Methods of Preparation of Some Carrier-Free Radioisotopes Involving Sorption on Alumina*

by

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Alumina, aluminum oxide, has been used for many years as an agent for separating both organic and inorganic materials, both by adsorption and by chromatography. Methods employing alumina have been developed recently in the Hot Laboratory at Brookhaven National Laboratory for the separation and purification of some of the radioisotopes produced and distributed by Brookhaven. In general, these methods have made possible the rapid and simple separation of the radioisotopes involved, in carrier-free condition, and with high isotopic purity. ("Carrier-free" is used in the sense that no stable element is added during separation. There may be some extremely small amounts of stable isotopes present that were produced by nuclear reactions.) Production has been in the millicurie range but scale-up to the curie level is feasible, since alumina is quite resistant to radiation damage, unlike ion exchange resins. Radioisotopes that are being separated by means of alumina include fluorine-18, molybdenum-99, technetium-99m, tellurium-132, and iodine-132.

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In general, although the exact mechanism is not agreed upon, alumina in acidic form, i.e. pH about 4, behaves as an anion exchanger and will adsorb anions from solution, allowing cations to pass through. In the basic form, pH about 10, it behaves as a cation exchanger, and will adsorb cations and have no effect on anions. By varying the pH, different ions may be selectively eluted, depending upon how firmly they are bound to the alumina. Relatively small volumes of reagents are required, and rapid separations may be effected.

The first application that was made of alumina in our work was in the development of an iodine-132 "generator" or "cow", by means of which iodine-132 could be "milked" from its parent tellurium-132 as desired in a medical or industrial laboratory. Iodine-132, emitting 5 betas ranging in maximum energy from 0.73 to 2.13 Mev and 9 gammas ranging from 0.520 to 2.2 Mev, has a 2.3-hour half-life. This is too short to make shipping any distance practical. This isotope is of interest to the medical and biological professions because of its harder radiations, and its shorter half-life, compared to 8-day iodine-131. While the first work with iodine-132 was in medical research, it has found application in industrial research, particularly in the petroleum industry. Studies have been made of uniformity of mixing of greases, catalyst flow in pilot plants, and similar subjects. Here the half-life is of prime importance, because tests can be made on full-scale runs of consumer products in production equipment without having to store the product while waiting

for activity to decay away. After a day or two iodine-132 has decayed to undetectably low levels.

Iodine-132 is formed by beta decay of tellurium-132, which is a fission product with a yield of $\sim 4.7\%$ and decays to stable xenon-132. The 3.2-day half-life of tellurium-132 is long enough to make shipment over considerable distances feasible, and to allow it to serve as a source of iodine-132 for practical lengths of time. For example, 100 mcs. of tellurium-132 will provide at least 10 mcs. of iodine-132 daily for nearly 2 weeks. Several years ago, a method and device, involving precipitation and redissolution of tellurium dioxide, was developed that provided the user with a simple means of separating or milking iodine from tellurium in his own laboratory. It was supplied routinely for about 4 years. While generally satisfactory, foaming would occasionally and unpredictably occur and cause trouble, and the product solution contained sufficient stable tellurium, about 2 mgs., to cause "garlic breath" in patients to whom it was administered.

A new generator has been developed that eliminates both of these difficulties. This generator consists of 20 grams of chromatographic alumina contained in a glass column about 1 inch in diameter and 6 inches long, with a coarse glass filter frit in the bottom to retain the alumina. This column is mounted inside of a Lucite cylinder, being retained in place by rings of plastic tubing. This outer tube protects the glass from breakage during

shipping and handling. Tellurium-132 is fixed on the alumina column by passing slowly through it a solution of the tellurium at any pH below 10.5, either carrier-free or containing up to 200 mgs. of carrier tellurium. Over 95% of the tellurium is retained by the alumina. The column is washed with water, and dilute ammonia, and is then ready for shipment and use. To milk iodine from the column, 25 ml. of 0.01 M ammonia is poured into the top of the generator. Almost immediately, product iodine-132 solution starts to drip from the bottom, and may be caught in any suitable receiver. Less than 5 minutes are required for a milking, and a subsequent milking can be made at any time by following the same simple procedure.

The tellurium is held on the alumina as the tellurite ion, as are the iodide, iodate, and periodate states of the iodine-132 as they are formed by decay of the tellurium. The 0.01 M ammonia is basic enough to remove the iodide but not basic enough to remove the iodate, periodate, or tellurite. Consequently, yields of iodine-132 are about 65% of the total iodine present, the remainder being retained on the column as iodate and periodate. Stronger base will remove all the iodine, but will also elute some of the tellurium. Under present conditions, stable tellurium contamination in the product solution is less than 0.01 µg/ml, since carrier tellurium is being used. This is at least a factor of 3 below the threshhold for the "garlic breath" effect. Carrier-free tellurium will be used shortly, and then there will be no stable tellurium in the product. The product solution is sterile and pyrogen-free as it comes from

the generator. The same generator is used for all size shipments, but whereas 10 mc. may be shipped unshielded in a suitably sized cardboard box, 100 mc. require 1 3/8" of lead shielding. The method of operation is the same in both cases; the shielded generator may be milked without removing it from its shield.

An extension of this work led to using alumina as a means of separating fission-product tellurium from uranium and the other fission products. As the source material, uranium oxide, U_3O_8, is irradiated in the Brookhaven reactor. After chemically removing the aluminum jacket, the uranium oxide is dissolved in nitric acid. The resultant solution is diluted with water until it is approximately 1 Molar in nitrate, and is then run under gravity flow through a 1 1/2" diameter column containing 40 grams of alumina. Under the acid conditions, the alumina retains the tellurium as the tellurite. No carrier tellurium is required. The uranyl nitrate and the other fission products pass through unaffected, with the single exception of molybdenum, which is retained as the molybdate. The only radioactive molybdenum isotope present is molybdenum-99, with negligibly small amounts of the stable isotopes formed in fission (95, 97, 98, 100). The alumina is washed first with dilute nitric acid, to remove the uranium and fission products, then with water, and then with dilute ammonia to neutralize the acid. Molybdate is removed by washing the column with 300 to 500 ml. of concentrated ammonia. Virtually all of the molybdenum-99 is removed by this treatment, less than 0.01% remaining. Less than 1% of the tellurium is lost during this washing. The tellurium is removed from the alumina by

washing with 100 ml. of 2 to 4 M sodium hydroxide. The resultant solution, after dilution and partial neutralization to a pH of about 10, is ready to be loaded on the iodine generator. The tellurium is predominantly tellurium-132, with small amounts of 30-hour tellurium-131. Under the conditions of use of the generator, the iodine product solution contains less than 0.3% iodine-131 contamination which grows in as the result of tellurium-131 decay. There are no other contaminating activities.

Since the fission-product tellurium is carrier-free, the same size alumina column may be used to handle practically any amount of tellurium, certainly up to the multicurie range. Adequate shielding and adequately sized dissolving and waste vessels, etc., are the only controlling factors. A complete run takes about 7 hours during most of which time the apparatus requires no attention by the operator.

As was mentioned, 67-hour molybdenum-99 is the only fission product that stayed on the alumina column when the tellurium-132 gross fission product solution was run through. Molybdenum-99 supplied by Oak Ridge is made by n,γ reaction on natural molybdenum, and thus has a large amount of stable molybdenum associated with it. Carrier-free molybdenum-99 in good yield and high purity may be obtained by washing the alumina column with 150 ml. of 1 M ammonia before eluting the tellurium from the column. Whereas a relatively large volume of concentrated ammonia is required to completely remove the molybdenum from the tellurium, 80% of the molybdenum is obtained by the dilute ammonia wash. Since the fission yield of molybdenum-99 is over 6%,

compared to 4.7% for tellurium-132, the amount of molybdenum activity produced is greater than the amount of tellurium activity. Molybdenum-99 has gammas ranging from 0.041 to 0.780 Mev, and emits betas 80% of which have a maximum energy of 1.23 Mev and 20% of 0.45 Mev.

When molybdenum-99 decays, 87% of it goes to 6-hour metastable technetium-99m, the balance going directly to the 2 x 10^5-year technetium-99. Technetium-99m in turn goes to technetium-99 by isomeric transition, emitting a single 0.140 Mev gamma. It, of course, grows into transient equilibrium with its longer-lived parent, molybdenum-99. In an analogous fashion to the tellurium-iodine-132 pair, technetium can be milked from molybdenum, providing a laboratory with a carrier-free 6-hour pure gamma emitting activity that can be available as desired. A milking system and generator consists of a glass column 1" in diameter containing five grams of chromatographic alumina in a bed 1/2" high, that has been treated with nitric acid to a pH of approximately 1.5. The alumina is retained by a coarse fritted disc. Carrier-free molybdenum-99 solution, obtained as described previously, is acidified to a pH of 1 to 2 with concentrated nitric acid and diluted to 25 ml. This is passed through the column and the column then washed with 0.1 M nitric acid. After technetium has grown in, it is milked from the column by eluting with 25 ml. of 0.1 M nitric acid. Yields of about 80% of the available technetium are obtained in less than 10 minutes. Radiopurity is greater than 99.99%. The technetium is removed as a cation, molybdenum remaining on the column as molybdate ion.

Fluorine-18, 112-minute half-life, is the longest lived radioisotope of fluorine known, and has been supplied by Brookhaven for several years. It emits a single 0.56 Mev positron, with which is associated, of course, the two coincident 0.51 Mev annihilation gammas. It is produced by a (t,n) reaction on oxygen-16, using the tritons produced by the (n,α) reaction on lithium-6 in the nuclear reactor. Lithium carbonate is the target material used.

The original separation method required the addition of fluoride carrier. In the present method, the irradiated lithium carbonate is dissolved in a minimum of hydrochloric acid and passed through a column of alumina that has been treated with 0.5 M hydrochloric acid and washed with water. Fluorine-18, as fluoride ion, is retained on the alumina, while the lithium, sodium-24, and any other cationic contaminant pass through. The column is then washed with water. The fluorine is eluted with 50 ml. of 0.1 M sodium hydroxide, with an over-all yield of over 95%. The product is carrier-free fluorine-18, with a greater than 99.99% radiopurity.

In all these methods, the apparatus required is simple, and very little manipulation is required. Consequently shielding is inexpensive, with very little remote handling equipment being required. Procedures are rapid, compared to those used previously, which involved precipitation and filtration, and little supervision is required once the initial dissolution of the irradiated material is accomplished.