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[Contribution from the Chemistry Department of Oregon State College]

Preparation of S^{35}-Labeled Sulfur Dioxide and Sulfuric Acid[1]

By B. J. Masters and T. H. Norris

A simple and convenient technique for the preparation of S^{35}-labeled sulfur dioxide and concentrated sulfuric acid is described. The method depends on the occurrence of an exchange reaction between these two compounds and leads to high specific activities and good percentage yields.

Sulfuric acid labeled with S^{35} has been shown by one of the present authors[2] to undergo isotopic exchange with sulfur dioxide at elevated temperatures, the observed half-time being *ca.* 7.5 hours at 211°. Extending this work, we have devised a simple and expedient method for preparing both labeled sulfur dioxide and concentrated sulfuric acid, with neutron-irradiated potassium chloride as starting material. The technique yields high specific activities with comparatively small activity waste. The heterogeneous, gas–liquid nature of the system makes separations and purification easy.

One evident advantage of the technique is that one may activate only a portion of a sulfuric acid solution, the remainder, of similar chemical composition, then being available for analysis, and further activation as necessary. The procedure also suggests a possible method of "counting" sulfuric acid in a gas counter. One could effect complete exchange between a little sulfur dioxide and excess acid. The gas, then of the same specific activity as the acid, could be counted by the technique described by Norris.[3]

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Experimental

The success of the procedure depends upon minimizing dilution of activity at each step. High specific activity barium sulfate, precipitated from a highly concentrated solution of irradiated potassium chloride, is dissolved in a minimum amount of concentrated sulfuric acid; a small excess of sulfur dioxide is then activated by complete exchange with this solution. This gas can thereupon be used to label a somewhat larger excess of concentrated acid in a second exchange. All operations are conducted by standard high vacuum techniques.

The following actual preparation of labeled acid illustrates the method. Irradiated potassium chloride was obtained from the U. S. Atomic Energy Commission (Item No. 17, Isotopes Catalog No. 3). Since the material used in this work was about fourteen months or almost five half-lives old, all activities quoted hereafter would, for fresh material, be greater by a factor of approximately 25. In a small centrifuge tube 1.79 g. of this salt, having *ca.* 0.25 mc. S^{35}, was dissolved in water containing 0.018 millimole of sulfuric acid carrier[4] and the volume was made up to 10 ml. After heating the solution, a small excess, 0.2 ml., of 0.2 *M* $BaCl_2$ was added and the resulting precipitate was digested for a time. Precipitation of activity was *ca.* 90% complete after one hour, as shown by rough checks of the activity of the clear solution before and after precipitation. Further digestion appeared to increase the completeness of precipitation somewhat.

After centrifugation, the supernatant was decanted for recovery of Cl^{36}, and the active barium sulfate (*ca.* 4 mg.) was washed with several small portions of water and finally with acetone, being centrifuged after each wash. Then, after drying in an oven, the sulfate was dissolved in 1.22 millimoles of 96% sulfuric acid. This solution, still in the original centrifuge tube, was sealed into a bomb tube (net volume 159 ml.) with 302 mm. of sulfur dioxide (2.57 millimoles). With the sealed tube in a furnace at 350° for six days complete exchange was obtained. The long period is presumably necessary because of the small amount of acid present; we are currently making a detailed study of the kinetics of this reaction.

The labeled sulfur dioxide thus prepared, recovered by opening the bomb *via* a break-off tip, was condensed and sealed into a second, similar bomb containing 35.7 millimoles of 96% sulfuric acid to be activated. Heating of this bomb at 270° for 20 hours yielded complete exchange; use of the lower temperature avoided excessive acid vapor pressure. For rapid exchange, it is apparently essential that the acid be exposed in the form of a thin layer. Finally the sulfur dioxide was again removed *via* a break-off tip and the preparation was complete.

The 3.65 g. of sulfuric acid thus prepared, counted as barium sulfate with an end-window counter, according to technique described by Norris,[2] showed a specific activity (corrected to zero thickness) of 1.4×10^6 c./m./mmole, corresponding to 60% of total starting activity. This acid was diluted fivefold with inactive acid before use in our experiments. With freshly irradiated potassium chloride, dilution by a factor of 125 would have been possible. The labeled sulfur dioxide fresh from the first exchange had a specific activity (calculated from the measured activity of the final sulfur dioxde) of 2.04×10^7 c./m./mmole counted as above, corresponding to 64% of starting activity. The use of a larger excess of sulfur dioxide in the first exchange would, naturally, lead to a higher percentage yield, with corresponding decrease in resulting specific activity.

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[1] Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 190, Department of Chemistry, School of Science.

[2] T. H. Norris, This Journal, **72**, 1220 (1950).

[3] T. H. Norris, *ibid.*, **74**, 2396 (1952).

[4] The presence of sulfate carrier *before* dissolution of the potassium chloride was found essential for obtaining any degree of completeness of activity precipitation. W. S. Koski, *ibid.*, **71**, 4042 (1949), has shown that the radiosulfur exists in such potassium chloride crystals almost exclusively in the +6 oxidation state, being carried by sulfate.