THE QUANTITATIVE DETERMINATION OF SELENIUM IN ORGANIC COMPOUNDS.

BY R. E. LYONS AND F. L. SHINN.

Received August 20, 1902.

THE difficulties encountered in the estimation of selenium in organic compounds led to a study of the analytical methods in use. We have found these methods impracticable in their application to selenium compounds which are to be decomposed with nitric acid. The results obtained were invariably too low.

It is stated in the literature,[1] and has been verified in this laboratory, that when metallic selenium is oxidized by nitric acid, the product is always selenious acid without a trace of selenic acid. This statement holds good in the case of organic compounds containing selenium when they are heated with red nitric acid in a sealed tube for several hours at temperatures between 180° and 260° C. Advantage has been taken of this deportment for the determination of selenium by methods based upon the reducibility of selenious acid by sulphur dioxide, hydrogen sulphide, sodium thiosulphate, hydriodic acid, etc.

The determination of selenium in solutions of selenious acid free from nitric acid is comparatively easy. Several of the methods proposed permit of a high degree of accuracy. The two following have best served our purpose:

(1) The old gravimetric method of Rose,[2] which consists in reducing the selenious acid, in the presence of hydrochloric acid, by means of sulphur dioxide, collecting the precipitate on a weighed paper, drying at 100° C., and weighing.

(2) The iodometric method of Norris and Fay,[3] whereby the selenious acid is reduced, in the presence of hydrochloric acid, by an excess of N/10 sodium thiosulphate solution and the excess determined by titrating back with a standard iodine solution.

Both methods when properly executed yield excellent results. The volumetric process is preferable when a number of estimations are to be made. It is simple, rapid and accurate.

Other methods deserving mention are those of Gooch and

---

[1] Wohlwill: *Ann. Chem. Pharm.*, **114**, 173; Dammer: Band **1**, 683; Roscoe and Schorlemmer: Vol. **1**, 362.

[2] Pogg. *Ann.*, **113**, 472; *Ztschr. anal. Chem.*, **1**, 73.

[3] *Am. Chem. J.*, **18**, 703; **23**, 119.

Pierce.[1] and Muthman and Schaeffer.[2] The latter method, however, has been studied by Gooch and Reynolds[3] and found to be inaccurate.

None of these methods are directly applicable to solutions of selenious acid containing free nitric acid, a condition obtaining from the customary oxidation of selenium and its compounds with nitric acid. To free such solutions from nitric acid without loss of selenium has afforded great difficulty from the time of the first attempts to estimate this metal.

Rose[4] states that solutions of selenious acid can not be heated above 100° C. without volatilization of selenium dioxide and provides for the removal of the nitric acid by evaporation on a water-bath. It has been our experience. and the experience of others, that with the most carefully conducted evaporations a loss of selenium invariably occurs.

Divers and Schimose[5] attribute the low results to the formation of selenic acid during the evaporation with nitric acid. They recommend boiling the residue with hydrochloric acid for the purpose of reducing any selenic acid to selenious acid. This precaution is manifestly unnecessary when nitric acid alone has been used to decompose the compound.

Rathke[6] recommended the addition of hydrochloric acid to the selenious acid solution previous to evaporation. Later,[7] he suggested the addition of sodium or potassium chloride to the solution to prevent volatilization of selenium chloride during the repeated evaporations with hydrochloric acid. The results of Rathke's analyses show a loss of from 1 to 5 per cent.

Michaelis,[8] finding that evaporation with hydrochloric acid always resulted in the loss of selenium, sought to avoid evaporation by boiling the solution with a great excess of concentrated hydrochloric acid until the nitric acid should be completely decomposed. The operation was conducted in a flask provided with a return condenser. Michaelis used this scheme success-

[1] *Am. J. Sci.*, **1**, (4), 36.

[2] *Ber. d. chem. Ges.*, **26**, 1008.

[3] *Am. J. Sci.*, **50**, 254.

[4] *Ztschr. anal. Chem.*, **1**, 73.

[5] *J. Chem. Soc.*, **57**, 439.

[6] *Ann. Chem. Pharm.*, **152**, 194 and 206.

[7] *J. prakt. Chem.*, **108**, 249.

[8] *Ber. d. chem. Ges.*, **30**, 2827.

fully, in connection with the gravimetric method, when ordinary nitric acid was employed to bring about the decomposition of the organic compound. It is our experience that when as little as 4 or 5 cc. of red fuming nitric acid are used, several hours' boiling under an inverted cooler is not sufficient to bring about complete decomposition and removal of the nitric acid. The method, even should it be successful, is a very great time-consumer and is troublesome from a mechanical standpoint. Further, the solution of selenious acid so treated would be unfit for direct titration, according to the method of Norris and Fay, on account of the large and unknown amount of hydrochloric acid present. It has been demonstrated that for accurate results with the method of Norris and Fay the amount of hydrochloric acid employed must fall within a certain, well-defined limit.[1]

The method suggested in this paper for the elimination of the nitric acid has the advantage of easy execution, requires less time and attention, and gives very accurate results when used in connection with either the gravimetric or volumetric methods for determining the selenium in solutions of selenious acid.

In the attempted estimations of selenium in a number of compounds, some of which contained mercury, we observed that in the case of a mercuric chloride compound the results always came nearer the theoretical than was true with the purely organic compounds. This deportment is verified in the analytical results reported by Rathke.[2] In a body, $C_3H_5Se_2OK$. the selenium found was 58.21 per cent. (theory 62.36 per cent.), while in the compound $2Se(C_2H_5)_3Cl + ZnCl_2$, containing the heavy metal zinc, the selenium found was 28.59 per cent. (theory 29.44 per cent.).

The plausible explanation of this deportment is that the heavy metal present forms with the selenious acid a selenite which is stable at the temperature of the water-bath, thus retaining all of the selenious acid in combination during the evaporation.

Accordingly, exactly equivalent portions of mercuric nitrate were weighed out and dissolved in the selenious acid solution previous to evaporation. The results were encouraging rather than satisfactory. The quantity of selenium usually lost by

---

[1] Norton: *Am. J. Sci.*, **157**, 287; Norris and Fay: *Am. Chem. J.*, **23**, 123.

[2] *Ann. Chem. Pharm.*, **152**, 207-212.

evaporation in the absence of a heavy metal was found much diminished. It would be impracticable, for obvious reasons, to have in the solution always a quantity of mercury salt exactly equivalent to the selenious acid. It became evident that the metal added to the solution to retain the selenious acid during the evaporation must form a selenite perfectly stable at 100° C., and sufficiently insoluble in cold water to permit of washing free from nitrates and nitric acid. A number of simple selenites, *e. g.*, cadmium, mercury, magnesium and silver, were tried but without success. All were found too soluble for quantitative purposes. A further search in the literature was rewarded by finding the statement of Boutzoureano[1] concerning the double selenite ammonia compounds. A number of selenites dissolve in ammonium hydroxide and upon evaporation of the solution on a water-bath, or in a vacuum, form double compounds, *e. g.*, $Ag_2SeO_3NH_3$. Silver and zinc selenite ammonia may be formed in this way. These compounds are insoluble in water, soluble in acids and perfectly stable at 100° C.

It was foreseen from this, that if to a solution of selenious acid containing nitric acid an excess of silver or zinc nitrate be added and the solution evaporated to dryness to expel the nitric acid, the residue, containing all of the selenium as selenite, could then be evaporated with ammonium hydroxide to form the double selenite ammonia. This compound, it was hoped, would permit of washing free from nitrates without appreciable loss. The residue of silver or zinc selenite ammonia could then be decomposed by means of hydrochloric acid, and the usual gravimetric or volumetric methods for the estimation of selenious acid applied. The method was tried and proved entirely successful.

EXPERIMENTAL PART.

Preparation of Pure Selenium Dioxide.—Pulverized selenium was oxidized with concentrated nitric acid and the reaction mixture evaporated to dryness on a water-bath. The residue was moistened with nitric acid and sublimed in a small beaker according to the method suggested by Norris and Fay.[2] To ensure greater purity the above product was resublimed in a current of

---

[1] *Jahresb. u. Fortschritte d. Chem.*, **42**, 398.

[2] *Am. Chem. J.*, **18**, 704.

dry oxygen in a combustion tube. The selenium dioxide so obtained, in the form of delicate, white needles, was dried to constant weight in a vacuum desiccator over phosphorus pentoxide. An accurately weighed quantity of pure selenium dioxide was dissolved in water, the solution acidulated with a drop of concentrated hydrochloric acid and diluted to 1000 cc.

In all of the following experiments the volumetric method of Norris and Fay[1] was used for the final estimation of the selenious acid.

Direct Titration of the Selenious Acid Solution.—Portions of the selenious acid solution, 25 cc. each, were titrated directly with the following result:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.05468	27.69	0.05469
(*b*)	0.05468	27.63	0.05457
(*c*)	0.05468	27.65	0.05461

Determination of Selenium in Solutions Containing Nitric Acid.—(*a*) Portions of 25 cc. of the selenious acid solution were treated with a slight excess of silver nitrate and about 2 cc. of fuming nitric acid. The evaporation to dryness and repeated treatment with ammonium hydroxide was then carried out according to the method to be described later. Following are the results:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.05468	27.83	0.05498
(*b*)	0.06491	32.78	0.06472
(*c*)	0.06491	32.88	0.06489
(*d*)	0.06491	32.75	0.06468
(*e*)	0.06491	32.77	0.06470

(*b*) An excess of zinc nitrate was used instead of silver nitrate in a series of experiments similar to (*a*), with the following result:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.06491	32.71	0.06460
(*b*)	0.06491	32.75	0.06468

(*c*) Similar experiments were made using cadmium nitrate in place of silver or zinc nitrate. The results were very much too low. Cadmium selenite ammonia, $CdSeO_3.NH_3$, does not withstand the washing.

---

[1] *Am. Chem. J.*, **18**, 704; **23**, 119.

(*d*) The selenium in the following aromatic selenium compounds was determined by this process:

	Weight of substance.[1]	Evaporated with zinc or silver nitrate.	N/10 $Na_2S_2O_3$ used. cc.	Se present.	Se found.	Theory. Per cent.	Found. Per cent.
(1)	0.10745	$AgNO_3$	27.52	0.05444	0.05436	50.67	50.59
(2)	0.21445	$Zn(NO_3)_2$	54.78	0.10866	0.10819	50.67	50.46
(3)	0.09065	$AgNO_3$	21.23	0.04212	0.04193	46.47	46.25
(4)	0.0945	$AgNO_3$	14.84	0.02950	0.02931	31.22	31.01

We recommend the following procedure for the determination of selenium in organic compounds:

Heat a weighed quantity of the substance in a sealed tube with red fuming nitric acid one hour, or longer, at a temperature of 235° or 240° C. Transfer the contents of the tube, together with the wash-water, to an evaporating dish of about 400 cc. capacity. Add about 1/4 more silver or zinc nitrate than is theoretically required to unite with the selenious acid present. Evaporate to dryness on a water-bath.[2] Wash down the sides of the dish with a little water and again evaporate to dryness. Treat the residue twice with about 50 cc. dilute ammonium hydroxide and evaporate after each addition. Add water and evaporate twice to ensure complete removal of free ammonia. When cool, wash the residue with water, decanting the wash-water on a filter, until free from nitrates. Place the filter-paper in the evaporating dish, decompose the silver or zinc selenite ammonia with 10 cc. hydrochloric acid (sp. gr. 1.124), dilute the solution to about 300 cc. with water and add a few pieces of ice.

Run in N/10 sodium thiosulphate solution in slight excess.[3] allow the mixture to stand one hour[4] and determine the excess of thiosulphate by titration with standard iodine solution.

1 cc. N/10 $Na_2S_2O_3$ solution = 0.001975 gram of metallic selenium.

To estimate the selenium gravimetrically:

(*a*) In case silver nitrate is used: Filter after decomposing the

---

[1] The substance used in (1) and (2) is di-phenyl-di-selenide; in (3) di-benzyl-di-selenide; and in (4) a compound, $C_{27}H_{24}Se_2$.

[2] The water-bath must not be allowed to go dry during this or any subsequent evaporation.

[3] We have found this method most accurate when the excess of N/10 thiosulphate employed does not exceed 5 to 7 cc. Compare Norton: *Am. J. Sci.*, **157**, 287; also Norris and Fay: *Am. Chem. J.*, **23**, 123.

[4] The mixture must be kept near the temperature of melting ice during the reduction with thiosulphate.

silver selenite ammonia with hydrochloric acid, wash the paper free from chlorine and reduce the selenious acid in the filtrate by means of sodium bisulphite.

(*b*) In case zinc nitrate is used: Filtering after the decomposition with hydrochloric acid may be omitted.

INDIANA UNIVERSITY, BLOOMINGTON, IND.,
August, 1902.

[CONTRIBUTION FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE EXPERIMENT STATION.]

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN PLANT SUBSTANCES.

BY C. P. BEISTLE.

Received September 3, 1902.

IT IS commonly known to chemists that plant materials, in their conversion to ash by burning, lose not only water, carbon dioxide, and nitrogen as the gaseous products of their ignition, but generally some portion of their sulphur and phosphorus as well.[1] Experience of other analysts has shown that such losses can not be avoided, like those of alkaline chlorides, by any simple precaution. The accurate determination of sulphur and phosphorus is of great importance in calculating the heat of combustion in plant substances from their elementary analysis, and the determination of phosphorus in estimating the soil-exhausting action of vegetable products. The ordinary ash analysis is insufficient for such purposes.

The following work was undertaken at the suggestion and under the direction of Dr. William Frear. The determination of sulphur and phosphorus in plant substances is carried on by a number of different methods and a comparison of results on a few of these methods is all that was attempted. The substances analyzed were cottonseed-meal and timothy hay. There were also a few determinations made on egg albumen. These substances were chosen on account of the wide difference in their sulphur and phosphorus content, the cottonseed-meal containing relatively large amounts, while the timothy hay is very poor in these elements. The methods used were as follows:

---

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. I, pp. 419-420; Vol. III, pp. 37, 430 and 446.