

PREPARATION OF METALLIC TELLURIUM.¹

BY VICTOR LENHER.

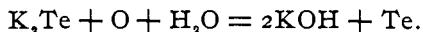
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JUST a year ago a study was begun on tellurium. The material at hand on which the research was to be made consisted of the so-called electrolytic copper slimes furnished by the Baltimore Electric Refining Company. The first step was naturally to extract the tellurium from these residues, then to work up the metal obtained into such derivatives as might be found convenient for study. The first method employed consisted in the treatment of the residues with concentrated hydrochloric acid; chlorides of the soluble elements were formed, while a highly siliceous residue remained insoluble. The resulting solution was poured into water, when the oxide of tellurium was precipitated along with more or less antimony oxychloride. This precipitate was again dissolved in hydrochloric acid and sulphur dioxide conducted into the solution, when tellurium was precipitated in a finely divided condition.

A process similar to the above is at present the general way by which the metal is obtained. The German tellurium which is on the market is obtained by treatment of the ore with aqua regia and the subsequent precipitation from a hydrochloric acid solution by sulphur dioxide.

A number of methods for obtaining metal are known, but most depend on the precipitation of the tellurium from a hydrochloric acid solution by sulphur dioxide.

Berzelius fused the naturally occurring tellurides with a mixture of oil and soda or potash, or with potassium tartrate. He obtained purple potassium telluride, which, subjected to the moderate oxidation of a current of air yielded tellurium according to the equation :



Berthier treats nagyagite, which is a combination of gold telluride and lead sulphide with hydrochloric acid ; hydrogen

¹ Read at the New York meeting of the American Chemical Society, December 27, 1898.

sulphide is evolved, lead, antimony, etc., pass into solution, while the gold telluride is unattacked. The latter is treated with nitric acid, which dissolves the tellurium away from the gold. The tellurium is brought into hydrochloric acid solution by evaporation with hydrochloric acid and the tellurium precipitated by sulphur dioxide. Petzite is fused with a mixture of sodium carbonate and potassium nitrate. He extracts the tellurate with water, treats with hydrochloric acid to reduce to tellurite, after which he precipitates with iron. Berzelius extracts in a similar manner, but reduces his tellurate to telluride by fusion with carbon.

Schroetter treats tellurides with either hot concentrated sulphuric acid or aqua regia. The gold is precipitated with ferrous sulphate or oxalic acid and the tellurium by zinc. He reprecipitates the tellurium from a hydrochloric acid solution by sulphur dioxide or an alkaline sulphite. Another method of extraction is to treat the ore with chlorine gas, when tellurium chloride is formed and distils from the non-volatile portion. The tellurium is subsequently precipitated from hydrochloric acid solution by sulphur dioxide. The method doubtless owes its origin to Berzelius. It has also been suggested to prepare tellurium by precipitation with the electric current.

In 1870 Stolba called attention to the precipitation of tellurium from its alkaline solutions by means of grape sugar; later, Kastner found that it was completely precipitated by grape or invert sugar. But after those two papers the sugar precipitation has been very little heard of; it seemed as though it should be an ideal means of producing metal from the electrolytic copper residues as the tellurium appears as a waste product and is already in alkaline solution.

A series of experiments was made to attempt the extraction of tellurium by different methods. The first thing to do was to prepare tellurium by a well-known method and obtain a product that it would be possible to use in comparison. To this end, five pounds of residues were treated with concentrated hydrochloric acid (sp. gr. 1.20). An amber-yellow liquid was obtained and a residue which was highly siliceous. It is possible to obtain a perfectly clear solution by filtration through asbestos wool, using a suction-pump. When sulphur dioxide is

brought into contact with such a strong acid solution, selenium should be precipitated free from tellurium according to Keller.¹ When sulphur dioxide was introduced into this solution a red precipitate formed showing selenium was 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. The filtrate from the strongly acid solution was diluted with water and more sulphur dioxide passed through the liquid, when the rest of the tellurium was precipitated. The lump of metal which was formed by fusion was finely powdered and fused with potassium cyanide; purple telluride of potassium was formed. The solution was filtered and a current of air passed through. The tellurium which was formed was fused, then distilled in hydrogen gas. This material was considered pure. When treated with aqua regia, dioxide is formed and may be obtained by evaporation. Tellurium oxide is completely volatile at a low temperature in hydrochloric acid gas, no residue remaining. Pure tellurium is likewise completely volatile when heated in hydrogen.

Since it seems most natural to prepare a metal from its oxide, the tellurium oxide was subjected to a number of reduction tests. In recent years, metallic magnesium and metallic aluminum have shown themselves to be of great value as reducing agents. When metallic aluminum and tellurium oxide are heated together in a crucible a violent reaction takes place; tellurium is formed, but immediately unites with the aluminum forming aluminum telluride. Metallic magnesium, even in very coarse condition, when heated with tellurium oxide, gives a very explosive reaction. So very energetic is the action that it has not been possible to collect any of the products formed.

When dry glucose is heated with the oxide, a coke is formed which becomes coated with the metal and is difficult to fuse into a button. The same may be said of a dry fusion of asphaltum

¹ This Journal, 19, 773.

with the oxide. Ignition of the oxide with dry oxalic acid does, however, give metal readily, and fusion into a globule is an easy matter.

The next series of experiments was made with the sugars. Tellurium oxide was dissolved in potassium hydrate, cane-sugar was added, and the solution warmed. When a saturated solution is used, purple telluride is formed, but boiling in contact with the air causes a rapid separation of black tellurium. After washing with water the precipitate can be dried and fused into a mass.

From a solution of an alkaline tellurite glucose precipitates black elementary tellurium. No intermediate formation of telluride could be noticed as with cane-sugar. Pure white, anhydrous grape-sugar was dissolved in water and added to a warm solution of the alkaline tellurite. Tellurium was precipitated in elementary form. During the process of washing, which always followed the precipitation, it was invariably noticed that grape-sugar was much more difficult to remove from the finely divided tellurium than any of the other sugars.

From these experiments it seemed natural to conclude that reducing sugars will give a very practical method for the preparation of metallic tellurium. Tellurium obtained by this method is completely volatile in hydrogen gas and its oxide is likewise volatile in hydrochloric acid gas.

Thanks to the kindness of Mr. Walker, of the Baltimore Electric Refining Company, who furnished the residues, and to Prof. P. de P. Ricketts, who in so many ways made the work possible, the author has been enabled to prepare a bar¹ of tellurium by fusion of the finely divided material obtained by reduction of tellurium in alkaline solution by means of sugar.

Among other experiments, I decided last year, while working on selenium, that as soon as I could obtain satisfactory compounds I should determine the atomic mass of tellurium by precipitation with hydroxylamine. As my work thus far on tellurium, which was begun with Prof. E. F. Smith at the University of Pennsylvania, and is now going on in this institution, had for one of its objects the determination of the atomic mass

¹ This bar was exhibited before the American Chemical Society, at New York, and weighed four pounds.

of tellurium by means of the hydroxylamine precipitation it seems quite proper that I should continue it, notwithstanding the fact that Prof. Jannasch, of the University of Heidelberg, announced in the *Berichte* for October, 1898, that he is engaged in work on the same line.

THE ASSAY OF NUX VOMICA.¹

BY EDWARD R. SQUIBB.

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IN the preparation of a paper on acetic acid as a substitute for ethyl alcohol in extracting the active principles of some officinal drugs, it became necessary to have a convenient and moderately accurate method of assaying nux vomica. The whole of this paper would interest very few members of the American Chemical Society, and such as it would interest may find it in the *American Journal of Pharmacy* for January, 1899. But the assay process that ends the paper may be far enough within the line of interest to this society to warrant the writer in offering it here.

The short and easy methods of Messrs. Dunstan and Short, given in the *British Pharm. Journ. and Trans.*, 3d Series, 13, 665-1055, and 14, 621, and given in the British Pharmacopœia, were found objectionable on some accounts, but chiefly because the results are too high. For example, a table is given on p. 1055, wherein from seven samples the percentage of total alkaloids ranged from 3.04 to 3.90 per cent. with an average of 3.29 per cent. This, in the writer's experience, is much too high, and there is a probability that the plus error may be due to weighing the chloroform extract as alkaloid. The most recent authority noticed is the new, 1898, British Pharmacopœia, but its method is liable to the same objection of weighing a chloroform extract as alkaloid. The U. S. Pharmacopœia of 1890 has an excellent method that avoids this source of error by titrating the alkaloids. This method² first makes a dry extract and then assays that for use in its standardized preparations.

Two grams of the dry extract are dissolved by shaking in a separator with twenty cc. of a previously-made mixture of two

¹ Read at the New York meeting of the American Chemical Society, December 28, 1898.

² U. S. Pharmacopœia (1890), pp. 152 *et seq.*