A STUDY OF THE AVAILABLE METHODS FOR THE DETERMINATION OF SELENIUM IN ORGANIC COMPOUNDS.

W. E. BRADT and R. E. LYONS, Indiana University.

The existing methods for the estimation of selenium, when applied to the determination of that element in organic compounds, either give results which are inaccurate or involve tedious manipulations.

It has been stated in the literature (1, 2, 3,) and has been verified in this laboratory (4) that nitric acid will oxidize selenium to selenious but not to selenic acid. Therefore the selenium in an organic compound, after treatment with fuming nitric acid in a sealed tube, will be converted into selenious acid and will be accompanied by an excess of nitric acid. Any method of analysis, which entails either the precipitation and weighing of the selenium as the element or the estimation by volumetric reduction of the dioxide, will be interfered with by this nitric acid or by the nitrates which may be formed by the neutralization of the acid.

J. Meyer (5) and later Gutbier and Engeroff (6) found that there is a notable loss of selenium while evaporating solutions of selenious acid on a water bath. This loss is considerable in the presence of hydrochloric acid. F. Konek and O. Schleifer (7) encountered the same difficulty. They also found that efforts to avoid the use of nitric acid as oxidizing agent, by the use of sodium peroxide or by combustion in a bomb in the presence of compressed oxygen, gave unsatisfactory results.

A method, to satisfactorily follow the Carius treatment, either must provide for the removal of the nitric acid without loss of selenium, or must be based on a reaction which will not be affected by nitrates or nitric acid. Several methods (Group I) have been proposed to meet these requirements, but they involve such an increase in laboratory manipulation that a rapid determination of selenium is impossible.

GROUP I.

Gravimetric methods.—These methods are objectionable either because of the tediousness of the process or because they are not applicable to solutions of selenium dioxide in nitric acid:

1. By the method of Michaelis and Rohmer (8) the mixture of selenium dioxide and nitric acid is boiled for a few hours, with a great excess of hydrochloric acid, under a reflux condenser. After the removal of the nitric acid is completed, the selenium dioxide is decomposed to selenium by heating for a long time with sodium sulphite. The selenium is thus converted into the black modification and is weighed as the element. H. Bauer (9) stated that this method gave good

"Proc. Ind. Acad. Sci., vol. 36, 1926 (1927)."

results if certain precautions were observed. Lyons and Shinn (10) encountered difficulty in removing all of the nitric acid when fuming nitric had been used in the Carius treatment.

2. The method of Gutbier and Rohn (11) is based on the reduction, by hypophosphorous acid, of selenium dioxide in an alkaline solution to the element. The precipitated selenium is collected, dried and weighed. The authors state that the precipitation is quantitative.

3. The method of Ivanov (12) is dependent on the formation and subsequent decomposition of the compound, $(HCNS)_2H_2SeO_3$. This, Ivanov states, decomposes to give a compact precipitate of selenium which can be more easily collected and weighed than can the selenium which has been precipitated by earlier methods. By this method the mixture of nitric acid and selenium dioxide is evaporated to dryness; a step which causes inevitable loss of selenium. An additional weakness of the procedure is the fact that it consumes an unusually long time.

4. The Perkins method (13) is based upon the reduction of selenium dioxide by hydriodic acid. This is done in the presence of specially prepared electrolytic silver with which the evolved iodine reacts. The percentage of selenium is calculated from the gain in weight of the silver. No precaution for the removal of nitrates is suggested, so this method is not feasible to follow the Carius treatment.

5. Meyer and Garn (14) developed a method which, although it is not gravimetric, will be discussed here because of its similarity to some of the gravimetric methods. It is based upon the colorimetric comparison of the mixture, resulting from the reduction of selenious acid by hydriodic acid, with similar mixtures of known selenium content. They state that the method is not practicable above 0.05 per cent selenium. It is obvious that the presence of nitrates would interfere with the action of hydriodic acid.

6. F. von Konek and O. Schleifer (15) decomposed the selenium organic compound by heating in sulphuric acid, reduced the resulting oxides by means of sulphur dioxide, and weighed the selenium as the element. The objectionable feature of this method is that the amount of heating necessary can not be accurately determined. Excessive heating leads to partial formation of selenium dioxide, the reduction of which in the presence of sulphuric acid "presents difficulties".

7. W. Smith (16) proposed a method which is designed for the removal of an excess of sulphur. This is done by treatment with bromine to form S_2Br_2. The selenium is precipitated with hydriodic acid in the usual manner and weighed as the element. This method, which would be affected by the presence of nitrates, is designed especially for the estimation of selenium in sulphur.

8. In 1923 V. Lenher (17) discussed in a general way the chemical principles utilized and some of the methods employed in the United States for the detection and estimation of selenium and tellurium.

9. Lenher and Kao (18) studied the precipitation of selenium by sulphur dioxide in hydrochloric acid and found that the temperature of the precipitating solutions should not exceed 30°C.

Volumetric methods.—These are unsatisfactory for the reasons given below:

1. The methods of Muthman and Shaeffer (19), which consists of the decomposition of selenious acid by hydriodic acid and subsequent titration with thiosulphate, has been studied by Gooch and Reynolds (20) and found to be inaccurate.

2. By the iodometric method of Norris and Fay (21, 22) the selenious acid is reduced in the presence of hydrochloric acid by an excess of tenth normal thiosulphate, and the excess thiosulphate is titrated with a standard iodine solution. This method, according to Lyons and Shinn (23), gives good results but is interfered with by the presence of nitrates.

3. The indirect iodometric method of Gooch and Pierce (24), according to Moser and Prinz (25), gives good results only when carried out in a distillation apparatus instead of in a flask. In 1924 Congdon and Bray (26) made a critical study of this method and found that the results averaged 0.7 per cent too high.

4. The Fredrich (27) method is based upon the following reaction: $4AgNO_3 + 3Se + 3HOH = 2Ag_2Se + H_2SeO_3 + 4HNO_3$. Since this method presupposes that the selenium is in the form of the element, it is not directly applicable for use after the Carius treatment. Furthermore the authors say that it is accurate only for very low concentrations of selenium.

5. Pellini and Spelta (28) proposed a method based on the reduction of selenium dioxide by hydrazine according to the following equation:

$$SeO_2 + N_2H_4 = Se + 2HOH + N_2$$

They measured the volume of the nitrogen which was evolved and calculated, from it, the percentage of selenium. It is obvious that nitrates would interfere with the reaction.

6. In 1925 Lenher and Kao (29) found that if selenium dioxide, dissolved in a very slight excess of sodium hydroxide solution and treated with tartaric acid, was subjected to the action of hydrazine sulphate for eight hours at 60°C., a separation of selenium and tellurium was effected. Proper temperature control prevented the precipitation of the tellurium.

7. The volumetric estimation of selenium by potassium permanganate in alkaline solution, of Marino (30), is based on the following reaction:

$$2KMnO_4 + 3SeO_2 = K_2O + 2MnO_2 + 3SeO_3$$

The oxidation is carried out in a hot alkaline solution; the mixture is then acidified, and an excess of oxalic acid solution added. The excess oxalic acid is titrated with potassium permanganate and the percentage of selenium calculated from these data. The original method was modified in 1919 by Moser and Prinz (31) in order to repress side reactions, and again in 1924 by Congdon and Bray (32) who state that their modification gives satisfactory results. The presence of nitric acid would interfere with the use of oxalic acid, and thus make this

method, which is also quite tedious, impracticable for use following the Carius treatment.

8. Klason and Mellquist (33) proposed a modification of the Norris and Fay method. The selenium dioxide solution, free from air, is just acidified with hydrochloric acid and an excess of potassium iodide added. The liberated iodine is titrated with twentieth normal sodium thiosulphate solution. The conditions forbid the presence of nitrates.

9. The method of Moser and Prinz (34) is based on the same reactions and is subject to the same limitations.

10. In 1922 Rosenhein and Krause (35) determined selenious acid by titrating it to sodium acid selenite with para-nitrophenol as indicator. This would be impracticable in the presence of nitric acid.

11. Losana (36) determined selenium by heating the material to be analyzed with iron powder and decomposing the resulting ferrous selenide by the addition of hydrochloric acid in an atmosphere of hydrogen. The hydrogen selenide generated was absorbed in a solution of zinc acetate and the selenide formed was titrated iodometrically. Losana designed this method for the analysis of ores and inorganic materials. He made no effort to apply it to the analysis of organic compounds.

12. In 1924 Stecker and Shartow (37), who were evidently unaware of the work of Pellini and Spelta, proposed again that method.

13. In 1925 Lang (38) used a modification of the Pellini and Spelta method. He reduced selenious acid in half normal sulphuric acid solution by means of a measured volume of hydrazine solution, and titrated the excess of the hydrazine with an iodate. The use of hydrazine is prohibited by the presence of nitrates.

GROUP II.

Some methods have been proposed for the estimation of selenium, which either avoid the use of nitric acid or successfully remove the nitric acid, or are able to permit its presence in the form of nitrates.

1. By the Frerichs (39) method, the Carius treatment is conducted in the presence of silver nitrate. The resulting silver selenite is then isolated and dissolved in nitric acid and titrated as soluble silver according to Volhard. Frerichs stated that selenium could be estimated in the presence of halogens by boiling the precipitate with dilute nitric acid, weighing the residue of silver halide and estimating the selenium as above.

2. In 1904 Becker and Meyer (40) used alcohol to rinse out the Carius tube and in the isolation of the silver selenite. Bauer (41) was unable to obtain good results with the Frerichs method. However Konek and Schleifer (42) stated that this method gave satisfactory results. It has been observed in this laboratory that the separation of the silver halide and silver selenite is difficult.

3. Lyons and Shinn (43) developed a method by which the nitric acid might be removed without loss of selenium. This then permitted the reduction of selenious acid by standard sodium thiosulphate solution. This was done by twice evaporating, on a water bath, the con-

tents of the Carius tube in the presence of silver or zinc nitrate. An insoluble ammonia compound ($Ag_2SeO_3NH_3$ or $ZnSeO_3NH_3$), which permitted the removal of nitrates by washing, was then formed by twice evaporating with ammonium hydroxide. After decomposition of the ammonia complex by acidification with hydrochloric acid, the resulting selenious acid was estimated by treatment with an excess of tenth normal sodium thiosulphate and subsequent titration with a standard iodine solution. The method has been found in this laboratory to give fairly satisfactory results with halogen-free compounds. However it consumes a great deal of time because of the fact that it is necessary to evaporate the solution to dryness on a water bath six times, and because the removal of nitrates is often very tedious. Nitrates, which are sometimes apparently surrounded by the insoluble silver or zinc selenite, cause errors in the iodometric titration.

4. Grabe and Petren (44) proposed a method which permits the presence of nitrates. However it is designed for the estimation of selenium in minerals and is not directly applicable to the analysis of organic compounds.

5. In 1920 Wrede (45) proposed the combustion of the selenium organic compound with oxygen in a tube in the presence of a platinum catalyst, and titration of the resulting selenious acid with tenth normal sodium hydroxide, with methyl orange as indicator, to sodium acid selenite.

6. In 1926 Reid (46) announced a method for the estimation of selenium in organic compounds, which was based on the fusion of the compound with sodium peroxide in the Parr bomb, and the subsequent precipitation of the selenium as the element.

A criticism of the methods available for the determination of selenium in 1914 was made by Konek and Norwall (47) who concluded that, at that time, there were no satisfactory methods available. In a discussion of the quantitative determination of selenium and tellurium, Lenher (48) said, "The separation of the two elements, selenium and tellurium, is not so perfect as commonly supposed. It is only by a fine distinction in choice of reagents and manipulation that it is possible to perfectly separate the two elements."

7. A review of the above methods shows plainly the need for a simple, rapid and direct procedure for the estimation of selenium. The writers (49) have developed such a method, applicable in the presence of nitrates, when the selenium is in the form of the dioxide or selenious acid; a condition which exists after the Carius treatment of halogen-free, selenium, organic compounds. In the analysis of organic compounds by this method, the contents of the Carius tube are first made alkaline with halogen-free potassium hydroxide solution, then slightly acidified with nitric acid, and finally neutralized by the addition of an excess of pure zinc oxide. This mixture is then titrated with a standard solution of silver nitrate according to Mohr's method for halogen determination, using sodium chromate as an external indicator. This procedure, which has not been successfully applied to halogen containing compounds, gives satisfactory results with halogen-free compounds.

BIBLIOGRAPHY.

1. E. Wohlwill. Beobachtungen ueber die Selensaure und einige selensaure Salze. Ann. CXIV, 173 (1860).
2. O. Dammar. Handbuch der Anorganischen Chemie. Band I, 683 (1892).
3. H. E. Roscoe and C. Schorlemmer. Treatise on Chemistry. Vol. I, 475 (1911).
4. R. E. Lyons and F. L. Shinn. The Quantitative Determination of Selenium in Organic Compounds. J. Am. Chem. Soc. XXIV, 1087-1093 (1902).
5. J. Meyer. The Gravimetric Determination of Selenium. Zeit. anal. Chem. LIII, 145-54 (1914).
6. A. Gutbier and F. Engeroff. The Gravimetric Determination of Selenium. Zeit. anal. Chem. LIV, 193-205 (1915).
7. F. Konek and O. Schleifer. Ueber neue selenhaltige Derivate des Antipyrins. Ber. LI, 842-855 (1918).
8. A. Michaelis and Roehmer. Ueber organische Selenverbindungen. Ber. XXX, 2827 (1915).
9. H. Bauer. Zur Bestimmung des Selens in Organischen Verbindungen. Ber. XLVIII, 507-508 (1915).
10. R. E. Lyons and F. L. Shinn. See Ref. 4, p. 1087.
11. A. Gutbier and E. Rohn. The Gravimetric Estimation of Selenium. Zeit. anorg. Chem. XXXIV, 448-52 (1903).
12. W. N. Ivanov. Thiocyanselenious Acid and the Determination of Selenium. Chem. Zeit. XXXII, 468 (1908).
13. C. C. Perkins. The Use of Silver in the Determination of Molybdenum, Vanadium, Selenium and Tellurium. Am. J. Sci. (4), XXIX, 540-542 (1910).
14. J. Meyer and W. Garn. The Detection and Determination of Small Quantities of Selenium. Zeit. anal. Chem. LIII, 29-33 (1914).
15. F. Konek and O. Schleifer. See Ref. 7.
16. W. Smith. The Estimation of Selenium in Sulphur. J. Ind. Eng. Chem. VII, 849-850 (1915).
17. V. Lenher. The Occurrence, Chemistry and Uses of Selenium and Tellurium. Trans. Am. Inst. Mining Met. Eng. Paper 1198-N.
18. V. Lenher and C. H. Kao. The Separation of Selenium and Tellurium by Sulphur Dioxide in Hydrochloric Acid Solution. J. Am. Chem. Soc. XLVII, 769-772 (1925).
19. W. Muthman and J. Shaefer. Untersuchungen ueber das Selen. Ber. XXVI, 1008-1016 (1893).
20. F. A. Gooch and W. G. Reynolds. The Reduction of Selenious and Selenic Acids by Hydriodic Acid. Am. J. Sci. (3), L, 249-252 (1895).
21. J. F. Norris and H. Fay. Iodometric Determination of Selenious and Selenic Acids. Am. Chem. J. XVIII, 703 (1896).
22. J. F. Norris and H. Fay. The Reduction of Selenium Dioxide by Thiosulphate. Am. Chem. J. XXIII, 119 (1900).
23. R. E. Lyons and F. L. Shinn. See Ref. 4.
24. F. A. Gooch and A. W. Pierce. The Estimation of Selenious and Selenic Acids. Am. J. Sci. (4), I, 31 (1896).

25. L. Moser and W. Prinz. The Volumetric Determination of Selenious Acid and Selenic Acid. Zeit. anal. Chem. LVII, 277-305 (1918).
26. L. A. Congdon and W. W. Bray. Critical Studies on Methods of Analysis. Part XI, Selenium. Chem. News. CXXVIII, 116 (1924).
27. K. Fredrich. Ueber eine Maassanalytische Bestimmungsmethode des Selens. Zeit. angew. Chem. XV, 852-56 (1902).
28. G. Pellini and E. Spelta. The Estimation of Selenium. Gazz. chim. ital. XXXIII, ii, 89-92 (1903).
29. V. Lenher and C. H. Kao. The Separation of Selenium and Tellurium. J. Am. Chem. Soc. XLVII, 2454-2461 (1925).
30. L. Marino. The Volumetric Determination of Selenious Acid by Permanganate in Alkaline Solution. Zeit. anorg. Chem. LXV, 32-37 (1910).
31. L. Moser and W. Prinz. See Ref. 25.
32. L. A. Congdon and W. W. Bray. See Ref. 26.
33. P. Klason and H. Mellquist. Iodometrische Methode zur Quantitativen Bestimmung kliner Mengen Selen in Schwefel und Kiessen. Zeit. angew. Chem. XXV, 514-518 (1912).
34. L. Moser and W. Prinz. See Ref. 25.
35. A. Rosenhein and L. Krause. Selenious Acid and Heteropolyselenites. Zeit. anorg. allgem. Chem. CXVIII, 177-192 (1921).
36. L. Losana. The Estimation of Selenium. Giorn. chim. ind. applicata. IV, 464-466 (1922).
37. W. Strecker and L. Shartow. A New Method for Determining Nitrites and Nitrates as Well as Selenium. Zeit. anal. Chem. LXIV, 218-224 (1924).
38. R. Lang. New Iodometric Studies which Depend upon the Formation and Measurement of Iodine cyanide. Zeit. anorg. allgem. Chem. CXLII, 280-298 (1925).
39. H. Frerichs. Eine neue Methode zur Bestimmung des Selens in organischen Verbingungen. Arch. Pharm. CCXL, 656-658 (1902).
40. W. Becker and J. Meyer. Ueber die Einwirkung von Selenwasserstoff auf Nitrile. Ber. XXXVII, 2550-2555 (1915).
41. H. Bauer. See Ref. 9, p. 508.
42. F. Konek and O. Schleifer. See Ref. 7, p. 584.
43. R. E. Lyons and F. L. Shinn, See Ref. 4.
44. A. Grabe and J. Petren. The Determination of Selenium. Svensk. Kem. Tid. XXIV, 128-134. (1913).
45. F. Wrede. The Estimation of Selenium in Organic Compounds. Zeit. physiol. Chem. CIX, 272-275 (1920).
46. E. E. Reid and E. H. Shaw. Some Derivatives of Ethyl Mercaptan. J. Am. Chem. Soc. XLVIII, 520-528 (1926).
47. F. Konek and F. Norwall. A New Oxygen Compound and the Behavior of Organic Selenium Compounds in the Calorimetric Bomb. Oesterr. Chem. Zeit. XVI, 288-289 (1914).
48. V. Lenher. The Quantitative Determination of Selenium and Tellurium. Proc. Am. Phil. Soc. LXV, 33-50 (1926).
49. R. E. Lyons and W. E. Bradt. A Short Method for the Estimation of Selenium in Organic Compounds. J. Am. Chem. Soc. *48*, 2642-7 (1926).