Atomic Energy Commission

Radiochemistry of Astatine

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of Astatine

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COMMITTEE ON NUCLEAR SCIENCE

The Radiochemistry of Astatine

By EVAN H. APPELMAN

Argonne National Laboratory
Lemont, Illinois
March 1960

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

FOREWORD

The Subcommittee on Radiochemistry is one of a number of sub-committees working under the Committee on Nuclear Science within the National Academy of Sciences- National Research Council. Its members represent government, industrial and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radio-chemically pure reagents, the problems of stockpiling uncontaminated materials, the availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Sub-committee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available informa-tion. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Sub-committee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

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INTRODUCTION

This volume which deals with the radiochemistry of astatine is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of astatine which might be included in a revised version of the monographs.

The Radiochemistry of Astatine[*]

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March 1960

I. General Reviews of Astatine Chemistry and Radiochemistry

> Edward Anders, Ann. Rev. Nucl. Sci. 9, 203 (1959).
>
> Earl K. Hyde, J. Chem. Ed. 36, 15 (1959).
>
> Earl K. Hyde, J. Phys. Chem. 58, 21 (1954)

II. Isotopes of Astatine[1]

Mass No.	Half-life	Principal modes of decay
< 202	43 sec.	electron capture, α
< 203	1.7 min.	e. c.
203	7 min.	e. c., α
204	25 min.	e. c.
205	25 min.	e. c., α
206	2.9 hr.	e. c.
207	1.8 hr.	90% e. c., 10% α
208	6.3 hr.	electron capture

[*]This monograph was prepared at the request of the Subcommittee on Radiochemistry of the Committee on Nuclear Science of the National Research Council.

Mass No.	Half-life	Principal modes of decay
208'	1.6 hr.	e. c. + 0.5% α + γ
209	5.5 hr.	95% e. c., 5% α,γ
210	8.3 hr.	electron capture + 0.2% α + γ
211	7.2 hr.	59% e. c., 41% α
212	0.22 sec.	α
213	?	α
214	2×10^{-6} sec.	α
215	10^{-4} sec.	α
216	3×10^{-4} sec.	α
217	0.018 sec.	α
218	2 sec.	α + 0.1% β
219	0.9 min.	97% α, 3% β

III. Hazards Involved in Handling Astatine

All the precautions customary in the handling of
highly radioactive substances must be observed in work
with astatine. The tendency of astatine to concentrate
in the thyroid makes it particularly dangerous,[2] and
its volatility makes it necessary to provide adequate
ventilation during all operations. At^{210} is addition-
ally hazardous because of its hard gamma ray and its
140-day, alpha-emitting Po^{210} daughter.

IV. Summary of the Chemical Properties of Astatine[3-7]

Since astatine has no long-lived isotopes, chemical
studies of it must be conducted at very low concentra-
tions--usually of the order of 10^{-15} $\underline{M}$. This makes the
astatine concentration comparable to that of the least
of the impurities in the experimental system. The re-

action of the astatine with such impurities often leads to irreproducible and uninterpretable--not to say exceedingly frustrating--results which lend considerable uncertainty to our knowledge of the chemistry of this element.

We might anticipate that astatine, as the heaviest halogen, would have properties roughly similar to those of its lighter brethren. However, a close examination of the chemistry of the halogens reveals marked differences among them, and the radiochemist must at all times be acutely aware of those properties which distinguish astatine from the other halogens.

At least four oxidation states of astatine have been identified in aqueous solution:

Astatide, At^-, is formed by reduction of higher states with SO_2, zinc, As(III) at pH > 5, or ferrocyanide at pH > 3 and ionic strength < 0.1. It is characterized by nearly complete coprecipitation (>90%) with AgI, TlI, or PbI_2.

The so-called "At(0)" is the form in which astatine is usually found when left to its own devices in acidic solution. In the absence of macro quantities of other halogens, At(0) is characterized by high volatility, a tendency to be adsorbed on metal or glass surfaces, and by ready, but quantitatively unpredictable extractability from acidic aqueous solutions into organic solvents. Thus in a single extraction CCl_4, benzene, toluene, cyclohexene, n-heptane, or isopropyl ether will remove from 70 to 98% of the astatine from an equal volume of an aqueous solution.

Various workers have reported degrees of coprecipitation of At(0) with insoluble iodides and iodates ranging

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from 0 to 90%. The astatine may be nearly quantitatively precipitated with elemental tellurium formed in situ in acid solutions, and will partially precipitate with insoluble sulfides and hydroxides.

The extractability of At(0) into hydrocarbons or CCl_4 decreases markedly with the addition of halide ions, while the extractability into ethers is not greatly altered.

The At(0) becomes unextractable into all organic solvents when an acid aqueous solution is rendered alkaline. The extractability is usually largely restored if the solution is reacidified within a short time. From the alkaline solution the astatine is completely coprecipitated with TlI or with AgI, the latter precipitated from an NH_4OH solution.

It has usually been assumed that the astatine species present in "At(0)" solutions is At_2. The effect of halide ions might then be explained in terms of the formation of such complexes as At_2I^-, which would not extract into CCl_4 or hydrocarbons, but might extract into ethers as HAt_2I. The behavior in alkaline solution is explicable in terms of reversible hydrolysis to At^- and $HOAt$.

However, as we have already noted, astatine is subject to reaction with impurities. At(0) should be especially vulnerable, since not only is At_2 expected to be extremely labile in its reactions, but any reaction which tends to break up the At_2 molecule becomes thermodynamically favored at these low astatine concentrations. To make matters worse, most of the experiments involving At(0) have been carried out without adequate control of the oxidation potentials of the solutions. Thus in addition to At_2 these solutions may contain assorted compounds of astatine with

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whatever organic impurities happen to be around, the exact species present varying from one solution to the next. It is small wonder that irreproducible behavior has been observed.

These complications may be largely avoided if another halogen and halide ion are present at macro concentrations. Now not only does the macro X^- -- X_2 couple control the oxidation potential of the system, but the astatine is in the form of a known interhalogen compound, since the reactions $At_2 + X_2 = 2AtX$ should be rapid and quantitative. Further, the macro halogen will react preferentially with many impurities which might otherwise react with the astatine.

In the presence of iodine and iodide the moderately extractable species AtI and the unextractable complex ion AtI_2^- appear to be formed. At 21°C. the distribution between aqueous solutions and CCl_4 is represented by

$$D = \text{organic astatine/aqueous astatine} = 5.5/1 + 2000(I^-)$$

From such solutions the astatine is not coprecipitated with AgI or $Pb(IO_3)_2$. Addition of Tl^+ to these solutions precipitates $TlI \cdot xI_2$, removing the iodide, most of the I_2, and all of the astatine from solution. The I_2 and astatine may readily be removed from the precipitate by washing it with acetone. PbI_2 does not coprecipitate astatine from these solutions if the stoichiometric I_2 concentration is low; when it is high, both I_2 and astatine are partially adsorbed by the precipitate but may be removed by acetone.

In a system containing I_2, IBr, and Br^-, the astatine is largely unextractable into CCl_4, being present primarily as the slightly extractable AtBr and the unextractable $AtBr_2^-$.

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The intermediate positive astatine state or states, which we may designate At(X), have been identified primarily on the basis of what they do not do. At(X) is completely unextractable into CCl_4 or benzene, though it may extract into ethers from several molar HCl solutions, and it does not coprecipitate with insoluble iodides or iodates.
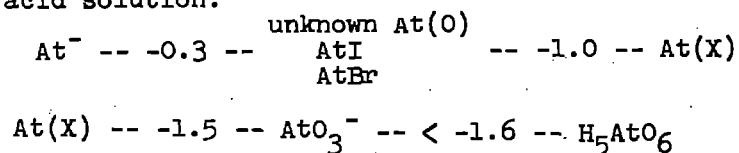
At(X) is formed by oxidation of At(O) with Br_2 or Cl_2 (but see following discussion of AtO_3^-) or by photochemical oxidation with a VO^{++} -- VO_2^+ mixture or with Fe^{+++} at low Fe^{++} concentrations. These photochemical oxidations are reversed in the dark, returning the astatine to the extractable At(O) state. The radiochemist must always consider the possibility of interference from such photochemical reactions.

Likely possibilities for At(X) are HOAt and $HAtO_2$, with the ether-extractable species being the corresponding polyhalo-acids $HAtCl_2$ and $HAtCl_4$. However organoastatine compounds cannot be excluded from consideration.

Astatate, AtO_3^-, has been identified as an unextractable species completely coprecipitated with $AgIO_3$, $Ba(IO_3)_2$, or $Pb(IO_3)_2$. It is formed by oxidation of lower astatine states with Ce^{+4}, hot persulfate, or hot periodic acid. It is also formed when Ag^+ is added to an I_2--I^- solution containing AtI, presumably in accordance with the reaction
$$AtI + 2I_2 + 3H_2O + 5Ag^+ = AtO_3^- + 5AgI + 6H^+.$$ Although the product of Cl_2 oxidation of At(O) is primarily At(X), when no chloride is present in solution other than that formed by hydrolysis of the chlorine, partial coprecipitation of the astatine with $Pb(IO_3)_2$ is observed, and this may indicate partial oxidation of the At(X) to AtO_3^-.

No evidence has been found for a perastatate.

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The following potential diagram, referred to 0.1 M.
acid, summarizes the oxidation-reduction behavior of asta-
tine in acid solution.

$$At^- \ \text{--} \ \text{-0.3} \ \text{--} \ \begin{matrix} \text{unknown At(0)} \\ \text{AtI} \\ \text{AtBr} \end{matrix} \ \text{--} \ \text{-1.0} \ \text{--} \ At(X)$$

$$At(X) \ \text{--} \ \text{-1.5} \ \text{--} \ AtO_3^- \ \text{--} \ < \text{-1.6} \ \text{--} \ H_5AtO_6$$

V. Preparation of Astatine

Astatine for chemical and medical studies and for
tracer use is prepared by bombardment of metallic bismuth
or bismuth oxide with alpha particles of energy exceeding
20 Mev, according to the reactions $Bi^{209}(\alpha,xn) \ At^{213-x}$.
The reactions with x = 2, 3, and 4 have threshold energies
of 20, 28, and 34 Mev, respectively.[8,9]

Metallic bismuth, the more common target material, is
customarily fused or vaporized onto aluminum or gold back-
ing plates. Since astatine may be volatilized from molten
bismuth it is necessary to cool the target carefully.
Bismuth is a poor thermal conductor, and the cooling prob-
lem increases with the thickness of the bismuth layer. The
back of the target is generally water-cooled. The face is
most effectively cooled by a flow of helium, though a static
helium atmosphere is often used. An 0.5 to 1 mil stainless
steel or copper cover foil pressed tightly to the surface
of the bismuth helps to dissipate the heat evolved and also
prevents astatine from escaping from the target.

When bismuth oxide is used, it is generally pressed
into small holes drilled in the face of a thick aluminum
plate and thereafter treated in the same manner as the
metallic targets. Melting of the target material is much
less likely in this case.

In all cases the beam of alpha particles should be de-
focussed as much as possible to avoid local hot spots on
the target.

Various astatine isotopes are also formed by spalla-
tion reactions brought about by high energy bombardment
of a variety of elements.

VI. Techniques for Counting Astatine Samples

Astatine^{211} may be assayed by counting either its
alpha particles or the x-rays accompanying its electron
capture. The alpha counting may be carried out in any
conventional alpha counters, such as gas-flow ionization
chambers or proportional counters, or zinc sulfide scin-
tillation counters, Reproducible and adherent astatine
samples may be obtained by evaporating astatine solutions
in about 2 $\underline{M}$ HCl to dryness on silver or platinum foils
under an infrared lamp. Under most other conditions such
evaporations show erratic losses of astatine.

The requirement of virtually weightless samples to
avoid self-absorption severely restricts alpha counting as
a means of assaying astatine. In coprecipitation experi-
ments one may circumvent this difficulty by counting in-
finitely thick samples of homogeneous precipitates, i.e.,
samples so thick that no alpha particles from the bottom
of the sample are counted. However, the absorption prob-
lem can be almost completely eliminated by the use of x-
ray counting methods, which permit the direct assay of
solutions and of bulky and inhomogeneous precipitates. Al-
though the x-rays may be counted with a Geiger counter,
much greater efficiency is obtained with a sodium-iodide

scintillator. It is advantageous to reduce the relative-
ly high background of the scintillator by operating it as
an energy analyzer registering only counts of energy in the
vicinity of the ca. 90 kv. k-x-ray of the astatine's
polonium daughter.

At^{211} decays in part to the long-lived Bi^{207} which
also decays by electron capture. The ratio of initial
At^{211} x-ray activity to residual Bi^{207} activity is of the
order of 10^5. The bismuth is usually present in colloidal
form — probably adsorbed on dust particles — and will be
carried along unpredictably through a surprisingly wide
variety of chemical procedures. Only distillation of the
astatine can be relied on to remove all of the Bi^{207}.
Samples x-ray assayed for astatine some time after purifi-
cation from Bi^{207} should be recounted after the astatine
has entirely decayed away, the resulting Bi^{207} count being
subtracted from the original count of the sample.

The techniques outlined here for At^{211} apply gener-
ally to the other astatine isotopes, with specific modifi-
cations arising from the decay scheme of the particular
isotope in question. Thus, for example, At^{210} may also
be assayed by scintillation counting of its 0.25 and 1.2
Mev gamma rays.

VII. Collection of Detailed Procedures for Isolation
and Purification of Astatine

A. Isolation of Astatine from Targets

Methods of two types are available for removing asta-
tine from bismuth targets--those involving distillation
of the astatine from the molten target and those involving
dissolution of the target in acid.

DISTILLATION OF ASTATINE FROM MOLTEN BISMUTH IN AIR[10]

For very rapid separation of astatine from the bismuth target, a method is used which gives astatine of somewhat uncertain purity but which is considered adequate for determination of short-lived alpha-emitters. The basis for the method is the distillation of astatine from molten bismuth. The bismuth target is dropped into a stainless steel crucible fitted on top with a water-cooled steel finger to which a collecting platinum disk is clamped. When the bismuth is kept slightly above its melting point (as measured by a thermocouple fitted into a well in the crucible), within a few seconds astatine distills onto the collecting plate. Polonium does not distill in appreciable quantities until considerably higher temperatures are reached. Using a vacuum carrier system to deliver the target, this procedure permits samples to be in the alpha-pulse analyzer within 90 seconds after the cyclotron beam is shut off.

Editor's Comments: This method was confirmed by the editor and Ralph D. McLaughlin.[7] Although the astatine begins to come off the target at the melting point of the bismuth, temperatures as high as 800°C. may be required to effect nearly quantitative removal. Astatine collected at such temperatures will be contaminated with any polonium which may have been present in the target, and also with some bismuth. The adherence of the astatine to the collecting plate is strongly dependent on the material of which the plate is made. Deposits on platinum or silver are strongly adherent, while those on aluminum are much less so.[11]

This procedure has also been found suitable for iso-
lating astatine prepared by heavy-ion bombardment of gold.
In this case the gold is dissolved in the molten bismuth.[12]

PROCEDURE 2

PURIFICATION OF ASTATINE ISOLATED BY PROCEDURE 1[7]

The astatine-containing plate from Procedure 1 is
placed in a tube on the end of an all-glass vacuum system
incorporating a U tube.[a] The plate is heated to 120°C. with
an electric furnace to drive off volatile impurities. A
liquid nitrogen cooling bath is placed around the U tube[b]
and the furnace temperature is raised to 500°C. over about
10 min.[c] The vacuum is broken and water or any desired
aqueous solution is added to the cold U tube. Upon thawing,
the solution is withdrawn, leaving virtually none of the
astatine behind. Yields are in the vicinity of 50%.

Notes:

[a]Several centimeters of glass tubing between the U tube
and the platinum plate is desirable to prevent polonium
from transferring to the U tube. If polonium contamination
is not a problem, this tubing may be heated to 100°C. or
more during the distillation to prevent adsorption of asta-
tine on the glass. Hydrocarbon greases should be avoided
between the U tube and the plate, since they have a strong
tendency to adsorb astatine. Dow Corning silicone grease
adsorbs relatively little astatine, as does a totally
fluorinated fluorocarbon fraction (e.g. Hooker Chemical
Company Fluorolube HG 1200).

[b]A bath at dry-ice temperature may be used, but in this

case a portion of the astatine may pass through the trap.

[c]A furnace is better for this heating than an induction heater, since when the latter is used the astatine has a tendency to leave the hot metal plate and become irretrievably imbedded in the cooler glass walls of the tube. The temperature of the furnace should be raised gradually.

PROCEDURE 3

DISTILLATION OF ASTATINE FROM MOLTEN BISMUTH IN HIGH VACUUM[4]

The procedure used was to distill the astatine from bismuth at its melting point in an all-glass system, and collect the carrier-free element in a four-millimeter diameter U tube cooled by liquid nitrogen. The U tube while still cold was washed with one drop of concentrated nitric acid, allowed to stand 1 hour, and then washed with distilled water into a stock bottle. By this method three-milliliter solutions were prepared containing 0.5-molar nitric acid and 10^7 disintegrations/sec. of astatine. Such a solution is 2.1 x 10^{-10} molar with respect to astatine. Yields up to 0.95 were obtained with less than 0.001 of any polonium present in the original target coming over.

Astatine evaporated on glass is very poorly held by this surface at room temperature. Based on this information, a double separation of astatine from bismuth and polonium was accomplished. A bismuth plate was bombarded in such a way as to accumulate in it approximately equal numbers of polonium and astatine atoms, after which a first distillation was carried out in the usual way. The tube containing the bismuth was sealed off and the astatine

then distilled at room temperature to a second U tube
cooled by liquid nitrogen. The yield of this experiment
was 0.83 of the astatine present on the original target,
with less than 10^{-6} of the polonium coming over.

Editor's Comments: This procedure is presented on a caveat
emptor basis. The editor and Ralph D. McLaughlin tested
the method but were unable to repeat it successfully.[7] In
our experiments the astatine did not distill below 600°C.
Above this temperature the bismuth itself began to distill,
carrying the astatine with it. Johnson, Leininger, and
Segré bombarded bismuth layers less than 40 mg/cm^2 thick on
1 mil aluminum backings. Our bismuth layers were from 0.5
to 1 g/cm^2 thick on 10 mil aluminum backings. It is pos-
sible that the difference in thickness of the bismuth is
in some way responsible for the difference in results.

We also had difficulty redistilling the astatine from
glass. It was often necessary to heat the glass to several
hundred degrees centigrade before the astatine was removed.
The astatine was probably being held by impurities which
condensed with it. A dark stain was often visible at the
point on the glass where the astatine had condensed.

PROCEDURE 4

DISTILLATION OF ASTATINE FROM MOLTEN BISMUTH
IN A STREAM OF INERT GAS[13]

About 220 mg/cm^2 of spectroscopically pure bismuth are
fused to a 10-mil gold disc, 3-3/8 inches in diameter, to
conform to the 2-by-7-cm. collimating slot in the cyclotron
window assembly, Fig. 1. The beam is sufficiently well

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collimated so that with centering of the bismuth more than 80% of the gold target may be recovered free of induced radioactivities. Enough platinum foil is placed in the path of the alpha beam at A (Fig. 1) to degrade the alpha-particle energy to 29 Mev. This is the optimum energy for the alpha-2n reaction with bismuth to form At^{211} without simultaneously producing At^{210} by the alpha-3n reaction.

Air is blown in along the side of the platinum foils to dissipate the heat produced by the beam. One-half atmosphere of helium is held in the area between the foils and the bismuth so that this area will be free of any oxygen. The presence of oxygen would lead to the formation of bismuth oxide, which could be carried over in the subsequent distillation operation. Because At^{211} is very volatile, even at room temperatures, water cooling is carried on just behind the gold target plate at B (Fig. 1). The total beam on the assembly in microampere hours is indicated by the integrator (Fig. 1).

At the end of the bombardment, the target and holder are allowed to cool for a short period of time to permit the decay of the short-lived radioisotopes produced in the aluminum, platinum, and gold foils. The target plate is then removed from the assembly and carefully dried. After the removal of the excess gold from either side of the gold-bismuth alloy, the target is cut lengthwise into two pieces, taking care to avoid flaking of the bismuth. These two pieces are placed in a small quartz boat, which is inserted into the large quartz tube shown at C (Fig. 2). Survey-meter readings are taken at the surface of the heating unit and at the cold finger D (Fig. 2) in order to
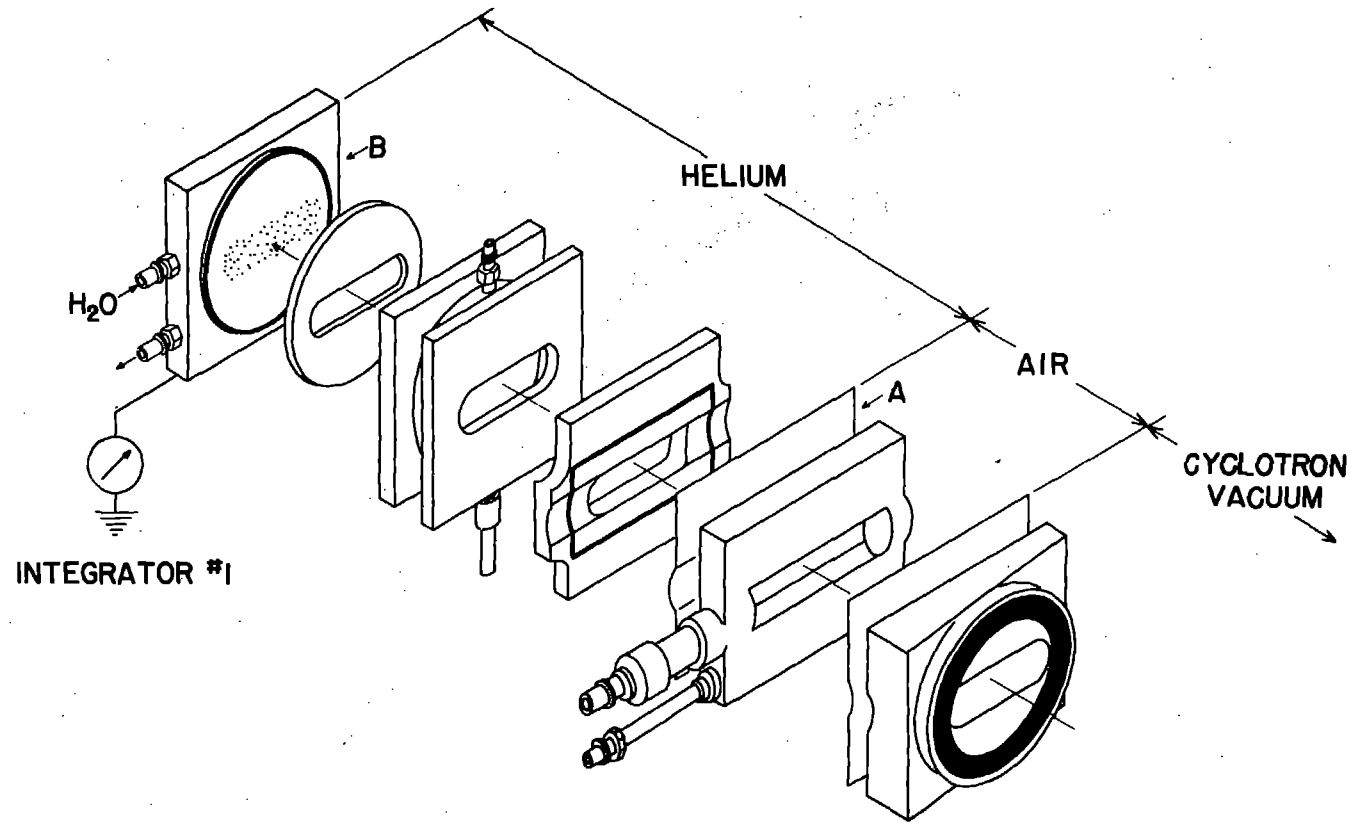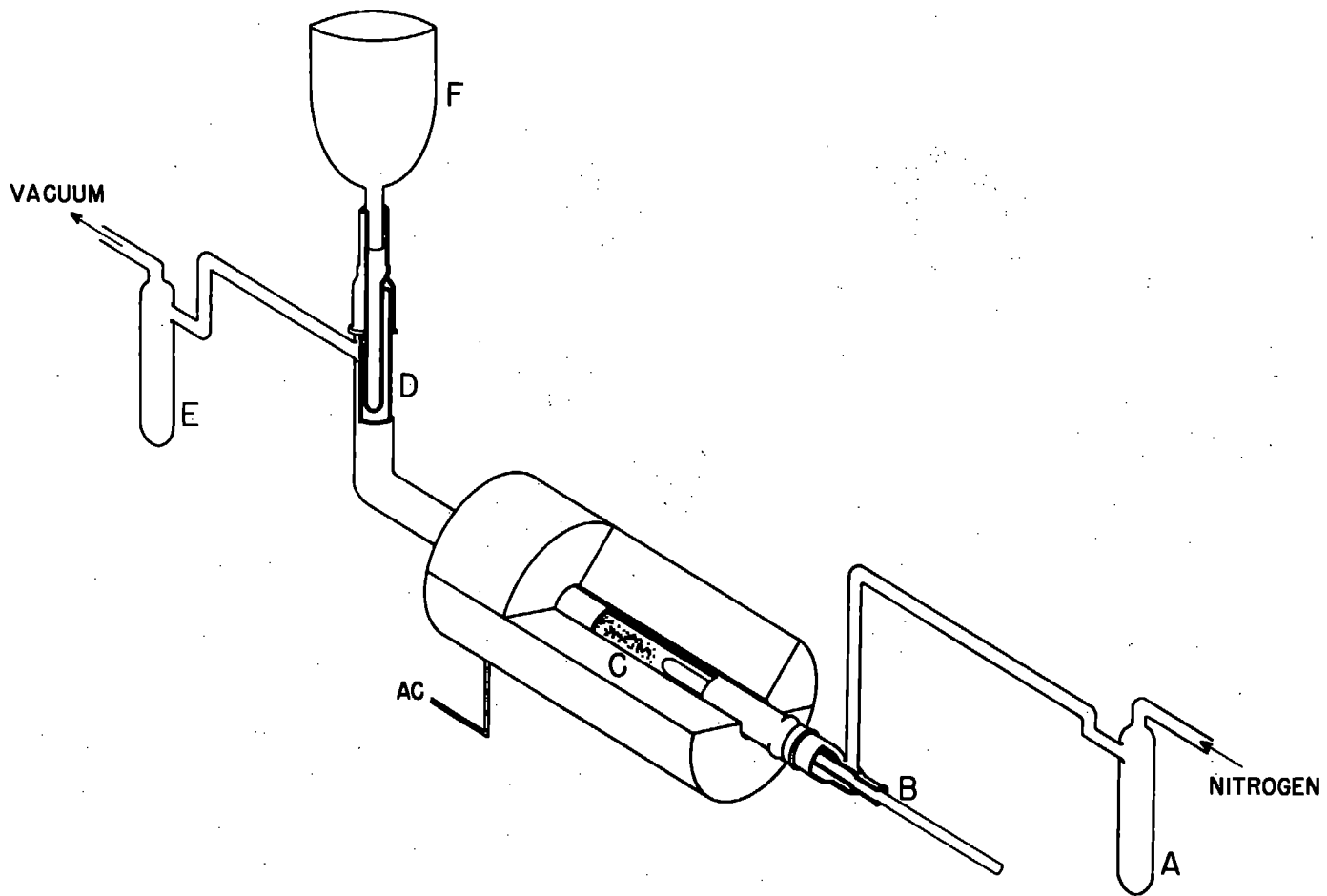
FIGURE 1.

FIGURE 2.

provide a reference point for later determination of completeness of the distillation of the At^{211}. Liquid nitrogen is put in the cold finger reservoir F (Fig. 2) and around the trap E (Fig. 2). In order to facilitate collection and to prevent the adsorption of the astatine on the glass of the cold finger, a thin film of ice is deposited on the finger by soft breathing. The entire system is evacuated with a Cenco-Megavac pump and tested with a Tesla coil. When a vacuum of less than 200 microns is obtained, an inert streaming gas--helium or nitrogen--is introduced through the capillary tube between A and B (Fig. 2). Two pounds of pressure is maintained on the tank side in order to permit a steady flow of gas over the bismuth to the cold finger. Neither water nor oxygen is permitted to enter the system, because it has been found that these tend to increase colloid formation.

The furnace is turned on, and the target is brought rapidly to 700°C as determined by a thermometer inserted in B (Fig. 2). Below this temperature the yield of At^{211} is low and above it a brown to black layer of bismuth may distill onto the cold finger and cause great loss of activity in subsequent centrifugation. The quartz tube between the furnace and the finger is flamed periodically to prevent adsorption of any activity on the walls of the quartz tube. The temperature is held at 700°C for approximately 40 minutes, or until survey-meter readings give no further indication of movement of activity from target to finger.

The furnace is turned off and opened, and the apparatus is allowed to cool to approximately 100°C. The vacuum

pump is turned off. When the system has returned to atmospheric pressure, the cold finger is carefully lifted straight up to prevent any of the ice from flaking off. The finger is washed with 10 ml of isotonic saline containing 5 mg/ml of Na_2SO_3. This solution is placed in an ultracentrifuge for 20 minutes at 30,000 rpm. The centrifuge cone is read with a survey meter and the value recorded. The supernatant is transferred to a 25-ml serum bottle. A 10-ml volume of water is added to the cone and shaken with the residue. The cone is again metered to determine the amount of activity remaining in the cone as colloid.

Editor's comments: The editor confirmed this procedure, obtaining yields of about 10%. Garrison et al.[14] report a similar procedure using a flow of nitrogen at 10^{-2} to 10^{-3} mm. of Hg. They heated the bismuth only to 425°C.

PROCEDURE 5

ISOLATION OF ASTATINE BY DISSOLUTION OF THE
TARGET AND EXTRACTION INTO ISOPROPYL ETHER[5]
(See also Procedure 6)

In making the isolation from the target, the bismuth is dissolved in nitric acid and the solution concentrated by boiling. The solution is not taken to dryness, as a little HNO_3 does not interfere. Concentrated HCl is added to bring the HCl concentration to 8 M, and the solution is cooled and extracted with isopropyl ether.[a] Isopropyl ether that has previously been equilibrated with 8 M HCl is somewhat better than pure ether for this purpose, since its use minimizes volume changes. The yields in a single extraction are better than 90%, the presence of Bi(III) salts increasing the extract-

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ability. Washing the ether phase with 8 $\underline{M}$ HCl removes about 10% of the activity. Less than 0.01% of the bismuth is retained in this procedure.

In the recovery of astatine from residues, higher oxidation states of astatine are reduced with hydrochloric acid, lower oxidation states are oxidized with Cl_2. Organic forms are apparently not affected by this treatment. Because of the large amount of sodium compounds that appeared in the residues, sodium chloride often precipitated from the 8 $\underline{M}$ HCl solutions. Separation by centrifugation is satisfactory, as there is no tendency for the complex to be retained on the precipitate. Iron salts, if present, are oxidized to Fe(III) and are extracted along with the astatine. Back-extraction with NaOH solution precipitates $Fe(OH)_3$, which will carry some of the astatine. Only about 5% of the astatine is carried if the amount of $Fe(OH)_3$ is not exorbitant. The extraction procedure also serves to separate from Po^{210}, which accumulates from the decay of At^{210}.

Note:

^{a}The isopropyl ether has previously been purified from peroxides by washing with three portions of saturated aqueous $FeSO_4$, followed by three portions of water.

Editor's comments: The editor has confirmed this method with certain exceptions: The HCl used to wash the astatine-containing ether should be about 1 $\underline{M}$ in HNO_3. If no nitrate is present up to half of the astatine activity may be backextracted in this wash. Neumann backextracted the astatine with 0.5 $\underline{M}$ NaOH. However I have found the complete-

ness of this back-extraction to be variable. Sometimes less than half of the astatine can be backextracted. I have not tested the use of this method for the recovery of astatine from residues.

PROCEDURE 6

ISOLATION OF ASTATINE BY DISSOLUTION OF THE TARGET AND EXTRACTION INTO ISOPROPYL ETHER, AND PURIFICATION FROM LEAD, BISMUTH, AND POLONIUM[10]

The method developed for removal of pure astatine consisted in its extraction, presumably while in the zero oxidation state, into diisopropyl ether (DIPE). The bismuth target was dissolved in such a manner as to end up with a solution in concentrated hydrochloric acid to which ferrous sulfate was added to make sure that the astatine was reduced to the zero state. This solution was contacted with DIPE. The DIPE solution was washed with dilute sulfuric acid, or hydrochloric acid, and so far as could be told by absence of polonium and bismuth alpha-activity, the astatine was pure. Samples of the DIPE solution could then be evaporated on platinum or stainless steel disks for radiation measurement.

A solution containing pure astatine isotopes begins to grow, successively, polonium and lower element daughters principally by electron capture decay. The polonium, bismuth, and lead may be removed periodically by adding one-tenth volume of 20 percent tributyl phosphate (TBP) in isobutyl ether to the DIPE solution and extracting into a 2M nitric acid--4M hydrochloric acid aqueous solution. These elements leave the organic phase, quantitatively,

in only about one minute contact time while the astatine
remains quantitatively in the organic layer. The polo-
nium can then be separated from bismuth and lead by ex-
tracting into TBP solution after destroying the nitrate
ion and making the aqueous solution 6M HCl. The bismuth
and lead are separated by precipitating the bismuth as
BiOCl and the lead as PbSO$_4$.

PROCEDURE 7

ISOLATION OF ASTATINE FROM BISMUTH OXIDE TARGETS[15]

The targets consisted of pockets of Bi$_2$O$_3$ imbedded
in the surface of an aluminum slab. After irradiation
the Bi$_2$O$_3$ was dissolved in HClO$_4$ containing a little
iodine, and the bismuth was precipitated as the phosphate.

B. Miscellaneous Radiochemical Methods

PROCEDURE 8

DETERMINATION OF ASTATINE IN BIOLOGICAL MATERIALS BY COPRECIPITATION WITH TELLURIUM[14]

A sample of astatine-containing tissue (less than 10
grams wet weight) is placed in a 100-ml. borosilicate glass
beaker and digested in a minimum volume of 9 N perchloric
acid containing 30% by volume of 16 N nitric acid. After
the organic material has been oxidized, the clear solution
is evaporated to 10 to 15 ml. of concentrated perchloric
acid. The solution is cooled and diluted to 3 N and 5 mg.
of tellurium as tellurous acid are added together with 1 ml.
of 12 N hydrochloric acid. (Tellurous acid is only slowly
reduced in cold 3 N perchloric acid in the absence of
dilute hydrochloric acid.) A stream of sulfur dioxide is
passed through the solution, precipitating metallic tellu-

rium which carries astatine quantitatively. The tellurium is separated by centrifugation, washed three times with distilled water, and transferred to a porcelain counting dish. After drying at 70°C., the dish is counted for alpha-activity.

Editor's comment: According to Corson, MacKenzie, and Segre, any polonium present remains quantitatively in solution when tellurium is precipitated in this way, and the astatine may subsequently be freed from tellurium by precipitating the latter from alkaline solution with sodium stannite.[3]

PROCEDURE 9

DETERMINATION OF ASTATINE IN BIOLOGICAL MATERIALS BY DEPOSITION ON SILVER[14]

A sample of astatine-containing tissue is digested in a mixture of perchloric-nitric acid.[a] After digestion is complete, the solution is evaporated until the perchloric acid fumes (approximately 10 ml.), diluted to 3 $\underline{N}$ with the addition of distilled water, and transferred to a 50-ml. beaker. A circular silver foil 2 mils thick of a size convenient for alpha counting is placed in the bottom of the beaker and the solution is stirred for 30 minutes. The foil is washed in water and acetone, dried in air, and counted for alpha-activity. Although the astatine deposits principally on the top surface of the silver foil, for quantitative results both sides of the foil should be counted for alpha-activity.

Note:

[a]The digestion procedure is that detailed in Procedure 8.

Editor's comments: The editor and Ralph D. McLaughlin
tested this method but were unable to obtain reproducible
results with it. In some experiments the astatine was
quantitatively removed from solution, while in others, less
than half of it could be removed. The method does not
provide a separation from polonium, which is also deposi-
ted to a large extent on silver foils.

PROCEDURE 10

CODETERMINATION OF I^{127}, I^{131} AND At^{211} IN TISSUE[16]

The apparatus consisted of a one-liter Claisen flask
fitted by a ground-glass joint to a thistle tube with a
stopcock and by a second joint to an all-glass water-jacket
condenser with a delivery tube bent nearly to a right angle.
Erlenmeyer flasks one-third full of CCl_4 and surrounded by
an ice bath served as receivers. The receiving flasks
were placed so that the delivery tube dipped well below
the surface of the CCl_4.

The thyroid glands were weighed, and no more than 50
grams was employed in a single determination. Thyroid
glands weighing more than 50 grams were divided into
approximately equal portions which were assayed separate-
ly. The tissue sample and some glass beads were placed
in the flask with approximately three times the tissue
weight of chromium trioxide. The neck of the flask was
washed with three times the tissue weight of water. After
the initial bubbling had subsided, a volume of 36 $\underline{N}$ sulfur-
ic acid equal to that of the water was added slowly through
the thistle tube. Since the reducing capacity of biologi-

cal materials is variable, it was sometimes necessary to use more than the stated amounts of reagents. The color of the reaction mixture usually was indicative of the progress of the oxidation. Persistence of the dark-green chromic ion indicated that the oxidation was not complete and more chromium trioxide, water, and sulfuric acid were added. All the reagents used were c.p. grade.

When the addition of the acid was complete, and the violent reaction had ceased, the flask was heated slowly to a boil, and water was distilled until the amount of water collected in the receiving flask was nearly equal to that originally added, or until excess chromium trioxide precipitated. A small amount of distilled water (10 to 20 ml) was added and the distillation was continued for a few minutes to insure the complete removal of chlorine and to wash out the condenser. Over-heating was avoided because of the possibility of carrying spattered dichromate over into the condenser.

The reaction flask was then allowed to cool to about 50°C, and the receiver was replaced by a 500-ml Erlenmeyer flask containing 200 ml of fresh CCl_4. Neither the At^{211} nor I^{131} was found in measurable quantities in the initial aqueous or organic phases in the first receiving flask.

From 50 to 200 grams of oxalic acid,[a] depending on the amount of tissue in the sample, were added slowly, a few crystals at a time until the evolution of CO_2 ceased and the solution was dark green in color. The flask was then heated and water, iodine, and some of the At^{211} were distilled over until the brown iodine color was no longer

discernable in the delivery tube. The distillation was
continued until another 20 to 30 ml of water had been
collected.

After the flask had cooled nearly to room temperature,
three times the tissue weight of anhydrous ferrous sulfate
was added, and the neck of the flask was washed with 20 ml
of water. The distillation was continued, using the same
receiving flask, until ferrous sulfate precipitated in the
bottom of the distilling flask as a greenish-white solid.
The distillate and the CCl_4 were transferred to a large
separatory funnel with enough $0.2\underline{M}$ Na_2SO_3 to completely
reduce the iodine. The layers were separated and the CCl_4
was discarded. The volume of the aqueous layer was re-
corded, and duplicate aliquots for radioactive assay
were pipetted into clean tinned bottle caps.[b] One ml of
$0.2\underline{N}$ KI in 0.1 $\underline{N}$ NaOH and an excess of 0.1 $\underline{N}$ $AgNO_3$ were
added. The samples were mixed by carefully rotating the
caps and were dried slowly under a heat lamp at 75°C.
The sampling technique described above is quantitative,
presumably as a result of the efficient scavenging of the
astatine by the mixed $AgI-Ag_2O$ precipitate, which, on
heating in contact with the tinned mount, is reduced to
form a thin uniform film of metallic silver completely
binding the astatine. The samples were assayed for
At^{211} alpha activity in an ionization chamber, and for
I^{131} gamma activity with a scintillation counter.[c]

The stable-iodine content of the samples was deter-
mined by oxidizing an aliquot of the iodine-containing
distillate with dilute HCl and H_2O_2 and re-extracting
into a known volume of CCl_4. The concentration of I_2

25

in the CCl_4 was measured with a previously calibrated Beckman spectrophotometer at a wave length of 570 mμ.

The accuracy of this method was checked by pilot experiments using samples of rat muscle or beef thyroid to which had been added known amounts of At^{211} and I^{131}. The recovery of the At^{211} was 90.2 ± 2.8% and that of I^{131} was 98 ± 1%.

The recovery of iodine, both stable and radioactive, was quantitative after the reduction with oxalic acid and the subsequent distillation as I_2. When the pilot experiments were performed, it was anticipated that At^{211} would be recovered quantitatively in the CCl_4 phase following the reduction with oxalic acid, as was iodine. It was found, however, that the recovery of the At^{211} was erratic so that the subsequent reduction with ferrous sulfate was included in the method to insure the accuracy of the determination of At^{211}.

Notes:

[a] The use of large crystals of oxalic acid is recommended, especially in the early stages of the reaction, which is quite violent.

[b] When these bottle caps are received from the dealer, they are coated with a thin film of lacquer. This is removed by soaking for a few hours in 6 $\underline{N}$ NaOH warmed on a hot plate.

[c] The scintillation counting was done through 0.5g/cm^2 of lead to remove α and β particles and At^{211} x-rays.

PROCEDURE 11

DETERMINATION OF ASTATINE BY COPRECIPITATION
WITH METALLIC SILVER OR PALLADIUM[15]

Silver or palladium ion is added to the astatine solution. Then sufficient sodium sulfite is added to precipitate all of the added cation as the metal. If a nitric acid solution is used, enough sulfite must be added to nearly completely neutralize the free acid. Less than 0.5% of the astatine remains in solution.

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