the X-ray diffraction pattern obtained. The pattern was different in certain respects from the hemihydrate pattern but was identical with the dehydrated hemihydrate pattern obtained from the dehydration of selenite at 130°.[1] Reproductions of the negatives showing the X-ray diffraction patterns of hemihydrate and dehydrated hemihydrate are given in Fig. 2. Patterns 3 and 4, showing the spots, are for the large crystals of hemihydrate and dehydrated hemihydrate, respectively; 1 and 2 are the respective patterns for the submicroscopic crystals obtained by dehydration of selenite. These observations show once more that the crystal structure of hemihydrate is similar to but not identical with that of dehydrated hemihydrate. When these results are taken together with the isobaric dehydration data, they show conclusively that calcium sulfate hemihydrate is not a zeolite but a definite chemical individual, irrespective of the method of preparation or the crystal size.

In the light of the above observations one is forced to conclude that Caspari is not justified in his contention that calcium sulfate hemihydrate and dehydrated hemihydrate are identical. His experimental results are not satisfactory either because he could not detect the differences between the two preparations by means of X-ray rotation spectrograms or because his unspecified precautions against rehydration of the dehydrated sample were inadequate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Quantitative Oxidation of Colloidal Selenium and its Application in the Volumetric Determination of Small Amounts of Selenium[1]

BY W. C. COLEMAN AND C. R. MCCROSKY

Selenium is an element that lends itself readily to colloidal dispersion. In this state it has been found to behave toward oxidizing reactants not unlike substances in homogeneous solution, and the following work is an application of this fact in the analytical determination of small amounts of the element. Apparently little work has been done on the direct titration of colloidal solutions, a type of reaction which has considerable chemical interest as well as the possibility of practical application.

Frequently in analytical operations selenium is precipitated in the elemental form. A rapid and accurate volumetric procedure applicable at this point would seem desirable. This is particularly true for the estimation of small amounts of selenium, a problem which recently has become of increasing importance. Such precipitates which would be free of interfering ions can be dissolved rapidly with a solution containing cyanide ion according to the reaction $CN^- + Se \longrightarrow SeCN^-$. When this reaction is reversed by adding an acid, red selenium precipitates and in the presence of a stabilizing agent remains in colloidal dispersion. It was found that the selenium in these colloidal solutions can be oxidized rapidly and quantitatively by certain volumetric oxidants. It seemed worth while to study the quantitative side of these reactions, first, with the idea of developing an accurate volumetric method for the determination of small amounts of selenium and, secondly, for the interest in chemical reactions of this kind which involve reactions between a solid in the dispersed phase and a reactant in true solution.

Lang[2] found that black selenium was oxidized incompletely by iodine monochloride but suggested that the red form might be oxidized successfully. The authors found that only in the colloidal state is selenium rapidly and completely oxidized by iodine monochloride.

Szebelledy and Schick[3] used colloidal selenium as an indicator in the bromate titration of arsenites.

Preparation of Materials

Pure selenium was prepared as described by Coleman and McCrosky.[4]

Sodium Selenocyanate.—A pure grade of sodium cyanide giving negative tests for ferricyanide and reducing agents was used for making the standard selenocyanate solutions by dissolving a weighed amount of the pure selenium with an excess of the salt and diluting to a definite

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[1] Original manuscript received April 29, 1936.

[2] R. Lang, *Z. anorg. allgem. Chem.*, **142**, 280 (1925).

[3] Szebelledy and Schick, *Z. anal. Chem.*, **97**, 186 (1934).

[4] Coleman and McCrosky, *Ind. Eng. Chem.*, **8**, 196 (1936).

volume. The solutions were also checked gravimetrically by precipitating and weighing the selenium.

Potassium Bromate, Potassium Iodate, Potassium Dichromate.—Baker's analyzed salts were twice recrystallized from water with centrifuging. These substances were used as primary standards.

Iodine Monochloride.—A 0.5 *N* solution was adjusted potentiometrically according to Kolthoff.[5]

Ceric Sulfate.—A solution of this substance 1 *N* with sulfuric acid was standardized potentiometrically against Bureau of Standards sodium oxalate.[6]

Potassium permanganate solution was standardized in the usual way against the same sample of sodium oxalate.

Experimental Part

The following equation gives the stoichiometrical relationship for the potassium bromate titration of colloidal selenium in the presence of a strong acid: $2BrO_3^- + 3Se + 3H_2O \longrightarrow 3H_2SeO_3 + 2Br^-$. The mechanism of the reaction may be such that the bromate ion oxidizes bromide to bromine which in turn oxidizes selenium to selenious acid.

Measured volumes of the standard sodium selenocyanate solution, containing an excess of sodium cyanide, were treated with a 1% solution of gum arabic (1 ml. for each 10 mg. of selenium). Sufficient hydrochloric acid (sp. gr. 1.18) was added to make the final volume 1 *N* and a rapid stream of air aspirated through the solution for fifteen minutes for the removal of hydrogen cyanide. The red colloidal solution of selenium was titrated with standard potassium bromate solution to the disappearance of red selenium. At the end-point the color changes are red to yellow, to colorless—an end-point that is defined satisfactorily but must be approached cautiously. In a series of twenty determinations where the selenium content in the solutions varied from 0.01333 to 0.04432 g. and the acidity for the final volume varied from one to six normal, the average deviation by using this method was less than 2 parts in 1000. Control tests showed that gum arabic does not reduce potassium bromate under the conditions existing in the solutions titrated. Hydrogen cyanide interferes with this titration due probably to the formation of cyanogen bromide which does not react with selenium. It was found that aspirating air through the solution removed hydrogen cyanide sufficiently so that it did not interfere. Using the above procedure with the initial presence of 0.200 g. of sodium cyanide in excess, the analysis of a solution containing 0.02193 g. of selenium was accomplished with the same degree of accuracy.

Colloidal selenium is oxidized by iodine monochloride, apparently, according to the equation

$$Se + 4ICl + 3H_2O \longrightarrow H_2SeO_3 + 2I_2 + 4H^+ + 4Cl^-$$

Use was made of this reaction in modifying the end-point in the bromate titration. This titration is carried on just short of the complete discharge of the selenium with 0.1 *N* potassium bromate when sufficient iodine monochloride to oxidize the remaining selenium and 4 ml. of carbon tetrachloride are added. The bromate titration is continued until the iodine color in the carbon tetrachloride is discharged, an end-point that is sharper than the one obtained by the disappearance of colloidal selenium. In a series of twelve determinations with solutions having a selenium content varying from 0.01333 to 0.02690 g. and an acidity varying from 1 to 6 *N*, results were obtained that showed a deviation of less than 2 parts in 1000. For the completion of this titration it is best to use flasks with ground glass stoppers. The technique of Swift and Gregory[7] is recommended.

When very small amounts of selenium (less than 10 mg.) are being determined, the use of gum arabic can be omitted by titrating in solutions 4 to 6 *N* in hydrochloric acid for the final volume through which air has been aspirated for ten minutes. In these cases the end-point was found to be sharper without the protective agent, which tends to form an emulsion with the carbon tetrachloride. If air is aspirated through the solution longer, or if it is allowed to stand before titration, small selenium aggregates may form. These are oxidized readily by iodine monochloride and do not interfere with the titration. Five determinations were made on solutions each containing 0.0006658 g. of selenium—using 0.005 *N* potassium bromate and the iodine monochloride end-point. The average deviation was less than 3 parts in 1000.

Colloidal selenium may be oxidized completely by iodine monochloride and the liberated iodine titrated with potassium bromate. Six determinations were made on solutions varying in selenium content from 0.01077 to 0.02194 g. The selenocyanate solutions were made 4 to 6 *N* with hydrochloric acid for the final volume. Hydrogen cyanide was removed by aspirating air through the solution as usual. An excess of iodine monochloride was added and the liberated iodine titrated with 0.1 *N* potassium bromate solution, adding carbon tetrachloride before the complete oxidation of the iodine. Closely agreeing results were obtained which showed an average deviation of less than 3 parts in 1000 from the amount of selenium present.

Potassium Iodate Titrations

Acid solutions of the iodate ion oxidize colloidal selenium readily, apparently according to the following stepwise equation.

$$5Se + 4IO_3^- + 3H_2O + 4H^+ \longrightarrow 5H_2SeO_3 + 2I_2$$
$$2I_2 + IO_3^- + 6H^+ + 5Cl^- \longrightarrow 5ICl + 3H_2O$$

When four-fifths of the iodate solution required for the complete titration is added, the colloidal selenium has been discharged and the solution is dark brown due to the presence of dissolved iodine which bleaches out on further addition of iodate. The end-point is determined with the aid of carbon tetrachloride (4 ml.) which is added before the complete oxidation of the iodine.

In the solutions containing varying amounts of selenium from 0.01333 to 0.02689 g. and with the acidity varying from 2 to 6 *N*, satisfactory results were obtained by titrating with 0.1 *N* potassium iodate. In a series of twelve determina-

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[5] Kolthoff, "Potentiometric Titrations," Second Edition, John Wiley and Sons, Inc., New York, 1931, p. 282.

[6] Willard and Young, THIS JOURNAL, **50**, 1322 (1928).

[7] Swift and Gregory, *ibid.*, **52**, 894 (1930).

tions the average deviation was less than 2 parts in 1000.

As in the case with the bromate titrations, if an excess of iodine monochloride is added to the colloidal selenium, quantitative oxidation takes place, with the liberation of an equivalent amount of iodine which can be titrated with standard potassium iodate solution. The procedure is the same as that for the analogous titration with potassium bromate. The results are equally satisfactory.

The successful and quantitative oxidation of colloidal selenium by the oxidants just discussed encouraged the authors to try others. At room temperature and in varying concentrations of hydrochloric acid, potassium dichromate does not oxidize colloidal selenium. However, accurate results are obtained in high concentrations of hydrochloric acid using iodine monochloride as a catalyst.

In a series of five determinations in solutions having selenium contents varying from 0.01330 to 0.02194 g. and final acidities of approximately 8 N with hydrochloric acid, titrations were made with 0.1 N potassium dichromate, after a few drops of iodine monochloride had been added as a catalyst. The end-point was determined as usual with the aid of carbon tetrachloride. The analyses agreed within 3 parts in 1000. The selenium must be oxidized completely before adding carbon tetrachloride for the latter dissolves selenium which then reacts so slowly that it results in over-running the end-point. The use of iodine monochloride to oxidize the selenium completely and the subsequent titration of the liberated iodine with dichromate solution gave decidedly inaccurate results.

Potassium permanganate was found to oxidize sulfuric acid solutions of colloidal selenium. An attempt was made to determine selenium by adding an excess of the permanganate and back titrating with standard ferrous sulfate solution, but the results were unsatisfactory. As gum arabic was omitted the inconsistent results were not due to its use. The results were consistently high when the titrations were carried out in the manner analogous to the dichromate titrations.

Ceric sulfate was found to oxidize colloidal selenium only in the presence of iodine monochloride as a catalyst. Satisfactory quantitative results could not be obtained with this oxidant. The results varied decidedly with changes in the acid concentration.

The following analyses were made to demonstrate the application of the bromate titration to the determination of selenium precipitated in the course of an analysis. A solution of selenious acid was standardized by the volumetric method of Norris and Fay[8] and the gravimetric method of V. Lenher and C. Kao.[9] The latter procedure was then used to precipitate the selenium from a measured volume of this solution. After careful washing the precipitate was converted to a sodium selenocyanate by adding three times the theoretical amount of sodium cyanide in 10 ml. of water and evaporating to dryness. The dried salts were dissolved in 10 ml. of water. After stabilizing with 2 ml. of 1% gum arabic, adding 10 ml. of hydrochloric acid (sp. gr. 1.18) and aspirating with air for fifteen minutes, the colloidal selenium was titrated with 0.1 N potassium bromate using the iodine monochloride end-point. The amount of selenium present in each of six determinations according to the standardization of the selenious acid was 0.02600 g. The results obtained by the bromate titration agreed with this value within 3 parts in 1000.

The authors believe that this method can be adapted to the determination of small amounts of selenium in a number of substances such as the determination of selenium in glass and the determination of free selenium in rubber, or wherever selenium can be precipitated as the free element. It can also be used for the determination of selenocyanates and is more generally applicable than the method reported by R. Ripan.[10]

Preliminary work shows that the behavior of colloidal tellurium with acid solutions of bromate, iodate and iodine monochloride is analogous to that of selenium. However, a quantitative study of these reactions has not been completed.

Summary

Colloidal selenium has been found to react quantitatively with volumetric oxidants and a rapid volumetric method for the determination of small amounts of selenium has been developed.

Reactions like these with colloidal substances have interesting chemical significance and suggest further study.

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[8] Norris and Fay, *Am. Chem. J.*, **18**, 703 (1896).

[9] V. Lenher and C. Kao, THIS JOURNAL, **47**, 2454 (1925).

[10] R. Ripan, *Z. anal. Chem.*, **94**, 331, 335 (1933).