

ines were prepared in the usual manner. They were recrystallized from hot absolute alcohol to which about 30% of acetone was added after solution, and were obtained as white non-hygroscopic crystals. The optically active β -methylcholine iodides were converted to the corresponding chlorides using silver chloride in alcohol according to standard procedures. The chlorides were recrystallized from butyl alcohol,⁵ and were obtained as white hygroscopic crystals. The optically active β -methylcholine chlorides were acetylated according to the method of Major and Cline.⁵ The acetyl esters thus obtained were white hygroscopic crystalline solids. The properties and analyses of the above-mentioned compounds are recorded in the table.

(5) Major and Cline, *THIS JOURNAL*, **54**, 247 (1932).

The authors wish to express their appreciation to Messrs. Douglass F. Hayman and Sol Adler for the analyses recorded in this paper.

Summary

1. *dl*-Dimethylaminoisopropanol has been resolved into its optically isomeric forms.
2. The dextro and levo isomers of β -methylcholine iodide, β -methylcholine chloride, and acetyl- β -methylcholine chloride have been prepared and characterized.

RAHWAY, N. J.

RECEIVED JULY 9, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Potassium Thiocyanate as a Primary Standard Substance

BY I. M. KOLTHOFF AND J. J. LINGANE

Although potassium thiocyanate has long been used as a reagent in the classical Volhard method for the titration of silver, the use of the pure salt as a primary standard substance in argentimetry has been discouraged in the literature.¹

The initial purpose of the present investigation was to investigate the possibility of preparing the pure salt for use as a standard substance. A secondary purpose was to determine the *accuracy* of the potentiometric and the Volhard methods for the titration of thiocyanate with silver, which has never been established, although the *precision* of the titration has been the subject of several studies.²

The second part of this work has led to the discovery of a hitherto unsuspected side reaction (or reactions) that takes place when thiocyanate is precipitated with silver.

Preparation of Pure Potassium Thiocyanate

Potassium thiocyanate from Kahlbaum and the reagent quality product of the Mallinckrodt Company have both been used in this study, and except for a considerable amount of hygroscopic water, the salts were found to be quite pure and suitable starting materials.

Samples of the salt were repeatedly recrystallized from water, ethanol and methanol. Recrystallization from the alcohols is somewhat simpler than from water, with respect to the manipulative details, but we have found that removal of chloride is incomplete on crystallization from alcohol and therefore it is preferable to recrystallize from

water when the original salt contains appreciable amounts of chloride. The yield in either case is approximately 50%.

Other samples of the pure salt were prepared by fractional precipitation from a saturated ethanol solution by the addition of ether; four successive fractions were collected.

In all cases, the crystals were collected on a Büchner funnel without paper, the adhering mother liquor was removed by suction, and the products were dried in a desiccator at room temperature. The samples were then heated for an hour at 150° and were finally heated to 200° (m. p. 172°) and kept melted for ten to twenty minutes, to remove the last traces of solvent.

Experiments were made to determine whether chloride and ammonium thiocyanate can be removed completely from potassium thiocyanate by recrystallization from water or alcohol. A sample to which 1% of potassium chloride had been added still contained 0.6% after three recrystallizations from alcohol, but after three recrystallizations from water the final product contained less than 0.005% of chloride.

A sample to which 1% of ammonium thiocyanate had been added contained less than 0.005% of ammonia after three recrystallizations from alcohol or from water.

It was found occasionally that the salt became colored yellow on heating and melting. Systematic study showed that this yellow discoloration was only obtained when the salt was heated in an atmosphere that was slightly contaminated by acid vapors. The discoloration also takes place at room temperature when the dried salt is exposed for some time in an acid contaminated atmosphere. The yellow coloration was more frequently observed with products that had been recrystallized from alcohol, even though the atmosphere in which the salt was heated was entirely free from acid fumes.

The yellow coloration is probably due to the formation of isoperthiocyanic acid ($\text{H}_2\text{C}_2\text{N}_2\text{S}_3$) and isodithiocyanic acid

(1) I. M. Kolthoff, "Die Massanalyse," 2 Aufl., Julius Springer, Berlin, 1931.

(2) Cf. I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, **70**, 369 (1927).

($\text{H}_2\text{C}_2\text{N}_2\text{S}_2$)³ or a mixture of these with the yellow oxidation products described by Offord.⁴

If reasonable care is taken to heat and melt the salt in a pure atmosphere, and to store the dried salt in glass-stoppered bottles in the dark, no trace of the yellow discoloration is formed. Samples prepared in this way are stable indefinitely. In direct sunlight the colorless crystals become yellow fairly quickly. Solutions of the pure salt in pure water are entirely stable, when protected from light. We have kept a solution of the pure salt for eleven months with no detectable change in titer.

Test for Impurities

Water (Alcohol).—Ten grams of the salt should not decrease in weight by more than 1 mg. (0.01%) when melted for ten minutes at 200°.

Chloride.—The test given by Murray⁵ was found to be entirely satisfactory. One gram of the salt is dissolved in 50 cc. of water and 20 cc. of chloride-free concentrated nitric acid is added. The solution is heated for two to three hours at 90 to 95° under reflux, and after cooling and addition of a few drops of 0.5 *N* silver nitrate solution, no opalescence due to silver chloride should be observable.

Ammonia.—One gram of the salt is placed on a watch glass and 1 cc. of 4 *N* sodium hydroxide solution is added. The watch glass is covered with a second inverted one of the same size which has a strip of moistened litmus paper adhering to its under side. The presence of 0.001% of ammonia is easily detectable by a blue coloration of the litmus paper after the apparatus has stood for fifteen minutes. The products used by us contained less than 0.001% of ammonia.

Other Impurities.—Other tests given by Murray were found to be satisfactory.

The samples of potassium thiocyanate used in the titrations against silver were pure white, and tests showed that they were entirely free from heavy metals, alkaline earth metals, chloride, ammonia, sulfate, sulfur, cyanate and cyanide.

Drying of Potassium Thiocyanate and Hygroscopicity of the Dried Salt

Three 23-g. samples of potassium thiocyanate, which had been thrice recrystallized from water and dried for a week over phosphorus pentoxide at room temperature, were ground to a fine powder in an agate mortar and placed in large tared weighing bottles with well fitting stoppers. The samples were then subjected to the drying treatment described in Table I. The results with the three samples agreed within the limits of the possible error in weighing; and we therefore give only the data obtained with one sample for the sake of brevity.

It is evident from these experiments that no more than 0.02% of water is retained by the salt after heating for one to two hours at 150°. The last trace of water is removed by melting for a short time at 200°.

It will be observed that there was a slight, but definite, increase in weight on prolonged heating of the molten salt at 200°. This increase in weight is probably caused

TABLE I

LOSS IN WEIGHT OF POTASSIUM THIOCYANATE ON HEATING

Treatment	Wt. of salt, %	Total change in weight, g.
25 hrs. over P_2O_5 at room temp.	23.6163	(0.000)
45 hrs. over P_2O_5 at room temp.	23.6170	+ .003
1 hr. at 100–105°	23.6136	– .011
4 hrs. at 100–105°	23.6125	– .016
1 hr. at 150–155°	23.6083	– .032
3 hrs. at 150–155°	23.6072	– .038
5 hrs. at 150–155°	23.6069	– .039
10 min. at 200–210° (m. p. 172°)	23.6055	– .045
30 min. at 200–210°	23.6036	– .053
1 hr. at 200–210°	23.6065	– .041
1 hr. 40 min. at 200–210°	23.6087	– .032

by a slow air oxidation and for this reason the melting period should not be unduly long.

Samples heated in the molten state for fifteen hours at 195° gained 0.05% in weight. Subsequent titration with pure silver solutions as described later showed that the effective strength of these samples was 0.04% less than samples which had been melted for only ten minutes at 200°.

Experiments were next made to determine the hygroscopicity of the dried salt. Twenty-three-gram samples of the solid melts from the drying experiments were crushed and ground to a fine powder in an agate mortar, and, after transferring to tared weighing bottles, they were redried at 150° to remove the water taken up during grinding (0.08%).

After standing for a week over deliquescent calcium chloride hexahydrate (relative humidity, 0.30), and for a week longer over deliquescent potassium carbonate dihydrate (r. h. 0.45), the weight of the dried samples remained unchanged. A sharp increase in weight, which increased rapidly with time, was found when the samples were placed over deliquescent sodium bromide dihydrate (r. h. 0.57). Therefore the dried salt is not hygroscopic at a relative humidity less than 45% but deliquesces rapidly at relative humidities greater than about 50%. This result is in accord with measurements of N. Schoorl (private communication), who found that the aqueous vapor pressure of a saturated potassium thiocyanate solution corresponds to a relative humidity of 0.50 at 13.5°.

Potentiometric Comparison of Potassium Thiocyanate against Silver.—We have studied the accuracy of this titration by direct comparison of pure potassium thiocyanate against pure silver.

Materials

Silver.—Pure silver was prepared according to the classical method of Richards and Wells⁶ by reducing twice recrystallized silver nitrate with redistilled ammonia and pure formic acid. Several samples of the metal so obtained were further purified by melting into buttons on charcoal, and electrolyzing these buttons in the usual way.

Silver Nitrate.—Mallinckrodt reagent quality silver nitrate was twice recrystallized from nitric acid and after

(3) H. N. Stokes and J. R. Cain, *THIS JOURNAL*, **29**, 443 (1907).

(4) H. R. Offord, *Ind. Eng. Chem., Anal. Ed.*, **7**, 93 (1935).

(5) Murray, "Standards and Tests for Reagent and c. p. Chemicals." D. Van Nostrand Company, New York City, 1927.

(6) T. W. Richards and R. C. Wells, *THIS JOURNAL*, **27**, 450 (1905).

drying at 110° the samples were melted for fifteen minutes at 225 to 250° in an electric oven, in platinum.

Water.—Twice distilled water was used for all standard solutions. All other materials used in this work were of a degree of purity consistent with the purposes for which they were used, as shown by appropriate tests.

Standard Solutions.—Standard solutions were prepared by weight, using a large Bunge balance which had a sensitivity of 1 mg. with a full load of two kilograms. Weighings below 200 g. were performed on an ordinary analytical balance. The set of weights used (10 mg. to 1000 g.) was carefully calibrated by the substitution method. Weighings were corrected to vacuum on the following density basis; weights 8.4, air 0.0012, potassium thiocyanate 1.91, silver nitrate 4.35 and silver 10.5 g. per cc.

The stock solutions were prepared and stored in specially constructed one-liter Erlenmeyer flasks, provided with finely ground glass stoppers carrying sealed-in delivery tubes similar to an ordinary wash bottle. The ends of the delivery tubes were closed with ground glass caps. These storage flasks were modeled after the storage bottles described by Lange and Schwartz.⁷

Potassium thiocyanate and neutral silver nitrate solutions were prepared from samples of the pure fused salts.

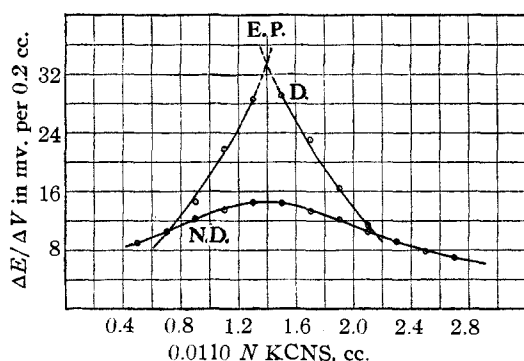


Fig. 1.— $\Delta E/\Delta V$ curves in region of equivalence point in final titrations of a digested and undigested precipitate: D., digested; N. D., not digested.

Acid silver solutions were prepared by dissolving carefully weighed buttons of the purified metal in an excess of 6 *N* nitric acid in a Kjeldahl flask. After diluting and heating to remove residual oxides of nitrogen, the solution was transferred to a previously weighed storage flask, diluted to *ca.* 800 cc. and weighed. The free acid concentration of these silver solutions (*ca.* 0.02 *N*) was determined by titrating suitable samples with standard sodium hydroxide, using brom cresol green indicator.

The standard stock solutions were approximately 0.2 molar. Twenty times diluted solutions (*ca.* 0.01 *N*) of each of the stock solutions were prepared using calibrated volumetric apparatus.

Apparatus and General Procedure of the Titrations

The usual potentiometric apparatus was used, allowing e. m. f. readings to ± 0.1 mv. The silver electrodes were prepared by plating small platinum gauze electrodes (cylinders of 1 cm. diameter and 1 cm. in length) with silver

from a potassium argenticyanide bath at low c. d. The saturated calomel and saturated mercurous sulfate reference electrodes were of the simple bottle type recommended by Müller.⁸ The bridge tubes were of the inverted U-type, filled with a gel of saturated potassium sulfate in 3% agar.

The titrations were performed in very faint diffuse daylight in a room with closely drawn shades. As a further precaution against light decomposition, the 250-cc. titration beaker was placed in a closely fitting brown glass jar. Efficient mechanical stirring was employed in all measurements and titrations, using a small electric induction motor and a glass stirrer of the propeller type.

The general procedure of titration consisted in weighing out 40 to 50 g. of the stock silver solution into a small tared and stoppered flask directly from the storage flask (silver solutions cannot be dispensed from weight burets with greased stopcocks), transferring to a 250-cc. beaker and diluting to 125 cc., with or without the addition of nitric acid. The stock thiocyanate solution was then added from a weight buret over a period of three to five minutes, with constant stirring, until the measured e. m. f. indicated close approach to the equivalence point.

In some titrations it was desired to add the titrating solution very slowly over a period of fifteen to thirty minutes and for this purpose a special dropping funnel, without a stopcock, similar to the one described by Johnson⁹ was used.

In some titrations a slight deficiency of potassium thiocyanate solution was added, and in others a slight excess was added. The titration was finally finished with the appropriate dilute solution (*ca.* 0.01 *N*), added from a 5-cc. microburet. The location of the equivalence point was found in the usual manner by calculating the point at which $\Delta E/\Delta V$ attained a maximum value.

The final titration was made very slowly, with care to obtain constant potential before adding successive increments of the dilute titrating solution. It required about one to one and a half hours for the final titration.

It was found that the titration could be made more quickly, and a more pronounced maximum in $\Delta E/\Delta V$ was obtained, when the mixture was heated to 70 to 90° for ten minutes after the addition of the stock thiocyanate solution, and cooled to room temperature again before the final titration. In this way the bulk of the precipitate is subjected to a drastic aging which causes a marked decrease in its adsorptive properties toward silver and thiocyanate ions.⁷ In Fig. 1 the data of two final titrations in the region of the equivalence point have been plotted to illustrate this difference in the behavior of digested and undigested precipitates. In both cases the maximum in $\Delta E/\Delta V$ comes at the same place, but the break is more pronounced with digested precipitates.

Considerable time is required to obtain constant e. m. f. readings during the titration, especially with undigested precipitates. Constant potential was obtained more quickly when an excess of thiocyanate solution was added, and the final titration was made with the dilute silver solution, than when the reverse procedure was employed. Ad

(8) E. Müller, "Elektrometrische (Potentiometrische) Massanalyse," 5 Aufl., Theodor Steinkopff, Dresden, Germany, 1931.

(9) C. R. Johnson, *J. Phys. Chem.*, **37**, 923 (1933).

(7) E. Lange and E. Schwartz, *Z. Elektrochem.*, **32**, 240 (1926).

dition of barium nitrate as recommended by Müller⁸ was not conducive to more rapid attainment of steady potential, the drift in potential, and the time required for the drift to decrease to a negligible magnitude, were practically the same as when no barium nitrate was present.

In order to show the precision of the comparisons the data of a typical titration are given in Table II.

TABLE II
DATA OF A TYPICAL TITRATION

52.476 grams of 0.17828 molar silver nitrate solution diluted to ca. 125 cc. and 1 cc. of concd. nitric acid added. 48.729 grams of 0.19131 molar potassium thiocyanate solution (salt recryst. once from alcohol) added from weight buret at room temperature. Mixture heated to 70 to 90°, digested ten minutes, and cooled to room temperature. Titration completed with 0.00955 *M* thiocyanate solution from microburet. Saturated mercurous sulfate reference electrode.

0.00955 <i>N</i> KCNS. cc.	<i>E</i> , volts	$\frac{\Delta E}{\Delta V}$	$\frac{\Delta^2 E}{\Delta V^2}$
0	+0.0800		
3.4	.1411		
3.6	.1558	147	+68
3.8	.1774	216	-23
4.0	.2058	284	
4.2	.2319	261	
4.4	.2519	200	

$V = 3.8 + 68/(68 + 23) \times 0.2 = 3.95$ cc. Correction to thiocyanate solution, +0.197 g. Total thiocyanate solution, 48.729 + 0.197 = 48.926 g. wt. AgNO₃ soln./wt. KCNS soln. = 52.476/48.926 = 1.0725 (calcd. 1.0731.) Effective strength of KCNS, 99.94%.

Five other titrations, using the same sample of potassium thiocyanate, yielded the following results, in terms of the effective strength of the salt: 99.96, 99.93, 99.90, 99.90 and 99.93%, or an average of 99.93% for the six titrations.

Products recrystallized two to five times from water and alcohol, and the samples obtained by fractional precipitation of a saturated alcohol solution of the salt with ether, were tested in a similar way.

The detailed results of these titrations are not given here but may be found in the thesis of the junior author.¹⁰ It suffices here to state that the final average obtained with twelve different products corresponded to an effective strength of 99.92% for the potassium thiocyanate.

Titrations carried out in neutral solution at room temperature, and with varying concentration of nitric acid (0–0.5 *N*), indicated that the acidity did not influence the results. However, when the potassium thiocyanate was added to a hot (80–90°) neutral or acid (nitric) silver solution, the average effective strength of the potassium thiocyanate was 100.05%. When the hot silver solution was acidified with sulfuric acid (0.06 *N*) the effective strength of the potassium thiocyanate was several tenths of a per cent. too high.

The reverse order of precipitation was also used in several titrations in neutral and dilute nitric acid solution; *i. e.*, the silver nitrate solution was added to the thiocyanate solution. The results agreed with the data of the

former experiments, which showed that the order of the precipitation is without influence in the titrations.

Titration to the Equivalence Potential.—Since the precision of this method is dependent on an exact knowledge of the equivalence potential, it is of prime importance to determine this value in an accurate way. A simple method has been proposed by Kolthoff¹¹ for determining the equivalence potential by titration. The method consists in performing a titration with very dilute solutions of known concentration, calculating an empirical equilibrium constant for the reaction from the titration data, and finally calculating the equivalence potential from the equilibrium constant. In this way the solubility product of silver thiocyanate in neutral 0.05 *N* potassium nitrate solution was found to be 3.2×10^{-12} at 24°, and the corresponding equivalence potential against the saturated mercurous sulfate electrode was +0.176 v., which agrees well with the value +0.175 v. found from the maximum in $\Delta E/\Delta V$. By a similar titration it was found that the equivalence potential in a solution 0.05 *N* in potassium nitrate and 0.032 *N* in nitric acid (which duplicates the conditions in the titrations described below) was +0.187 ± 0.002 v.

Titrations were performed by adding thiocyanate solution to a slight excess of silver solution, and finally adding dilute thiocyanate solution until the measured e. m. f. remained constant at +0.187 ± 0.002 v. for at least fifteen minutes. In four such titrations to the equivalence potential, the average effective strength of the potassium thiocyanate was found to be 99.92%. These results are in exact agreement with those obtained by locating the equivalence point from the maximum in $\Delta E/\Delta V$.

Titration by the Volhard Method.—Some titrations were made by the classical Volhard method employing ferric iron as indicator. The thiocyanate solution was added to a slight excess of silver solution and the excess was titrated back with the dilute thiocyanate solution. The indicator blank was found to be 0.10 cc. of 0.01 *N* thiocyanate, using 4 cc. of a saturated ferric alum solution as indicator, in a final volume of 200 cc., and this value was applied as a correction in the titrations. A comparison flask, containing the same amount of precipitate and ferric alum indicator with a slight excess of silver present, was used to assist in locating the color change. The end-point was taken when the yellowish-brown coloration persisted after a minute or two of vigorous shaking.

The results showed an effective strength for the potassium thiocyanate that varied between 100.01 and 100.05%, the average being 100.02%. These results, 0.10% higher than the potentiometric comparisons, indicate that adsorption equilibrium is not reached in the relatively rapid Volhard titration, and that an excess of silver is retained by the precipitate at the visual end-point. In the potentiometric titrations, which require more than an hour, the silver nitrate, co-precipitated by the precipitate, is given off during the time required to obtain constant e. m. f.

The correctness of this conclusion was verified by adding a slight known excess of silver nitrate to the suspension remaining after potentiometric titrations in which the pre-

(10) J. J. Lingane, Senior Thesis, University of Minnesota, June, 1935

(11) I. M. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928).

precipitate had been digested. The slight excess of silver was then titrated back with the dilute thiocyanate solution after the addition of 4 cc. of saturated ferric alum indicator. The effective strength of the potassium thiocyanate calculated from the results of two such titrations was only 0.01% higher in both cases than the value determined from the potentiometric end-point.

A Side Reaction During the Precipitation of Thiocyanate with Silver.—Although the methodical precision of the potentiometric titrations was better than 0.01%, the results frequently varied by as much as 0.05% under identical conditions of titration. Furthermore, the effective strength of the various preparations of potassium thiocyanate was consistently in the neighborhood of 99.92% instead of exactly 100.00%, although no impurities could be found in any of the products. These facts pointed to the occurrence of a side reaction (or reactions) accompanying the precipitation of silver thiocyanate.

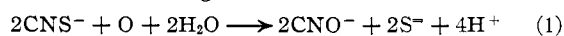
When a hot, acid silver solution was precipitated with thiocyanate the effective strength of the thiocyanate was definitely greater than 100%. Further, when a hot, neutral silver solution was treated with thiocyanate, the precipitate was colored a light tan, even when the precipitation was made in the dark. From hot dilute sulfuric acid solution the precipitates were pure white, but the effective strength of the potassium thiocyanate was several tenths of a per cent. greater than 100%.

Some of the tan precipitates from hot neutral solution were washed with water and suspended in a weak acetic acid solution containing excess potassium iodide. A strong odor of hydrogen sulfide was observed and a test for hydrogen sulfide was obtained with a moistened lead acetate paper placed in the mouth of the flask.

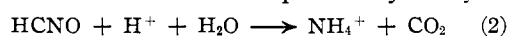
It was thought that an air oxidation of thiocyanate might have been induced during the precipitation, but the results obtained in potentiometric titrations in an atmosphere of nitrogen were the same as in air, and tan colored precipitates were also obtained in the absence of air.

Another possibility was that silver, being a rather strong oxidizing agent under certain conditions, might oxidize a minute fraction of the thiocyanate with the formation of cyanide, or cyanate, and thionic acids. A test was developed which was capable of detecting as little as 0.01% of cyanide in the precipitate but no indication of the presence of cyanide was obtained.

It was thought that some cyanate might be formed according to the reaction



with the simultaneous precipitation of the sulfide by silver or its oxidation to thionic acids or sulfate, depending on the conditions. Cyanic acid is a weak acid which decomposes very easily



Thus, if cyanate were an intermediate product of the side reaction, ammonia should be present in the final solution. This was actually found to be true.

The traces of ammonia, formed under various conditions of precipitation of thiocyanate with silver, were determined in the supernatant solution by making alkaline with ammonia-free sodium hydroxide, distilling in an all-glass apparatus and collecting the distillate in 10 cc. of 0.001 *N* sulfuric acid. The amount of ammonia in the distillate was estimated colorimetrically with Nessler's reagent. Ammonia-free reagents were used. According to the procedure developed, 0.005 mg. of ammonia in 90 cc. of solution could be detected with certainty.

TABLE III
FORMATION OF AMMONIA DURING PRECIPITATION OF SILVER THIOCYANATE

1.75 g. of AgNO_3 in 100 cc. of water and 0.97 g. of KCNS in 75 cc. of water for each experiment. 1 cc. excess of 4 *N* NaOH added to 90 cc. of supernatant solution and distilled for 30 min. in current of pure air.

Conditions of precipitation		NH_3 in 10 cc. of distil- late, mg.
1	$\text{KCNS} \longrightarrow \text{AgNO}_3$, 0.2 <i>N</i> in HNO_3 , room temp.	0.03
2	As (1), except at 80–90°	.07
3	As (1), except both solutions boiled 2 min. before mixing, and boiled during precipitation	.04
4	As (1), except air displaced with NaHCO_3	.03
5	$\text{KCNS} \longrightarrow \text{AgNO}_3$, neutral, room temp.	.03
6	$\text{KCNS} \longrightarrow \text{AgNO}_3$, neutral, 80–90°	.05
7	As (5), except 0.5 g. of borax present	.03
8	As (7), except $\text{AgNO}_3 \longrightarrow \text{KCNS}$.02
9	$\text{KCNS} \longrightarrow \text{AgNO}_3$, 0.2 <i>N</i> in H_2SO_4 , room temp.	.03
10	As (9), except at 80–90°	.07

It will be observed that practically the same amount of ammonia was formed in the absence as in the presence of air. More ammonia was found when the precipitation was made in hot solution than when the precipitation was made at room temperature.

Discussion of Results

Although the end-point of the potentiometric titration can be found with a precision of better than 0.01%, the titration of silver with thiocyanate is not suited to work of a highly exact nature. As a result of the side reactions, the variations between duplicate titrations at room temperature may amount to as much as 0.05%, the average result corresponding to an effective strength of the potassium thiocyanate of 0.08% less than the theoretical.

The Volhard method of locating the end-point leads to the same result when the precipitate is digested with a slight excess of silver before the final titration. In the ordinary Volhard method at room temperature without digestion, the average effective strength of the potassium thiocyanate is 0.02% higher than the theoretical, and 0.10% greater than the effective strength found potentiometrically or after digestion, because 0.10% of the silver nitrate is still adsorbed or occluded by the precipitate at the end-point. The relatively good results obtained by the ordinary Volhard method are thus due to a compensation of errors.

Potassium thiocyanate may be recommended as a standard substance in work of ordinary accuracy.

Summary

1. Potassium thiocyanate is easily obtained

in a pure state and is a suitable standard substance for work of ordinary accuracy ($\pm 0.1\%$).

2. During the precipitation of silver with thiocyanate, or the reverse, slight side reactions occur in which cyanic acid is an intermediate product decomposing to ammonia and carbon dioxide. When a hot neutral silver solution is precipitated with thiocyanate the precipitate is colored tan by silver sulfide. The side reactions also take place in the absence of oxygen.

3. As a result of the side reactions, the average effective strength of the potassium thiocyanate in the potentiometric titration with silver at room temperature is only 99.92%.

4. If titrated at 70 to 90° an effective strength slightly greater than 100% is found. If the precipitation is carried out in hot dilute sulfuric acid (0.06 *N*), the deviation is several tenths of a per cent. greater.

5. The ordinary Volhard titration at room temperature leads to an effective strength 0.10% greater than the potentiometric titration, due to occlusion of silver nitrate at the end-point. If the precipitate is digested just before the end-point, the Volhard method gives results practically identical with the potentiometric method.

6. The solubility product of silver thiocyanate at 24° in 0.05 *N* neutral potassium nitrate solution is equal to 3.2×10^{-12} .

MINNEAPOLIS, MINNESOTA

RECEIVED JUNE 4, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Formation of Zirconate Hydrosols and their Disintegration by Certain Neutral Salts

BY ARTHUR W. THOMAS AND HARRY S. OWENS

In a previous publication,¹ the *pH* raising action of neutral salts upon basic zirconium chloride (sometimes designated as "zirconium oxide") hydrosols was ascribed to the replacement of OH groups from the polyolated micelles by the anions of the added neutral salts. If the strongly coördinatively bound OH group can thus be displaced from the central metallic atom by added anions, one would expect other coördinatively bound groups also to be displaceable.

Increases in chloride ion activity of "oxide"

(1) A. W. Thomas and H. S. Owens, *THIS JOURNAL*, **57**, 1825 (1935).

hydrosols have been reported to result upon addition of neutral salts.² Inasmuch as the order of effectiveness of the anions of the salts in raising the chloride ion activity is in general similar to those reported from this Laboratory for displacing OH groups from the micelle, the writers submit this as evidence for the expected displacement of chlorido groups. Removal and replacement of aquo groups from the central metallic atom by

(2) (a) P. S. Wassiliev and A. J. Rabinowitch, *Kolloid Z.*, **56**, 305 (1931); (b) H. B. Weiser, *J. Phys. Chem.*, **35**, 1, 1368 (1931); (c) A. Lottermoser and T. Chang, *Kolloid Z.*, **65**, 62 (1933); (d) W. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929, p. 527.