Constant Current Coulometric Method in Argentometric Titration of Thiourea

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(Received May 15, 1953)

Introduction

Several methods are available for the determination of thiourea in which are included, besides well-known Volhard's silver nitrate method in an ammoniacal solution, iodine titration by Reynolds⁽¹⁾, oxidimetric method by Cuthill⁽²⁾, selenious acid method by Werner⁽³⁾ and sulfur determination method proposed by Wiesenberger⁽⁴⁾ and Akita⁽⁵⁾. When thiourea is mixed with ammonium thiocyanate, the analysis of the former only, or of both is carried out according to the methods published by Salkowski⁽⁶⁾, Reynolds⁽¹⁾ and Kodama⁽⁷⁾.

These methods are, however, limited to a comparatively larger amount of thiourea. It is desirable to find out a reliable and accurate micromethod by which a milligram amount or less of thiourea is precisely determined. The object of this paper is to present a coulometric titration method for the microanalysis of thiourea.

The constant current coulometric method was applied to this purpose and the results obtained were satisfactory. As is observed in Table 1 and 2, milligram and submilligram quantities of thiourea were determined with a tolerable precision.

In the method described below, thiourea was treated with silver bromide solution in ammonia and the liberated bromide ion, which is equivalent to thiourea, was titrated with the anodically generated silver ion rather than with a standard solution. The electrolysis current was automatically controlled to be constant during the electrolysis; thus the amount of the generated silver ion was exactly determined as the product of current and time according to Faraday's law.

Because the titrant could be added in very small increments, the coulometric titration is a suitable means to the microanalytical treatment. In contrast to the ordinary titration, the standardization and storage problems of solutions are avoided, therefore high precision is attained by the constant current coulometric titration especially when it is applied to microanalyses.

In the preliminary experiments a small amount of thiourea was titrated in an ammoniacal medium with the anodically generated silver ion, which procedure is analogous to the Volhard's titration of thiourea. Results obtained were fairly accurate when the concentration of ammonia exceeds $2N$ in the electrolyte. But the objection is that the reaction is somewhat time-consuming. This difficulty was overcome by the present method, replacing thiourea by the equivalent bromide ion.

Apparatus

A weighing bottle of brown glass (about 70 ml.) with the ground glass stopper was used as the

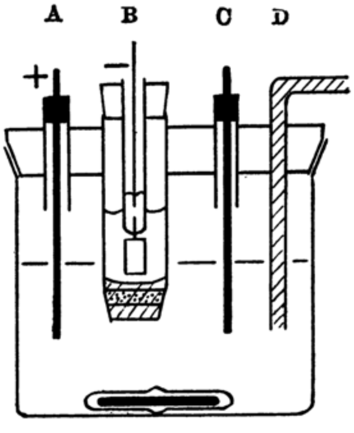

Fig. 1. Schematic diagram of the electrolysis cell
A: Generator anode, Ag rod.
B: Generator cathode, Pt sheet.
C: Indicator electrode, Ag rod.
D: Agar KNO_3 bridge.

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(1) J. E. Reynolds and E. A. Werner, *J. Chem. Soc.*, **83**, 6 (1903).

(2) R. Cuthill and C. Atkins, *J. Soc. Chem. Ind.*, **56**, 5 (1937).

(3) A. E. A. Werner, *Analyst*, **65**, 286 (1940).

(4) E. Wiesenberger, *Mikrochimie ver. Mikrochim. Acta*, **29**, 73 (1941).

(5) T. Akita and K. Takagishi, *Plastics* (in Japanese), **1**, 22 (1950).

(6) Salkowski, *Ber.*, **26**, 2498 (1893).

(7) S. Kodama and others, *J. Chem. Ind. Japan*, **54**, 184 (1951).

electrolysis cell. The sample to be analysed was weighed directly in it. Another rubber stopper was prepared to which electrodes were firmly settled and arranged for electrolysis as shown in Fig. 1. Generator cathode (B in the figure) is a smooth platinum plate (6×15mm) dipped in the saturated potassium nitrate solution, which is isolated from the solution to be analysed with a sintered glass disk and agar.

The solution was vigorously stirred with a magnetic stirrer. The whole cell is preferably enclosed in a dark case to eliminate the photochemical change of silver bromide.

As the source of the constant current for electrolysis the line-operated device of Carson8) was utilized. The value of current was measured at intervals during electrolysis from the IR-drop across a standard resistor to ascertain the constancy. Actually the current was stable enough and no appreciable drift was observed. The quantity of silver ion generated is calculated as the product of current and time, the latter having been measured with a stop-watch.

The electrolysis was interrupted at appropriate intervals and followed by the measurement of potential of the indicator electrode. The end-point of the titration was determined in the same way as in the conventional potentiometric titration.

Procedure and Results

Procedure. The aqueous solution or the solid sample of thiourea is weighed directly in the electrolysis cell. When a larger volume of solution than several milliliters is dealt with, evaporate to a few milliliters. Then the silver bromide solution in ammonia is added drop by drop to a slight excess. Without filtering the precipitate of silver sulfide formed, the solution is gently warmed at 60 to 70°C till the odour of ammonia disappears. Precautions must be taken against drying up the solution. This process is accomplished in a dark place to avoid the photochemical decomposition of silver bromide which has been separated out. Next about 5g. of potassium nitrate is added and the solution is made up to about 50ml. with water, acidified with dilute sulfuric acid. After arranging the electrodes to the cell, the electrolysis is started with a constant current of an appropriate value. The end-point is informed with the aid of the potentiometric method.

NOTES. The ammoniacal silver bromide solution is prepared as follows. The purified silver bromide which is prepared from silver nitrate and potassium bromide and recrystallised from ammonia is dissolved to saturation in concentrated ammonia. This work is performed under a photographic lamp in a dark room. The ammoniacal solution thus prepared is stable against light if no residue of the solute is present.

Sulfuric acid is the most preferable to acidify the solution after the reaction between thiourea and silver bromide has been completed. With acetic acid, the measuring process is time-consuming although no serious interference results. Nitric acid is disapproved because it attacks silver electrodes even when diltute and gives considerable negative results.

To bring the reaction between thiourea and silver bromide to completion, subsequent removal of ammonia is inevitable. Expelling ammonia with a strong base is not recommended. In the procedure described above the solution was gently warmed at 60 to 70°C over an electric heater of small wattage. Precautions must be taken against bubbling and complete evaporation. To make the removal of ammonia easy, the preliminary concentration of the original solution to a small volume is advisable and the large excess of the silver bromide solution is rather objectionable.

Repeatability. To have a knowledge of the repeatability of this method a series of experiments were made taking about 3.9 mg. of thiourea in each. About 4ml. of the silver bromide solution was added and the constant current of about 10 mA. was used for electrolysis. The results obtained are shown in Table 1. Observed values are fairly accurate. The mean of the errors is −0.0076 mg. for these seven samples and the standard deviation 0.011 mg. for each value.

Table 1

Determination of Thiourea, (A)

Amount of Thiourea	Current	Equiv. Point (sec.)		Error	
(mg.)	(mA.)	Calc.	Found	mg.	%
3.936	10.010	997.5	999.7	0.009	0.22
3.942	9.999	999.1	996.9	−0.009	−0.22
3.940	9.996	998.9	996.0	−0.011	−0.29
3.995	10.005	999.5	992.4	−0.027	−0.71
3.937	10.000	998.1	998.9	0.003	0.08
3.939	10.010	998.8	997.3	−0.006	−0.15
3.939	10.021	997.4	999.6	0.009	0.22

Table 2

Determination of Thiourea, (B)

Amount of Thiourea	Current	Equiv. Point (sec.)		Error	
(mg.)	(mA.)	Calc.	Found	mg.	%
0.3982	10.001	100.9	101.7	0.0031	0.79
0.3926	10.003	99.5	103.6	0.0161	4.1
0.1969	5.986	83.4	86.2	0.0067	3.4
0.1963	5.959	83.5	85.3	0.0043	2.2
0.1965	5.783	86.2	87.2	0.0024	1.2
0.0312	0.876	87.6	89.2	0.0006	1.8
0.0312	0.882	88.2	95.5	0.0026	8.3
0.0312	0.899	88.1	93.5	0.0019	6.1
0.0312	0.889	89.0	83.3	−0.0020	−6.4

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8) W. N. Carson, *Anal. Chem.*, **22**, 1565 (1950).

Analysis of Decreased Amounts of Thiourea. As this method is intended rather for the microanalysis, decreased amounts of thiourea were treated, the results of which are shown in Table 2. Absolute errors in mg. are passably small, but the relative errors are no longer ignored, therefore the limitation lies at several hundredths milligram of thiourea. It is obvious from the table that the use of smaller electrolysis current is profitable for smaller amounts of thiourea, because the smaller the current is, the longer time is taken to the end-point. Thus the error due to time-measurement is reduced.

Simultaneous Analysis of Thiourea and Thiocyanate

Microanalytical determination of thiourea and ammonium thiocyanate in the mixture is often sought for.

The present method, when applied to the mixture, gives the sum of both substances, because thiocyanate is titrated argentometrically together with bromide and only one inflection occurs on the potentiometric curve owing to the similar solubilities of their silver salts.

Titration of thiourea only with the electrolytically generated iodine, modified method of Reynolds[1], was also not available because iodine titration is valid only for macroanalysis.

Léon's device[9] gives a useful information to the present purpose, as be succeeded in the simultaneous analysis of bromide and thiocyanate with the potentiometric titration in an 80 to 90% acetone solution. This device was introduced and the simultaneous analysis of thiourea and thiocyanate was attempted in an acetone solution using the present method. The acetone solution made a clear-cut distinction of thiourea from thiocyanate and two inflections appeared on the potential-time curve due to bromide and thiocyanate respectively. Mixtures of various proportions were treated, the results of which are tabulated in Table 3.

Table 3

Simultaneous Analysis of Thiourea and Thiocyanate in 90% Acetone Solution
1 coulomb = 0.3945mg. thiourea, 0.7889mg. thiocyanate

Thiourea	Thiocyanate	Current	Equiv. Point Found (sec.)		Error (%)	
(coulomb)	(coulomb)	(mA.)	Thiourea	Thiocyanate	Thiourea	Thiocyanate
7.484	2.526	10.013	760.4	252.6	1.7	0.12
7.482	2.526	10.011	757.2	255.4	1.3	1.2
7.978	3.959	10.032	816.6	391.3	2.5	−0.68
7.971	3.956	10.009	804.9	402.2	1.1	1.7
4.806	5.435	10.019	488.3	539.8	1.6	−0.22
4.806	5.435	10.067	483.5	544.0	1.3	0.95
4.806	5.435	10.018	485.2	553.7	1.1	2.0
4.983	9.782	10.008	514.0	985.5	3.2	1.1
4.981	9.777	10.006	514.1	983.3	3.3	0.58
2.502	7.547	10.001	254.0	758.4	1.6	0.48
2.504	7.553	9.993	252.9	756.4	1.0	0.01

A little less accurate values are found compared with those in a pure solution. This procedure is, however, simple and easy for the simultaneous analysis, if such an error is within allowance.

Summary

The coulometric method with a constant current was used for the microanalysis of thiourea.

An ammoniacal solution of silver bromide was added to thiourea solution and the liberated bromide equivalent to thiourea was titrated with electrolytically generated silver ion in an acid solution. A milligram amount of thiourea was satisfactorily determined with the standard deviation of about 0.01 mg. and the method is also applicable to submilligram amounts of thiourea.

Simultaneous analysis of thiourea and ammonium thiocyanate in a mixture was made using 90% acetone solution.

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[9] C. Léon, *Compt. Rend.*, **232**, 170 (1951).