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Application of 2-thiouracil and 2,4-dithiouracil for the Determination of Metal Ions.
II. Potentiometric Titration of Silver and Mercury (II)

Zastosowanie 2-tiouracylu i 2,4-ditiouracylu do oznaczania jonów metali. II. Miareczkowanie potencjometryczne srebra i rtęci (II)

Применение 2-тиоурацила и 2,4-дитиоурацила для обозначения ионов металлов.
Потенциометрическое титрование серебра и ртути (II)

Complex-forming properties of 2-thiouracil, 2,4-dithiouracil and derivatives, so as their use for spectrophotometric determination of metal ions, were reviewed in part I [1]. However, the named compounds did not find an application as reagents in another methods of analysis, e.g. electrochemical ones. Nevertheless, reverse employment of the reactions of thiouracils with metal ions is known. G a n b Ź c k [2] and later V i e b Ź c k [3] have described the determination of 6-methyl- and 6-propyl-2-thiouracil by the reaction with AgNO_3 , whence equivalent amount of H^+ was titrated with sodium

hydroxide solution; M i d d e l d o r f [4] has proposed similar procedure for 6-methyl-2-thiouracil, but an excess of AgNO_3 was back-titrated with ammonium thiocyanate solution; N e s h k o v a and coworkers [5] have assayed 2-thiouracil, 6-methyl-2-thiouracil and 2,4-dithiouracil potentiometrically with AgNO_3 against ion-selective electrode. 6-Methyl-2-thiouracil was determined also by precipitation with mercuric nitrate solution and titration of the excess of Hg^{2+} with SCN^- or EDTA solution [6] or by amperometric titration with mercuric chloride [7]; the reaction with cupric sulfate was used for colorimetric procedure [8]. Colorimetric determination of 6-propyl-2-thiouracil was elaborated, based on the reaction with RuCl_3 [9].

In present work we stated that 2-thiouracil and 2,4-dithiouracil may be used as titrants for the determination of Ag^+ and Hg^{2+} ions with an application of silver sulfide indicator electrode.

EXPERIMENTAL

Reagents and apparatus

2-Thiouracil, a.r. - Fluka (Buchs, Switzerland).

2,4-Dithiouracil was synthesized after W h e e l e r and L i d d l e [10], and was purified and analyzed as previously reported [1].

Solutions 0.1 mole/dm^3 of thiouracil or dithiouracil sodium salts were prepared by dissolving of weighed amount of the sample in equivalent volume of 0.1 mole/dm^3 NaOH solution.

Buffer solutions: pH 3.30-6.65 - acetate after Walpole, pH 7.20-11.85 - borate after Michaelis.

All reagents used were analytical grade, prod. by POCh (Gliwice, Poland).

Potentiometer type PHM-22 with scale expander 630P - Radiometer (Copenhagen, Denmark) with electrodes: glas G-202 C, calomel K-401, mercuric P901, silver P4011; silver sulfide electrode was prepared by electrolytic coating of silver electrode in ammonium sulfide solution.

All measurements were carried out at $20^{\circ}\text{C} \pm 1^{\circ}$.

Preliminary investigations

It was previously stated [1] that silver complexes of 2-thiouracil and 2,4-dithiouracil are stable in weak acidic or neutral solutions. Now pH range of suitable medium was examined, when a series of samples (standard AgNO_3 solutions) with different volumes ($5 - 15 \text{ cm}^3$) of acetate buffer solutions pH 3.30-6.30 varying every ca. 0.5 pH, or without buffer were titrated with thiouracil or dithiouracil sodium salt solutions, - in respect of reproducibility, sensitivity and time of equilibration. Similar examinations were undertaken with the samples of Hg^{2+} salts (mercuric acetate). The conclusions of these tests resulted in following recommended procedures.

Determination of Ag^+

- with 2-thiouracil. The solutions ($0.50-5.0 \text{ cm}^3$) of silver salts, containing 5.30-49.30 mg of Ag, were pipetted into titration vessel, added to each 10 cm^3 buffer solution pH ca. 5.20 (5.0-5.5) and water to the volume 100 cm^3 and titrated with 0.1 mole/dm^3 solution of 2-thiouracil sodium salt against silver sulfide indicator electrode and saturated calomel electrode, the last connected with titration vessel by salt (sat. KNO_3) bridge.

- with 2,4-dithiouracil. Potentiometric determination of silver using 0.1 mole/dm^3 solution of 2,4-dithiouracil sodium salt was performed on analogous way, only without an addition of buffer solution.

The ratio of metal-ion to ligand in equivalence point, taken for stoichiometric calculation of silver concentration in solution, was 2:1 in both cases for thiouracil and dithiouracil. Results of determinations carried out with known amounts of silver in samples are presented in tab. 1.

Tab. 1. Potentiometric determination of silver with 2-thiouracil and 2,4-dithiouracil - statistical evaluation of results

Reagent	Number of variables n	Standard deviation, %	Standard deviation of the mean %	Confidence interval prob. level 95%
2-Thiouracil	7	0.61	0.23	98.24 ± 0.44
2,4-Dithiouracil	7	0,85	0.32	98.43 ± 0.62

Determination of Hg^{2+}

- with 2-thiouracil. To the volumes ($0.5-4.0 \text{ cm}^3$) containing 9.90-79.20 mg Hg (II) were added 10 cm^3 buffer pH ca. 5.30 (5.0-5.5) each, filled up with water and titrated potentiometrically as by Ag^+ . One of titration curves is shown on Fig. 1. As it is to be seen, in equivalence point corresponding to molar ratio 1:1 (first "potential jump") considerably higher potential change was obtained, hence a higher sensitivity of the procedure and easy to estimate end point; this was assumed for statistical evaluation of the method.

- with 2,4-dithiouracil. Similar titration was carried out using standard solution of sodium salt of this reagent, but now in neutral medium, without buffer. Molar ratio 1:1 was found at end point of the titration. Statistical evaluation for both cases is presented in tab. 2.

Tab. 2. Potentiometric determination of mercuric ions with 2-thiouracil and 2,4-dithiouracil -statistical evaluation

Reagent	Number of variables n	Standard deviation, %	Standard deviation of the mean %	Confidence interval prob. level 95%
2-Thiouracil	9	0.59	0.20	99.02 ± 0.39
2,4-Dithiouracil	7	0.42	0.16	100.95 ± 0.31

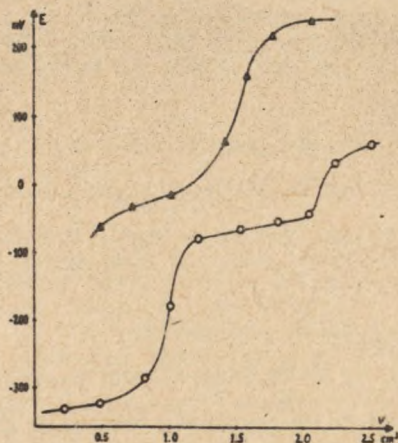


Fig. 1. Titration curves of mercuric ions with the solutions: 0.1 mole/dm³ 2-thiouracil sodium salt (an example : 19,96 mg Hg; —○—○—) and 0.1 mole/dm³ 2,4-dithiouracil sodium salt (ex.: 29,61 mg Hg; —△—△—)

Simultaneous determination of Ag^+ and Hg^{2+}

It was proved that in given above conditions for the application of the solutions of each reagent. they may be used for the determination of a sum of both metal ions, with accuracy parall to that of particular ions; simultaneous in one titration procedure differentiating determination of Ag^+ and Hg^{2+} did not succeeded.

Interferences

Titration of silver or mercuric ions were carried out with 2-thiouracil or 2,4-dithiouracil sodium salt solutions, but now in the presence of following metal ions: Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} . It appeared that these "foreign" ions - as well single as all together - did not interfere if present in concn. fivefold that of Ag^+ or Hg^{2+} to be determined. However, Bi^{3+} -ions in high concentrations (5 - 10 fold) and Fe^{3+} -ions in amounts equal Ag^+ and Hg^{2+} interfere and should be removed.

Discussion of results

An application of 2-thiouracil and 2,4-dithiouracil as analytical reagents was not much used, though these compounds are commercially available in pure form or may be easily synthesized in analytical laboratory.

The solutions of 2-thiouracil and 2,4-dithiouracil sodium salts proved to be suitable titrants for potentiometric determination of silver and mercury (II).

Quantitative composition of complexes formed by thiouracils with metal ions at end point of the titration was estimated by means of stoichiometric calculations, but also by the precipitation of the complexes from more concentrated

solutions of components and following elemental analysis (determination of N, S and Ag or Hg). At equivalence point of silver determination the complexes of the molar ratio 2:1 (Ag:reagent) are formed, but mercuric complexes 1:1 are here utilized; the complexes of another composition were found to be not useful for titrimetric determinations.

Silver sulfide indicator and saturated calomel reference electrode system was employed and the titration with 2-thiouracil was performed in optimal weak acidic (pH 5 - 5.5) medium, with 2,4-dithiouracil - in neutral medium. Definite conditions assure the determination of milligramme amounts of silver (5-50 mg) and mercury (II) 9-80 mg with fair precision (tab. 1 and 2). A method is sufficiently specific for Ag and Hg (II); from the midst of often accompanying ions - Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} and many anions do not interfere with the determination of silver and/or mercury, some (as Fe^{3+}) may be removed by usual analytical procedure.

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S t r e s z c z e n i e

2-Thiouracyl i 2,4-dithiouracyl zastosowano w postaci roztworów soli sodowych do potencjometrycznego oznaczania srebra i rtęci (II), wobec elektrod siarczkosrebrowej (wskaźnikowa) i kalomelowej.

Miareczkowanie za pomocą 2-thiouracylu wykonano przy pH 5.-5.5, a za pomocą 2,4-dithiouracylu ok. pH 7. Do obliczenia wyników wykorzystano powstanie kompleksów srebrowych 2:1 (Ag : odczynnik), a dla oznaczenia rtęci (II) - stosunek molarowy 1:1. W oznaczeniach nie przeszkadza obecność ołowiu, kadmu, miedzi, cynku; przeszkadza obecność Fe (III).

Р Е З Ю М Е

2-тиоурацил и 2,4-дитиоурацил применяются в виде растворов натриевых солей для потенциметрического обозначения серебра и ртути /II/ в присутствии электродов - сернисто-серебряного /указательный/ и каломельного.

Титрование при помощи 2-тиоурацила проведено при pH 5 - 5,5, а при помощи 2,4-дитиоурацила около pH 7.

Для вычисления результатов использовано создание серебряных комплексов 2:I /Ag :реактив/, а для обозначения ртути /II/- отношение молярное 1:1. В обозначениях не мешает присутствие свинца, кадмия, меди, цинка, мешает присутствие Fe /III/.