

ART. XXVII.—*On a Method for the Quantitative Determination of Cæsium, and the Preparation of Pure Cæsium and Rubidium Compounds*; by H. L. WELLS.

SINCE no method has heretofore been devised for the accurate quantitative determination of cæsium in the presence of both rubidium and potassium, some experiments have been made in order to test the availability of the plumbic chloride, described in the preceding article, for this purpose. The results have not been as accurate as could be desired, but the method will be useful until a better one is found.

The solubility of Cs_2PbCl_6 in a hydrochloric acid solution (fuming acid diluted with water 1:1), containing twice the theoretical amount of lead chloride and saturated with chlorine, was determined by making a precipitation of about 1^g of Cs_2PbCl_6 under these conditions in 350^{cc} and determining the cæsium in the filtrate. The whole filtrate gave 0.0119^g of Cs_2SO_4 , which corresponds to a solubility of 0.000068^g of Cs_2PbCl_6 in 1^{cc}. A similar experiment in which concentrated hydrochloric acid was used, and also a larger excess of lead chloride, gave a solubility of 0.000049^g of Cs_2PbCl_6 in 1^{cc}. It has been shown in the preceding article that the solubility of Rb_2PbCl_6 is 0.003^g in 1^{cc} under similar conditions.

Some actual determinations of cæsium were made as follows: Known quantities of Cs_2PbCl_6 and about an equal weight of PbCl_2 were dissolved in hot HCl (1:1). Chlorine was passed into the solutions until they became cold, and, after standing about three hours, the precipitates were collected in porcelain Gooch crucibles and washed with hydrochloric acid containing chlorine. The precipitates were decomposed with hot water and the cæsium in the resulting solutions was determined as sulphate. In one case a comparatively large amount of potassium chloride was present. The details are as follows:

	Cs_2PbCl_6 taken.	KCl taken.	Volume 1:1 HCl.	Cs_2SO_4 found.	Deficiency as Cs_2SO_4 .
A	·1674 ^g	----	35 ^{cc}	·0856	·0026
B	·1592	----	35	·0807	·0031
C	·1280	0.5 ^g	35	·0638	·0035

These results indicate greater errors than were expected from the previous solubility determinations. It is suspected that a little of the precipitate was dissolved by washing, and the use of hydrochloric acid containing lead chloride as well as chlorine would probably diminish the error. The last experiment shows that the presence of a considerable amount of potassium has no influence upon the result.

The determination of cæsium by this method can be simplified by weighing the precipitated cæsium-plumbic chloride directly. The salt is perfectly stable at 100°. The following table gives the details of a number of determinations made in this way. The precipitates were all thoroughly washed with hydrochloric acid containing chlorine and dried on an asbestos filter at 100°.

	Cs ₂ PbCl ₆ taken.	PbCl ₂ taken.	KCl taken.	Volume HCl.	Cs ₂ PbCl ₆ found.	Cs ₂ PbCl ₆ lost.
A	·2761 ^g	0·25 ^g	---	28 ^{cc} 1:1	·2650 ^g	·0111 ^g
B	·0878	1·0	0·5 ^g	52 1:1	·0833	·0035
C	·1202	1·0	---	52 1:1	·1071	·0131
D	·7558	0·1	---	28 conc.	·7369	·0189
E	·2483	0·1	---	20 conc.	·2359	·0124

The results show considerable losses in cæsium, which apparently do not entirely depend upon the volume in which the precipitation is made. It is believed that the losses occur chiefly in washing, for large quantities usually show a larger total loss than small ones.

When cæsium and rubidium are together, the precipitation of cæsium plumbic chloride is accompanied by a partial precipitation of the rubidium, unless the quantity of the latter is small. It is possible, however, to make an indirect determination of the cæsium in such a precipitate by weighing it and afterwards determining the weight of the cæsium and rubidium sulphates. Two experiments have been made on this plan, where not only rubidium, but also potassium, sodium and lithium were present.

	A	B
Cs ₂ PbCl ₆ taken,	0·3561 ^g	0·1545 ^g
Rb ₂ PbCl ₆ taken,	0·2845	0·4101

To each of these were added about 0·15^g each of potassium and sodium chlorides, 0·25^g of lithium carbonate and 0·1^g of lead chloride. The substances were dissolved by boiling with dilute hydrochloric acid, about an equal volume of concentrated acid was added, and chlorine was passed until the solutions became cold.

	A	B
Volume of solution,	30 ^{cc}	50 ^{cc}

After standing several hours the precipitates were collected on asbestos filters in porcelain Gooch crucibles, washed with dilute hydrochloric acid saturated with chlorine, dried at 100° and weighed.

	A	B
Cs_2PbCl_6 and Rb_2PbCl_6 found,	0.5621	0.4538

The precipitates were treated on the filters with hot water, the resulting solutions were evaporated with sulphuric acid, the lead sulphate was removed by filtration, the filtrates were evaporated and finally ignited in an ammoniacal atmosphere and the mixed sulphates were weighed.

	A	B
Cs_2SO_4 and Rb_2SO_4 found,	0.2826	0.2164

For calculating the results, the following formulæ were used :

(P = weight of $\text{Cs}_2\text{PbCl}_6 + \text{Rb}_2\text{PbCl}_6$)

(S = weight of $\text{Cs}_2\text{SO}_4 + \text{Rb}_2\text{SO}_4$)

Weight of Cs = $5.095\text{S} - 2.301\text{P}$

Weight of Rb = $2.006\text{P} - 3.801\text{S}$

	A	B
Cæsium taken	0.1381	0.0599
Cæsium found	0.1464	0.0584
Error in cæsium	0.0083 +	0.0015 —
Rubidium taken	0.0823	0.1186
Rubidium precipitated ..	0.0534	0.0876

The results show that approximate determinations of cæsium can be made by this method when all the alkali-metals are present. The process leaves a part of the rubidium with the potassium, and these two metals can be precipitated as platinic chlorides and their amounts determined indirectly.

The method which has been described is useful for the extraction of cæsium and rubidium from their natural sources. The following method of procedure may be suggested, supposing all the alkali-metals to be present as chlorides in a concentrated aqueous solution :

At least an equal volume of concentrated hydrochloric acid is added, and any precipitated sodium and potassium chlorides are removed. The solution is diluted somewhat to avoid a subsequent precipitation of these chlorides, a solution of lead chloride, made by boiling lead oxide with a large excess of hydrochloric acid, is gradually added while chlorine is passed into the solution until it is cold and until fresh additions of lead chloride fail to produce a yellow precipitate. According to my solubility determinations, this precipitation leaves less than 1% of rubidium and a much smaller quantity of cæsium in each liter of the solution. The precipitate is usually almost

free from potassium. To ensure the complete purification of the cæsium and rubidium, the precipitate is washed with hydrochloric acid containing chlorine and lead chloride, then it is treated repeatedly with small quantities of boiling water until completely decomposed, and the resulting solution is subjected to a repetition of the foregoing process. The mixed plumbic salts are decomposed with hot water and the resulting, filtered solution is evaporated to dryness to remove hydrochloric acid. The residue is dissolved in hot water,* the lead is precipitated by the addition of a slight excess of ammonium sulphide and the precipitate is removed by filtration. The solution is evaporated to dryness and the residue consists of cæsium and rubidium chlorides and some ammonium chloride.

The following directions for the separation and purification of the cæsium and rubidium do not involve any new methods, but the course of procedure has been arrived at after a considerable amount of experience, and it may be of use to others. It is assumed that rubidium is more abundant than cæsium in the mixture. If cæsium predominated it would be more advantageous to extract that metal first by an obvious modification of the process.

The mixed chlorides of rubidium and cæsium are dissolved in at least five parts of concentrated nitric acid and the solution is evaporated to dryness and heated until the excess of nitric acid is removed. The residue is dissolved in a small amount of water, and as much oxalic acid as corresponds to twice the weight of the original chlorides is added. The whole is evaporated to dryness and the residue is ignited in platinum until the oxalates are completely converted into carbonates.† The carbonates are dissolved in water, the solution is filtered and exactly neutralized with a measured solution of tartaric acid, as much more tartaric acid as has been used for the neutralization is added, and the solution is evaporated until it becomes saturated while hot. The solution on cooling deposits acid rubidium tartrate, which is washed with a small quantity of water and is recrystallized two or three times from a hot saturated solution in the same way until it gives no cæsium spectrum.‡ The united mother-liquors from the acid rubidium tartrate are evaporated to dryness and ignited in platinum. The resulting carbonates are converted into chlorides, and, to a solution of these in a small volume of 1:1 hydrochloric acid, a solution of antimony trichloride in the same acid is

* No part of this residue should be thrown away on the assumption that it is lead chloride, for the salt CsPb_2Cl_5 is difficultly soluble and resembles PbCl_2 .

† This method of converting alkaline chlorides into carbonates is due to J. L. Smith, this Journal, II. xvi. 373.

‡ This method is due to O. D. Allen, this Journal, II, xxxiv, 367.

added as long as a precipitate forms.* The precipitate is collected on a filter and washed with hydrochloric acid. To remove traces of rubidium, the precipitate is thoroughly decomposed with successive, small quantities of hot water, then hydrochloric acid and a little antimony trichloride are added to the whole in order to repeat the precipitation. The last precipitate is washed with hydrochloric acid. It usually shows no rubidium when tested with the spectroscope. The caesium antimony chloride is decomposed with hot water and hydrogen sulphide is passed into the resulting solution. The filtrate from the antimony sulphide gives, on evaporation, pure caesium chloride. The filtrates from the antimony double salt are freed from antimony, evaporated to dryness and the mixture of caesium and rubidium chlorides, which should be very small in amount, is preserved for use in subsequent purifications.

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