TABLE VI

DATA ON TYPE $2Q.2C_2H_5XHgX_2$

$X.HgX_2$	Color	Crystal form	M. p., °C.	X, %		Hg, %	
				Calcd.	Found	Calcd.	Found
$Cl.HgCl_2$	white	hexagonal	232–235	21.53	21.76		
$Cl.HgBr_2$	yellow	rhombic	221–223	30.87	30.65		
$Cl.HgI_2$	yellow	rhombic	173–175	38.59	39.06		
$Br.HgCl_2$	white	rhombic	177–180	30.87	30.46		
$Br.HgBr_2$	white	prisms	189–190	38.21	37.76	23.98	24.20
$Br.HgI_2$	yellow	prisms	173	44.46	44.02	21.56	21.85
$I.HgCl_2$	yellow	prisms	155	38.59	39.22	23.66	23.88
$I.HgBr_2$	yellow	plates	174	44.46	44.88		
$I.HgI_2$	yellow	hexagonal[a]	188	49.55	49.10	19.58	19.97

[a] When molecular equivalents such as to form $3Q.3C_2H_5I.2HgI_2$ were dissolved in acetone, only $2Q.2C_2H_5I.HgI_2$ precipitated while $Q.C_2H_5I.HgI_2$ remained in solution. With iodide the reaction $2Q.2RI.HgI_2 + I_2 = QRI.HgI_2 + QC_2H_5I.I_2$ took place.

Summary

1. Possible types of complex salts containing quinoline, alkyl halides and mercuric halides were studied and were found to be quite numerous.
2. Analogous salts hitherto described, of Types II, VI and VII, only, were found. The homologous salts of these respective types alternately show irregularities of melting point.
3. Other types of complex salts involving alkyl halides are described.
4. Some isomeric salts are described and discussed.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF INDIANA UNIVERSITY]

A SHORT METHOD FOR THE ESTIMATION OF SELENIUM IN ORGANIC COMPOUNDS

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Introduction

In an effort to choose a method for the determination of selenium in organic compounds, 21 methods, which had been proposed in the literature, were studied. Each of these failed to fulfil at least one of the conditions obtaining in our work. Any determination of selenium in organic compounds presupposes the decomposition of that compound, usually by means of the Carius method. The presence of nitric acid, or of nitrates, however, makes the use of 16 of these methods impossible. Two of the remaining methods, the Frerichs[1] and the Lyons and Shinn[2] methods, avoid this difficulty only by means of long and tedious manipulation. Of the three

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[1] Frerichs, *Arch. Pharm.*, **240**, 656 (1902).

[2] Lyons and Shinn, THIS JOURNAL, **24**, 1087 (1902).

remaining methods, two are designed for the estimation of selenium in minerals and could not be readily adapted to the use in mind, while the remaining one, the method of Wrede,[3] is based upon the catalytic oxidation of the compound and the subsequent titration to sodium acid selenite with methyl orange as indicator, a procedure which the authors hesitated to adopt. A review of these methods shows the need for a simple, rapid and accurate procedure for the estimation of selenium in organic compounds. The writers have developed such a method designed to follow the Carius treatment, which is based on the negligible solubility of silver selenite in neutral solutions, and upon the fact that silver chromate is more soluble than silver selenite.

It has been shown in this Laboratory that the Carius treatment of halogen-free seleno-organic compounds quantitatively converts the selenium to selenious acid.[2] Therefore, the contents of the Carius tube will, after the complete combustion of any such compound, consist of selenious acid in the presence of more or less diluted fuming nitric acid. The following experimental work will show that the proposed method can be satisfactorily used to estimate the selenium of selenious acid in the presence of fuming nitric acid, and can be applied to halogen-free seleno-organic compounds after decomposition by heating with nitric acid.

Experimental Part

Preliminary Experiments.—In the following experiments pure, dry, sublimed selenium dioxide was used as a source of selenium. Although silver selenite and silver chromate are soluble in nitric acid, they are quite insoluble in exactly neutral solutions. After neutralization of the nitric acid, a modification of the Mohr method for halogen determination can be used for the estimation of the selenium. By this method the selenium is precipitated as silver selenite by titration with a standard silver nitrate solution.

It was found that the use of sodium hydroxide, with methyl orange as indicator (the color of phenolphthalein obscured the end-point), was impracticable for neutralization because the color change occurred at the formation of sodium acid selenite. This compound then reacted according to the following equations to prevent both the complete precipitation of the selenious acid and the formation and detection of the silver chromate end-point.

$$\begin{aligned} 4NaHSeO_3 + 8AgNO_3 &= 4Ag_2SeO_3 + 4NaNO_3 + 4HNO_3 \\ Na_2CrO_4 + 2AgNO_3 &= Ag_2CrO_4 + 2NaNO_3 \\ Ag_2SeO_3 + 2HNO_3 &= 2AgNO_3 + H_2SeO_3 \\ Ag_2CrO_4 + 2HNO_3 &= 2AgNO_3 + H_2CrO_4 \end{aligned}$$

An excess of sodium hydroxide interfered by causing the formation of silver oxide. Sodium acetate, ammonium hydroxide, calcium and mag-

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[3] Wrede, *Z. physiol. Chem.*, **109**, 272 (1920).

nesium oxides were also unsatisfactory; the first, because it did not sufficiently reduce the acidity; the second, because it induced the formation of complex ions; and the last two, because they caused the formation of silver oxide. The use of zinc oxide was quite satisfactory. It maintained the Sörensen (P_H) value of the solution between 10^{-5} and 10^{-6}, a condition that neither permitted the formation of silver oxide nor prevented the precipitation of silver chromate.

When sodium chromate was used as an internal indicator, the red color of the silver chromate was indefinite (probably because of the adsorption of the chromate by the precipitating silver selenite). Therefore, it was necessary to use the chromate as an external indicator. The silver nitrate solution was restandardized in this way both against dry resublimed selenium dioxide and against freshly fused, C. P. (Baker's Analyzed) sodium chloride. The data given in Table I were obtained.

TABLE I

THE STANDARDIZATION OF SILVER NITRATE

Method used: modified Mohr method for halogen determination. Indicator: sodium chromate, used externally. Neutrality was maintained by the presence of an excess of zinc oxide.

Expt.	$AgNO_3$ (corr.), cc.	NaCl, g.	SeO_2, g.	$AgNO_3$ 0.1 N coeff.
1	32.67	0.1912	....	1.00107
2	32.56	.1904	....	1.00027
		Av. accepted 0.1 N coeff. per NaCl		1.00068
3	21.43	....	0.1192	1.00041
4	22.46	....	.1250	1.00089
		Av. accepted 0.1 N coeff. per SeO_2		1.00065

The data of Table I show that silver nitrate may be standardized either against pure sodium chloride, or against pure selenium dioxide by neutralizing with zinc oxide and using the Mohr method with an external indicator. In each case, a blank was run under identical conditions as to temperature and volume to determine the amount of silver nitrate solution necessary to give an end-point,[4] and this amount subtracted from the total used. The close agreement of the coefficients obtained demonstrates the accuracy of the titration of the selenious acid.

When a known weight, 0.15–0.2 g., of selenium dioxide was dissolved in 2 cc. of fuming nitric acid, diluted to 20 cc., and the mixture neutralized with zinc oxide, titration with silver nitrate gave low results. This could have been due either to the presence of the zinc nitrate, which would have been formed, or to the mechanical incorporation of the selenious acid by the solid zinc oxide. The latter supposition was supported by the fact that long-continued stirring lessened the error. The first was eliminated by titration of selenium dioxide, in the presence of zinc nitrate, with silver

van Eck, *Pharm. Weekblad,* **53,** 1554 (1916).

nitrate. The zinc nitrate did not affect the accuracy of the titration.[5] The low results were evidently caused by the mechanical separation of the silver nitrate and the selenium dioxide by the zinc oxide. This difficulty was avoided by the following procedure.

Recommended Procedure.—Subject a weighed quantity of the halogen-free seleno-organic compound to be analyzed to the Carius treatment until decomposition is complete.[6] With a minimum amount of water, wash the contents of the tube into a graduated cylinder of about 100 cc. capacity. Place a small piece of litmus paper in the solution and make alkaline by the addition of halogen-free sodium hydroxide or potassium hydroxide solution.[7] Add two drops of methyl orange solution and slightly acidify with nitric acid. Add halogen-free zinc oxide in slight excess and stir until alkaline toward methyl orange.[8] Titrate with 0.1 *N* silver nitrate solution using a halogen-free soluble chromate as an external indicator. Observe the final volume of the solution, the temperature and the volume of the silver nitrate solution used. Make a blank determination with a suspension of zinc oxide under identical conditions of volume and temperature and correct the volume of silver nitrate solution accordingly.

TABLE II

ACCURACY OF THE PROPOSED METHOD

Materials analyzed: A, resublimed SeO_2 dissolved in 2 cc. of fuming HNO_3; B, twice steam-distilled diseleno-acetone, $C_6H_{12}Se_2$; C, recrystallized diphenyldiselenide (m. p., 63.5°).

Silver nitrate solution: 1 cc. (for Expts. 10 to 16, incl.) = 0.0039625 g. of Se. 1 cc. (for Expts. 17 to 20, incl.) = 0.00400985 g. of Se.

Expt.	Cpd. anal.	$AgNO_3$, cc.	Se present, g.	Se found, g.	Error, Se, g.	Error, Se, %
10	A	21.71	0.08596	0.08602	+0.00006	+0.07
11	A	38.08	.1514	.1509	− .00050	− .33
12	A	30.50	.12093	.12085	− .00008	− .07
13	A	21.43	.08490	.08492	+ .00002	+ .025
14	A	22.46	.08903	.08900	− .00003	− .04
15[a]	A	33.29	.1318	.1319	+ .00010	+ .07
16[b]	A	41.61	.1650	.1649	− .00010	− .07
17	B	17.00	.06806	.06816	+ .00010	+ .14
18	B	53.20	.21370	.21332	− .00038	− .18
19	C	11.80	.04743	.04732	− .00011	− .2
20	C	45.55	.18309	.18265	− .00044	− .24

[a] Mixture to be titrated contained 5 g. of $Zn(NO_3)_2.6H_2O$.

[b] Mixture to be titrated contained 10 g. of $Zn(NO_3)_2.6H_2O$.

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[5] See Expts. 15 and 16 in Table II, this paper.

[6] The temperature of the combustion will vary, according to the nature of the compound, from 240° to 300°.

[7] An alkali solution of known halogen content is equally satisfactory if the amount used is observed and the amount of silver nitrate corrected accordingly.

[8] At this point the litmus will indicate an acid, and the methyl orange, an alkaline solution.

Calculate the percentage of selenium, basing the calculations on the following equation: $H_2SeO_3 + 2AgNO_3 + ZnO = Ag_2SeO_3 + Zn(NO_3)_2 + H_2O$.

The end-point, which with 0.1 *N* silver nitrate solution can be detected to one drop of excess, may be anticipated by observing the amount of silver selenite precipitated by one drop of the silver nitrate solution, by the curdling and rapid settling of the precipitate after stirring, and by the failure of the silver nitrate to form a temporary acidity. This last is easily observed by the reddening of the methyl orange.

Accuracy of the Proposed Method.—By the above procedure the results in Table II were obtained.

In Expts. 10 to 16, inclusive, the starting mixture consisted of selenium dioxide dissolved in 2 cc. of fuming nitric acid; d., 1.52. This mixture was chosen because, after the Carius treatment of any halogen-free seleno-organic compound, the selenium is present, and must be analyzed, as selenium dioxide dissolved in fuming nitric acid. The data of Table II show that the proposed method gives results well within the customary limits of accuracy both with selenium dioxide and with organic compounds.

Summary

1. A study of the literature dealing with methods for the estimation of selenium revealed the fact that no simple, accurate method, suitable to follow the Carius treatment of selenium organic compounds, has been available.

2. Since, in neutral solutions, silver selenite is less soluble than silver chromate, the writers have developed a method for the estimation of selenium in selenious acid which is based on the volumetric precipitation, from neutral solutions, of silver selenite according to a modification of the Mohr method for halogen determination.

3. Since the Carius treatment of seleno-organic (halogen-free) compounds converts the selenium to selenious acid, this method is applicable to the analysis of any such compound that has been completely decomposed by the Carius treatment.

4. Diseleno-acetone, diphenyldiselenide and solutions of selenious acid in fuming nitric acid were analyzed by the proposed method with satisfactory results.

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