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A GENERALIZED PROCEDURE FOR THE
ISOLATION OF IODINE WITHOUT CARRIER--
ITS DETERMINATION BY NEUTRON ACTIVATION
USING I^{129} AS AN ISOTOPIC TRACER

by

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ABSTRACT

In order to make the 1.7×10^7 -year I^{129} useful as an iodine tracer, a neutron-activation procedure was used for its determination. A procedure involving high-temperature ignition in a stream of oxygen was devised for the isolation of iodine from a variety of materials. After activation and decontamination, a large sodium iodide, well-type crystal was used as a selective detector for the I^{130} activation product. The normal iodine content of a sample is readily determined at the same time.

Eight-day I^{131} is readily available and has been used extensively as an iodine tracer. Its short half-life, however, limits its usefulness for long-term experiments, such as may be involved in biological studies. The 1.7×10^7 -year I^{129} promises to be a useful isotope for such experiments. It does not occur in nature except in minute quantities as a result of fission in uranium ores.⁽¹⁾ Although its specific activity (370 disintegrations per minute per microgram) is too low for convenient use as a direct radioactive tracer, the technique of neutron-activation can be used to increase the sensitivity for its detection by a factor of 10^6 or more.

The pertinent reactions in the neutron activation of I^{129} and I^{127} are as follows:

Interfering iodine activities are produced by the following reactions:

Since reaction (3) is produced by very energetic neutrons (greater than 9 Mev) only, the use of a well-moderated neutron flux is helpful. Although the fission product iodine from as little as 10^{-12} gm of natural uranium can limit the sensitivity of the method, this interference can be eliminated by very careful purification from uranium before irradiation.

The analysis of a sample for I^{129} and I^{127} involves the following steps:

- (1) Isolation of an iodine fraction from the sample without the addition of carrier, but with I^{131} tracer for determination of yield.
- (2) Packaging in a container suitable for neutron irradiation with a minimum of chemical impurities.
- (3) Irradiation of the isolated iodine in a moderated neutron flux.
- (4) Irradiation of an I^{127} monitor containing a known amount of I^{129} in a separate container adjacent to sample.
- (5) Decontamination of the irradiated sample and monitor from extraneous activities.
- (6) Measurement and resolution of the various iodine activities which may be present.

- (7) Determination of the specific activities of the monitor with respect to the 25-min I^{128} , the 12.5-hr I^{130} , and the 13.3-day I^{126} . From these data, the I^{127} and I^{129} content of the sample can be determined by direct comparison with the same activities in the sample, corrected for chemical yield.

THE CHEMICAL ISOLATION OF IODINE

A satisfactory procedure that has been devised for the isolation of iodine from many different types of samples involves the following steps:

- (1) Ignition of the sample in a stream of oxygen in a quartz apparatus.
- (2) Trapping of the iodine in a dilute solution of sulphurous acid.
- (3) Carrying of the iodide ion on a precipitate of silver chloride.
- (4) Decomposition of the silver chloride by heating with aluminum metal in a vacuum and the distillation of the iodine into a quartz tube.

A quartz ignition apparatus [modifications of an apparatus described by Godfrey *et al.*⁽²⁾] coupled to a Pyrex scrubbing tower by means of a semi-ball joint is illustrated in Figure 1. The apparatus is suitable for samples weighing as much as 100 g. A scaled-down version may be used for smaller samples. After insertion of a quartz wool plug into the bottom of the inner quartz tube, the sample is packed in with a glass rod with periodic additions of a solution containing I^{131} tracer. The apparatus is assembled and initially oxygen is passed between the concentric quartz tubes at a rate of 2000 cc/min. About 30 ml of water is added to the scrubbing tower and a flow of gaseous sulphur dioxide is started. This gas enters through the side arm of the scrubbing tower. The first step in the burning is a gradual downward destructive distillation of the sample using ring burners, with ignition of the volatile decomposition products in the region of 2-mm holes. For complete combustion of these volatile products, the rate of destructive distillation must be sufficiently slow that an excess of oxygen is maintained, but must be sufficiently fast that the flame produced is hot enough to prevent the formation of soot. The area of the 2-mm holes is kept hot at all times. Oxygen enters through these holes and the flame is contained within the inner quartz tube. In this manner the outer tube is protected from extensive strains due to the hot flame and fused salts. After the destructive distillation is complete, the carbonaceous residue is ignited in a stream of oxygen. The oxygen flow between the tubes is reduced by half, and oxygen is passed up the inner tube. The area of the 2-mm holes is heated and then the sample ignited at the bottom. The flow rate of oxygen up the inner tube is gradually increased. The rate is limited by necessity for complete combustion of additional volatile

material at the top of the combustion tube. After all combustible material has been burned, the entire quartz apparatus is baked out at a temperature of about 800°C in a stream of oxygen to remove the last traces of iodine.

Figure 1
Ignition Apparatus

After the scrubbing solution has been transferred to a suitable container and acidified with sulphuric acid, the excess sulphur dioxide is removed by bubbling nitrogen through the solution. Silver chloride is precipitated by the addition of silver nitrate. Usually, enough chlorides distil from the sample so that none need be added; however, if no precipitate forms, hydrochloric acid is added, followed by the addition of more silver nitrate. Two or three milligrams of silver are sufficient for adequate carrying of the iodine. After digestion to coagulate the silver chloride, the precipitate is centrifuged, washed with water, and dissolved in a solution of sodium cyanide. At this point, any insoluble material (such as traces of soot) is removed by centrifugation and the silver chloride is reprecipitated by acidification. The precipitate is washed with acid and water, and then transferred with acetone to the quartz tube of Figure 2. After centrifugation, the bulk of the acetone is removed with a transfer pipet and the last traces by evaporation.

After the addition of about 0.3 g aluminum wire, the tube is sealed to the quartz distillation apparatus below the quartz frit. The apparatus is evacuated with gentle flaming to a pressure of 3μ or less. The U-tube is immersed in liquid nitrogen and the temperature of the aluminum-silver chloride mixture raised to a red heat with a small furnace. The iodine distils into the U-tube along with aluminum chloride. Normally the iodine distils in 2 fractions. The more volatile of these appears in the U-tube as soon as the aluminum melts. The less volatile fraction must be moved into the U-tube by flaming to a temperature of 300 to 400°C. After sealing off

both ends of the U-tube, the iodine is moved into the arm opposite the reaction vessel by cooling that end in liquid nitrogen while flaming the rest of the tube. This end is sealed off at a convenient length and irradiated along with an I^{127} , I^{129} monitor in a separate tube. Before irradiation, it is convenient to check the chemical yield by dropping the quartz tube into the well of a sodium iodide crystal and counting the 0.36-Mev gamma ray of I^{131} .

Figure 2
Quartz Distillation
Apparatus

DECONTAMINATION PROCEDURE

After irradiation, the iodine is decontaminated from all extraneous activities. The most troublesome contaminant has been that of the 36-hr Br^{82} which has a decay scheme similar to that of I^{130} . Since iodine is not separated from other halogens before irradiation, radiobromine is always produced to some extent. Because of its volatility in the elemental form, precautions must be taken to prevent contamination of reagents and apparatus which may result in subsequent recontamination of the iodine fraction. This is particularly troublesome when solvent-extraction procedures are used along with oxidation-reduction cycles.

The addition of milligram quantities of iodine and bromine improves yields and decontamination factors. If exchange between the radionuclides and the added carriers is complete, adequate yields and decontamination factors can be achieved by a variety of procedures. Frequently, however, poor yields and low decontamination factors resulted when the radiohalogens reacted with traces of organic matter and the resulting organic halides did not exchange with the carriers. The conditions of irradiation in the reactor are particularly favorable for the production of organic halides.⁽³⁾ The effects were exaggerated by the deliberate addition of organic matter.

The problem was solved by the high-temperature ignition of the irradiated sample followed by distillation of the iodine. The procedure is as follows:

(1) The irradiated quartz ampule is washed in strong acid to remove surface contaminants.

(2) The ampule is placed in the apparatus of Figure 3 such that the file scratch is at the edge of the ball joint. With the furnace at 800°C and a slow constant stream of oxygen following, the semi-ball joint is twisted to break the tube at the scribed mark.

Figure 3
Decontamination Apparatus

(3) The halogens are distilled from the ampule by heating with a torch. They pass through hot copper oxide furnace and are absorbed by a solution of 1N sodium hydroxide containing iodide, iodate, bromide, and bromate in the distillation apparatus.

(4) A few milligrams of sodium peroxide are added to the distillation flask to promote exchange of halogens by oxidation to a common state. Excess peroxide is decomposed by boiling and the solution is acidified with sulfuric acid saturated with sulfur dioxide to reduce the halogens to a common reduced state. Excess sulfur dioxide is removed by boiling in a stream of nitrogen.

(5) After cooling the solution to prevent air oxidation, ferric sulfate is added to oxidize iodide to iodine, leaving bromide in solution.

(6) The iodine is distilled in a small volume with reflux by vigorous boiling with a slow nitrogen stream.

(7) The iodine is trapped in a small volume of sulfurous acid. The distillation procedure is repeated as often as required. When exchange is complete, the iodine is quantitatively distilled with decontamination from bromine by a factor of 10^4 or more for each distillation. The iodine is finally precipitated as silver iodide in a tube suitable for counting in the well of a sodium iodide scintillator.

(8) The irradiated I^{127} , I^{129} monitor is decontaminated, precipitated as silver iodide, weighed and counted.

COUNTING PROCEDURE

The use of a gamma-ray spectrometer has simplified the measurement and resolution of the iodine activities involved in the determination of I^{129} by activation. The spectrometer used consists of a well-type sodium iodide scintillator, multiplier phototube, amplifier, and a single-channel pulse-height selector. A one-mil nickel sheath within the well served as a beta shield.

In Figure 4 is illustrated the decay scheme⁽⁴⁾ of I^{130} . Associated with each disintegration is a total gamma energy of 1.9 Mev or greater. Although this energy is liberated by relatively low-energy gamma rays in cascade, a large fraction of the events will be recorded as high-energy coincidences of the cascade gamma rays when the sample is placed in the center of a large sodium iodide scintillator. As the size of the crystal is increased, the fraction of the disintegrations which appear at high energies is increased, with a consequent decrease in the low-energy events. This is illustrated in Figure 4, in which differential curves of counting rates versus energy for 3 different sizes of crystals are shown. It seems probable that an integration of all the events observed with the 5-in. crystal represents a counting efficiency approaching 100%.

Figure 4

Gamma Spectra of I^{130} in Various Size Sodium Iodide Crystals

- Crystal size = 2" x 2", Well = 5/8" x 1-1/2"
- - - - - Crystal size = 3" x 3", Well = 1/4" x 1-1/2"
- - - - - Crystal size = 5" x 5", Well = 5/16" x 2-1/2"

Note: All curves are normalized to the same disintegration rate.

In addition to I^{130} , three other radioactive isotopes are always present during the counting procedure. They are the 8-day I^{131} , the 25-min I^{128} , and the 13-day I^{126} with maximum gamma decay energies of 0.72, 0.98, and 1.42 Mev (in low abundance), respectively. The I^{131} is added at the beginning of the isolation procedure as tracer to determine the chemical yield of the iodine. The others are formed by neutron reactions with normal I^{127} during the activation. With the 5-in. crystal it is possible to measure the disintegration rate of I^{130} with a high counting efficiency while discriminating severely against the activities of the other 3 isotopes of iodine. After consideration of backgrounds in addition to counting efficiencies and discrimination against activities other than that of I^{130} , two operating conditions were chosen for measurements of I^{130} activity with the 5-in. crystal. When the I^{126} activity is a serious problem (e.g., when the sample contains large amounts of natural iodine), the I^{130} is measured in the energy region from 1.6 to 2.5 Mev. Under these conditions, the counting efficiency for I^{130} is ~40% and the background is 40 counts per minute. When the activity of I^{126} is low, the I^{130} measurements are made in the energy band between 1.2 and 2.5 Mev. Under these conditions, the counting efficiency is ~70% and the background is 90 counts per minute. The abundances of the other 3 activities are determined by measurements in a narrow energy band in the region of low gamma energy (0.25 to 0.50 Mev).

RESULTS AND DISCUSSION

A variety of biological samples (leaves, grain, soil, roots, bark, twigs, thyroids, and other animal tissues) to which I^{129} had been added in varying amounts were analyzed for I^{127} and I^{129} to check the procedures as they were developed. Typical chemical yields were about 50 per cent through the entire isolation and decontamination procedures. The I^{127} content of samples varied from 5 parts per billion for a wheat sample to 2150 parts per billion for a lake weed.

To demonstrate the sensitivity of the method for I^{129} the iodine from 100 g of leaves was isolated without addition of I^{129} , activated, and measured. An upper limit of 6×10^{-16} g of I^{129} per gram of leaf was determined. The same sample was found to contain 143 parts per billion of normal iodine.

Samples were irradiated in Argonne's CP-5 reactor at a flux of 3×10^{13} neutrons/cm²-sec. At this flux, the method can determine as little as 10^{-10} g of I^{127} and 10^{-13} g of I^{129} .

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