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NOTES ON SELENIUM AND TELLURIUM.

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IN a paper under the above title,[1] published some years ago, I pointed out the difference of behavior of selenium and tellurium, in the dioxide state, towards sulphur dioxide and ferrous sulphate in solutions of hydrochloric acid of various strength. The experiments were conducted under definite conditions, as stated in my original paper, the quantities of the two elements being in every case 0.1 gram each, the quantity of the solution 100 cc., and the acidity varying from 0.5 to 100 per cent., the pure hydrochloric acid meaning the aqueous product of 1.175 sp. gr. Based on quantitative determinations of the two elements precipitated by sulphur dioxide in the cold, and other conditions as already stated, the conclusions reached, were as follows: Selenium is most readily precipitated by sulphur dioxide in strong hydrochloric acid. This precipitation continues to be complete until an acidity of 25 per cent. is reached, the solution being allowed to stand about twenty hours. The precipitation, within that time, becomes nil at an acidity of approximately 3 per cent. The precipitation of tellurium in strong hydrochloric

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[1] This Journal, 19, 771.

acid is nil. It begins with an acidity of about 80 per cent. (the time of standing as above), becomes complete at about 60 per cent., and continues to be so until the acidity is reduced to about 10 per cent.

On page 774 of the paper cited is found the following remark : " From the above facts we learn that even with sulphur dioxide in a hydrochloric acid solution of over 80 per cent. acid a separation is possible" (meaning a separation of selenium and tellurium).

A NEW METHOD OF QUANTITATIVE SEPARATION OF SELENIUM AND TELLURIUM.

That selenium is more readily precipitated by sulphur dioxide than tellurium has long been known and the principle has been practically applied, but, it seems, never to quantitative analysis. Since the publication of my paper, above referred to, I have had occasion in numerous instances to determine the two elements in copper analysis, and I have in all cases applied this hydrochloric acid-sulphur dioxide method. When working with a Gooch filter and a suction pump (filter-paper, of course, cannot be used) this separation is a rapid and simple one. My mode of operation is as follows : 100 grams of copper with from 2 to 4 grams of ferrous sulphate, are dissolved in 400 cc. nitric acid (sp. gr. 1.42) and the nitrous fumes expelled. This solution, after diluting and cooling, is made sufficiently ammoniacal to dissolve all the copper. After boiling and settling, the ferric hydroxide containing the selenium and tellurium is gathered on a filter. It must be freed from copper by washing with ammoniacal water, redissolving in acid, and reprecipitation with ammonia (repeatedly if necessary). This ferric hydroxide is then brought into dilute hydrochloric acid solution (not more acid being used than is necessary to dissolve the precipitate), and hydrogen sulphide passed through the cold liquid until saturation. The solution must be cold to retain the selenium sulphide in soluble form in sodium sulphide, and copper must be absent to guard against insoluble cupric selenide. The sulphides are filtered and washed and digested with a solution of sodium sulphide, which latter takes up the sulphides of selenium and tellurium. The solution, after filtering, is acidified with nitric acid and evaporated to dryness. The latter operation must be performed with care, to avoid loss of selenium dioxide. The residue now contains the dioxides of selenium and tellurium and sodium nitrate, besides some sulphur. To this residue is added 200 cc. of strong hydrochloric acid, and boiled until all the nitrohydrochloric acid (its presence being due to the nitrate) is destroyed, and the two elements, which may have been oxidized to the selenic and telluric form, are reduced to the selenous and tellurous state. After cooling, the solution is filtered off from the sulphur and the insoluble halide through a Gooch filter, and the residue washed several times with strong hydrochloric acid; the latter, however, need not be of more than 90 per cent. strength. The filtrate is now ready to be saturated with sulphur dioxide gas, conveniently generated by copper borings and concentrated sulphuric acid, which will precipitate the selenium alone under the given conditions. After settling, which may be accelerated by warming, the selenium is gathered on a weighed Gooch filter and washed with hydrochloric acid (90 per cent.) about three times. Here the filtrate is set aside, and the selenium freed of salts, etc., by washing successively with warm, dilute hydrochloric acid, pure water, and strong alcohol. After drying it is weighed. The filtrate containing the tellurium is increased to double its volume with pure water. With the small quantities of tellurium present in copper, the amount of sulphur dioxide held in solution is generally sufficient to precipitate that element completely upon boiling ; however, it is safer to boil the dilute solution for some minutes, and while doing so to conduct more sulphur dioxide through it. After cooling and settling, the tellurium is filtered, washed, and weighed in the same manner as the selenium.

The following quantitative determinations, for which commercial accuracy only is claimed, were made in proof of the method, the conditions being that 0.1 gram of selenium and 0.1 gram of tellurium, previously converted into dioxide, were jointly dissolved in 100 cc. of 90 per cent. hydrochloric acid, and the further operations performed as previously described :

DETERMINATION OF SELENIUM AND TELLURIUM BY PRECIPITATION WITH SULPHUR DIOXIDE IN HYDROCHLORIC ACID.

	Selenium.		Tellurium.	
	Weighed in. Gram.	Found. Gram.	Weighed in. Gram.	Found. Gram.
	0.1000	0.0983	0.1000	0.0998
	0.1000	0.1000	0.1000	0.0986
	0.1000	0.1006	0.1000	0.1010
	0.1000	0.0994	0.1000	....
	0.1000	0.1002	0.1000	0.0993
	0.1000	0.1010	0.1000	0.1013
Av'r'ge	0.1000	0.0999	0.1000	0.1000

The selenium in every case proved to be free of tellurium by its complete solubility in potassium cyanide. Nor could selenium be detected in the filtrates with ferrous sulphate by either increasing or decreasing the strength of the acid. In short, the separation is complete.

In a paper by Mr. Victor Lenher[1] are to be found the following remarks: "When sulphur dioxide is brought into contact with such a strong solution, selenium should be precipitated free from tellurium according to Keller. When sulphur dioxide was introduced into this solution a red precipitate formed, showing selenium just precipitated. It appeared to darken, however, when the liquid was saturated. On boiling, the precipitate agglomerated into a mass which much resembled selenium, but on separating it by means of potassium cyanide it was found to consist of 3.2 grams of selenium and 28.3 grams of tellurium. This seems to indicate that tellurium and selenium cannot be perfectly separated by sulphur dioxide in strong hydrochloric acid solution."

Mr. Lenher worked with 5 pounds of tellurous and selenous material. He does not mention the quantity of acid he used. His conditions were, therefore, probably radically different from those as given in my own experiments.

As I could not doubt my own results of often repeated tests, nor Mr. Lenher's assertions, I inferred that the difference in the conclusions arrived at must be due to the difference in the relative masses of tellurium and acid present in the experiments, and I corroborated this by a few simple tests: The oxides of 0.1 gram of selenium and 5 grams of tellurium were dissolved in

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[1] "Preparation of Metallic Tellurium," This Journal, 21, 347.

100 cc. of 90 per cent. hydrochloric acid, and the solution saturated with sulphur dioxide. The precipitate, after standing about twenty hours, contained all of the selenium with 2.1 grams of tellurium. In the subsequent tests the acid of the same strength was increased each time by 50 cc., the quantities of selenium and tellurium remaining constant. The quantity of tellurium decreased in each successive precipitation, and became nil when the quantity of acid reached 450 cc. It follows, therefore, that to obtain a perfect separation of selenium and tellurium in strong hydrochloric acid solution by means of sulphur dioxide, the quantity of acid must be about 100 times that of the tellurium.

Numerous chemists have pointed out the error made in determining tellurium in its metallic state, it being due to slight oxidation. Mr. F. H. D. Crane[1] found this error to be from 0.3–0.6 per cent. over the correct result, when no precautions were taken. Criticism for using this method in industrial practice seems to me entirely unjustified. Although accuracy is always essential, the practical chemist must be able to discriminate between accuracy and pedantry. For example: Our copper rarely contains as much as 0.01 per cent. of tellurium, and we should find, according to Mr. Crane, when using 100 grams of copper, from 0.01003 to 0.01006 instead of 0.01 gram of the element, a difference absolutely beyond detection and of no importance whatsoever in ordinary work. In fact, the chemist would find, in practice, that with more scientific methods ±3 or 6 per cent. would often be far from covering the differences between his own duplicates, or those of other equally conscientious workers. In substantiation of this I need only refer to the determination of small percentages of precious metals,[2] upon which large commercial interests depend. With silver, which occurs in larger quantity than tellurium, determinations often differ ±3 to 5 per cent. from the mean. With gold, occurring in smaller quantities, these variations rise as high as ±25 per cent.

BALTIMORE, March, 1900.

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[1] "A Contribution to the Knowledge of Tellurium," Dissertation, Johns Hopkins University, 1898.

[2] "Assays of Copper and Copper Matte," *Trans. A. I. M. E.*, 25, 250.