ART. XIII.—*The Quantitative Precipitation of Tellurium Dioxide and its Application to the Separation of Tellurium from Selenium;* by PHILIP E. BROWNING and WILLIAM R. FLINT.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cci.]

ALL those processes for the estimation of tellurium in which the tellurium is precipitated and weighed in elementary condition are open to the objections that, first, there is more or less difficulty in securing completeness of precipitation owing to the rapid increase of free acid* in the solution; and, second, the product is extremely susceptible to oxidation. On the other hand, those methods in which compounds decomposable by heat are transformed to the dioxide by ignition are generally both tedious by reason of the length of time required (as for example, the basic nitrate process as described by Norris†) and, what is more to the point, liable to errors caused not only by lack of constancy of composition, but also by the volatilization of the product to be weighed.

Of all the forms in which tellurium has been weighed there is no doubt that the dioxide is the best. It is unaffected by the air, is anhydrous, is not hydroscopic, and can easily be obtained in pure condition. Likewise it can be heated to any temperature below low redness without any danger of volatilization. It was in view of these facts that some results obtained from an extensive study, about to be published, of the hydrolytic behavior of hydrochloric acid solutions of tellurium tetrachloride suggested the process about to be described.

When a tetrachloride solution containing the least possible excess of hydrochloric acid is sufficiently diluted with hot water, but a small portion, if any, of the tellurium is at first precipitated. By the addition of as little ammonia in excess as may be, and the restoration of the acidity by acetic acid in the faintest possible excess and then allowing the liquid to stand until cold, the tellurium is precipitated completely, as TeO_2, but in very finely crystalline condition. The precipitate is insoluble in cold water and alcohol, in acetic acid and ammonium acetate solutions of one per cent strength if cold, and filters, washes, and dries with the greatest facility.

In the first testing of the method, portions of pure dioxide were weighed out, dissolved in two cubic centimeters of concentrated hydrochloric acid, diluted with two hundred cubic centimeters of boiling water, and the ammonia, and subse-

* Crane, Am. Chem. J., xxiii, 409. See also Lenher and Homburger, J. Am. Chem. Soc., xxx, 387.

† J. Am. Chem. Soc., xxviii, 1675.

quently acetic acid, added with great care. After standing over night, the liquid was decanted through the asbestos of a Gooch crucible, and the precipitate transferred and washed with cold water, and dried to constant weight at about 105°. In Table I, experiments 1 to 4, are gathered the results obtained.

TABLE I.

	TeO_2 taken grm.	TeO_2 found grm.	Error grm.
(1)	0·2002	0·2000	—0·0002
(2)	0·2019	0·2017	—0·0002
(3)	0·2904	0·2002	—0·0002
(4)	0·2006	0·2004	—0·0002
(5)	0·2011	0·2010	—0·0001
(6)	0·2003	0·2003	0·0000

In experiments 5 and 6, one and one-half cubic centimeters of ten per cent potassium hydroxide solution were used to dissolve the dioxide, instead of hydrochloric acid. The solution was then acidified slightly with hydrochloric acid, and the determinations completed from this point as before. The results seem to be equally good.

Next, weighed amounts of basic nitrate were dissolved in two cubic centimeters of hydrochloric acid. The small quantity of nitric acid holds up a little of the tellurium* and consequently before dilution resort was had to evaporation to remove as much of the free acid as possible. This had to be done with extreme care, since the least tendency on the part of the solution to boil was accompanied by the volatilization of the tetrachloride formed. With a not unreasonable amount of care, however, good results were obtained. In all of the experiments of Table II the dilution was with hot water, two hundred cubic centimeters being sufficient, but in several the treatment was varied, as given below.

TABLE II.

	$2TeO_2.HNO_3$ taken grm.	TeO_2 theory grm.	TeO_2 found grm.	Error grm.
(1)	0·2508	0·2094	0·2079	—0·0015
(2)	0·2501	0·2088	0·2086	—0·0002
(3)	0·2521	0·2105	0·2101	—0·0004
(4)	0·2500	0·2088	not completed	
(5)	0·2537	0·2118	0·2115	—0·0003
(6)	0·2510	0·2096	0·2091	—0·0005

* Gutbier, Studien über das Tellur, 46.

In experiment I, during the evaporation of the acid, there was noticed a slight volatilization of the tetrachloride, which accounts for the increased error. In 2, filtration was performed after twelve hours, and the same length of time elapsed in 5 and 6. Experiment 3 stood for two hours, and in this and number 4 potassium hydroxide was used in place of ammonia. So much tellurium was found in the filtrate from 4 that the determination was not completed. In 5 and 6, the basic nitrate was dissolved with two cubic centimeters of ten per cent potassium hydroxide solution, instead of the usual hydrochloric acid. Before dilution with hot water, hydrochloric acid was added in very slight excess. The ammonia added in number 6 was so much in excess as to dissolve completely the precipitate formed. The increased amount of ammonium acetate produced in the solution probably held up a trace of tellurium.

In order to observe the effects produced by variations in the factors concerned in the process, several experiments were performed, the figures for which are given in Table III.

TABLE III.

	$2TeO_2.HNO_3$ taken grm.	TeO_2 theory: Te taken as 127·5 grm.	TeO_2 found grm.	Error grm.
(1)	0·2502	0·2089	0·2083	−0·0006
(2)	0·2524	0·2108	0·2110	+0·0002
(3)	0·2505	0·2092	0·2089	−0·0003
(4)	0·2528	0·2111	0·2106	−0·0005
(5)	0·2531	0·2113	0·2106	−0·0007
(6)	0·5008	0·4182	0·4182	0·0000
(7)	0·5010	0·4183	0·4175	−0·0008
(8)	0·5005	0·4179	0·4178	−0·0001

The first four and the eighth were allowed to stand over night before the precipitate was removed; in the fifth one quarter hour, and in the sixth and seventh one half hour, elapsed. By a comparison of the results it appears that very little difference is made whether the time allowed to elapse be from 15 to 30 minutes or 12 or more hours, so long as the liquid is thoroughly cooled.

In all of the experiments of this series, the basic nitrate was dissolved with ten per cent potassium hydroxide solution, two cubic centimeters being sufficient in the first five, and four in the last three numbers. The solution in the case of the first two was then acidified slightly with hydrochloric acid, before dilution with hot water. In the rest, the alkaline solution was simply diluted with boiling water and faintly

acidified with acetic acid, the precipitate being afterwards made crystalline* by further heating. It was noted that the precipitate formed by this variation of the method is not so quickly transformed to the crystalline condition as when the procedure of the experiments described in Table I is followed. It is, besides, still more finely divided and does not settle quite so well. There seems to be a distinct advantage in the use of ammonia, when added to the solution acidified with hydrochloric acid, since, if the diluted solution is sufficiently hot, the precipitate formed by the ammonia begins to become crystalline, apparently, at about the time when the point of neutrality is reached. Under these conditions, a few drops of dilute ammonia in excess have an inappreciable solvent effect upon the TeO_2 and consequently there is also no opportunity for the slight excess of acetic acid subsequently introduced to dissolve and thus hold up a trace of the tellurium. On the other hand, it seems probable that, when the acetic acid is introduced, in faint excess, into the hot, diluted solution, alkaline with potassium hydroxide, since the tellurium is precipitated in floccy form which does not become entirely crystalline until again heated, the excess of acid must dissolve up a more or less minute portion of the precipitate and retain it in solution in such a form as not to be again thrown down upon cooling. Two facts may be adduced in support of this theory, namely: first, that the errors in Table III show much greater irregularity than those of Table I; and second, that whereas the filtrates of I were shown by testing with stannous chloride to be free from tellurium, several of those in II, notably experiments 4, 5, and 7, were proved to contain it in traces.

And finally, the last three experiments of Table III show that it is perfectly possible to use quite as successfully one half gram of the basic nitrate, equivalent to four tenths gram of dioxide, in a single determination, employing a bulk of solution no greater than 200 to 250 cubic centimeters.

Attempts to separate tellurium from copper and bismuth by treatment with small amounts of potassium hydroxide solution, and to estimate the tellurium in the filtrate by this ammonia-acetic acid process, met with only moderate success. Under the conditions, the copper and bismuth apparently tend to form insoluble tellurites undecomposable by the allowable excess of alkali,† and consequently there was always a loss of tellurium. And further, if the bismuth or copper is precipitated together with the tellurium, it is practically impossible to dissolve out from the mixed precipitate all the tellurium by a hot

* Berzelius. Ann. de Chim. et de Phys., 2 serie, lviii, 134 sq.
† Ibid., lviii, 114.

solution of the alkali. The results of two experiments with mixtures of bismuth and tellurium oxides are given in Table IV.

TABLE IV.

	TeO_2 taken grm.	Bi_2O_3 taken grm.	TeO_2 found grm.	Error grm.
(1)	0·2027	0·005	0·2015	−0·0012
(2)	0·2009	0 005	0·1997	−0·0012

In both cases, the mixed oxides were heated with two cubic centimeters of potassium hydroxide solution (10 per cent), the precipitate filtered out, and the filtrate diluted with hot water and precipitated by addition of acetic acid.

If hydrochloric acid solutions of tellurium and selenium dioxides be mixed, abundantly diluted with boiling hot water, and the operation of the above described process properly applied, only the tellurium is precipitated, the selenium remaining entirely in solution in the filtrate. This not only provides a simple and rapid preparative process for the purification of tellurium from selenium, but also makes possible the estimation of tellurium directly in the presence of the latter element.

TABLE V.

	TeO_2 taken grm.	SeO_2 taken grm.	TeO_2 found grm.	Error grm.
(1)	0·2015	0·2	0·2010	−0·0005
(2)	0·2013	0·1	0·1996	−0·0017
(3)	0·2003	0·1	0·1992	−0·0011
(4)	0·2009	0·1	0·2003	−0·0006
(5)	0·2000	0·1	0·2002	+0·0002
(6)	0·2015	0·1	0·2016	+0·0001
(7)	0·2038	0·1	0·2040	+0·0002
(8)	0·2028	0·05	0·2019	−0·0009
(9)	0·2024	0·05	0·2024	0·0000

Experiment 1 in Table V was made upon 0·2 grm. of TeO_2 in the presence of 0·2 grm. of SeO_3, which was later found to contain a little copper. After solution of the oxides in two cubic centimeters of hydrochloric acid and dilution to 200 cubic centimeters with hot water, precipitation was effected as usual by ammonia and acetic acid. Copper was carried down in the precipitate, as shown by its greenish color, the total weight after thorough drying being 0·2054 grm. In order to determine the amount of TeO_2 per cent, the precipitate was washed with ten per cent potassium hydroxide solution, the tellurium being carried away in solution as tellurite; the residue was

washed with water until free from soluble matter, and dried to constant weight, yielding 0·0044 grm. The amount of TeO_2 by difference was consequently 0·2010 grm. But the residue, when dissolved in hydrochloric acid and tested with stannous chloride, showed the presence of a trace of tellurium.

In experiment 2, two cubic centimeters of the potassium hydroxide solution were used, and the hot, diluted solution acidified with acetic acid. In 3 and 4, after the solution in two cubic centimeters of potassium hydroxide, hydrochloric acid was added in faint excess, and the hot, diluted solution treated with ammonia and then acetic acid; the difference between these two determinations is apparently explained by the fact that in 3 the solution was allowed to cool a little before addition of ammonia, and thus the floccy precipitate was attacked by the acetic acid. In experiments 5, 6, and 7, potassium hydroxide was used to dissolve the oxides, hydrochloric acid was added to faint acidity, and the dilution made with cold water, which was then heated to boiling. It was evident that the floccy precipitation caused by the cold water included some selenium, which was not released by the change to crystalline form, since not only are the errors positive, but also the precipitate, when tested for selenium with potassium iodide by the delicate method of Norris, Fay, and Edgerly,* showed the presence of a trace of that element. In order to be certain that this is the true explanation of the fact, two more experiments, 8 and 9, were performed, in the first of which special care was taken to dilute with water actively boiling, and to carry out the subsequent operations as quickly as possible in order that the change of condition of the precipitate might occur before the acetic acid was introduced. No selenium could be detected in the precipitate of experiment 8. In the case of 9, the hot solution was allowed to cool somewhat before the precipitation, in consequence of which the abundant, floccy precipitate included a minute trace of selenium, as afterwards proved by the above mentioned test.

In order, therefore, to estimate tellurium as the dioxide by this method, it is evident that fairly accurate and concordant results can be obtained by dissolving the material in ten per cent potassium hydroxide solution, about two cubic centimeters for 0·2 grm. of dioxide, acidifying this solution slightly with hydrochloric acid, diluting to 200 cubic centimeters with boiling hot water, and precipitating the tellurium in a finely crystalline form of dioxide from the still hot solution by the careful addition of dilute ammonia in faint excess and the restoration of the acidity by the faintest possible excess of

* Am. Chem. J., xxiii, 105.

acetic acid. If these simple operations are properly carried out, the precipitate will have become crystalline by the time when the excess of ammonia has been reached; the addition of a few drops of acetic acid will cause the precipitation to become entirely quantitative when the solution has cooled, so that no tellurium will be detectable in the filtrate by stannous chloride; the precipitate can be transferred, and safely and rapidly washed with cold water, and dried to constant weight at about 105° (or even up to just below low redness) in a quarter of an hour. Furthermore, the filtration can be performed at the end of half an hour or so, or after 12 to 24 hours, as most convenient. And, as shown by the experiments of Table V, selenium does not interfere, providing precautions are taken.