

### 204. Polonium Monosulphide.

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Polonium monosulphide has been prepared on the milligram scale; its decomposition under vacuum has been used as the basis of a new method for the preparation of pure polonium metal.

TRACER studies<sup>1</sup> have shown that polonium can be precipitated from acid solution together with other insoluble sulphides by hydrogen sulphide. The composition of the precipitate was, however, uncertain although Guillot<sup>2</sup> had suggested that it was polonium sesqui-sulphide, presumably analogous to bismuth sulphide; analytical data could not be produced to support this assumption owing to the very small amounts of polonium then available. More recently, the precipitation of milligram amounts of polonium from dilute hydrochloric acid solution was found to yield a black solid, which was not analysed owing to the presence of large amounts of sulphur resulting from the radiation-induced oxidation of the hydrogen sulphide. Since the black solid yielded a sublimate of polonium metal when heated in a vacuum it was possible that the precipitate was elementary polonium.<sup>3</sup> The attempted preparation of a sulphide from the elements has also been reported, but this was unsuccessful.<sup>4</sup>

The decomposition of the sulphide precipitate into the elements has been investigated in some detail since it affords a convenient and rapid method of preparing pure, lead-free polonium in good yield from aged polonium residues, the precipitated lead sulphide being involatile under the conditions used for the sublimation of the polonium. The procedure is, however, useless for the separation of polonium from irradiated bismuth since bismuth sulphide decomposes appreciably to the metal at 500° and 5  $\mu$  pressure, the resulting sublimate consisting of a mixture of bismuth and its sulphide. The separation of tracer polonium from bismuth-polonium sulphide precipitates at 700° under vacuum<sup>1</sup> cannot, therefore, have been very efficient.

The analytical data obtained in the present work show that the black precipitate obtained by passing hydrogen sulphide into a solution of polonium dichloride or tetrachloride in dilute hydrochloric acid is the monosulphide, PoS. The first step in the precipitation from solutions of the tetrachloride is evidently reduction to the bivalent state and this appears to be confirmed by experiments on the precipitation from solutions in concentrated (*ca.* 6*N*) hydrochloric acid, when it was found that very little polonium was precipitated, owing to the repression of the ionisation of the hydrogen sulphide, and the solution became pink, a characteristic of solutions of bivalent polonium.

The monosulphide is soluble in concentrated hydrochloric acid, insoluble in ethyl alcohol, acetone, or toluene and is decomposed by bromine, sodium hypochlorite, and aqua regia. It is also insoluble in ammonium sulphide, as previously reported for tracer polonium.<sup>1</sup>

The solubility product of polonium monosulphide was determined by precipitating the compound from solutions of varying hydrochloric acid concentration which had been saturated with hydrogen sulphide; the polonium concentration was determined by  $\alpha$ -particle counting and the sulphide ion concentration was calculated from the solubility data of Kendall and Andrews<sup>5</sup> and the known dissociation constants of hydrogen sulphide. Activity corrections were not applied. The results are given in the Table, but the reproducibility was not good and the attainment of equilibrium required some time, during which a considerable amount of sulphur was precipitated owing to the oxidation

<sup>1</sup> Curie and Curie, *Compt. rend.*, 1898, **127**, 175.

<sup>2</sup> Guillot, *J. Chim. phys.*, 1931, **28**, 107.

<sup>3</sup> Bagnall, D'Eye, and Freeman, *J.*, 1955, 2320.

<sup>4</sup> Burbage, *Record Chem. Progr.*, 1953, **44**, 157.

<sup>5</sup> Kendall and Andrews, *J. Amer. Chem. Soc.*, 1921, **43**, 1545.

of the hydrogen sulphide by radiation; this could lead to anomalous solubility results if any of the polonium was carried down with the sulphur. All the determinations were made with freshly prepared, lead-free polonium.

Concn. of HCl	Concn. of polonium		Concn. of sulphide	Solubility
	mc/ml.	moles/l. $\times 10^4$	ion (moles/l.) (calc.)	product
N	4.7	5.03	$1.09 \times 10^{-23}$	$5.5 \times 10^{-29}$
2N	18.5	19.8	$2.73 \times 10^{-24}$	$5.4 \times 10^{-29}$
4.4N	90.0	96.4	$2.65 \times 10^{-25}$	$5.5 \times 10^{-29}$

The monosulphide decomposes into the elements at about 275° and 5  $\mu$  pressure at which temperature the sulphur sublimes from the residue of lead sulphide and polonium metal. The latter can be sublimed from the lead sulphide at 450–500° at the same pressure giving an extremely pure product. X-Ray powder photographs of the metal so prepared were much better than those of the metal obtained as reported earlier<sup>6</sup> and the specimens of metal could be easily melted under vacuum to form small silvery globules. The X-ray powder photographs of the monosulphide were unfortunately too poor to index.

The formation of polonium monosulphide is in marked contrast to the rather ill-defined behaviour of the tellurium-sulphur system and is further evidence of the increased basic character of polonium expected from its position in the Periodic Table.

#### EXPERIMENTAL

All the work was carried out in dry-boxes in order to minimise the hazards associated with the handling of high levels of  $\alpha$ -activity.

*Analytical.*—Specimens for analysis were precipitated from dilute (1–2N) hydrochloric acid solution, filtered through a 1 cm. diameter sintered disc (No. 3 or No. 4 porosity) and washed with a mixture of equal volumes of toluene and absolute alcohol (3  $\times$  1 ml.) to remove precipitated sulphur. Some of the preparations were then dissolved in a 3:1 (v/v) nitric acid-hydrochloric acid oxidising mixture (0.2 ml.) containing a little bromine; the resulting solution was boiled for 15 min. with 1 ml. of concentrated hydrochloric acid in order to eliminate the bromine and the nitric acid. The solution was then analysed for sulphate and polonium by the methods used for the polonium sulphates.<sup>7</sup> Other specimens were analysed by heating the sulphide under vacuum and collecting the sulphur and polonium sublimates. The separation was quite efficient, the sulphur sublimate containing a maximum of 0.2% of the polonium. The sulphur was then estimated by oxidation to sulphate and analysis as above; preliminary experiments on the oxidation of milligram amounts of sulphur had shown that this procedure was quantitative. The polonium was determined by calorimetry and also by dissolving the metal in hydrochloric acid and counting  $\alpha$ -particles from aliquot portions of the solution. The results obtained by the second procedure for the determination of sulphur were low [S:Po (g.-atom) = 0.85–0.90] for samples containing between 250 and 500  $\mu$ g. of polonium monosulphide; this is probably due to the comparatively high vapour pressure of sulphur at room temperature. The S:Po ratios for the larger specimens were  $1.00 \pm 0.04$ , and the specimens analysed ranged in weight from 125  $\mu$ g. to 3.6 mg. (approx. 15 curies of  $^{210}\text{Po}$ ).

*Solubility Determinations.*—The techniques used for the polonium sulphates<sup>7</sup> were used.

*Application as a Purification Procedure.*—The polonium is best precipitated from N-hydrochloric acid solution containing at least 100 mc/ml. of  $^{210}\text{Po}$ ; more dilute solutions should be concentrated by precipitation with lanthanum hydroxide before treatment with hydrogen sulphide. The attempted precipitation of the polonium from dilute solution (20 mc/ml.) with lead carrier gave poor yields. The precipitated sulphide is "unwettable" and tends to float on the surface of the liquid and stick to the walls of the glass tube in which the precipitation is carried out; this is overcome by adding a little absolute alcohol or alcohol-toluene. The sulphide precipitate was filtered off on a No. 3 porosity filter stick mounted on a modified Buchner flask, washed with alcohol-toluene to remove sulphur, and then sealed into a distillation tube of the type described earlier.<sup>3</sup>

The sulphide was decomposed by heating at 275° for 10 min., and the polonium distilled by heating at 450–500° for 15 min.; the metal was then sealed off under vacuum until required.

<sup>6</sup> Bagnall and D'Eye, *J.*, 1954, 4295.

<sup>7</sup> Bagnall and Freeman, *J.*, 1956, 4579.

The filter sticks can be re-used a number of times. The micro-filter sticks described in an earlier paper <sup>3</sup> can be used for smaller (1 c) preparations. The time required for the complete purification cycle is less than 1 hr. and the overall recoveries at the curie level are in the range 96—99% and depend on the precipitation efficiency, since the distillation efficiency is about 99.7%. The method compares favourably with other procedures used for the purification of polonium and it provides a very pure product.

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