McCarthy¹ is convenient but of small capacity. On a larger scale excellent results may be obtained with a stout-walled 250 cc. Erlenmeyer flask of rather hard glass, charged with 75 g. arsenious oxide evenly spread over the bottom. The flask is set in a flat sand bath, and the sand brought about one-half inch above the level of the material within. The mouth of the flask is covered with a porcelain crucible cover, and the bath is heated under a hood with a sufficiently powerful burner of the ring or stove type. The sublimation may require 7 hrs. and should not be intermittent for the flask, once cooled, is likely to crack when reheated. It is finished when a line of clear glass appears all around the flask above the sand. When completely cool, the flask is removed from the bath and with cautious handling the bottom is cut off with a hot point just below the line of the sublimate. The latter may then be easily removed with a knife blade. It is best to reject the portion in the neck of the flask, for volatile impurities will tend to concentrate there. The writer prefers to reject also the glassy ring of sublimate just above the sand level. With proper management the yield is excellent, very little being lost by volatilization.

CONCLUSION

It must be admitted that arsenious oxide lacks some of the qualities desirable in a standard substance for volumetric analysis. Nevertheless it is capable of affording extremely accurate results and for the purpose of directly standardizing iodine solutions there seems to be no other substance² which can fully take its place. Since it must be used, the chemist must possess practical and reliable methods for determining whether commercial samples are sufficiently pure for ordinary analytical work, while in case of deficiency, or when the material must be of the highest purity, dependable methods of preparation must be available. It is believed that these needs are met by the methods of preparation and testing here presented. Especially are methods given for detecting and eliminating an impurity to which far too little attention has been given in the past, *viz.*, antimonous oxide.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY
DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

THE BISULFATE METHOD OF DETERMINING RADIUM

By HOWARD H. BARKER

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The quantitative determination of the small amounts of radium in radioactive ores and various products obtained in their treatment for the recovery of radium is generally conducted by the emanation method. It is based upon the fact that the gaseous disintegration product of radium—the emanation—can be completely separated from radioactive materials and that the equilibrium quantity is proportional to the radium content. Very small quantities of radium emanation

are capable of exact measurement by electrical methods, for which carefully standardized electroscopes have come into general use.

The care and accuracy with which the emanation is separated from the specimen under examination are very essential in quantitative work and demand skillful manipulation, especially in the case of solids. Since heat alone rarely affects a complete separation of the emanation from the radioactive solids, the recognized methods of determining radium involve chemical treatment that will result in a solution or in decomposition of the material by fusion. Our experiments test the applicability of fusion with bisulfate, for the separation of radium emanation, and afford a comparison of this method with other methods recognized as more or less standard.

Our work deals with substances which are not susceptible of direct solution in water or acids. The emanation is separated by direct fusion with sodium or potassium bisulfate or mixtures of the two. Since solids generally emit, at ordinary temperatures, variable proportions of the emanation continually produced by the radium present, the customary procedure is to first expel the emanation, that is, reduce it to zero, and then seal up the sample, allow it to stand for a definite time—a day or longer—and finally separate the accumulated emanation by fusing again. The equilibrium amount is then conveniently obtained by reference to a table of growth of radium emanation.¹

Plum² made use of potassium bisulfate for radium determination in his study of methods of separating the radioactive constituents from carnotite ores. Schlundt³ employed potassium bisulfate in a few of his experiments on the quantitative determination of radium mainly by fusion with mixed alkali carbonates. The experiments that follow I hope will serve to establish the reliability of the bisulfate method and also its range of applicability.

PLAN OF EXPERIMENTS

Representative carnotite ores and the radium-bearing products obtained therefrom were selected for the determinations of radium which were conducted by at least two other methods for comparison with the bisulfate method. The samples include (1) two carnotite-bearing sandstones from different localities and differing considerably in composition and radium content, (2) a siliceous concentrate obtained from an ore by chemical treatment in which the radium has been concentrated about fifteen-fold, (3) a sample of first sulfate containing about 600 parts of radium per billion of total weight, one-fourth of which is barium sulfate, (4) one sample of tailings, the sandy residue left after the extraction of radium from the ore, (5) a by-product very rich in gypsum, but containing also vanadium, iron and uranium compounds.

The radium was determined in case of these samples by at least three methods.

¹ *Loc. cit.*

² Antimony potassium tartrate, advocated by Metzl (*Z. anorg. Chem.*, **48** (1906), 156), is well known to be efflorescent when crystallized. The present writer has been unable to dry it to strictly constant weight in agreement with the theoretical composition of the anhydrous salt.

³ Kolowrat, *Le Radium*, **6**, 195; also Curie, "Traité de Radioactivité," I, p. 419; *Chem. Kalender*, **2** (1914), 361; Rutherford, "Radioactive Substances and Their Radiations," **1913**, 665.

² *J. Am. Chem. Soc.*, **37** (1915), 1811.

³ *Trans. Am. Electrochem. Soc.*, **26** (1914), 163.

METHODS OF SEPARATING THE EMANATION

1—Preparation of a refined radium-barium sulfate by fusing a weighed sample, to which a small quantity of barium compound has been added, with 3 to 5 times its weight of a mixture of sodium and potassium carbonates. After leaching the melt with water, the insoluble carbonates are dissolved in dilute hydrochloric acid and pure radium-barium sulfate is precipitated by the addition of a few drops of sulfuric acid. The

FIG. I—TYPE OF APPARATUS FOR BOILING OFF EMANATION FROM MIXED CARBONATE FUSION

refined sulfate thus obtained is fused in a platinum boat with a mixture of sodium and potassium carbonates and is then sealed and stored for a certain period after which the accumulated emanation is again separated, collected and transferred to a standardized electro-scope.¹

2—Direct separation of the emanation from the melt is obtained by fusion of the sample in a platinum crucible with mixed carbonates of sodium and potas-

sium. The melt is poured into a clean iron mortar. The crucible may be rinsed out by fusing a little more of the carbonates in it. The melt is powdered and sealed up in a thin-walled glass bulb, B, shown in Fig. I. After standing for a day or longer the emanation that has accumulated during the period of storage is separated by dissolving the carbonate in nitric or hydrochloric acid. The gas burette E of the apparatus used for this operation (Fig. I) is filled with a boiling hot solution of caustic soda through the levelling reservoir G by closing cock D and having F open. Then, after closing F, the levelling bulb G is lowered to a position below the outlet tube D in order that subsequent boiling will be conducted under slightly diminished pressure. This precaution also enables one to detect small air leaks in the apparatus. The bulb B containing the powdered carbonate is so adjusted in the 3-hole rubber stopper of the wide-mouth flask A, the boiler, that it is cracked by forcing down the stopper. The cock D is then opened and moderately strong acid is admitted gradually from the drop funnel C. When the sample is siliceous and the carbonate fusion exceeds 5 g., the capacity of the boiler should be at least 250 cc., and it is sometimes advantageous to have a little water in it to distribute the carbonate when the bulb is broken and in this way prevent the formation of a coating of silicic acid over the dry powder when acid is admitted. If the volume of air remaining in the boiler still exceeds the capacity of the burette, the air may be partly displaced by carbon dioxide before connecting up with the burette. As the decomposition of the carbonate proceeds the solution is heated and finally boiled until the liquid in the gas burette is forced down by water vapor to the level of D. The gas is then transferred quantitatively to an air-tight electro-scope.

3—The bisulfate method consists in making a fusion of the material whose radium content is to be determined with either sodium or potassium bisulfate alone, or better, a mixture of the two in a hard glass pyrex tube of suitable dimensions. Hard glass pyrex tubes 25 cm. by 2.5 cm. were used in most of the determinations. The material and the bisulfate are thoroughly mixed before introducing into the tube, after which they are fused and boiling continued long enough to expel the last traces of emanation. The sides of the tube are washed down by introducing a little fresh bisulfate into the tube, allowing it to fuse and run down into the melt. The test tube is sealed with a stopper carrying two outlet tubes, one extending to within an inch or two of the melt, and the other just reaching through the stopper. After the emanation has been allowed to accumulate for a given definite period, the tube is connected up with the evacuated ionization chamber of an electro-scope as shown in Fig. II. The micro drying bulb next to the ionization chamber contains concentrated sulfuric acid, whose function is to remove moisture from the air and emanation before entering the electro-scope. The other drying bulb connected to the test tube on the ionization chamber side of the apparatus contains a fairly strong solution of caustic soda to remove any traces of sulfuric acid distilled over in the operation. The drying bulb hitched

¹ Further details are given by Lind, *THIS JOURNAL*, 7 (1915), 1024, and in U. S. Bureau of Mines, *Bull.* 104, 94.

to the other side of the test tube contains concentrated sulfuric acid or water, and is there primarily for noting the inflow of air into the system. It also serves for detecting any leaks in the line of connection. All rubber connections are wired, and the tips of the glass tubes are not broken until all connections have been made. Before breaking the capillary tips, the intermediate system is placed under a slight vacuum. The tips are then broken and by adjusting the stopcocks of the evacuated ionization chamber the flow of air through the chain is regulated. Heat is now gently applied until the mass is molten, after which it is boiled for about 5 min. Sometimes it is a little difficult to get good boiling at this stage, but I find where an equal mixture of the fused bisulfate and crystals is used, that this difficulty seldom appears. The emanation is swept into the chamber by a slow, steady current of air which is maintained during heating until atmospheric pressure is nearly attained in the chamber.

FIG. II

Readings of the rate of discharge are made 3 hrs. after the introduction of the gas, the same as in the other methods.

RESULTS AND DISCUSSION

The results obtained are summarized in the following table. The values represent duplicate determinations for the most part, but some of them are triplicate. The values in the table represent grams of radium per gram of material $\times 10^{-9}$.

Material	Wt. of Sample	TABLE I		
		Refined Sulfate	Mixed Carbonate	Bisulfate
Carnotite No. 1.....	1.00	5.15	5.18	5.22
Carnotite No. 2.....	1.00	10.60	10.00	10.40
Concentrate.....	0.50	29.90	30.00	29.40
Tailings.....	3.00	0.90	0.94	1.00
First Sulfate.....	0.05	676.00	680.00	678.00
By-products.....	2.00	1.26	1.24	1.27

The good agreement in the values shows that from the standpoint of accuracy in radium determination, no one method has any advantage for the classes of materials examined. The bisulfate method, however, presents some advantages which deserve recognition.

I—It has been established that the bisulfate method may be used in liberating the emanation from samples of pitchblende, whose radium content is known, used in the standardization of electroscopes. There are two advantages worthy of mention which the bisulfate

method has in this operation over the solution method: (a) It is not necessary to take into consideration the "emanating power" of the pitchblende in the case of the bisulfate method, while it is in the case of the solution method; (b) The same carefully weighed samples of pitchblende may be used for several standardizations by resealing the bisulfate melt after the emanation has been driven off and collected for standardization.

II—Besides simplicity of operation, the bisulfate method is by far the most rapid procedure. Not only is the actual time required for the final separation of the emanation shorter than in the other procedure, but the time in work expended in preparing a sample and getting it sealed up is reduced to a few minutes.

III—The chances for loss due to manipulation are reduced to one operation, when the material is transferred to the test tube. In both of the other methods great care must be exercised in avoiding losses when fusions are in progress. Instead of one, two to three transfers of materials occur in the other methods.

IV—The cost of the operation is reduced. If one is careful the test tubes may be used for several determinations. In the refined sulfate method the small platinum boats, costing at least a dollar each are not good for more than 5 to 6 determinations. The use of larger platinum vessels is essential in the other methods, while in the bisulfate method all fusions are made in hard glass test tubes.

V—After the final separation of emanation by the bisulfate method, the material remains and is ready for another determination in case an accident occurs.

When the material under examination contains thorium, then the gas cannot be transferred directly to the electroscope during fusion, but must be collected in a gas burette to allow the decay of thorium emanation.

I wish to thank Mr. J. C. Simpkins, who assisted me at the outset in this work, and Dr. H. Schlundt for his helpful suggestions.

CHEMICAL PRODUCTS COMPANY
DENVER, COLORADO

A RAPID PRESSURE METHOD FOR THE DETERMINATION OF CARBON DIOXIDE IN CARBONATES

By W. H. CHAPIN

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By use of the apparatus sketched below carbon dioxide may be very quickly determined in any carbonate which is soluble in cold hydrochloric acid. The accuracy of the method is equal to that attainable with the absorption method, except possibly when the latter is in the hands of a very skilled manipulator who has had long practice with the method.

The principle is very simple: The carbonate is allowed to dissolve in dilute HCl contained in a flask of known volume to which is attached a small mercury manometer. The change in pressure is read off, and by a simple calculation the weight and percentage of CO₂ are obtained. The necessary details are given in the procedure.