

A final determination will be carried out later with new tin tetrabromide, using silver prepared expressly by Richards' method.

PRAGUE, CZECHOSLOVAKIA.

---

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF BOHEMIAN CHARLES UNIVERSITY OF PRAGUE.]

## A REVISION OF THE ATOMIC WEIGHT OF TIN.<sup>1</sup> II.

BY HENRY KREPELKA.

Received February 13, 1920.

We have determined in a new and more careful series of trials, the ratio  $\text{SnBr}_4 : 4\text{Ag}$  by analysis of newly prepared tetrabromide of tin.

The materials for this purpose were prepared with great care and cleanliness, and chief attention was paid to removing all traces of moisture from the bromine used for the synthesis of the tetrabromide and to keeping the latter in an absolutely dry state. Individual analyses were carried out in the same way as before,<sup>2</sup> although one profited, of course, by the experience gained in the earlier work. The details follow:

### Preparation of New Materials.<sup>3</sup>

**Bromine.**—Ordinary bromine was shaken in portions in a separatory funnel containing distilled water, every portion being thus treated 3 times. This bromine was then redistilled from a saturated solution of potassium bromide. The distillate was allowed to drip into a solution of potassium oxalate prepared by neutralizing pure oxalic acid with pure potassium carbonate. The potassium bromide thus obtained was recrystallized 3 times, and its solution was evaporated with a small quantity of potassium dichromate and twice distilled sulfuric acid. The bromine thus set free removed all iodine that may have been present. This evaporation was repeated 3 times. In order to remove organic matter the dry bromide was melted in small quantities in a platinum crucible. From this re-melted bromide, bromine was set free by means of an amount of potassium dichromate and sulfuric acid, such as to leave undecomposed bromide in the distilling flask. The bromine was then redistilled and from a portion of this distillate was prepared the calcium bromide used to dry the remaining part of the bromine, which was then further dried by shaking it with phosphorus pentoxide (twice sublimed in a stream of oxygen), and was afterwards distilled directly into the apparatus in which the synthesis of tetrabromide took place.

**Tetrabromide of tin** was prepared in the modified Lorenz apparatus. During the preparation the communication with the outside air was ef-

<sup>1</sup> Presented to the Bohemian Academy of Sciences, Prague, 1919.

<sup>2</sup> B. Brauner and H. Krepelka, *THIS JOURNAL* (preceding paper).

<sup>3</sup> The remaining reagents not mentioned here were prepared in the same way as stated in the preliminary work.

fectured by a drying system (described in the preceding communication) to which were added tubes containing sublimed phosphorus pentoxide.

The course of the reaction showed that both the bromine used and atmosphere of the reaction bottle were absolutely free from moisture, since the first drop of bromine did not at once react with the tin foil—only after 5 minutes did the reaction begin slowly to take place. As soon as the first foil was covered with tetrabromide the reaction became violent and accompanied by such heat that the surrounding pieces of foil were melted into a ball, and the whole reaction bottle had to be quickly cooled.

The tetrabromide obtained was introduced into glass bulbs provided with cone-shaped necks and there sealed. This arrangement removed the difficulties encountered at the same operation during the preliminary work, when the bulbs used had straight necks.

**Silver.**—750 g. of pure ordinary silver was dissolved in portions in distilled nitric acid (1 : 2) in such a way as to leave a small part of the silver undissolved.

The solution of silver nitrate thus obtained was heated to the boiling point and, after the expulsion of nitrous gases, was filtered. The clear solution, colored pale blue by copper, was allowed to crystallize by evaporation. Silver nitrate thus obtained was fused in a porcelain dish until the melted mass became black. This black substance was dissolved in water and the solution was filtered and allowed to crystallize by evaporation. The crystallization was repeated 3 times. A spectroscopic examination of the last crystals showed only the lead line 3683.62 (intensity 1000), proving thus that all other metals had been removed.

The silver nitrate obtained in this manner was reduced by ammonium formate (prepared from pure formic acid and freshly distilled ammonia) and the reduced silver was washed with distilled water until the Nessler reagent gave no test for ammonia, dried in an electric drying oven at 150° and then melted in a current of pure hydrogen according to the method elaborated by T. W. Richards.<sup>1</sup>

Pure hydrogen for this purpose was obtained by the electrolysis of a solution of pure sodium hydroxide prepared from *pure metallic sodium*. The apparatus used consisted of a long U-shaped tube, in one arm of which was evolved oxygen and in the other hydrogen. The arms were long in order to prevent the mixing of the 2 gases. The hydrogen was conducted into a purifying system composed of 2 Richards' washing flasks filled with a saturated solution of silver sulfate, a U-tube containing fused sodium hydroxide, a tube filled with red hot pumice stone covered with platinum and of another U-tube containing fused sodium hydroxide. The individual parts of the apparatus were connected by means of air-tight ground joints.

<sup>1</sup> THIS JOURNAL, 27, 472 (1905).

Grains of remelted silver were etched with dil. nitric acid which had been redistilled, then washed successively in distilled water, ammonia water, and again in distilled water.

The final delicate operation, namely the preparation of small pieces of pure silver for weighing, was carried out in the following manner. The greater portion of the silver buttons was cut up into small pieces on a slab of pure silver with a sharp steel chisel—the pieces were then etched and washed as above. The remaining grains were rolled between clean steel rollers in such a way that after each passing through the roller the silver was etched and washed in order to remove any trace of iron which it might have acquired. The silver foil was then cut by scissors into small pieces, which were then etched and washed as before.

Weighing was done on the same balance as in the preliminary work, but not until after the weights had been tested and corrected.

Six analyses were made in this series and the following results were obtained:

No. of analysis.	No. of bulb.	SnBr <sub>4</sub> G.	Corr. for vacuum. G.	Silver corr. for vacuum. G.	SnBr <sub>4</sub> :4Ag.	At. wt.	Difference from the mean.
1.....	19	5.11681	5.11788	5.03796	1.01586	118.702	0.003
2.....	8	2.46823	2.46875	2.43035	1.01580	118.674	+0.025
3.....	9	0.99489	0.99510	0.97961	1.01581	118.679	+0.020
4.....	18	1.69798	1.69834	1.67172	1.01592	118.727	-0.028
5.....	21	3.54191	3.54265	3.48737	1.01585	118.697	+0.002
6.....	15	3.82100	3.82180	3.76199	1.01590	118.717	-0.018
				Mean,	1.01586	118.699	±0.016
				Maximum	=	118.727	
				Minimum	=	118.674	
				Difference	=	0.053	

**Discussion.**—The mean value from 6 determinations is 118.699 ( $\pm 0.016$ ). The maximum figure, 118.727, found only once, was arrived at by the analysis of Bulb No. 18, which was filled as far as to the neck. The minimum was 118.674 and this was the result of the analysis of Bulb No. 8, likewise filled up to the neck. The maximum difference between the highest and lowest values is thus 0.053. The mean value of all 6 ratios, SnBr<sub>4</sub>:4Ag, is 1.01586. The only probable source of error of this series of analyses appears to have been the space in the necks of the bulbs not filled with tetrabromide.

The agreement of the resulting mean value of the atomic weight of this series of analyses with the mean value of the preliminary determination increases the probability of this figure, and supports the value of the atomic weight of tin, 118.699 (118.70), as determined by Briscoe<sup>1</sup> and by Bax-

<sup>1</sup> *J. Chem. Soc.*, 107, 76 (1915).

ter and Starkweather.<sup>1</sup> This value has been accepted by the International Committee on Atomic Weights.

In conclusion I wish to express my gratitude to The Bohemian Academy of Arts and Sciences in Prague, with whose financial support this work was carried out. I am also obliged to Professors Dr. B. Brauner and Dr. Sterba-Böhn for their valuable advice as well as to Dr. Sveda for his kind assistance.

WOLCOTT GIBBS MEMORIAL LABORATORY,  
CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

## THE ATOMIC WEIGHT OF LEAD FROM A JAPANESE RADIO-ACTIVE MINERAL.

BY THEODORE W. RICHARDS AND JITSUSABURO SAMESHIMA.

Received February 14, 1920.

The lead used in this work came from Hokuto, Formosa, Japan, and was separated from a crystalline mineral crust containing lead and barium<sup>2</sup> which had been formed in the bottom of a hot spring. According to Hayakawa and Nakano<sup>3</sup> this mixture of minerals contains (besides cerium and lanthanum) some radioactive elements, namely, ionium, polonium and radium, but no uranium. With their apparatus, however, they were unable to discover radioactivity in the lead chloride obtained from it.

About 10 g. of metallic lead obtained from this specimen was dissolved in pure nitric acid and the lead nitrate was recrystallized several times and then converted into chloride by freshly distilled pure hydrochloric acid. The lead chloride was recrystallized 4 times by dissolving the crystals in hot water in a quartz dish and adding hydrochloric acid. Before the last crystallization the hot solution of chloride was filtered through a Gooch-Munroe crucible. Owing to the small amount of material, no further purification was attempted. This lead chloride was then used for the determination of the atomic weight of lead.

The ordinary lead used for comparison was obtained from lead acetate, converted into chloride and recrystallized 5 times in the same manner as the Japanese lead.

The method of analysis was similar to that already often described<sup>4</sup> in other papers. Moist crystals of lead chloride (after washing the last crop with pure water) were transferred directly into a platinum boat which

<sup>1</sup> *Proc. Nat. Acad. Sci.*, **2**, 718 (1916).

<sup>2</sup> Okamoto, *Beitr. Mineral. Japan*, **4**, 178 (1912).

<sup>3</sup> Okamoto, *J. Geol. Soc. Tokyo*, **18**, 19 (1911); Hayakawa and Nakano, *Z. anorg. Chem.*, **78**, 183 (1912).

<sup>4</sup> Baxter and Wilson, *Proc. Am. Acad.*, **43**, 363 (1907); Richards and Lambert, *This Journal*, **36**, 1335 (1914); Richards and Wadsworth, *ibid.*, **38**, 2613 (1916); Richards and Hall, *ibid.*, **39**, 536 (1917).