold formed. 2. Titration of the oxide with standard reducing agents and weighing of the gold formed.

Gas-Evolution Methods

Gas-evolution methods were investigated in this connection and several types of apparatus devised for measuring the oxygen. In one quantitative experiment the apparatus cracked and the presence of ozone[7] was detected both by its odor and by means of starch-iodide paper. Various factors were incidentally observed which would entirely vitiate the results of analysis by gas evolution: (1) ozone has a greater density than molecular oxygen; (2) the decomposition of the ozone catalytically by means of platinum sponge involves uncertainty on account of adsorption of gases by platinum; (3) the difference in density of auric oxide and metallic gold. However, the gas-evolution method could be used if the oxygen were absorbed in a suitable reducing agent, but this procedure involves rather large samples of the oxide for analysis.

Titration with Standard Reducing Agents

Titration with standard reducing agents gave promise of accurate results because gold in the trivalent form is very easily reduced at ordinary temperatures. Ferrous sulfate has been used by French.[8] Its reducing action is prompt and complete. In our experiments titration was made in a carbon dioxide atmosphere, an excess of standard ferrous sulfate solution being added and the remainder titrated back with permanganate. The solution was boiled to coagulate the gold, which was filtered off, ignited and weighed. Since the oxide does not dissolve extensively in any except the halogen acids and since there is great danger of redissolving some of the gold formed at the instant when the permanganate is added to a halide solution of gold, it was necessary to carry out

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[7] This confirms the observation made by Brunck [*Z. anorg. Chem.*, **10**, 247 (1895)], who reported the evolution of ozone when silver, mercuric, auric, chromic and other oxides were heated.

[8] French, *Min. Eng. World*, **37**, 853 (1913).

this titration in sulfuric acid solution. Under this condition the oxide particles remained in suspension, and when the ferrous sulfate solution was added they were quickly coated over with a layer of metallic gold. It then became necessary to boil the solution for some time to make reduction complete. To counteract the possible solvent action of ferric ion on the finely divided gold, the residual titration was in some cases made after the metal had been filtered off; in others, sodium fluoride was added to remove the ferric ions in the form of the complex FeF_6^{---} ion. As a result of these disturbing factors, the results given in the table are found to be somewhat erratic, the chief source of error arising from the fact that the oxide was titrated in the solid form.

Titration with Standard Titanous Chloride Solution

To make possible the titration of the gold in hydrochloric acid solution, the combination titanous chloride–ferric chloride was tried. Titanous chloride has been applied by Zintl[9] to the potentiometric titration of gold. Since it was necessary, in the present investigation, to weigh the gold formed, the potentiometric method could not be employed. However, the addition of an excess of titanous chloride solution and back titration with ferric chloride proved successful.

An apparatus was devised in which titration could be carried out in a carbon dioxide atmosphere. Two burets were fitted with three-way stopcocks connecting, respectively, with a reagent bottle and a rubber stopper fitted into a 150cc. Pyrex extraction flask. This rubber stopper also carried a tube by way of which the carbon dioxide was introduced, the gas serving simultaneously to stir the solution during the titration. It also held a bent glass rod to serve in touching off the last drops from the buret tips, and another small tube which served as an exit for the carbon dioxide and for the introduction of potassium thiocyanate indicator solution.

The sample of auric oxide, in the form of a dense suspension, was transferred to the extraction flask by means of a pipet, 10 cc. of suspension being generally sufficient to yield approximately 0.1 g. of gold. Five cc. of concd. hydrochloric acid was added and the air washed out of the apparatus by means of the carbon dioxide. An excess volume of titanous chloride was added, so that after most of the gold had been coagulated, the solution had a distinct violet tinge characteristic of titanous chloride. One cc. of 25% potassium thiocyanate solution was then added and back titration completed with ferric chloride to a distinct reddish tinge. At this point care must be taken not to add the indicator too soon, that is, before the titanous chloride is present in excess, for the reason that potassium thiocyanate reduces auric to aurous gold, forming the orange-red aurous thiocyanate, and leading to low results. The finely divided gold which has separated out does not interfere with recognition of the end-point, if the solu-

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[9] Zintl and Rauch, *Z. anorg. Chem.*, **147**, 256 (1925); *Z. Elektrochem.*, **31**, 428 (1925). See also Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, New York, **1926**, p. 297.

tion is heated nearly to boiling to cause the gold to settle. Heating the solution has the additional advantage that it hastens the reaction of chloro-auric acid with titanous chloride, so that the titration can be carried out within a reasonably short time.

The results[10] are shown in Table I.

Table I

The Analysis of Auric Oxide

1. By Titration of Solid Oxide with $FeSO_4$ and $KMnO_4$ Solutions

Net $FeSO_4$, cc.	$FeSO_4$, N	O_2, g.	Au, g.	Ratio, Au:O	O_2, %	O_2 in Au_2O_3, %
21.09	0.1008	0.01662	0.1368	8.23	10.84	10.85
31.84	.1018	.02590	.2119	8.18	10.89	
18.28	.1008	.01473	.1202	8.16	10.91	
8.75	.1018	.00713	.0583	8.17	10.90	
61.87[a]	.04943	.02446	.2014	8.24	10.83	
37.38[a]	.04943	.01477	.1212	8.21	10.86	
				Av.	10.87	

2. By Titration of Oxide (Dissolved in HCl) with $TiCl_3$ and $FeCl_3$ Solutions

Net $TiCl_3$, cc.	$TiCl_3$, N	O_2, g.	Au, g.	Ratio, Au:O	O_2, %
16.57	0.1023	0.01257	0.1028	8.18	10.89
21.35	.1023	.01747	.1434	8.21	10.86
25.09	.1023	.01903	.1563	8.21	10.86
23.74	.1023	.01801	.1479	8.22	10.85
				Av.	10.87

[a] Titrated in the presence of sodium fluoride.

Discussion

The results given in Table I show that the ferrous sulfate-permanganate method is reproducible to 0.3% and that the titanous chloride-ferric chloride titration is reproducible to 0.15%. The agreement of the experimental results, 10.87%, with the calculated percentage of oxygen in auric oxide, namely, 10.85%, indicates that the oxide is substantially uniform in composition and the gold is in the trivalent form.

Summary

1. A method advanced by Fremy for the preparation of auric oxide has been studied critically and a satisfactory method of purification of the precipitate established.

2. Several methods of analysis of auric oxide have been studied, and sources of error in each case are pointed out.

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[10] Since auric ion liberates iodine and is reduced to aurous ion by iodide ion, an attempt was also made to analyze the oxide by titration of the iodine formed with thiosulfate. Gooch and Morley [*Am. J. Sci.*, [4] **8**, 261 (1899)] have shown that the iodimetric method is accurate if very small amounts of gold, 0.05 to 10 mg., are determined. When applied to the analysis of auric oxide, the method failed on account of partial reduction to metallic gold, and the extraordinary slowness of the reaction between chloro-aurate ion and iodide ion.

3. The oxide so prepared is shown to contain 10.87% of oxygen as compared with the calculated percentage, 10.85, of oxygen in auric oxide. Qualitative evidence is also adduced to show that the product is pure within the limits of experimental error.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

A STUDY OF THE PROPERTIES OF THE SYSTEM LITHIUM CHLORATE-WATER. I. INTRODUCTION. II. PHASE RELATIONS

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I. Introduction

The present investigation was undertaken for the purpose of gaining some knowledge of the influence of small additions of water on the properties of a fused electrolyte. It was anticipated that if a salt of sufficiently low melting point could be found, the properties of its mixtures with water might be studied over the whole concentration range from pure salt to pure water. According to the literature, lithium chlorate melts at 127° and it was thought that this salt would prove to be completely miscible with water at and above its melting point. This proved to be the case.

With the exception of some electrochemical data due to Ostwald,[2] the literature relating to lithium chlorate is concerned chiefly with the nature of the solid phases that exist in equilibrium with its aqueous solutions. The salt appears to have been prepared first by Wächter,[3] who obtained what corresponds to a hemihydrate, $LiClO_3.{}^1/_2H_2O$. Troost,[4] who prepared the same compound a little later, agrees with Wächter regarding the hydrate, and states that it melts at 50° and decomposes at 100°. Potilitzin[5] placed the melting point of the anhydrous salt at 124° and reports a hemihydrate, $LiClO_3.{}^1/_2H_2O$, melting at 50° and losing water at 90°. Retgers,[6] who studied the crystalline form of the salt, and Mylius and Funk,[7] who determined its solubility in water, hold that no hydrate is formed. Brühl[8] investigated the salt by crystallographic methods and described three anhydrous modifications, as well as a hemihydrate, melting at 63–65°. The highest temperature modification melted at 125–127°.

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[1] Metcalf Fellow in Chemistry at Brown University, 1924–1925.

[2] Ostwald, *Z. physik. Chem.*, **1**, 83 (1887).

[3] Wächter, *J. prakt. Chem.*, **30**, 321 (1843).

[4] Troost, *Ann. chim. phys.*, [3] **51**, 136 (1857).

[5] Potilitzin, *J. Russ. Phys.-Chem. Soc.*, **16**, 840 (1883).

[6] Retgers, *Z. physik. Chem.*, **5**, 449 (1890).

[7] Mylius and Funk, *Ber.*, **30**, 1716 (1887).

[8] Brühl, *Bull. soc. ind. minérale*, **35**, 155 (1912).