THE DETERMINATION OF SELENIUM AND TELLURIUM IN BLISTER COPPER AND COPPER CONCENTRATES

by

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Introduction.

Selenium and tellurium do not occur to any great extent in Nature and they are seldom studied in any detail. However, a general understanding of their properties, both physical and chemical, is essential in an investigation of their analytical determination. A general account may be found in many of the text-books on inorganic chemistry, but the following resumé has been included in this dissertation for the sake of completeness.

The elements occur in group VI B of the Periodic Table, of which sulphur and oxygen are the typical elements. Selenium has an atomic number of 34 and atomic weight of 79.2, while tellurium an atomic number of 52 and atomic weight of 127.5. The resemblance between these elements and sulphur is very marked and they generally occur naturally in conjunction with sulphide ores, though in very subordinate quantities. Occasionally the elements are found as mineral selenides and tellurides. Tellurium occurs as a gold telluride in Transylvania, and it was in this form that the element was first discovered.

As might be expected by analogy with the properties of sulphur, both elements display allotropy. Selenium occurs in amorphous, monoclinic, and metallic forms. The metallic is the most stable modification, and all other forms revert to it with a rate which is accelerated by heating. It is this form which displays the photo-electric effect for which the element is noted. Metallic selenium is insoluble in carbon disulphide while the other two modifications are soluble. Tellurium occurs in two allotropic forms, namely the amorphous and crystalline varieties. The amorphous resembles the crystalline form in all properties except those influenced by fineness of division, and on heating yields the crystalline form with evolution of heat. The crystalline modification is brittle and easily powdered and melts at 452°C. The elements bear a fairly close resemblance to sulphur in their chemical properties. Like sulphur they form hydrides, di- and tri-oxides and their corresponding acids, and various halogen compounds which correspond to the sulphur halides. Tellurium tends to be rather more metallic than either selenium or sulphur, and if two electrodes of the element are placed in an alkaline solution, the element dissolves at both electrodes when an electric current is passed through the solution, giving Te^{++++} ions at the anode and Te^{--} ions at the cathode. Corresponding with the increase in metallic tendency tellurium appears to enter less readily than selenium and sulphur into the composition of organic compounds.

Both selenium and tellurium form hydrides which resemble sulphuretted hydrogen and may be prepared in much the same way as the sulphur derivative. Both hydrides are gaseous and have odours which resemble hydrogen sulphide but are much more pungent. Hydrogen telluride is very poisonous when inhaled. Many metallic tellurides are unstable and yield the hydride by reaction with water alone. The selenides, in general, decompose with evolution of the hydride, by reaction with dilute hydrochloric or sulphuric acid solution, while aluminium selenide reacts with water alone. The gases are both unstable and may be easily decomposed. It is rather interesting to note that the ionisation of a decinormal aqueous solution of hydrogen telluride is 50 per cent. while a similar solution of hydrogen selenide is only 4.1 per cent ionised. Hydrogen sulphide undergoes an even smaller degree of ionisation in solution. The selenides and tellurides of many of the heavier metals are precipitated under similar conditions to the sulphides, though they are generally less stable than the sulphides.

As might be expected from the properties of sulphur, selenium and tellurium each yield two oxidation products, namely, the dioxide and trioxide. In addition to these derivatives tellurium also forms a monoxide which is of relatively little importance on account of its instability. Both dioxides are colourless crystals, at normal temperatures, as opposed to the gaseous form of sulphur dioxide. Selenium dioxide readily sublimes on warming, a process which is used for the purification of the compound, but tellurium dioxide must be heated to 400 to 500°C before it begins to volatilize. Tellurium dioxide is very sparingly soluble in water whereas the dioxide of selenium is hygroscopic in moist air. Despite its sparing solubility, tellurium dioxide forms a basic nitrate and sulphate both of which are soluble in water. If a concentrated aqueous solution of selenium dioxide is evaporated over sulphuric acid, crystals having the composition of selenious acid (H_2SeO_3) may be obtained. These crystals are deliquescent in moist air but in dry air tend to lose their water of crystallisation yielding the dioxide. As might be expected from the metallic affinities of tellurium, tellurium dioxide not only exhibits acidic tendencies but also basic properties, as is evidenced by the formation of the basic nitrate and sulphate. A compound approximating to tellurous acid (possibly with the formula H_2TeO_3) is produced as a bulky crystalline precipitate by the treatment of tellurium tetrachloride with water or by the decomposition of an aqueous solution of a tellurium salt by an aqueous alkaline solution. The product however is very unstable and spontaneously dehydrates to form the dioxide. Corresponding to the sulphites, selenium and tellurium form selenites and tellurites. Though the selenites all appear to be derived from selenious acid (H_2SeO_3), the tellurite salts are not all related to the monohydrated acid but are apparently derived from the hypothetically condensed acids of the system ($H_2Te_2O_5$- di-tellurous, and $H_2Te_4O_9$- tetratellurous acid). Solutions of selenious and tellurous acids may be reduced in acid solution by various reducing agents, the best known being sulphur dioxide, hydroxylamine and hydrazine. This property is also exhibited by solutions of selenites and tellurites. It is interesting to note that selenium dioxide is used in organic chemistry as an oxidising agent, on account of the ease with which the compound decomposes to give elementary selenium. However, in solution it has slight reducing properties, showing its relation to sulphur dioxide.

The trioxides of the elements are of little importance in comparison with the corresponding acids. While tellurium trioxide is comparatively easy to prepare the preparation of selenium trioxide is an extremely difficult task. However, selenic acid is easily prepared by the oxidation of selenious acid and forms a well defined series of selenates which resemble the sulphates in many respects. Tellurium trioxide gives rise to a number of hydration products which may be regarded as telluric acids, but which can more conveniently be considered as products of further hydration of "normal" telluric acid (H_2TeO_4), the dihydrate ($H_2TeO_4.2H_2O$) being the most stable. Selenic acid crystallises in long hexagonal prisms, apparently isomorphous with crystalline sulphuric acid and having a melting point of 57 to 58°C. The molten substance is easily cooled below its melting point and the presence of small quantities of water considerably lowers the melting point. The acid is easily decomposed with the formation of selenious acid and oxygen on heating to above 160°C. It is interesting to note that sulphuric and selenic acids have approximately the same heats of neutralisation and are, therefore, of approximately comparable strength. Concentrated selenic acid does resemble sulphuric acid in many ways though its characteristics are less strongly marked. The acid has greater oxidising powers than sulphuric acid and is consequently less stable. Generally the reduction of selenic acid to elementary selenium does not proceed as readily as with selenious acid, and it is generally advisable to convert all the selenate present to selenite by boiling the solution with hydrochloric acid. It is interesting to note that selenic acid will dissolve metallic gold, though this power must be ascribed as much to the oxidation powers of the acid as to its acidity.

Telluric acid generally occurs as the dihydrate, a white powder which is easily soluble in water. The solution is only feebly acid. It is interesting to note that the allotelluric acid (H_2TeO_4) is a stronger acid than the dihydrate. The acid will attack such metals as lead, tin, silver and gold, though this property is probably due to its oxidising powers.

The selenates are isomorphous with and bear a very marked resemblance to the sulphates though they are not as stable. Calcium selenate gives a hemihydrate resembling plaster of Paris and also a hydrate of the composition $CaSeO_4.1.5H_2O$. Copper selenate, also, bears a very marked resemblance to its sulphate analogue. The selenates will readily form double salts and even alums have been prepared which are of the orthodox crystalline form.

Telluric acid is notably different from what might be expected by analogy with sulphuric and selenic acids. Isomorphism is exceedingly rare between the tellurates and sulphates and selenates, and the tellurates do not form alums, or as a rule mixed crystals with the sulphates and selenates.

The halides of selenium and tellurium are an interesting series of compounds. In general selenium displays a greater affinity for the halogens than does sulphur. Both selenium and tellurium form stable hexafluorides. These are the only hexahalides known, the tetrahalides being more common. There are, as is the case with sulphur, no known combinations between selenium and iodine. Tellurium, however, does give a tetriodide. The halides of tellurium are not very stable and tend to decompose to the more normal types. Selenium forms monohalides while tellurium forms dihalides. Selenium tetrabromide is interesting on account of its volatility.

A standard method for the separation of selenium is to distil it from a solution in the form of the tetrabromide. Selenium tetrachloride is also volatile but requires a higher temperature to effect its distillation.

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The investigation which is described in the following text was undertaken with the object of providing a simple analytical procedure by which the selenium and tellurium content of blister copper and copper concentrates could be determined in the course of a few hours. The procedure generally recommended for the estimation of these elements involves their gravimetric separation, and it may be seen from the analysis of typical samples of blister copper and copper concentrates, given below, that such a procedure demands the use of a large sample (about 100 gm.) if reasonably accurate results are to be obtained.

	Blister.	Concentrate.
% Se.	0.01	0.005
% Te.	0.001	0.0005

The analysis of the concentrate is still further complicated by the presence of approximately 20 per cent. of sulphur, which renders the solution of a large sample a difficult task, which can only be accomplished by the use of a large volume of liquid bromine. It is obvious that such a process is unsatisfactory and it is desirable to find a better method of solution, or alternatively, to usė micro-methods for estimating the elements and thus permit the use of a smaller sample. The necessity for the complete solution of sulphur becomes evident when the resemblance between that element and selenium and tellurium is considered. If sulphur is allowed to separate from the solution in its elementary form it is likely that it will occlude the two latter elements with a resulting error in the determination of their amount,

The following method for the determination of selenium and tellurium in refined copper given in "Standard Methods of Chemical Analysis" by W. Scott (1) is reproduced below, as it appears to be fairly representative of the procedures outlined for the analytical determination of traces of selenium and tellurium in the presence of copper recommended by many of the text-books on analytical chemistry.

"Weigh 100 grams of drillings into a 1300 ml. beaker, cover with water and add gradually 350 ml. HNO_3(1.42). When the copper is in solution, boil out all red fumes, dilute to 700 ml. with warm water and neutralize with NH_4OH until just enough copper hydroxide has been formed to cover the bottom of the beaker; then add the required amount of oxidised ferrous sulphate in solution. Stir well, dilute to 900 ml. and boil for at least one hour, settling on the warm plate overnight. Filter on a 15 cm. filter.

Treat the filtrate with ammonia until a precipitate of copper hydroxide has formed on the bottom of the beaker; half the quantity of oxidised $FeSO_4 . 7H_2O$ added previously, is again added and the solution boiled for one hour, allowing to settle overnight on the warm plate. Filter on a 15 cm. filter. It is absolutely necessary that no iron salts be left in this filtrate, either in solution, or as hydrate, therefore, this filtrate had best be tested with ammonia and refiltered on a 15 cm. filter. The three precipitates on the 15 cm. papers are treated as one, dissolved in the least quantity of warm H_2SO_4(1-1), the papers washed well with hot dilute H_2SO_4(1-20) and filtered into a 600 ml. beaker. Make strongly ammoniacal, boil well and filter, washing the precipitate well and free from the folds into the apex of the filter. Refilter the filtrate to catch any iron that has washed through. The papers are spread open and the precipitates dissolved in 25 ml. warm HCl(1-1) in a 250 ml. beaker, using as little hot water as possible to remove the yellow stains.

Filter the solution into a 400 ml. beaker, washing with as little hot water as possible. To the filtrate add four times its volume of concentrated HCl and cool.

Add a saturated water solution of SO_2 to precipitate the selenium.

Filter off the precipitated Se on a tared Gooch crucible, wash with cold water and alcohol, dry at 60°C. for two hours, then at 105°C. to constant weight.

Weigh as metallic Se.

Expel the Se from the crucible and reweigh as a check on the weight and purity of the precipitate.

Tellurium.

To the filtrate from the precipitated Se add 2 grams of tartaric acid in order to keep the Sb in solution, dilute to 600 ml. with hot water, add 50 ml. concentrated NH_4OH, and saturate the solution with SO_2 gas. Boil for two minutes and allow to settle 4 - 6 hours.

Filter the Te on a tared Gooch crucible, wash with hot water and finally with alcohol, dry at 115°C. to constant weight.

Weigh as metallic Te."

It is evident that this procedure is slow and wasteful of reagents.

A knowledge of the impurity content of the various products in the refining of copper is of considerable importance, as traces of impurities often have an appreciable effect on the properties of refined copper. It is said that the presence of 0.009 per cent. of selenium will effect the conductivity of copper by an amount depending on the annealing temperature. The decrease in conductivity may be up to 2 per cent. There is no reliable data of the effect of selenium on the mechanical properties. Traces of tellurium in the presence of bismuth have a profound effect on the brittleness of copper.

The problem has been divided into five parts, each of which is treated separately in the order in which it occurs in the general procedure,

viz., (1) The Solution of the Sample.
(2) The Separation of Selenium and Tellurium from Solution.
(3) The Separation of Selenium from Tellurium.
(4) The Estimation of Selenium.
(5) The Estimation of Tellurium.

1. The Solution of the Sample.

The solution of samples for the estimation of their selenium content is complicated by the fact that selenium is volatilized as $SeO_2.2HCl$ (2) from boiling hydrochloric acid solutions and strong hydrochloric acid solutions heated on a water-bath, though the loss is not appreciable at temperatures below 100°C. when the solution is less than 6N in hydrochloric acid. Tellurium, however, will volatilize only from boiling concentrated hydrochloric acid solution. In selecting a procedure for the solution of a sample containing selenium and tellurium it is necessary therefore to avoid one which might involve loss of selenium or tellurium by volatilisation.

Blister copper is easily soluble in dilute nitric acid, though it was found advisable to add a few drops of liquid bromine to oxidise any sulphur which might have been liberated during the process of solution. After standing for about half an hour the solution was boiled to expel any free bromine.

Concentrates, on the other hand, are much more difficult to dissolve, since they contain almost 20 per cent. of sulphur. If a gravimetric method be used for the determination approximately 100 grams of the sample should be taken to obtain weighable amounts of selenium and tellurium. The solution of this sample, containing approximately 20 grams of sulphur, is a task which can only be accomplished with considerable difficulty and it therefore becomes advisable to use a smaller quantity.

A 5-gram sample of concentrate may be dissolved quite easily if the sample is treated with 15 mls. of a mixture of two parts of liquid bromine and three parts of carbon tetrachloride by volume (3). This should be allowed to stand for half an hour or more with occasional shaking, and then about 60 ml. of concentrated nitric acid added and the solution slowly evaporated to dryness. If any sulphur remains in the residue it will have separated out in the form of globules, which may be dissolved by further treatment with a few ml. of the bromine-carbon tetrachloride mixture, followed by further evaporation to dryness with concentrated nitric acid.

An attempt was made to dissolve 5-gram samples of concentrate by electrolytic oxidation at a high current density, in sulphuric acid solution. This method did not, however, yield satisfactory results, and no solution of the copper appeared to take place until a few ml. of nitric acid solution had been added. Even then sulphur separated from the solution and formed a layer on the surface, which did not dissolve with further treatment. The addition of a few crystals of potassium bromide appeared to aid solution though it did not proceed to completion. It is possible however, that this method, if subjected to a more extensive study, may yield interesting and valuable results.

11. The Separation of Selenium and Tellurium from Solution.

(a) Separation.

In general the methods for the estimation of selenium and tellurium depend on the reduction of selenates and selenites, tellurates and tellurites, to elementary selenium and tellurium. It is evident that the presence of any substance which might interfere with the reduction is undesirable, and it is therefore advisable to separate the selenium and tellurium content of the solution from such interfering substances. For this purpose there are two methods in common application. One of these depends on the volatility of certain selenium compounds which may be isolated under special conditions from the rest of the solution by distillation processes (4) (5). The distillation methods are only useful for the separation of selenium but the alternative procedure will also separate tellurium and consists of the precipitation of the elements on a ferric hydroxide precipitate as insoluble ferric compounds. C. Whitehead (6) used this separation for the determination of selenium and tellurium in copper bullion, and recommended the solution of 25 to 50 grams of the bullion in nitric acid and addition of an amount of ferric nitrate solution equivalent to 250 milligrams of iron. The separation is carried out as follows:-

"Precipitate while hot with an excess of ammonia, filter, and wash with dilute ammonia until the copper salts are entirely removed, redissolving and reprecipitating if necessary. The residue on the filter contains the tellurium and selenium present in the bullion as ferric tellurites and selenites."

W. R. Schoeller (7) who recommends this method of separation states:-

"If the material is high in copper this step must be applied, and it is convenient for the removal of nitric acid instead of by evaporation. The nitrate solution is diluted and treated with a suitable quantity of solution of iron in nitric acid unless sufficient iron is already present. The quantity of iron should be 30 to 50 times that of the selenium and tellurium. The hot solution is treated with a moderate excess of ammonia and the precipitate allowed to settle, collected on a large filter, and washed with water containing a little ammonium chloride and hydroxide. Only if the amount of copper is very large (e.g. in the analysis of refined copper) is it necessary to dissolve the precipitate in dilute hydrochloric acid and repeat the precipitation with ammonia."

The literature consulted on the separation indicates that this procedure is quite satisfactory. However, experiments conducted on solutions containing a known quantity of selenium showed that if an excess of ammonia was used precipitation of the selenium was incomplete, whereas, when ammonia was not present in excess the results obtained were quite satisfactory. This was confirmed by experiments which were conducted as follows: A known quantity of selenium was added to solutions of copper nitrate, to which solutions of ferric nitrate had been added. The precipitation of ferric hydroxide was carried out under the conditions specified in the table below. The precipitate was carefully washed (with hot water in the case of 1. and with dilute ammonium hydroxide in 2. and 3.), and then dissolved in dilute (1:1) hydrochloric acid. The selenium was precipitated by reduction with stannous chloride solution, and estimated iodometrically with an N/100 sodium thiosulphate solution, in accordance with a method which will be described later.

	mg. Fe added.	mg. Se added.	mg. Se found.	Conditions
1.	85	2.00	1.99	Just enough ammonia to precipitate Fe.
2.	85	2.00	1.04	Copper complex + excess ammonia.
3.	85	2.00	0.81	Copper complex + excess ammonia + ammonium chloride.

It will be seen from the above results that the presence of an excess of ammonia results in incomplete precipitation of selenium, in amount about 50 to 60 per cent. No mention of this fact was made in the available literature and the use of an excess of ammonia seems to be universally recommended. The following extract from a paper by Marvin and Schumb is interesting in the light of these results. (4).

"In order to obtain a definite quantity of selenium the following procedure was used:-

A 10-cc. pipet of standard selenious acid solution was delivered into a 250-cc. beaker, 25cc. of concentrated hydrochloric acid were added, followed by 25 cc. of hydrochloric acid saturated with sulfur dioxide, and the solution was allowed to stand for at least 24 hours. At the end of this time the red modification was completely precipitated and had settled out upon the bottom of the beaker. This precipitated selenium was then filtered upon asbestos or a layer of sulfur about 3.8 cm. (1.5 inches) thick. The red selenium was dissolved from the asbestos or sulfur pad by means of concentrated nitric acid, the solution concentrated to a small volume, made alkaline with ammonium hydroxide to precipitate ferric hydroxide, and after filtration again acidified with nitric acid.

Urea was added to destroy nitrous acid, the solution cooled, an excess of potassium iodide added, and the liberated iodine titrated with standard sodium thiosulfate. Using the same pipet in order to obtain the same quantity of selenious acid, hydrochloric acid and potassium iodide were added and the mixture was titrated with sodium thiosulfate solution. The two procedures required the same amount of sodium thiosulfate solution."

It is rather interesting to note that the authors of this paper obtained exact agreement between the two procedures, one of which entailed removal of ferric hydroxide with an excess of ammonia, though it is difficult to discover where iron was introduced in the course of the determination. If the ferric hydroxide procedure were satisfactory in the presence of an excess of ammonia, even though the amount of iron present was very small, one would expect a slight loss in the selenium content of the solution. This, however, was not the case, and it would seem that no ferric selenite separated with the ferric hydroxide precipitate.

Further experiments were conducted to determine the effect of varying quantities of iron in the presence of an excess of ammonia. Measured quantities of ferric nitrate solution containing known amounts of iron, were added to known amounts of selenious acid, and the iron precipitated as hydroxide with excess ammonia. The solutions were then filtered, the precipitate carefully washed with hot water, dissolved in hot dilute hydrochloric acid and the selenium estimated iodometrically after precipitation as elemental selenium with stannous chloride. The results obtained are given in the following table:-

mg. Fe added.	mg. Se added.	mg. Se found.
28	0.418	0.134
56	0.418	0.233
142	0.418	0.356
224	0.418	0.374

It appears from these results that the efficiency of precipitation of selenium in the presence of excess ammonia increases as the amount of iron present increases.

Keller (8) has conducted some interesting experiments to determine the amounts of iron which must be present in the solution to effect complete separation of the selenium and tellurium content. He took one gram of each element and by oxidation with dilute nitric acid obtained a solution of selenious and one of tellurous acid. One gram of ferrous sulphate was dissolved and oxidised, and that amount of iron added to each solution, as well as to each succeeding filtrate (previously acidified) after the ferric hydroxide, precipitated with ammonium hydroxide, was collected on a filter and washed.

The ferric hydroxide precipitates were each dissolved in hydrochloric acid and the selenium precipitated with ferrous sulphate and the tellurium with sulphur dioxide and their amounts determined on tared filters. The quantitative results were as follows:-

Element.		Se.	Te.
Quantity taken (gms.)		1.0	1.0
No. of pptn.	1.	0.0892	0.9548
	2.	0.0973	0.0448
	3.	0.1546	-
	4.	0.1297	-
	5.	0.2219	-
	6.	0.1416	-
	7.	0.1236	-
	8.	0.0513	-
	9.	0.0121	-
	10.	-	-
Quantity found (gms.)		1.0213	0.9996

Keller concludes by stating that it is clear that the reaction is quantitative only when a certain excess of iron is present, which for selenium must be many times that for tellurium.

To investigate the cause of the incomplete separation of selenium in the presence of an excess of ammonia a quantity of ferric selenite was isolated by the treatment of a fairly concentrated solution of selenious acid, which had been neutralised with ammonia, with an excess of neutral ferric nitrate solution. The finely divided greenish precipitate was isolated, washed with distilled water and dried at 100°C. A yellowish powder was obtained which was apparently insoluble in hot or cold water. It was, however, soluble in dilute acid and was decomposed in the presence of ammonium hydroxide with the formation of ferric hydroxide. This reaction probably proceeds according to the equation $Fe_2(SeO_3)_3 + 6NH_4OH = 2Fe(OH)_3 + 3(NH_4)_2SeO_3$.

Ammonium selenite is soluble and is liberated into the solution. The reaction proceeds in a forward direction in the presence of an excess of ammonia, whereas it would appear from the results given above that the presence of an excess of ferric hydroxide favours the reverse reaction, though there is still a tendency for the formation of ammonium selenite. It seems essential, therefore, to keep the ammonia concentration as low as possible in the precipitation of ferric selenite.

Ferric selenate appears to be precipitated under similar conditions to the selenite. A neutral ferric chloride solution was added to a solution of sodium selenate and a fine brownish precipitate was formed. This after careful washing was found to contain selenium and was presumed to be a form of ferric selenate. The precipitate underwent reactions similar to those of the selenite. The reaction

$$Fe_2(SeO_4)_3 + 6NH_4OH = 2\ Fe(OH)_3 + 3\ (NH_4)_2SeO_4,$$

however, appears to proceed to completion in the presence of an excess of ammonia, and an excess of ferric hydroxide seems to have little or no effect on the direction of the reaction. To 10 ml. of a solution of sodium selenate containing 1.55 mg. of selenium, 6 ml. of a solution of ferric nitrate containing 85 mg. of iron were added. Ferric hydroxide was precipitated, with an excess of ammonium hydroxide, the solution was boiled, filtered, and the hydroxide precipitate well washed with hot water. The precipitate was then dissolved in hot dilute hydrochloric acid solution and the solution obtained was reduced with stannous chloride to precipitate selenium, but no deposit formed. However, when the solution was carefully neutralised with ammonia and an excess was carefully avoided the precipitation of ferric selenate appeared to be complete.

If nitric acid is used for the solution of the sample selenium is converted directly to the selenite and no selenate is produced. However, when it is necessary to use strong oxidising agents in this process the selenium is partly oxidised to selenate. When bromine is used in the process of solution for the oxidation of sulphur, it is probable that some of the selenium will be present as selenate in the final solution, and it becomes necessary to take account of the behaviour of both selenate and selenite in the ferric hydroxide separation.

An investigation was conducted on the effect of copper hydroxide on ferric selenate and selenite. This involves a consideration of the occurrence of the reactions

$$3Cu(OH)_2 + Fe_2(SeO_3)_3 = 2Fe(OH)_3 + 3CuSeO_3 \;.......(a),$$

and

$$3Cu(OH)_2 + Fe_2(SeO_4)_3 = 2Fe(OH)_3 + 3CuSeO_4 \;.......(b)$$

Copper selenite was isolated by precipitation from a solution of neutral ammonium selenite with copper sulphate. At first a greenish-white precipitate was obtained, but on warming the solution it became blue and finely crystalline. The precipitate was insoluble in water and was copper selenite. Copper selenate (9) is soluble in water and it is likely that there will be a marked tendency for the reaction denoted in (b) to proceed in the forward direction. It, therefore, seems desirable to avoid precipitation of copper hydroxide during the precipitation of a selenate as ferric selenate, though it is unlikely that its presence will effect the results in separating a selenite, other than its possible interference with the filtration of the hydroxide precipitate.

From a consideration of the above data it became apparent that some method of pH control would have to be used if complete precipitation of ferric hydroxide is to be obtained without separation of copper hydroxide. The precipitation of ferric hydroxide takes place when the pH of the solution is between 3 and 5, whereas no copper hydroxide is formed until the pH has reached 6. It is, therefore, possible by careful regulation of the conditions to obtain complete separation of ferric hydroxide without precipitation of copper hydroxide taking place. The correct regulation of pH was obtained by the use of the acetic acid-ammonium acetate buffer which is used in the 'basic acetate' method.

In the case of blister copper samples it was found necessary to add iron to the solutions to effect the separation of selenium and tellurium, since their iron content is very small. In general it is recommended that the iron content of the solution should be about 30-50 times that of the selenium and tellurium present in order to effect complete precipitation. This quantity was found by experiment to be quite sufficient, provided the pH of the solution was carefully controlled in the manner described above. Iron was added as a 10 per cent. ferric nitrate ($Fe(NO_3)_3.9H_2O$) solution containing 1 per cent concentrated nitric acid. This process was unnecessary for the treatment of concentrates as these contained more than sufficient iron. The ferric hydroxide was found to be completely precipitated from the solution without any separation of copper hydroxide when the following procedure was adopted. The solution was neutralised with a strong solution of ammonium carbonate until a slight permanent precipitate was obtained. Six ml. of 2N acetic acid was added and the solution was allowed to boil for a few minutes. Then 14 ml. of 2N ammonium acetate was added to the solution which was allowed to boil for another minute. Macerated filter paper was stirred into the solution to coagulate the precipitate, and the solution was filtered while still hot. The buffer mixture used produced a solution of approximately pH 5.

The tellurate and tellurite of ferric iron seem to be precipitated under similar conditions to the corresponding selenium compounds. Ferric tellurate has been described by J. J. Berzelius as consisting of pale yellow flakes, which are apparently insoluble in water but which are soluble in an excess of ferric salt solution. He also describes the tellurite which consists of insoluble yellow flakes (10). It is, therefore, reasonable to assume that the same conditions govern their precipitation as those for selenates and selenites.

The most satisfactory method for the separation of selenium and tellurium from the ferric hydroxide precipitate, consists of the solution of the precipitate in hydrochloric acid, and the reduction of the solution obtained with a solution of stannous chloride, which causes separation of elemental selenium and tellurium.

The use of stannous chloride as a quantitative reagent, proposed by W. R. Schoeller (7), depends on the reduction of selenates and selenites, tellurates and tellurites, in acid solution to the elementary form. With regard to this method Schoeller states:-

"The most generally applied procedure for the precipitation of selenium and tellurium in metallurgical analysis consists in saturating the solution with sulphur dioxide, a manipulation by no means free from disadvantages. The action of the gas in dilute solutions is slow, small quantities of these elements, especially tellurium requiring protracted treatment; the precipitate is finely divided and does not settle readily. Sulphur dioxide does not reduce selenic and telluric acids. It readily reduces pure, not too dilute solutions of the tetrachlorides, but in solutions charged with other metals (copper, iron, antimony and bismuth) interfering reactions take place. Hydrazine used by itself or in conjunction with sulphur dioxide is a very efficient reducing agent, but its high price discourages its lavish use. Sulphur dioxide is harmful to the respiratory passages, and the manipulation and filtration of large quantities of liquid saturated with the gas is most unpleasant.

The stannous chloride method is free from these drawbacks, the action of the reagent being immediately and stoichiometrically defined; an excess is required only to keep the solution reduced, time must be allowed for small precipitates to settle. Ferric chloride is unobjectionable, being reduced at the start to ferrous salt ....The presence of smaller amounts of copper retained in the precipitated ferric hydroxide, far from being prejudicial, assist the precipitation of selenium and tellurium by stannous chloride, as the precipitate produced is not pulverulent, but flocculent; it contains copper, and is most probably cuprous selenide (telluride) formed by virtue of the reaction

$$SeCl_4 + 2CuCl_2 + 4\,SnCl_2 = Cu_2Se + 4SnCl_4.$$

As for the objection that the precipitated elements occlude tin (and copper as well, if present), the essential feature of the stannous chloride process is, that it utilises the reagent merely as a convenient means for recovering the two elements in the form of a concentrate suitable for their separate determination." He recommends that the following procedure be adopted;

"The warm fairly acid solution is stirred and treated with a freshly prepared, acid 20 per cent. solution of stannous chloride, the yellow colour of the ferric chloride being first discharged; continued addition of the reagent produces a pale reddish-brown, brown or brownish black colour, and on standing the solution is decolorised with deposition of a reddish to black precipitate. If very little selenium or tellurium is present, the solution must be set aside overnight. The acid concentration (which may be about 1 of acid to 2 of water) in this procedure is not high enough to cause the precipitation of arsenic,but should some arsenic find its way into the precipitate, it will not interfere later on. Antimony and bismuth chlorides are not reduced."

S. T. Volkov (11) recommends that the reduction should be carried out in a solution containing 5 per cent. by volume of concentrated hydrochloric acid and that solid stannous chloride in excess should be introduced into the boiling solution. The solution should then be boiled for five minutes and allowed to stand overnight. T.L. Pokrovskaya (12), however, suggests that the reduction with stannous chloride should be carried out at 70°C. It appears however, from experiments conducted that the most satisfactory method of reduction consisted in boiling the solution in the presence of an excess of stannous chloride for 5 to 10 minutes. The selenium and tellurium coagulate rapidly under these conditions and on standing for about an hour the precipitate settles on the bottom of the beaker. Selenate solutions appear to reduce incompletely when the reaction is allowed to take place at a low temperature, but the reduction rapidly proceeds to completion on boiling. The loss of selenium which normally occurs from boiling hydrochloric acid solution is prevented in the presence of an excess of reducing agent.

After reduction the selenium and tellurium precipitate may be separated from the solution by filtration through a pad of filter paper pulp, about 3mm. thick, packed tightly in a gooch crucible. It is then washed with a dilute hydrochloric acid solution containing a few drops of stannous chloride solution, and finally with a little dilute hydrochloric acid.

(b) Solution of the Selenium and Tellurium Residue.

The choice of a solvent for the precipitate was carefully considered as each has its particular advantages. W,R. Schoeller (7) recommends that it be treated with a solution of bromine in strong hydrochloric acid added drop by drop through a glass tube. The precipitate is left on the pad of filter pulp during this process, and the drop-wise addition of the brominated acid is continued until the precipitate has dissolved, care being taken to avoid an excess. The filter pad is finally washed with small portions of hydrochloric acid (4 acid : 1 water). This method is followed by reduction of the solution with sulphur dioxide. Experiments conducted showed that the solution of the precipitate was rapid when this method was used, and that it was probably the most suitable method of solution if it was to be followed by reduction with sulphur dioxide.

Cousen (13) has described a method in which he estimates the selenium in glass colorimetrically by means of phenyl hydrazine hydrochloride. He separates the selenium from the solution of the glass by saturation with sulphur dioxide, and collects the precipitate on a filter pad which is transferred after washing, into a beaker containing 10 ml. of water, 5 ml. concentrated hydrochloric acid and 3-4 ml. of very dilute chlorine water (about N/60). The solution is then gently warmed and the pad disintegrated with a glass rod. Selenium is apparently readily dissolved with such treatment, though there is no evidence of the solution of tellurium.

Volkov (11) recommends the solution of the selenium and tellurium precipitate on the filter pad in hydrochloric acid containing a few drops of nitric acid, with subsequent digestion at 60°C to complete solution. This method is very satisfactory and results in complete solution.

Pokrovskaya (12) collects the precipitate in a sintered glass crucible, and dissolves it from the crucible by wetting with a few drops of nitric acid followed by the addition of 2-3 ml. of concentrated sulphuric acid in a few ml. of water. The two latter methods precede reduction with hydroxylamine hydrochloride and hydrazine sulphate respectively.

Marvin and Schumb (4) use hot, concentrated nitric acid with considerable success for the solution of precipitated selenium, and estimate the selenium content of the resulting solution iodometrically. Experiment has shown that nitric acid is also a solvent for tellurium.

Nitric acid is the only solvent which is suitable when selenium is to be determined iodometrically, provided all trace of nitrous acid is eliminated with urea in the resulting solution. All the other methods described above involve the presence of free halogen to effect the solution which would complicate an iodometric method. This method will be discussed later.

111. The Separation of Selenium from Tellurium.

The selenium and tellurium in the sample may be separated from the other elements present by the process just described, but, since most of the methods for the estimation of these elements depend on the absence of the other it is necessary, if these are to be used, to separate them.

Volkov (11) recommends the solution of the selenium and tellurium concentrate in 5 ml. of hydrochloric acid containing 3-4 drops of nitric acid with digestion at 60°C to complete solution. The solution is then diluted with 5-7 ml. of water and filtered into an evaporating basin, 5 ml. hydrochloric acid are added and the filter washed to a total volume of 25 ml. Two ml. of 25 per cent. hydroxylamine hydrochloride are introduced into the solution which is then digested on a water bath for 2-3 hours. This procedure is said to separate selenium from tellurium, but tests conducted on the concentrate of these elements obtained from a 5 gm. portion of blister copper showed the separation to be incomplete. A modification of this method was suggested by Pokrovskaya (12) using hydrazine sulphate instead of hydroxylamine. A trial, however, did not yield any more satisfactory results than before.

Selenium is quantitatively precipitated by sulphur dioxide in hydrochloric acid solutions, and when the acidity is carefully regulated, it may be separated from tellurium if both of these elements are present in the solution. The effect of the acidity of the solution on the precipitation of these two elements by sulphur dioxide was the subject of some important experiments conducted by E. Keller (8). Using hydrochloric acid of specific gravity 1.175 and with solutions containing 0.1000 grams each of tellurium and selenium he obtained the following results for the amount of reduction under different conditions of acidity.

Acidity per cent.	Selenium.	Tellurium.
0.5	..	total
1	0	0.0761
2	..	0.0600
3	Trace.	0.0653
5	0.0124	0.0745
8	..	0.0931
10	0.0349	total
20	0.0800	total
30	total	total
40	total	total
50	total	total
60	total	total
65	total	0.0965
70	total	0.0882
75	total	0.0411
80	total	nil
90	total	nil
100	total	nil

It may be seen from these results that if the solution contains 80 per cent or more hydrochloric acid (specific gravity 1.175), complete separation of selenium from tellurium may be obtained by reduction with sulphur dioxide. This method of separation was applied satisfactorily to the separation of the selenium and tellurium content of the concentrate obtained by reduction with stannous chloride. This was dissolved from the filter pad with a solution of bromine in concentrated hydrochloric acid according to the method described by Schoeller (7), which has already been discussed. The pad was washed several times with small quantities of concentrated hydrochloric acid and the filtrate and washings were collected. Separation of selenium and tellurium was effected by saturating the solution with sulphur dioxide. The saturated solution was boiled for a few minutes to coagulate the selenium precipitate, allowed to cool, and again saturated with sulphur dioxide. The precipitate was allowed to settle overnight, though generally a shorter period sufficed, and filtration could be performed with success after a few hours. The precipitate was collected on a pad of filter paper pulp in a gooch crucible, and washed a few times with hot distilled water. The filtrate was reserved for the estimation of tellurium. It was unnecessary to collect the washings as the tellurium content of the solution was very low and the loss involved was very slight.

Selenium can be distilled from a mixture with tellurium under certain conditions and it is possible that this might be used as a method of separation, though it is slower than the separation with sulphur dioxide.

IV. The Estimation of Selenium.

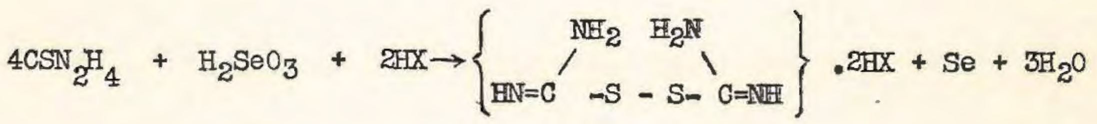
The gravimetric estimation of selenium depends on its separation and weighing in the elementary form. The determination is generally performed by reduction of alkali selenites and selenious acid in a solution containing about 30 per cent concentrated hydrochloric acid, with sulphur dioxide. A number of other reducing agents have been proposed but sulphur dioxide is of more common application. Alkali selenates and selenic acid are not reduced by the gas, but must first be reduced to the selenious condition by prolonged heating with concentrated hydrochloric acid under reflux. Gravimetric determination of selenium is of more general application in the quantitative analysis of the element than any alternative procedure. This process, however, is not eminently suited to the determination of the amount of the element when it is present as a trace, as in blister copper and copper concentrates, since such a procedure requires that large samples are taken to obtain a weighable amount of the element. In an attempt to provide a more suitable alternative, colorimetric and volumetric procedures were investigated.

In general the colorimetric methods for selenium depend on the red Colour of solutions of colloidal selenium. The colloid is generally produced by the reduction of alkali selenites and selenious acid with various reducing agents in the presence of a solution of gum arabic which acts as a protective colloid, and prevents precipitation of the selenium produced by reduction. The tint of the unknown solution may be compared with that produced in solutions containing known quantities of selenium. prepared under similar conditions. The pink colour is quite easily detectable in solutions where there is only 0.1 mg. of selenium in 100 ml.

of solution. The reducing agents generally used for the colorimetric reduction are sodium hyposulphite, hydroxylamine, hydrazine, mercurous chloride and stannous chloride. Stannous chloride has the advantage of reducing both selenate and selenite, but it will also reduce tellurates and tellurites if they are present. The other reductants will not generally reduce selenates and tellurates and tellurites, and are suitable for the estimation of selenium in the presence of tellurium provided the selenium is present as selenite. In all cases the reduction will only proceed in acid solution. Stannous chloride is well suited to the determination of selenium provided any tellurium present is removed prior to the reduction. The reduction is carried out in a solution containing about 10 per cent of hydrochloric acid, and is not inhibited by the presence of a small quantity of nitric acid. The action is rapid, even in cold solution, only about fifteen minutes being necessary for full reduction to be attained.

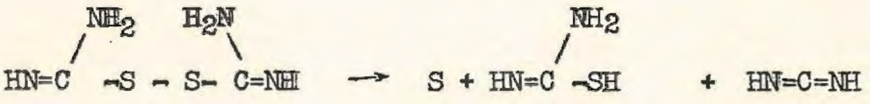
The application of thiourea as a reducing agent for selenious acid was first demonstrated by P. Falciola (14). The reduction takes place instantaneously even when selenium is present only as a trace, provided there is an excess of hydrogen ions. There are very few substances which inhibit the reduction, but copper in large quantities forms an insoluble compound with thiourea, and the nitrate ion must be removed prior to the addition of the reagent. Falciola claims the reduction is quantitative, and applied it to the separation of selenium and tellurium, since tellurium is not liberated from solution by thiourea in acid or neutral solutions. When tellurium is present, however, the solution becomes yellow though no separation of the element takes place. Falciola claims that this yellow colour is produced when one part of tellurium is present in 500,000 parts of solution (15) .

In a paper published in the 'Analyst' in 1940 (16), A. E. A. Werner described a method by which thiourea may be determined quantitatively by oxidation with selenious acid. In principle the method depends on the quantitative reduction of selenious acid to selenium with thiourea, and the estimation of any excess of selenious acid by iodometric means, or by neutralising the excess acid with standard sodium hydroxide. The reduction takes place in the following manner;



$$4CSN_2H_4 + H_2SeO_3 + 2HX \rightarrow \left\{ HN{=}\overset{NH_2}{C}{-}S-S{-}\overset{H_2N}{C}{=}NH \right\} .2HX + Se + 3H_2O$$

It will be seen from the above equation that four molecules of thiourea reduce one molecule of selenious acid with the production of a salt of bis-(amino-imino-methyl)-disulphide. Werner states that the reaction proceeds quantitatively over a wide range of thiourea concentrations. He points out that the salt of bis-(amino-imino-methyl)-disulphide slowly decomposes when the acid concentration is low with the precipitation of suplhur and the generation of more thiourea, the decomposition being represented by the following equation:



$$HN{=}\overset{NH_2}{C}{-}S-S{-}\overset{H_2N}{C}{=}NH \rightarrow S + HN{=}\overset{NH_2}{C}{-}SH + HN{=}C{=}NH$$

Experiments conducted on this reduction indicated that the decomposition is inhibited by a fairly high acid concentration, though this in turn slows down the reduction. The presence of 3 per cent. of concentrated hydrochloric acid appeared to be sufficient to delay precipitation for about twenty- four hours.

Both Falciola and Werner claim that the reduction is quantitative, but this does not appear to be the case. It is very probable that if the conditions of reduction are carefully controlled quantitative results may be obtained, and experiment indicates that the most important of these conditions is the pH of the solution. When thiourea is added to an acid solution it will raise the pH of the solution, the rise in pH depending on the amount of thiourea added. The following results will illustrate this point:

(all measurements of pH were carried out using the quinhydrone electrode).

Normality HCl.	ml. Molar thiourea per 100 ml. soln.	pH
0.1	1.0	1.7
	2.0	3.7
	4.0	5.2
0.2	2.0	4.3
	4.0	4.6
0.5	2.0	4.2
	4.0	4.8
1.0	2.0	4.3
	4.0	4.9
5.0	2.0	3.6
	4.0	4.5
	8.0	5.5

It may be seen from the above results that the acid concentration is of secondary importance as the pH of the solution depends on the amount of thiourea added.

The efficiency of reduction of selenious acid by thiourea was tested at different pH values using varying quantities of thiourea in excess. To an HCl solution of known normality containing a known quantity of selenium as selenious acid, the requisite quantity of thiourea was added. After 15 minutes the precipitate was collected on a pad of filter paper, washed with water, and then dissolved from the pad in hot concentrated nitric acid. The selenium content of the solution obtained was estimated iodometrically by the method of v. d. Meulen (17) which will be explained later in this section. The results are given in the table below :

Normality Solution. (HCl.)	mg.Se added.	ml.Molar Thiourea per 50 ml. soln.	mg. Se. found.
0.5	0.393	2	0.369
	0.393	1	0.342
0.2	0.393	2	0.361
	0.393	1	0.318

It becomes evident from these results that the reduction of selenite solutions with thiourea is not complete under normal conditions, though as previously remarked with careful control the reaction may become complete. The incomplete reduction is not caused by an insufficient acid strength as the presence of excess acid seems to render the reaction even less complete. Two solutions of 10 ml. of standard selenious acid solution containing 0.00938 gm. of selenium per ml. were treated with 20 ml. of molar thiourea under different conditions of acidity. To the first solution 1 ml. of concentrated hydrochloric acid was added and to the second 10 ml. Both solutions were made up to a total volume of 50 ml. and after 15 minutes the solutions were filtered through sintered glass crucibles and the precipitate carefully washed with water, once with alcohol and finally with ether. The selenium precipitate was dried at 105° C, and weighed. The results obtained were as follows :

ml. conc. HCl per 50 ml.	gm. Se present.	gm. Se found.
1	0.0938	0.0843
10	0.0938	0.0750

It can be seen from these results, that strong acid has a very marked effect on the reduction, and that it is therefore necessary to keep the acid concentration fairly low. The optimum acid strength was not investigated but it seems desirable that the pH of the solution should be below 5.0 if reduction is to be achieved at all. In all the experiments conducted no complete reduction was obtained and it appeared that thiourea had no quantitative application. It is possible that the reaction may proceed quantitatively under certain conditions, but these conditions, if they exist, were not determined. However, thiourea is useful in that it will rapidly reduce cold, dilute hydrochloric or sulphuric acid solutions of selenites to red amorphous selenium, a reaction which has an application in the qualitative detection of selenium.

Selenious acid is reduced by, and liberates iodine quantitatively from potassium iodide according to the equation

$$4KI + H_2SeO_3 + 4HCl = 4KCl + Se + 3H_2O + 2I_2.$$

This reaction was applied to the colorimetric determination of selenium by J. Meyer and W. von Garn in 1914 (18). The method is more sensitive than those already described as the yellow colour of the iodine reinforces that of the reduced selenium. Gum arabic must be added as a protective colloid for the selenium produced, and the reaction can be performed in solutions containing sulphuric, hydrochloric or nitric (free from nitrous acid) acids. Tellurium does not interfere.

The liberation of iodine from potassium iodide by reduction with selenious acid has also found application in the volumetric estimation of selenium. Muthmann and Schafer (19) claimed that the estimation of selenium may be effected with reasonable accuracy by adding a hydrochloric acid solution of potassium iodide and determining the iodine liberated with a standard sodium thiosulphate solution. They state the presence of elemental selenium in the solution obscures the end-point with starch. Werner (16) used this reaction as a volumetric method for the estimation of selenious acid and states : -

"This reaction forms an admirable method for its determination, the liberated iodine being determined in the usual manner with N/10 sodium thiosulphate solution; the end-point is very sharp and the violet colour of the colloidal selenium does not interfere, as the selenium precipitate is readily coagulated on shaking to a bulky precipitate, leaving a colourless supernatant liquid."

Other investigators have found that there is a certain amount of absorption and occlusion of iodine by the precipitated selenium which causes low results, and the coloured precipitate interferes with the recognition of the end-point. Several modifications have been proposed to avoid these drawbacks. Moser and Prinz (20) and others have suggested distillation of the iodine from the reaction mixture. However the process is somewhat complex, and Berg and Teitelbaum (21) obviate the difficulty by the simple expedient of adding carbon disulphide which dissolves the selenium as well as the iodine. The selenite solution is diluted in a glass stoppered flask to 100 ml. and acidified with 10 ml. of 25 per cent. hydrochloric acid. Carbon disulphide (20 ml.) is added, then 1.5 times the required quantity of 0.2 N potassium iodide solution in a thin stream while the flask is given a rotatory motion. After one minutes vigorous shaking the iodine is titrated with thiosulphate, the liquid being well shaken after each decolourization of the aqueous layer, and finally titrated after addition of starch. The end-point is sharp. The results obtained using this method for the determination of the selenium content of a selenious acid solution of known strength were entirely satisfactory. An N/100 sodium thiosulphate solution was used. The procedure will give reproducible results in the presence of nitric acid (free from nitrous acid), but the solution must be shaken vigorously and the titration should be carried out in a stoppered vessel to avoid atmospheric oxidation.

A still simpler modification was proposed by J. H. van der Meulen (17). He claims that selenites can be sharply titrated in acid potassium iodide solution with sodium thiosulphate if the selenium formed is kept in colloidal suspension by means of sufficient starch indicator. He proposes that 20 ml. of selenite solution (about 0.05

molar) be diluted with 150 ml. of water and 15 ml. 2 per cent. starch solution, followed by 10 ml. N potassium iodide and 10 ml. of 5 N hydrochloric acid. After a few minutes the solution is titrated with 0.1 N sodium thiosulphate, the colour change being from dirty brown to clear red.

This procedure was subjected to an examination, as it appeared to be more simple than the alternative techniques, and gave good reproducible results when used for the determination of small quantities of selenium, using N/100 and N/200 thiosulphate solutions. The method was adopted as proposed by v.d. Meulen, and was found to act quite satisfactorily in this form provided there was only a small quantity of selenium present in the solution. However, if the quantity of selenium was large, the consequent liberation of iodine was large, and the decomposition of the starch-iodide complex formed, with thiosulphate, became a somewhat difficult task. When the concentration of selenium in the sample was high it was found advisable to use a 5 per cent. solution of gum arabic in preference to the 2 per cent. starch solution. This permitted the titration of the iodine liberated with sodium thiosulphate until the vicinity of the end-point was reached before it became necessary to add starch indicator, a procedure which is in accordance with the normal practice for iodometric titrations. The end-point colour may be determined if a blank is prepared from a solution of selenite of approximately the same concentration as that in the unknown, placed in a vessel similar to that in which the titration is being performed, and made up to the same volume. The solution should contain ten per cent. of concentrated hydrochloric acid, and the same quantity of protective colloid as the solution in which the iodine is being estimated. The selenium in the blank is reduced with the production of colloidal selenium by the use of a quantity of freshly prepared stannous chloride solution. The titration with thiosulphate is allowed to proceed until the blue colour produced by the starch indicator is no longer visible and the pink colour of colloidal selenium remains.

It was observed that about half-a-minute after the completion of the titration the blue starch colour began to reappear. This was thought to be due to atmospheric oxidation of the colloidal selenium formed during the titration, with the formation of selenious acid and the production of iodine by the oxidation of potassium iodide. It was found that if an atmosphere of carbon dioxide was maintained above the solution it appeared to be more stable, and it is desirable to maintain such an atmosphere during the course of the titration. These conditions are obtained if half to one gram of sodium bicarbonate is added to the titration solution, after acidification, and just prior to the titration. Care must be taken to ensure that there is sufficient acid present to allow complete reaction with the bicarbonate, and to ensure that there is still an excess of acid.

The method is applicable in the presence of tellurium since tellurites are not reduced by potassium iodide in acid solution.

Thus the estimation of selenium may be carried out in a solution in which tellurium is also present. Since 1 ml. of an N/200 sodium thiosulphate solution is equivalent to 0.099 mg. of selenium it may be seen that the use of dilute thiosulphate solutions provides a method for the estimation of small quantities of selenium. The end-point for the titration is not very sharp, but the amount of selenium may be determined with reasonable agreement between determinations as is evidenced by the results given below.

mls. selenite soln. used.	mls. $Na_2S_2O_3$ reqd. 1 ml. = 0.0987 mg.Se	mg. Se per ml. selenite soln.
3	9.1	0.273
4	12.3	0.270
5	15.0	0.270
10	27.5	0.2714

For the purpose of comparison of the accuracy of this method with that of the standard gravimetric procedure for selenium using sulphur dioxide as reducing agent, a solution of selenious acid containing approximately 6 mg. of selenium per ml. was prepared. Two 20 ml. portions of the solution were acidified with hydrochloric acid so that the acid concentration of the resulting solution was about 30 per cent. of concentrated hydrochloric acid. The solution obtained was then saturated with sulphur dioxide, the red selenium precipitate allowed to settle, collected in a sintered glass crucible, washed with alcohol and ether and dried at 105°C. The solution was found to contain 5.57 mg. per ml. Two 10 ml. portions of this solution were diluted to 200 ml. and 10 ml. portions of the dilute solutions were standardised volumetrically with sodium thiosulphate solution (1 ml. = 0.0943 mg. Se). The mean result for six determinations was 1 ml. of this solution = 0.273 mg. selenium, whereas according to the gravimetric determination the solution should contain 0.279 mg. selenium per ml. The gravimetric method used is accurate and reliable and it may be assumed that the results obtained by its use are very close to the absolute selenium content of the solution. The deviation of the value obtained by the volumetric procedure from the theoretical content of the solution seems quite permissible in view of the errors which might have been introduced in the process of dilution. On this basis, therefore, the method seems quite satisfactory for small quantities of selenium. It is probable, however, that the results which would be obtained from solutions of fairly high selenium content would be unsatisfactory, as there would be difficulty in keeping all the selenium in colloidal suspension. Probably the Berg and Teitelbaum method (21) would be more satisfactory in such cases.

Norris and Fay (22) proposed the following method of determination of selenious acid:-

A measured portion of the solution containing selenious acid is mixed with ice-cold water and 10 ml. of hydrochloric acid (sp. gr. 1.12). An excess of N/10 sodium thiosulphate solution is then added and the excess of thiosulphate measured with a standard iodine solution. A later paper by the same authors (23) described the chemical reactions which appeared to take place. They found that the interaction between selenium dioxide and sodium thiosulphate was as follows:-

$$SeO_2 + 4Na_2S_2O_3 = 2Na_2S_4O_6 + Se + 2Na_2O.$$

In concentrated solutions selenium is precipitated, and the solution becomes alkaline, but in dilute solution no selenium is precipitated and the reaction is not complete according to the equation, owing to the sodium hydroxide formed neutralising part of the selenious acid, which therefore does not enter into reaction. In the presence of hydrochloric acid the reaction occurs according to the equation:

$$SeO_2 + 4Na_2S_2O_3 + 4HCl = Na_2S_4SeO_6 + Na_2S_4O_6 + 4NaCl + 2H_2O.$$

Coleman and McCrosky (24) in 1937, submitted the Norris and Fay method to a critical examination, and concluded that so long as the excess of thiosulphate is no greater than 5 ml. of the 0.1 N solution, an accuracy of one part in a thousand may be obtained regardless of whether the titration is carried out at 0 or at 20°C. They studied the effect of potassium iodide on the starch-iodide end-point and concluded that with 0.1 N sodium thiosulphate solutions the results are equally satisfactory in the presence or absence of potassium iodide. However, with 0.01 N solutions, potassium iodide should be employed, and its use is imperative with 0.001 N solutions. Their researches showed that the method is equally satisfactory in solutions of hydrobromic, sulphuric and perchloric acids, though weak acids and nitric acid are unsatisfactory.

A comparison was made of the results obtained by the methods of Norris and Fay, van der Meulen, and Berg and Teitelbaum, and these have been tabulated below. The determinations were conducted on 10 ml. portions of standard selenite solution, using N/100 sodium thiosulphate.

Method used.	mg. Se found.
v. d. Meulen	2.046
Berg and Teitelbaum	2.024
Norris and Fay	2.046

The agreement between the methods seems to be quite satisfactory. The deviation of the Berg and Teitelbaum method is equivalent to 0.1 ml. of sodium thiosulphate solution.

V. The Estimation of Tellurium.

Tellurium is also reduced in acid solution though the precipitation of the element is slow in dilute hydrochloric acid solution, and does not take place at all when the concentration of acid is too high; moreover, the precipitated element is so finely divided that it oxidises readily in the subsequent washing process. The fact that no precipitation takes place in the presence of excess acid has been used for the separation of the element from selenium, and is one of the most important procedures for this purpose. A satisfactory precipitation of tellurium is obtained if a mixture of sulphur dioxide and hydrazine hydrochloride is used for reduction, the method being applicable to both tellurates and tellurites.

Another method, generally recommended, consists of the hydrolytic precipitation of tellurous acid. The solution if alkaline is just acidified with hydrochloric acid, rendered just alkaline to to methyl orange with ammonium hydroxide, and reacidified with a few drops of acetic or formic acid. It is then diluted with a large volume of boiling water, and on cooling crystalline tellurous acid separates out. This can be collected, dried and weighed. This method was tested but yielded inconsistent results, probably because the solution was insufficiently diluted.

The chief difficulty in determining the tellurium content in the blister and concentrate samples is due to the extremely small amount present. A gravimetric method is impracticable unless a large sample (3-400 gm.) is taken, and the manipulation of such a quantity is complicated by other factors. It is, therefore, necessary to find a method sufficiently sensitive to determine amounts of tellurium of the order 0.05 mg. and less. The obvious alternatives appear to be volumetric or colorimetric procedures.

A volumetric procedure for tellurium was proposed by B. S. Evans (25). It involves the reduction of a tellurate solution in the presence of sufficient gum arabic to keep the tellurium in colloidal form, followed by the oxidation of the colloidal tellurium back into solution by titration with an N/100 iodine solution, an excess of iodine being indicated by the appearance of a violet colour in a layer of carbon tetrachloride. The reduction is carried out by sodium hypophosphite in a solution which has been acidified with phosphoric acid. The solution is heated to the boiling point, and then cooled and diluted. Apparently the cooling and subsequent dilution stops the reduction completely, and the oxidation with iodine will proceed without any danger of complication. The method is said to be suitable for the determination of quantities of about 0.5 mg tellurium.

With very small quantities of iodine carbon tetrachloride does not give a very marked colour, and if a more dilute iodine solution were to be used it would be very difficult to obtain a satisfactory end-point. Since 1 ml. of 0.01 N iodine solution is equivalent to 0.319 mg. of tellurium the method does not seem to be particularly suited to the determination of 0.05 mg. of the element, which is approximately its amount in a 10 gm. blister copper sample.

Tellurium in colloidal suspension imparts a brown colour to a solution and this property has been used for the colorimetric determination of the element. The colour is quite perceptible when the element is present only to the extent of 0.02 mg. per 10 ml. of solution. The colloidal suspension of the tellurium is generally obtained by the reduction of a tellurate or tellurite in the presence of gum arabic. A number of reducing agents have been proposed of which stannous chloride seems to be the most efficient on account of its rapid action. Care should be taken to ensure that the solution contains sufficient gum arabic to keep the tellurium completely in colloidal suspension, and that there is about 10 per cent. of hydrochloric acid present. The volume of the solution should be kept as small as possible since the tellurium concentration is very low.

An attempt was made to use the yellow colour developed by tellurium in the presence of thiourea (15) for colorimetric determination. However, this colour was not appreciable for the quantities of tellurium under discussion.

The Procedure for Determining Selenium and Tellurium in Blister Copper.

Five grams of the sample were weighed into a 400 ml. beaker. This was treated with 10 ml. of concentrated nitric acid in 10 ml. of distilled water, and the beaker was covered with a watch glass. When all reaction had ceased a further 20 ml. of concentrated nitric acid was added in small quantities, all reaction being allowed to subside before each addition. This quantity of nitric acid was found to be sufficient for the complete solution of the sample. When all the blister copper had dissolved, the solution was allowed to cool and a few drops of liquid bromine were added to oxidise any free sulphur. After about 15 to 30 minutes it was warmed to expel the bromine, and when most of the gas had been evolved, boiled until it assumed a blue colour. After cooling, 5 ml. of a 10 per cent. solution of ferric nitrate ($Fe_2(NO_3)_3.9H_2O$) containing 1 per cent. nitric acid was added and the excess acid was neutralised with a strong solution of ammonium carbonate until a slight permanent precipitate was present in the solution. Six ml. of 2 N acetic acid was added, the solution was diluted to 200 ml, raised to the boil, and boiled for a few minutes. A precipitate of ferric hydroxide began to form when the temperature of the solution reached about 60°C. After boiling for a few minutes 14 ml. of a 2 N ammonium acetate solution was added and the solution was boiled for another minute. Macerated filter paper was then stirred into the solution, and the precipitate allowed to settle. The solution was filtered while hot, and the precipitate washed three times with hot water, the filtrate being discarded. The ferric hydroxide precipitate was dissolved from the filter paper on which it had collected with a hot solution of dilute hydrochloric acid (1:1), and the filter was carefully washed with hot water to remove all traces of ferric salt, the solution and filter paper washings being collected in the beaker in which the precipitation had been performed. More hydrochloric acid was added so that the solution contained about 10 per cent. of the acid, and selenium and tellurium were precipitated by reduction with stannous chloride solution. The precipitate was flocculated by boiling the solution for five minutes, and allowed to settle. The solution was filtered through a pad of filter paper pulp placed in a gooch crucible (the pad being about $\frac{1}{8}$th of an inch thick) the precipitate being washed with dilute hydrochloric acid (N) solution containing a little stannous chloride, and finally, two or three times with a 2 per cent solution of hydrochloric acid. The filtrate and washings were discarded.

The residue on the filter pad was treated with a solution of bromine in concentrated hydrochloric acid, added drop by drop until solution of the precipitate appeared to be complete. Any precipitate adhering to the sides of the beaker in which the original precipitation was performed was dissolved by a similar treatment, and added to the main bulk of solution. The filter pad was finally washed with small portions of concentrated hydrochloric acid, the solution and washings being reserved for further treatment. An excess of the brominated hydrochloric acid was avoided. The procedure was found to be most satisfactory if the pad was left in the gooch crucible and the solution and washings were collected in a clean Buchner flask.

The solution was transferred from the Buchner flask to a 250 ml. beaker, the flask being washed with small portions of concentrated hydrochloric acid, and the solution obtained saturated with sulphur dioxide. When saturated the solution was heated to boiling, and allowed to boil for a few minutes in order to coagulate the selenium precipitate. It was then cooled, again saturated with sulphur dioxide, and allowed to stand overnight to allow the selenium precipitate to settle. The selenium was collected on a pad of filter paper pulp in a gooch crucible, and washed with a little dilute hydrochloric acid. The filtrate was reserved and the washings were discarded.

Two alternative procedures were considered for the treatment of the selenium residue which remained on the filter pad.

The first consisted in transferring the residue and the filter pad from the gooch crucible to the beaker in which the reduction was performed and treating it with hot concentrated nitric acid. When solution appeared to be complete the solution was diluted with a little water and filtered to remove the filter pulp which composed the pad. The residue on the filter was carefully washed with hot water, and the filtrate and washings were collected. Two to three grams of urea were added to the solution which was boiled. This treatment eliminated nitrous acid. The solution was cooled, 2 ml. of a 2 per cent. starch solution and 2 ml. of a normal solution of potassium iodide were added. After five minutes a half gram of sodium bicarbonate was added to provide an atmosphere of carbon dioxide, and the iodine liberated titrated with N/200 sodium thiosulphate. The results yielded by this process occasionally appeared to be somewhat low, apparently due to incomplete solution of the selenium precipitate. Possibly the use of fuming nitric acid would have yielded better results, but this was not determined. The other alternative was a colorimetric method. The precipitate adhering to the sides of the beaker was dissolved by adding 5 ml. of a boiling solution of concentrated hydrochloric acid containing a little nitric acid. This solution, while hot, was used to dissolve the main bulk of the precipitate on the pad. The filter pad was washed with small quantities of distilled water, and the solution and washings were made up to 50 ml. in a Nessler tube. Two ml. of a five per cent. solution of gum arabic was added, with 1 ml. of a 20 per cent. freshly prepared stannous chloride solution. The colour developed was compared with that of solutions of selenious acid reduced in the presence of 5 ml. of the hydrochloric acid - nitric acid mixture under similar conditions. The results obtained by this method were entirely satisfactory, and solution of the selenium appeared to be complete. It is advisable to avoid too great an acid strength, as it is possible that hydrolysis of gum arabic will take place under such conditions and impair its action as a protective colloid.

The filtrates from duplicate estimations after the separation of selenium were combined, and boiled to expel sulphur dioxide. When all the gas had been evolved (after about ten minutes vigorous boiling), a few ml. of freshly prepared stannous chloride solution was added and boiling was continued for another ten minutes. The solution was allowed to stand for about half an hour and filtered through a pad of filter paper pulp in a small gooch crucible following the procedure which had been adopted previously. There was no noticeable precipitate in the solution but a visible deposit was left on the pad. The pad was washed with a normal solution of hydrochloric acid containing a little stannous chloride and finally with a 2 per cent. solution of hydrochloric acid. The tellurium residue on the filter pad was dissolved with a solution of concentrated hydrochloric acid containing a few drops of concentrated nitric acid, the pad being washed with distilled water. The solution so obtained was evaporated to dryness in a small porcelain basin. This process has the advantage of eliminating any possible trace of selenium, which is volatile in hydrochloric acid solution, as well as reducing the bulk of the solution. The residue in the basin was dissolved in 1 ml. of concentrated hydrochloric acid solution, and transferred to a test-tube with a little distilled water. 0.5 ml. of a five per cent. solution of gum arabic and 0.5 ml. of a freshly prepared 20 per cent. stannous chloride solution were added to the solution in the test-tube which was up to a total volume of 10 ml. and compared with sodium tellurite standard solutions reduced under similar conditions.

Two samples of blister copper A and B were analysed by this procedure and the results are tabulated below. (Except where stated the determination was made on 5 gm. portions of the sample:

Sample.	Number.	% Se.	%Te.	Remarks.
A.	1.	0.008	0.0003	Se was estimated colorimetrically with stannous chloride Te was estimated in combination of all four filtrates.
	2.	0.0086		
	3.	0.0094		
	4.	lost.		
	5.	0.0060	0.0004	Se estimated by titration with sodium thiosulphate (N/100):
	6.	0.0083		
	7.	0.0097	± 0.0006	2.5 gm. portions used for analysis. Se estimated with thiosulphate. Te estimated in each individually.
	8.	0.0090		
	9.	0.0087		
	10.	0.0080	not determined	2.5 gm. portions used for analysis. Se estimated by thiosulphate in the presence of Te in concentrate obtained with stannous chloride.
	11.	0.0064		
	12.	0.0104	not determined.	Se estimated gravimetrically in a 100 gm. portion, by reduction with SO_2.

Independent analyses made on sample A gave the following results:-

Analyst.	%Se.	%Te.
a. British Copper Refiners.	0.0082	0.0025
b. Ledoux & Co., New York.	0.010	not found.
c. Griffith, London.	0.0062	Nil.
d. Roan Antelope.	0.010	0.0003

(Figures supplied by the Chief Chemist of the Roan Antelope Mine Laboratory.)

No details of the method of analysis used in any case except d. are available. It would seem that the high result obtained for tellurium in a. is the product of incomplete separation from selenium. The amounts of the elements in the sample are probably

Se. 0.01%. Te ± 0.0003%.

These are the results obtained in case d., in which the analysis was conducted on a hundred gram sample, the selenium and tellurium separated on a ferric hydroxide precipitate (care being taken to avoid an excess of ammonia) which when dissolved in hydrochloric acid was saturated with sulphur dioxide, and the selenium was estimated gravimetrically. Finally, the tellurium was precipitated in the combined filtrates from a triplicate selenium determination by reduction with hydrazine sulphate and sulphur dioxide after the acid content of the solution had been reduced to 30 per cent. concentrated hydrochloric acid by neutralisation with ammonia.

Sample.	Number.	%Se.	%Te.	Remarks.
B.	1.	0.0103	0.0002	Se estimated colorimetrically with stannous chloride.
	2.	0.0103		
	3.	0.0115	-	
	4.	0.0081	0.0004	Se estimated volumetrically with N/200 sodium thiosulphate.
	5.	0.0057		
	6.	0.0120	not determined.	2.5 gm. portions taken. Se determined by thiosulphate.
	7.	0.0098		
	8.	0.0083		
	9.	0.0106	not determined.	2.5 gm. portions taken. Se determined by thiosulphate in the presence of Te in concentrate obtained with $SnCl_2$.
	10.	0.0098		
	11.	0.0119		

The Procedure for Concentrates.

Five grams of the concentrate were treated in a covered 400 ml. beaker with 15 ml. of a mixture of two parts of liquid bromine and three parts of carbon tetrachloride by volume. After standing for half-an-hour with occasional shaking, about 60 ml. of concentrated nitric acid was added and the solution slowly evaporated to dryness. It was found that all the sulphur in the sample had not been dissolved in this process, and the residue was treated with a further 5 ml. of the bromine-carbon tetrachloride mixture and evaporated to dryness with another 10 ml. of concentrated nitric acid. The residue was dissolved in a few ml. of nitric acid and diluted to 50 ml. with distilled water. The solution obtained was boiled for five minutes and filtered to remove the silica. The residue was washed with hot water and the filtrate treated with a strong solution of ammonium carbonate until a slight permanent precipitate was obtained. (It was unnecessary to add iron to this solution as the sample contained about 10 per cent.) The process was continued in the same manner as for blister copper, the selenium and tellurium being removed with ferric hydroxide. One sample of concentrate was analysed and the results are tabulated below.

Number.	%Se.	%Te.	Remarks.
1.	0.0052	0.0002	Se estimated colorimetrically with $SnCl_2$.
2.	lost.		
3.	0.0052	0.0006	Se estimated volumetrically with sodium thiosulphate.
4.	0.0047		
5.	0.0050		
6.	0.0061		

Number.	%Se.	%Te.	Remarks.
7.	0.0058	-	Se estimated with thiosulphate in the presence of Te in $SnCl_2$ concentrate.
8.	0.0070	-	

The selenium and tellurium content of a sample of chalcopyrite was determined using the procedure for concentrates. The results obtained are given below. The method appeared to be entirely satisfactory.

%Se.	%Te.	Remarks.
0.0128	0.0014	Se determined volumetrically by sodium thiosulphate.
-		
0.0137		Se determined with thiosulphate in presence of Te in concentrate obtained with stannous chloride.

From the results given above it appears that the stannous chloride colorimetric method gives the most consistent values for the selenium content. As has already been stated there appears to be some slight discrepancy in the volumetric procedure possibly due to incomplete solubility of selenium in the nitric acid which was used for the determination. Possibly fuming nitric acid will eliminate any error from this source.

The utmost care should be observed during the colorimetric determination of selenium with stannous chloride to avoid contamination of the solution with any impurities, as these may cause a deviation from the true tint developed in a pure solution. The visual comparison of the colour developed with that of standards is quite sufficient, and any attempt at more accurate comparison is unjustifiable in view of the errors which may be introduced in the procedure. The probable error of visual comparison for selenium determination, discounting any errors introduced in the treatment of the sample to separate the element, is approximately 5 per cent. of the amount of selenium present, if this is about 0.01 per cent. Such a discrepancy may be disregarded.

The Preparation of Selenium and Tellurium Standards.

(a). Selenium.

A convenient standard containing selenium consists of a solution of selenious acid prepared by dissolving selenium dioxide in water. Selenium dioxide is readily prepared by the oxidation of elemental selenium with nitric acid, evaporating the solution to dryness and subliming the residue. A very satisfactory method for the preparation and purification given in "Inorganic Syntheses" volume I, edited by H.S. Booth (26) is quoted in the following text as it was found to be most suitable and efficient.

"Place 100 ml. of concentrated nitric acid in a casserole (or evaporating dish) on a sand bath. Apply heat to the sand bath. At the same time add crude selenium cautiously in small portions until a total of 60 g. has been used. The selenium should be scattered over the surface of the acid, and the frothing allowed to subside after each addition before more selenium is added. By the time the reaction is completed, the sand bath should be at such a temperature that evaporation will have started. Continue heating until the residue appears to be dry...........

..... Pulverize the crude selenium dioxide, contaminated with impurities of copper and other heavy metals that may have been present in the ore from which the selenium was obtained, and place in an evaporating dish. Moisten the selenium dioxide with a small amount of nitric acid, invert two nested funnels over the evaporating dish, the larger funnel having a plug of glass wool in its neck, and heat with an open flame. (One funnel may be used but the percentage yield is decreased). The material sublimes at 317°C; and upon striking the funnels, which are considerably cooler, it solidifies into long needle-like crystals. The melting point of the resublimed selenium dioxide, taken in a sealed tube, agrees with that found in the International Critical Tables, i.e., 340°C."

Selenium dioxide is hygroscopic and must be kept in a desiccator. The pure substance is white but after a few days the crystals become reddish due to slight decomposition with the production of red amorphous selenium. It is interesting to note that this decomposition is catalysed by alkaline substances (e.g. glass) while it is inhibited by acidic substances. It is for this reason that it is sometimes recommended that the dioxide should be prepared in quartz apparatus rather than glass.

Selenium dioxide is not a primary standard but its solution may be standardized either gravimetrically or volumetrically. Reduction with sulphur dioxide is most suitable for gravimetric standardisation, but when the standard is very weak (1 ml.= 0.1 mg Se) it is advisable to use a volumetric method to determine its selenium content. The Norris and Fay (22) and the v.d. Meulen (17) methods were found to be most satisfactory for this purpose. These procedures have already been discussed in detail.

The solution used for the colorimetric estimation of selenium in the samples of blister copper and copper concentrates, according to the method described in the foregoing text, contained 0.086 mg. selenium per ml., and was standardised volumetrically using v.d. Meulen's procedure.

(b) Tellurium.

Unlike selenium dioxide, tellurium dioxide is insoluble in water and is unsuitable for the preparation of solutions of tellurium.

A satisfactory solution was prepared by dissolving 0.2 gm. of elementary tellurium in concentrated nitric acid and evaporating the resulting solution to dryness. The residue was dissolved in a little caustic soda solution, filtered to remove any insoluble matter and the filtrate diluted to 100 ml. Twenty ml. portions of the resulting solution were acidified with hydrochloric acid and standardised by reduction to elementary tellurium with sulphur dioxide and hydrazine sulphate according to the following procedure:

(Standardisation is advisable as generally part of the tellurium remains undissolved after treatment with nitric acid):

The solution was diluted with 20 ml. of water and 8 ml. of concentrated hydrochloric acid, and heated to boiling. Fifteen ml. of freshly saturated solution of sulphur dioxide was added. Then 10 ml. of a 15 per cent. aqueous solution of hydrazine sulphate, and finally 25 ml. more of the saturated sulphur dioxide solution. The solution was boiled for five minutes, the precipitate was allowed to settle, filtered through a tared sintered glass crucible, and washed with hot water to remove chloride. The precipitate was finally washed with alcohol, and dried to constant weight at 105°C.

One ml. of the tellurium solution was diluted to 200 ml. and a solution containing approximately 0.01 mg. of tellurium per ml. was obtained. This was quite suitable for the colorimetric estimation of the quantities of tellurium obtained in the samples of blister copper and copper concentrate analysed.

SUMMARY.

A method by which traces of selenium and tellurium may be estimated in blister copper and copper concentrates using manageable quantities of the sample has been outlined.

Attention has been drawn to the precautions necessary for the separation of selenium and tellurium from copper solutions by precipitation as ferric salts.

The relative merits of the colorimetric and volumetric methods of estimating selenium and tellurium are discussed. The value of thiourea as a quantitative reagent for the reduction of selenite solutions has been investigated.

The conditions governing the colorimetric estimation of quantities of tellurium of the order 0.05 mg. have been studied.

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