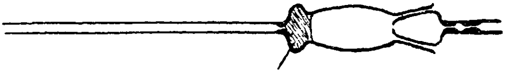
CCLXXI.—*The Micro-estimation of Selenium and Tellurium in Organic Compounds.*

By HARRY DUGALD KEITH DREW and CHARLES RAYMOND PORTER.

NO microchemical method has yet been worked out for the quantitative precipitation and filtration of either selenium or tellurium. In the present paper we describe processes which enable these elements to be estimated in some 5—20 mg. of initial material; the degree of accuracy attained is at least equal to that on the macro-scale, and the processes offer very material advantages in respect of time and labour.

Selenium.—The usual process for the estimation of selenium in organic substances is that described by Bauer (*Ber.*, 1915, **48**, 507), in which the selenium is transformed to the dioxide by heating at 250° with nitric acid in a Carius tube. The contents of the tube are washed with water into a flask and boiled under reflux with at least 100 c.c. of concentrated hydrochloric acid until nitrous fumes have been driven off, and the selenium is then precipitated by means of sodium sulphite. Other reducing agents (*e.g.*, sulphurous acid) have been used by other investigators.

Capped filter tube.



After many trials, we found that this procedure, when applied on a microchemical scale, results in loss of selenium, small but appreciable and inconstant amounts escaping with the acid fumes, in which, after condensation, its presence may be detected. We tried next to remove the nitric acid by evaporation on a water-bath; but here again we found a loss of selenium owing to the not-negligible volatility of the dioxide (contrast Gutbier and Engeroff, *Z. anal. Chem.*, 1915, **54**, 193). The problem was solved, however, when we observed, somewhat unexpectedly, that the removal of the nitric acid was superfluous, the simple passage of sulphur dioxide into the solution, in presence of an excess of hydrochloric acid, being sufficient to destroy the nitric acid and bring about after an interval the quantitative precipitation of selenium.

The filtration of the element was first tried in sintered-glass micro-filters, but penetration of the diaphragm by finely divided selenium occurred. The difficulty was obviated by coagulating the selenium by further heating at 100°, and filtering through a Pregl micro-Gooch crucible fitted with a capillary cap (see fig.) to stabilise the humidity condition of the asbestos.

The preliminary decomposition of the material was attempted, in suitable cases, by heating with fuming nitric acid in micro-Kjeldahl flasks, but it was found preferable to use the Carius method. The handling of Carius tubes on the micro-scale becomes a much simplified process.

The method finally adopted may be summarised as follows:

The material (5—20 mg., corresponding to 3—5 mg. of selenium) is decomposed in the Carius tube with some 0·3 c.c. of fuming nitric acid (*d* 1·50). The contents of the tube are washed into a boiling-tube with alternate rinsings of water and concentrated hydrochloric acid, and the liquid (about 10 c.c.) is heated on a boiling water-bath while a stream of sulphur dioxide is being passed through it. When the whole of the selenium has been transformed to the black variety (about 20 minutes), the liquid is cooled and filtered through the micro-Gooch crucible with the aid of a siphon tube, the vessel and delivery tube are thoroughly rinsed with water and alcohol, and the capped crucible is then dried at 110° during ten minutes in a stream of filtered air, in the manner described by Pregl for halogen precipitates, and weighed with the usual precautions. Table I shows the results of analyses, all weights being given in milligrams.

TABLE I.

Substance.	Amount taken.	Se found.	Se, %.	
			Found.	Calc.
Selenium (pure, recrystallised)	5·665	5·635	99·5	100·0
,, ,, ,,	5·313	5·339	100·5	100·0
Selenium acetylacetone	15·456	6·918	44·75	44·7
,, ,,	19·059	8·505	44·6	44·7
Selenium benzoylacetone	17·904	5·874	32·8	33·1
Selenium dehydrobisdibenzoylmethane	22·839	3·461	15·15	15·1
Selenium ω-phenylacetylacetone	19·350	5·965	30·85	31·25
,, ,, ,,	6·623	2·065	31·1	31·25
Selenium β-phenylpropionylacetylmethane	13·900	4·075	29·35	29·65
,, ,, ,, ,,	18·495	5·460	29·5	29·65
,, ,, ,, ,,	11·350	3·382	29·8	29·65

We concluded from other experiments that, in order to avoid the possibility of interference by atmospheric humidity effects, it was not advisable to weigh less than about 2·5 mg. of selenium. The contents of the filter need not be changed for a further estimation, even after long standing; but, unless analyses are carried out in succession on the same day, the filter should be re-washed with water and alcohol, dried, and weighed again, before a fresh determination is made.

Tellurium.—The standard process for the estimation of tellurium is that of Lenher and Homberger (*J. Amer. Chem. Soc.*, 1908 **30**, 387; compare Gutbier and Huber, *Z. anal. Chem.*, 1914, **53**, 430). We had little difficulty in applying this method on a micro-scale. Owing to the low vapour pressure at 100° of tellurium dioxide and oxychloride, solutions of the dioxide in dilute nitric or hydrochloric acid may be evaporated to dryness on a water-bath without detectable loss of tellurium. Precipitation of tellurium by sulphurous acid and hydrazine hydrochloride is microchemically quantitative in the presence of 15% hydrochloric acid and no trace of tellurium afterwards redissolves in the acid (contrast Menke, *Z. anorg. Chem.*, 1912, **77**, 282). The preliminary decomposition of the organic tellurium compound may be effected in a micro-Carius tube, but in the case of most non-aromatic tellurium compounds decomposition is safely carried out by heating with fuming nitric acid in micro-Kjeldahl flasks. Filtration of the precipitated tellurium is quantitative in the micro-Gooch crucible used for selenium. Sintered glass filters are equally serviceable, since tellurium is much more readily filtered than selenium.

The experimental details are as follows: The substance (about 10—15 mg.) is decomposed with fuming nitric acid (*d* 1·50) in a Carius tube (0·3 c.c. of acid) or in a micro-Kjeldahl flask (3—4 c.c. of acid), and the liquid is rinsed into a small porcelain evaporating dish with water and taken to dryness on the water-bath. The residue is dissolved by adding 10% hydrochloric acid (3 c.c.) and the solution again evaporated on the water-bath to a syrup. The dish is covered with a small clock glass, and 10% hydrochloric acid (3 c.c.) is added, followed by freshly prepared, saturated, aqueous sulphurous acid (3 c.c.) and 15% aqueous hydrazine hydrochloride (2 c.c.). The mixture is heated during ten minutes on the water-bath with gradual addition of more sulphurous acid (2 c.c.), and the tellurium is then filtered and washed with the aid of hot water and alcohol. The filter crucible is dried and weighed as in the case of selenium. Table II shows the results of analyses.

TABLE II.

Substance.	Amount taken.	Te found.	Te, %. Found.	Te, %. Calc.
Tellurium acetylacetone	8·221	4·676	56·9	56·55
Tellurium ethylacetylacetone	12·628	6·433	50·9	50·3
,, ,, ,,	6·058	3·078	50·8	50·3
Tellurium ethylacetylacetone dichloride	13·777	5·418	39·35	39·4
Tellurium dimethylacetylacetone	11·770	5·916	50·25	50·3

The same filter crucible may be used repeatedly without renewal of the filter plug or removal of the precipitate, even when it has stood for many days. In spite of observations to the contrary in the literature, we have observed no tendency of precipitated selenium or tellurium to become oxidised.

The Estimation of Halogen in Tellurium Compounds.—We observed during the above investigation that chlorine, bromine, and iodine can be estimated with accuracy on a micro-chemical scale even in presence of tellurium. Chlorides and bromides may be decomposed by heating in micro-Kjeldahl flasks with concentrated nitric acid containing an excess of silver nitrate; but iodides should be decomposed first with aqueous halogen-free potash before the iodine is precipitated, in the cold, with nitric acid containing silver nitrate. Fuming nitric acid should never be used, as its presence occasions minute but appreciable losses of halogen whether tellurium is present or not, as is shown by the results with pure sodium chloride given in Table III.

TABLE III.

Substance.	Amount taken.	Halogen, %. Found.	Halogen, %. Calc.
Tellurium ethylacetylacetone dichloride	5·762	21·65	21·85
,, ,, ,, ,, ...	2·485	21·85	21·85
,, ,, ,, ,, ...	9·281	21·6	21·85
Tellurium butyrylpropionylmethane dichloride	5·846	20·65	20·95
Tellurium methyltribromide	22·578	62·85	62·7
Tellurium methyltri-iodide	2·555	72·75	72·35
Sodium chloride	6·899	60·65	60·65
,, ,, ...	4·504	60·4	60·65

When fuming nitric acid (*d* 1·50) was used, the following variable and inaccurate results were obtained :

Sodium chloride (4—8 mg.) gave Cl, 59·65, 59·5, 58·85, 56·4%; tellurium ethylacetylacetone dichloride (5—14 mg.) gave Cl, 20·75, 21·35, 21·55, 21·0%. Possibly, under these conditions traces of nitrosyl halide escape before full contact with the silver salt can be established.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, July* 17*th*, 1929.]