A STUDY OF THE FEASIBILITY OF A TRACER SYSTEM FOR LOCATING A FUEL-ELEMENT FAILURE IN REACTORS

by

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A FUEL-ELEMENT FAILURE IN THE REACTORS

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The results of this investigation indicated that a system of tracer
elements for location of fuel-element failure merited further development.
The proposed method consists in adding very small amounts of different
pairs of elements to the fuel alloy of each subassembly. In most cases
this is less than 0.1 w/o. These elements become activated during
operation of the reactor, producing radioisotopes. When a fuel-element
failure has occurred, a portion of the coolant is analyzed radiochemically
for the elements added to the fuel as tracers. The radioactive species
of the elements that are detected indicate the subassembly in which the
failure has occurred.

The elements which were found to be suitable tracers were erbium,
gallium, holmium, iridium, osmium, platinum, rhenium, scandium, terbium,
thorium, and ytterbium. Radiochemical separation procedures were
developed for these elements and checked out on irradiated alloy
specimens. It was determined that the tracer elements did not already
exist in reactor coolant water. Metallurgical studies indicated
that fuel alloy could be prepared with the tracer elements. The
physical properties, particularly hardness, ductility, and corrosion
resistance, of the tracer fuel alloys were similar to those of fuel alloy
without tracers.

INTRODUCTION

In a reactor in which the subassemblies are self-contained and welded
into the pressure vessel to form the reactor core, it would be desirable
to be able to replace a unit subassembly in the core, rather than the entire
core, if a fuel-element failure occurred. In order to do this, it is necessary
to locate the specific subassembly in which this failure has occurred.

The fact that failure has occurred is determined from the radiation
level in the coolant system. It has been defined as a condition under which
access to the lower reactor compartment must be prohibited fifteen min­
utes after reactor shutdown. For practical purposes, a radiation level
greater than 200 mr per hr under these circumstances is taken as the indi­
cation of failure.
Location of the subassembly in which the fuel-element failure has occurred, however, presents great difficulties. Instrumental methods, based on the detection of a suddenly increased concentration of fission products in the coolant channel for a single subassembly, have been developed for production-type reactors.

Although research on instrumental methods for failure location was continued, study of an alternative tracer technique was initiated. Generally speaking, this technique consisted of adding a specific tracer species to the fuel elements of a given subassembly. Upon the occurrence of a failure in an element, or elements, the tracer species would be released to the coolant stream. Analysis of a sample of the coolant for the tracer species would permit direct identification of the subassembly within which a fuel-element failure had occurred. Battelle undertook a study of the feasibility of the proposed tracer technique for the Knolls Atomic Power Laboratory.

PRELIMINARY CONSIDERATIONS

At the start of the investigation, consideration of the general characteristics of the system led to the establishment of certain criteria which the tracers had to satisfy. For instance, the possibility of placing the tracer between the core and the cladding was studied. Such a system appeared most likely to change the fuel-element characteristics, and, additionally, might not be a truly representative tracer of the fuel alloy. Accordingly, it was agreed that the tracer must not significantly alter the properties of the fuel alloy.

Other criteria, which were agreed upon by Battelle and KAPL personnel were:

1. The tracer must not significantly alter the properties of the fuel alloy.

2. The tracer must not be present in the fuel alloy or the coolant system generally, in a quantity sufficient to obscure the effect of the added tracer element.

As the survey proceeded, more stringent specifications were developed for the tracer species to satisfy.
Initially, three general tracer systems were considered. The first was based on the use of separated stable isotopes, the second on the use of isotopes of uranium, and the third on the use of tracer elements which produced radioactive isotopes by neutron irradiation. The first two types of systems had been investigated by KAPL, and were given further consideration in this study. Since the radioactive-tracer system appeared to offer the greatest promise, however, the major effort was concentrated on this system.

**Separated Isotopes**

A tracer system based on identifying different subassemblies by means of separated isotopes or combinations of separated isotopes is theoretically possible. Such a system based on the separated stable isotopes of titanium was considered by KAPL. It was proposed that subassemblies be identified by different ratios of specific isotopes.

The following drawbacks to this system were noted:

1. Mass-ratio changes would occur with time.

2. In the event of two or more failures in different subassemblies, it would be almost impossible to resolve the mass ratios.

3. The analysis would require highly skilled personnel because of the extreme sensitivity required. The requisite skill was available only in three or four mass-spectrometric groups in the whole country.

Separated isotopes which would yield radioactive species by neutron activation were also considered. Among the isotopes which appeared useful for this purpose were: erbium-170, iridium-193, platinum-192, platinum-198, rhenium-188, tungsten-180, tungsten-184, tungsten-186, and ytterbium-176. Use of these isotopes appeared to be more practical than the use of stable separated isotopes because radiochemical analysis could be performed by technicians, and multiple failures might still be located at least within a relatively small number of subassemblies.

Investigation of the availability and cost of separated isotopes, however, resulted in the decision to eliminate this technique from any further consideration on economic grounds. The only commercial source of separated isotopes at the present time is the Stable Isotopes Division of Oak Ridge National Laboratory operated for the United States Atomic Energy Commission by the Union Carbide Nuclear Company.
with Dr. C. P. Keim at the Oak Ridge National Laboratory indicated that the following separated isotopes were available at the prices listed:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Quantity on Hand (a) g</th>
<th>Enrichment, per cent</th>
<th>Form</th>
<th>Price, dollars per mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium-50</td>
<td>1.8</td>
<td>94.0</td>
<td>Cr₂O₃</td>
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<td>Copper-63</td>
<td>2.0</td>
<td>99.1</td>
<td>CuO</td>
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<td>Palladium-108</td>
<td>3.7</td>
<td>94.2</td>
<td>Palladium</td>
<td>1.70</td>
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<tr>
<td>Tungsten-180(b)</td>
<td>0.003</td>
<td>7.0</td>
<td>WO₃</td>
<td>104.00</td>
</tr>
<tr>
<td>Tungsten-184(b)</td>
<td>0.005</td>
<td>95.0</td>
<td>WO₃</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.034</td>
<td>91.0</td>
<td>WO₃</td>
<td>0.85</td>
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<tr>
<td>Tungsten-186(b)</td>
<td>0.40</td>
<td>97.2</td>
<td>WO₃</td>
<td>1.00</td>
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<td>Iridium-191</td>
<td>0.080</td>
<td>85.9</td>
<td>Iridium</td>
<td>24.75</td>
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<tr>
<td>Iridium-193</td>
<td>0.470</td>
<td>89.1</td>
<td>Iridium</td>
<td>21.00</td>
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<tr>
<td>Platinum-196</td>
<td>6.0</td>
<td>65.9</td>
<td>Platinum</td>
<td>1.60</td>
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<tr>
<td>Platinum-198</td>
<td>0.27</td>
<td>60.0</td>
<td>Platinum</td>
<td>7.75</td>
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<tr>
<td>Rhenium-185</td>
<td>0.31</td>
<td>85.4</td>
<td>Rhenium</td>
<td>1.40</td>
</tr>
<tr>
<td>Rhenium-187</td>
<td>0.025</td>
<td>98.2</td>
<td>Rhenium</td>
<td>1.70</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>Not yet separated</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Quantities on hand subject to prior allocation.
(b) New run now in process. Quantities and enrichments not yet known.

These prices are for less than gram quantities. The quantities required for the application of this tracer system are not available at the present time and could be made available only with great expenditure of time and effort due to the low mass-handling capacity of the calutrons. The costs themselves would make large-scale use prohibitive. At the nominal cost of $1 per mg about $1,000,000 would be required per reactor for tracers alone.

### Uranium Isotopes

A second system of tracer identification investigated by KAPL involved the use of different ratios of the isotopes of uranium. The advantage of this system over the previously discussed stable-isotope system was that two of the isotopes, uranium-233 and uranium-235, were interchangeable as fuels. Otherwise, it suffered from the same drawbacks; that is, the difficulty of resolving a multiple failure, and the requirement for highly skilled personnel to perform the analyses.
Activated Elements

A third method of applying the tracer technique is by use of elements that would produce identifiable radioisotopes. Ideally, a different element would be added to the fuel alloy in each subassembly. Following a failure, the detection in the coolant of a radioisotope produced by neutron activation in the tracer element would indicate without ambiguity the subassembly at fault. If there were more subassemblies to be tagged than there were elements available for tagging, combinations of elements could be used. A unique combination would be used in each subassembly. Desirable tracer elements would have neutron-absorption cross sections which would allow them to become activated readily during the operation of the reactor. This formation of radioisotopes would increase the sensitivity as well as the specificity of the detection process. The analyses of the coolant would be of the radiochemical type, requiring neither highly trained analysts nor extensive equipment. Cost of the tracers would be much lower than that required by the use of separated isotopes. It was decided on these considerations that the tracer method, employing elements with naturally occurring isotopic composition, held the most promise at the present time.

THE TRACER-SYSTEM DEVELOPMENT PROGRAM

In order to determine the feasibility of the proposed system of elemental tracers for failure location, a two-phase development program was undertaken. First, in collaboration with KAPL, criteria were established for the selection of promising tracer elements. On the basis of these criteria, and the available literature on known isotopic species, eleven promising elements were selected for experimental evaluation.

The second phase of the study consisted of a laboratory-scale metallurgical investigation of the selected tracer systems and development of the radiochemical procedures for analysis and separation of the elemental tracers and their associated radioisotopes.

Criteria for Choice of Tracer Elements

The Element Must Not be a Fission Product

The fission-product activity of even low-yield nuclides is larger than the activity induced in the tracer elements. Calculations based upon the
Way-Wigner formula for the growth and decay of fission-product activity indicate that a gross fission-product activity greater by a factor of $10^6$ than the average tracer activity can be expected. Exceptions were established, however, for gallium and terbium.

The Element Must Have a Sufficiently Long Half Life for Detection

A period of 2 to 4 days after shutdown of the reactor may be necessary before analysis and identification of the tracer elements can be completed. Thus a minimum half life of several hours is required for the induced tracer activity.

The Induced Activity Must Emit Detectable and Identifiable Nuclear Radiation

In general, some gamma radiation is desirable, since it can be identified readily by means of a gamma-ray spectrometer. Beta radiation of less than 0.1 mev presents problems in detection and occasionally requires special equipment. A relatively short half life is useful for verification of isotope identity.

The Activation Cross Section Must be Lower Than the Fission Cross Section of Uranium-235

This requirement was established in order to assure a tracer system that will retain its usefulness throughout the operating life of the reactor. A tracer element with a very high cross section will "burn out" and be no longer available as tracer before the end of the life of the reactor. By the same token, too low a cross section will result in insufficient activation.

The Tracer System May Cost a Maximum of $50,000 Per Reactor Core

This requirement rules out the use of separated isotopes at the present time. Their cost, based upon a nominal $1 per mg of separated isotope tracer, would be about $1,000,000. The approximate costs of the proposed tracer elements are listed in Table 1.
## Table 1. Cost of Tracer Elements

<table>
<thead>
<tr>
<th>Tracer Element</th>
<th>Cost, dollars per g</th>
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</thead>
<tbody>
<tr>
<td>Erbium</td>
<td>28</td>
</tr>
<tr>
<td>Gallium</td>
<td>11</td>
</tr>
<tr>
<td>Holmium</td>
<td>137</td>
</tr>
<tr>
<td>Iridium</td>
<td>62</td>
</tr>
<tr>
<td>Osmium</td>
<td>61</td>
</tr>
<tr>
<td>Platinum</td>
<td>30</td>
</tr>
<tr>
<td>Rhenium</td>
<td>13</td>
</tr>
<tr>
<td>Scandium</td>
<td>73</td>
</tr>
<tr>
<td>Terbium</td>
<td>137</td>
</tr>
<tr>
<td>Thulium</td>
<td>410</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>34</td>
</tr>
</tbody>
</table>

The Concentration of an Individual Tracer Should be Less Than 0.1 w/o of the Fuel Alloy

This is based upon a reasonable sequence of reactor operation and shutdown producing a detectable and identifiable activity in 1 liter of coolant following what is defined as a minimum failure.

A calculation was made of the individual tracer concentrations which satisfy these requirements. The basic parameters for the calculations were the following:

- **Neutron Flux.** $5 \times 10^{13}$ n/s.
- **Activation Cross Section.** BNL-325 value for thermal neutrons corrected by a factor of 0.53 for higher neutron energy.
- **Criterion of Reactor Operation.** Detectable tracer activities must be present in 1 liter or less of primary coolant following a minimum failure after either 15 days of reactor operation and 8 days of shutdown or 10 hr of operation and 2 days of shutdown.
- **Minimum Failure.** The release of 0.13 g or 0.5 w/o of fuel alloy into the primary coolant was defined as the minimum failure. A thorough analysis of this parameter has been made by Dewes and Sherman of KAPL.
Hafnium Equivalent. The number of parts per million of hafnium to which the tracer is equivalent in neutron-poisoning effect, based upon thermal neutron absorption cross sections. This should be less than 250 ppm for the tracer system.

Minimum Detectable Radioactivity. This was defined as 80 disintegrations per sec at the point of measurement. This activity must be present in 1 liter or less of primary coolant. Detection efficiency, including geometry, was taken as 20 per cent.

Nuclear Constants. Isotopic abundances, decay schemes, and half lives were taken from NBS-499 or UCRL-1928. In several cases, two isotopes contribute to the detectable activity of the tracers. The nuclear properties of the eleven tracer elements are shown in Table 2.

Chemical Yields. Chemical yields were determined experimentally, as described later, and represent the average of four determinations.

The required concentrations calculated for the eleven tracers which were established as a result of the initial feasibility study are shown in Table 3.

Taking all these factors into consideration, the growth of tracer radioisotopes during reactor operation was calculated and is shown in Figures 1 through 11. Curves are given for all the isotopes which contribute appreciably to the tracer activity 2 days after reactor shutdown. Decay curves are given for convenience in estimating the activity level of a tracer following irradiation and shutdown. The radioactivity levels are those present in the indicated volume of primary coolant following the "minimum failure". Solid curves represent actual induced activities and dashed curves are relative half lives.

Experimental Criteria for Tracer Elements

The second phase of the experimental study was the laboratory investigation. The literature survey and consultation period had indicated that eleven elements were suitable for further study for the tracer application. The next step was a laboratory study to evaluate the conformance of these eleven elements to the experimental criteria.

The performance of the tracer elements was evaluated on the basis of the following experimental criteria:
<table>
<thead>
<tr>
<th>Element</th>
<th>Parent Nuclide</th>
<th>Abundance, per cent</th>
<th>Activation Cross Section, barns</th>
<th>Daughter Nuclide</th>
<th>Half Life</th>
<th>Radiation Beta</th>
<th>Gamma</th>
<th>Other</th>
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<tbody>
<tr>
<td>Erbium</td>
<td>159</td>
<td>27</td>
<td>2</td>
<td>169</td>
<td>9.4 days</td>
<td>0.51</td>
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<tr>
<td></td>
<td>170</td>
<td>15</td>
<td>9</td>
<td>171</td>
<td>7.5 hr</td>
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<tr>
<td>Gallium</td>
<td>71</td>
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<tr>
<td>Holmium</td>
<td>165</td>
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<td></td>
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<td>1.5</td>
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<tr>
<td>Rhenium</td>
<td>187</td>
<td>63</td>
<td>75</td>
<td>187</td>
<td>85 days</td>
<td>0.56</td>
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</tr>
<tr>
<td>Scandium</td>
<td>45</td>
<td>100</td>
<td>22</td>
<td>46</td>
<td>85 days</td>
<td>0.56</td>
<td>0.9</td>
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</tr>
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<td>1.2</td>
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<tr>
<td>Element</td>
<td>Parent Nuclide</td>
<td>Abundance, per cent</td>
<td>Activation Cross Section, barns</td>
<td>Daughter Nuclide</td>
<td>Half Life</td>
<td>Beta</td>
<td>Gamma</td>
<td>Other</td>
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<tr>
<td>Terbium</td>
<td>159</td>
<td>100</td>
<td>22</td>
<td>160</td>
<td>73 days</td>
<td>0.86</td>
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<td></td>
<td></td>
<td>0.095</td>
<td>0.087</td>
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</tr>
<tr>
<td>Thulium</td>
<td>169</td>
<td>100</td>
<td>130</td>
<td>170</td>
<td>129 days</td>
<td>0.97</td>
<td>0.89</td>
<td>0.086</td>
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<tr>
<td>Tiberium</td>
<td>168</td>
<td>0.14</td>
<td>11,000</td>
<td>169</td>
<td>31 days</td>
<td>0.023</td>
<td>E. C.</td>
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<td>174</td>
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<td>60</td>
<td>175</td>
<td>101 hr</td>
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<td>0.196</td>
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<tr>
<td>Element</td>
<td>Concentration, w/o of alloy</td>
<td>Hafnium Equivalent, ppm</td>
<td>Sample Volume, liter</td>
<td>Chemical Yield, per cent</td>
<td>Type of Radiation Detected</td>
<td>Tracer Cost per Unit Cell, dollars</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------</td>
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<td>----------------------</td>
<td>--------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erbium</td>
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<td>565</td>
<td>1</td>
<td>92</td>
<td>Beta</td>
<td>315</td>
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<tr>
<td>Gallium</td>
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<td>77</td>
<td>Beta</td>
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<tr>
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<td>0.1</td>
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<td>Beta</td>
<td>88</td>
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<td>Osmium</td>
<td>0.154</td>
<td>208</td>
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<td>Beta</td>
<td>3080</td>
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<td>Gamma</td>
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<tr>
<td>Rhenium</td>
<td>0.039</td>
<td>226</td>
<td>0.1</td>
<td>28</td>
<td>Beta</td>
<td>166</td>
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<tr>
<td>Scandium</td>
<td>0.017</td>
<td>155</td>
<td>0.1</td>
<td>42</td>
<td>Beta</td>
<td>408</td>
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<tr>
<td>Terbium</td>
<td>0.024</td>
<td>120</td>
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<td>92</td>
<td>Beta</td>
<td>1080</td>
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<td>Thulium</td>
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<td>92</td>
<td>Beta</td>
<td>1012</td>
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<tr>
<td>Ytterbium</td>
<td>0.0087</td>
<td>31</td>
<td>0.1</td>
<td>92</td>
<td>Gamma</td>
<td>98</td>
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</table>
Relative decay intensity of radioactivity, based on $5 \times 10^{13}$ nu and $9.6 \times 10^{3}$ g of tracer element.

**FIGURE 1. THE DEGREE OF ACTIVATION OF GALLIUM AS A FUNCTION OF REACTOR-OPERATING TIME**
Relative decay
Intensity of radioactivity, based on $5 \times 10^{13}$ n and $0.23 \times 10^{-9}$ g of tracer element

Radioactivity, disintegrations per sec

Scandium-46

Scandium-46

Reactor-Operating Time, days

FIGURE 2. THE DEGREE OF ACTIVATION OF SCANDIUM AS A FUNCTION OF REACTOR-OPERATING TIME
Rhenium-188

Rhenium-186

Relative decay

Intensity of radioactivity, based on $5 \times 10^{13} \text{ nV}$ and $5.3 \times 10^{-9} \text{ g}$ of tracer element

\[ 10^5 \]

\[ 10^3 \]

\[ 0 \]

Radioactivity, disintegrations per sec

Reactor-Operating Time, days

FIGURE 3. THE DEGREE OF ACTIVATION OF Rhenium AS A FUNCTION OF REACTOR-OPERATING TIME
Radioactivity, disintegrations per sec

Osmium-193

Relative decay

Intensity of radioactivity, based on $5 \times 10^{13}$ f.w and $21.0 \times 10^{-9}$ g of tracer element

Osmium-191

Osmium-193

Reactor-Operating Time, days

FIGURE 4. THE DEGREE OF ACTIVATION OF OSMIUM AS A FUNCTION OF REACTOR-OPERATING TIME
FIGURE 5. THE DEGREE OF ACTIVATION OF IRIDIUM AS A FUNCTION OF REACTOR-OPERATING TIME

Radioactivity, disintegrations per sec

Iridium-194

Iridium-192

Relative decay

Intensity of radioactivity, based on $5 \times 10^{18}$ nu and $0.6 \times 10^{-9}$ g of tracer element

Reactor-Operating Time, days

10

20

30

40

50

60

70
FIGURE 6. THE DEGREE OF ACTIVATION OF PLATINUM AS A FUNCTION OF REACTOR-OPERATING TIME

Radioactivity, disintegrations per sec

10^3

10^2

10^1

10^0

Platinum-193

Platinum-197

Relative decay

Intensity of radioactivity, based on 5 \times 10^{13} \text{nv} and 11.0 \times 10^{-9} \text{g}

of tracer element

Reactor-Operating Time, days
Terbium-160

Relative decay
Intensity of radioactivity, based on $5 \times 10^{13}$ neutrons and $0.32 \times 10^{-9}$ g of tracer element

Reactor-Operating Time, days

FIGURE 7. THE DEGREE OF ACTIVATION OF TERBIUM AS A FUNCTION OF REACTOR-OPERATING TIME
FIGURE 8. THE DEGREE OF ACTIVATION OF HOLMIUM AS A FUNCTION OF REACTOR-OPERATING TIME
Relative decoy

Intensity of radioactivity, based on $5 \times 10^{13}$ nu and $4.6 \times 10^{-9}$ g of tracer element

FIGURE 9. THE DEGREE OF ACTIVATION OF ERBIUM AS A FUNCTION OF REACTOR-OPERATING TIME
FIGURE 10. THE DEGREE OF ACTIVATION OF THULIUM AS A FUNCTION OF REACTOR-OPERATING TIME

Radioactivity, disintegrations per sec

Relative decay
Intensity of radioactivity, based on $5 \times 10^{19}$ neutrons and $0.10 \times 10^{-8}$ g of tracer element

Thulium-170

Reactor-Operating Time, days
FIGURE 11. THE DEGREE OF ACTIVATION OF YTTERBIUM AS A FUNCTION OF REACTOR-OPERATING TIME
(1) It must be possible to separate the tracer elements chemically from gross fission products. Purification from gross fission products by a factor of $10^6$ is necessary. The chemical yield must be sufficiently high to be measured and to allow the tracers to be identified by their radiation.

(2) It must be shown that these tracers are not already present as cooling-water contaminants. The "minimum failure" condition will result in the presence of $1.35 \times 10^{-8}$ g of tracer element if present initially at 0.1 w/o in the fuel, in 1 liter of coolant. In general, this is a lower concentration than can be measured chemically. Thus the presence of measurable amounts of an element in the coolant as an impurity prevents its use as a tracer element. This was the reason for the exclusion of the possible tracers copper, tantalum, and tungsten. These had been detected in the coolant.

(3) These tracers must be metallurgically compatible with the fuel alloy. The presence of the tracer elements in fuel alloy may not change significantly the physical and chemical properties of the fuel. These properties include hardness, ductility, and resistance to corrosion.

Results

The initial phase of the program resulted in the selection of eleven elements for further study. These elements were erbium, gallium, holmium, iridium, osmium, platinum, rhenium, scandium, terbium, thulium, and ytterbium. This selection was based upon the criteria, which could be evaluated without experimental work, listed in the previous section.

This selection of elements was then evaluated experimentally for suitability as tracers on the basis of the second group of criteria. The experimental investigation consisted of two parts: (1) a chemical investigation in which methods for separation of these elements from fission products, cooling-water contaminants, and each other were developed and means for identification of their radioisotopes established, and (2) a metallurgical investigation which determined the ability of these elements to alloy with the fuel material and produce alloys with physical and chemical properties unchanged from those of the original fuel.
Development of Separation and Identification Procedures

Analytical Methods. A literature search was conducted to obtain radiochemical methods for the separation of the tracer elements. Manuals and compilations of the national laboratories furnished the majority of the chemical-separation procedures. The rare-earth separation procedure was found in the open literature. These methods were adapted to the needs of this particular problem, the conditions of operation were determined, and the chemical yields obtained by a number of experimental runs with nonradioactive material. The methods in their final form appear in the Appendix to this report. The averages of four representative yield determinations are shown in Table 4.

Fission-Product Decontamination. These chemical procedures were performed in the presence of gross fission products containing $5 \times 10^6$ to $2 \times 10^7$ counts per min of beta-gamma activity. The fission products were obtained from Oak Ridge National Laboratory and were a mixture of short- and long-lived species with an average half life of about 18 days when used. Decontamination factors were determined for the separation of each of the tracer elements from this fission-product mixture and the results are reported in Table 4. The decontamination factor is defined as the ratio of the activity present with the desired constituent prior to separation to that present with it at completion of the separation procedure. Factors of about $10^6$ were found for all the tracer elements. These results are the averages of duplicate determinations.

Cooling-Water Contaminants. The chemical procedures were carried out in the presence of 10 ml of reactor cooling water. The results of these experiments are shown in Table 4, the values being averages of duplicate determinations. The reactor cooling water was received three days after removal from the reactor and had beta activity level of 600 counts/(min)(ml). This decayed with an average half life of about 3 days. The results indicated, that no appreciable quantity of the tracer elements existed in the coolant.

Pure-Tracer-Element Standards. The identification of the tracer elements was made on the basis of three major characteristics: beta energies, gamma energies, and half life. Specimens of the pure tracer elements were sealed in quart vials and irradiated in the Oak Ridge X-10 reactor for 1 min at a flux of $5 \times 10^{11}$ nev. Scans were made of each
<table>
<thead>
<tr>
<th>Element</th>
<th>Chemical Yield, per cent</th>
<th>Decontamination Factor</th>
<th>Activity Found From Reactor Coolant, counts per min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erbium</td>
<td>92</td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>Gallium</td>
<td>77</td>
<td>&gt;10^6</td>
<td>10</td>
</tr>
<tr>
<td>Holmium</td>
<td>92</td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>Iridium</td>
<td>37</td>
<td>5 x 10^5</td>
<td>10</td>
</tr>
<tr>
<td>Osmium</td>
<td>65</td>
<td>10^6</td>
<td>None</td>
</tr>
<tr>
<td>Platinum</td>
<td>50</td>
<td>&gt;10^6</td>
<td>16</td>
</tr>
<tr>
<td>Rhenium</td>
<td>28</td>
<td>&gt;10^6</td>
<td>None</td>
</tr>
<tr>
<td>Scandium</td>
<td>42</td>
<td>8 x 10^5</td>
<td>27</td>
</tr>
<tr>
<td>Terbium</td>
<td>92</td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>Thulium</td>
<td>92</td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>92</td>
<td>(a)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

(a) No activity detected from 5 x 10^6 counts per min other than fission-product rare earths.
(b) No activity detected other than fission-product cerium and its praseodymium daughter.
element with the gamma-ray spectrometer. These scans established the most useful gamma-ray energies for identification of each species. Half lives were determined by successive counts on the scintillation counter and were very close to those previously reported for these isotopes.

**Detection of the Tracer Elements in Irradiated Fuel Specimens.** In the course of the metallurgical investigations, specimens were prepared which were to contain each of the tracer metals. These specimens were rectangular pieces of zirconium-7, 1 w/o uranium about 1 cm square and 2 mm thick. They weighed about 2 g each. In order to further test the reliability of the chemical-separation methods, a selection of these specimens, each of which was to contain one of the tracer elements, was irradiated in the Oak Ridge X-10 reactor for 1 hr at a flux of $5 \times 10^{11}$ nvt. The results of the analysis of these specimens prior to irradiation are shown in Table 5.

The specimens were stacked in the irradiation can with alternate disks of 2S aluminum to aid heat dissipation during the irradiation. Following irradiation, the specimens were dissolved in a combination of 1:1 nitric acid and 1:1 hydrofluoric acid. The solutions were diluted to 100 ml and aliquots were taken for radiochemical analyses. The size of these aliquots and the calculated activities are shown in Table 5. The osmium specimen was dissolved in a flask with a reflux condenser to prevent loss of osmium tetroxide by volatilization. Following the radiochemical separation of the tracer elements, beta-absorption curves and gamma-ray-spectrometer scans were taken for identification purposes. Half lives were also determined for the short-lived isotopes to aid in characterization. The gross gamma activity of the solutions was about $10^7$ counts/(min)(ml). The observed activity of the tracers is shown in Table 5. A correlation of the calculated values with the experimentally determined values for the activity is only qualitative, since the chemical yields, flux values, and weights of specimens were only approximate. In addition, average values were taken for the efficiency of the counting equipment rather than calibrate the equipment for the radiations of each of the isotopes formed.

Because of the sensitivity of the activation method, thulium was detected even though it had not been found spectrographically. This was also true of rhenium. Ytterbium, however, was not detected.

Since gallium is a fission product of very low yield ($10^{-5}$ per cent), a specimen which had no gallium added was also analyzed radiochemically as well as the specimen containing gallium. No gallium was found in the specimens to which no tracer gallium had been added. Thus the amount of radiogallium produced by fission will not interfere with the use of gallium.
### TABLE 5. RADIOCHEMICAL ANALYSIS OF IRRADIATED SPECIMENS FOR TRACER ACTIVITIES

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tracer</th>
<th>Analytical Value for Concentration of Tracer, w/o</th>
<th>Radiochemical-Analysis Data</th>
<th>Activity, counts per min</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>Specimen Analyzed</td>
<td>Fraction of Specimen Analyzed</td>
<td>Calculated</td>
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<tr>
<td>1</td>
<td>Erbium</td>
<td>0.02</td>
<td>0.1</td>
<td>$1 \times 10^4$</td>
</tr>
<tr>
<td>2</td>
<td>Gallium</td>
<td>0.05</td>
<td>0.1</td>
<td>$2.5 \times 10^3$</td>
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<tr>
<td>3</td>
<td>Holmium</td>
<td>0.02</td>
<td>0.01</td>
<td>$2.4 \times 10^4$</td>
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<tr>
<td>4</td>
<td>Iridium</td>
<td>0.04</td>
<td>0.01</td>
<td>$1.7 \times 10^4$</td>
</tr>
<tr>
<td>5</td>
<td>Osmium</td>
<td>0.02</td>
<td>0.1</td>
<td>$2 \times 10^3$</td>
</tr>
<tr>
<td>6</td>
<td>Platinum</td>
<td>0.05</td>
<td>0.1</td>
<td>$5 \times 10^2$</td>
</tr>
<tr>
<td>7</td>
<td>Rhenium</td>
<td>None detected</td>
<td>0.01</td>
<td>$2 \times 10^4$</td>
</tr>
<tr>
<td>8</td>
<td>Scandium</td>
<td>0.01</td>
<td>0.1</td>
<td>$5 \times 10^3$</td>
</tr>
<tr>
<td>9</td>
<td>Terbium</td>
<td>0.05</td>
<td>0.1</td>
<td>$1.6 \times 10^4$</td>
</tr>
<tr>
<td>10</td>
<td>Thulium</td>
<td>None detected</td>
<td>0.1</td>
<td>$1 \times 10^4$</td>
</tr>
<tr>
<td>11</td>
<td>Ytterbium</td>
<td>None detected</td>
<td>0.1</td>
<td>$1.3 \times 10^4$</td>
</tr>
</tbody>
</table>

(a) The correlation between calculated activity and found activity is only qualitative since the conversion factor for disintegrations per minute to counts per minute were estimated and not established experimentally. Chemical yields, flux, and sample size are also approximations.

(b) Based upon minimum analytically detectable concentration furnished by analytical laboratory.
as a tracer. The isotope of terbium which is formed in fission is not that formed by the \((n,\gamma)\) reaction and no interference was anticipated.

As a result of these analyses, all of the tracers except ytterbium have been found suitable for this application to the extent that these experiments may be presumed to simulate reactor conditions.

Study of Metallurgical Factors

While it is not an infallible criterion with respect to zirconium alloys, it is a good general rule that elements having boiling points below 1600 C cannot be alloyed with zirconium by usual procedures to the extent of 0.1 w/o. After eliminating elements on this basis and on the basis of previously discussed criteria, only eleven chemical elements were left for evaluation as tracers in the fuel alloy. The selected elements were erbium, gallium, holmium, iridium, osmium, platinum, rhenium, scandium, terbium, thulium, and ytterbium.

Alloying Procedure. Metallurgical evaluation of the effect of a 0.1 w/o or less tracer addition upon the fuel alloy, sponge zirconium-7 w/o uranium, was carried out on 50-g ingots prepared in a tungsten-electrode arc-melting furnace. Because raw sponge zirconium cannot be melted in this type of furnace, the sponge zirconium used was prepared by premelting in a consumable-electrode furnace. The resulting ingot was then rolled to sheet and the sheet cut into small squares. The uranium used was biscuit uranium. The gallium, iridium, osmium, platinum, and scandium used were obtained from the Fairmont Chemical Company, Newark, New Jersey. No analyses were supplied or obtained on these metals, but, except for the scandium, the purities were probably 99 per cent or better. The scandium was in powder form and its purity is unknown. The rhenium used was obtained at Battelle Memorial Institute in the form of metal foil, and its purity was 98 per cent or better. The remaining rare-earth elements, erbium, holmium, terbium, thulium, and ytterbium were obtained in the form of small metallic buttons from the Ames Laboratory, Ames, Iowa, through the courtesy of Dr. F. H. Spedding.

Each alloy was melted, turned over, and remelted at least five times, using an arc current varying from 200 to 500 amp. No variation in the ingots was detected which could be attributed to varying the arc current.

Alloy Properties. All alloys were hot rolled to 0.08-in. sheet at 700 C. This operation produced no cracking in any alloy and resulted in sheet covered with a very thin layer of oxide. Alloys prepared from one
batch of sponge zirconium had hardnesses ranging from 175 to 225 DPH; alloys prepared from another batch of sponge zirconium had hardnesses ranging from 225 to 270 DPH. There was no correlation between hardness and the amount of tracer found in the alloys.

Pieces of each alloy were cold rolled. All alloys could be cold reduced 20 per cent in thickness without any cracking, most could be cold reduced 25 per cent without cracking, and some withstood 40 per cent reduction without cracking. Again no correlation could be found between tracer content and ductility in cold rolling.

The cold-rolled alloys were annealed by heating to 800 °C for 1 hr and furnace cooling. The annealed alloys were given a sharp 90-deg bend as a final test of their ductilities. This test showed no differences between alloys of comparable thickness, regardless of the tracer content. Some of the thicker alloys cracked in bending 90 deg; the thinner pieces bent without cracking.

No effect of tracer content upon the microstructure of the alloys was observed either in the hot-rolled condition or in the annealed condition. Figure 12 shows the microstructure of one of the sponge zirconium-7 w/o uranium base tracer alloys after cold working and annealing for 1 hr at 800 °C. The angular white particles in the structure are grains of alpha zirconium. These particles were formed by recrystallization at 800 °C and were unchanged by cooling to room temperature. The dark intergranular constituent was beta-zirconium solid solution at 800 °C. In cooling from 800 °C, the beta-zirconium regions have transformed by precipitation of alpha zirconium, zirconium-uranium compound, and zirconium-tracer compounds. This precipitation accounts for its dark-etching behavior.

One alloy was analyzed for uranium content and this alloy was found to contain 7.1 w/o uranium. All alloys were analyzed spectrographically for the presence of the added tracers. The accuracy of the spectrographic analyses varied from element to element, but in no case is it believed that the error of analysis was greater than 50 per cent of the amount detected. The results of the analyses are listed in Tables 6 and 7. Where more than one analysis is given, the analyses refer to separate ingots and the analyses are listed in the order in which the ingots were prepared.

The behavior of scandium, thulium, and ytterbium in these alloying attempts was not considered entirely satisfactory and an attempt was made to discover the reason. Three 11-g charges consisting of 10 g of zirconium and 1 g of each of the tracers were prepared and melted. Severe spattering was observed in melting the charges containing thulium and ytterbium and less than 10 g of metal was recovered. It must be presumed that the boiling points of these metals are below the melting point of zirconium and that,
therefore, they cannot be alloyed with zirconium by normal procedures. Some spattering, possibly attributable to the use of powdered scandium, was observed in melting the charge containing scandium. However, an ingot weighing 10.6 g was recovered and it follows that scandium can be alloyed with zirconium.

FIGURE 12. SPONGE ZIRCONIUM-7 w/o URANIUM TRACER ALLOY AFTER COLD WORKING, ANNEALING 1 HR AT 800 C, AND FURNACE COOLING

Corrosion Properties. Corrosion tests have been run in 680 F water on samples of each tracer alloy and on a reference alloy containing no tracer addition. After approximately 2 months, no differences in corrosion behavior attributable to the tracer additions have been detected. The mean corrosion rate of samples from these 50-g ingots is of the order of +0.001 mg/(cm²)(hr). These samples were tested as arc melted and hot rolled at 700 C.
### TABLE 6. ANALYSES OF SPONGE ZIRCONIUM-7 w/o URANIUM-TRACER ALLOYS

<table>
<thead>
<tr>
<th>Tracer Element</th>
<th>Spectographic Analysis, w/o</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ingot 1</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.010</td>
</tr>
<tr>
<td>Thulium</td>
<td>N. D. (a)</td>
</tr>
<tr>
<td>Erbium</td>
<td>0.02</td>
</tr>
<tr>
<td>Holmium</td>
<td>0.02</td>
</tr>
<tr>
<td>Terbium</td>
<td>0.05</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>N. D. (b)</td>
</tr>
<tr>
<td>Rhenium</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Osmium</td>
<td>0.02</td>
</tr>
<tr>
<td>Iridium</td>
<td>0.04</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.05</td>
</tr>
<tr>
<td>Gallium</td>
<td>0.025</td>
</tr>
</tbody>
</table>

(a) Not detected. Limit of detection is about 0.03 w/o thulium.
(b) Not detected. Limit of detection is about 0.005 w/o ytterbium.
<table>
<thead>
<tr>
<th>Tracer Elements Added</th>
<th>Ingot Spectrographic Analysis, w/o</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmium</td>
<td>0.02</td>
</tr>
<tr>
<td>Scandium</td>
<td>0.02</td>
</tr>
<tr>
<td>Osmium</td>
<td>0.02</td>
</tr>
<tr>
<td>Terbium</td>
<td>0.08</td>
</tr>
<tr>
<td>Osmium</td>
<td>0.02</td>
</tr>
<tr>
<td>Holmium</td>
<td>0.02</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.08</td>
</tr>
<tr>
<td>Erbium</td>
<td>0.03</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.08</td>
</tr>
<tr>
<td>Thulium</td>
<td>Not detected</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.08</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>Not detected</td>
</tr>
<tr>
<td>Gallium</td>
<td>0.15</td>
</tr>
<tr>
<td>Rhenium</td>
<td>0.03</td>
</tr>
<tr>
<td>Gallium</td>
<td>0.15</td>
</tr>
<tr>
<td>Iridium</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The foregoing data are believed to show the metallurgical feasibility of using the elements erbium, gallium, holmium, iridium, osmium, platinum, rhenium, scandium, terbium, and thulium as tracers in fuel elements. Thulium is included in this group because it was detected by activation analysis in its alloy. Although ytterbium was not detected, even by activation analysis, it should be investigated further in any larger scale metallurgical development program. It should be borne in mind that the feasibility of using these tracers has been demonstrated on 50-g ingots only, and that in some cases less than 20 per cent of the added tracer has been detected by analysis of the ingot. The problem of obtaining homogeneous ingots weighing 10 or 20 lbs and having the desired analyses will require considerable developmental work.

DISCUSSION AND CONCLUSIONS

Selection of Tracer Elements

It may become possible on the basis of more complete knowledge of cooling-water contaminant activities to add several more tracer elements to the selection. Copper, tantalum, and tungsten were eliminated on the basis of reported contamination studies, but greater experience with the reactor system may show that these or other elements could be used.

The availability of separated isotopes of the tracer elements at reasonable cost would also increase the number of useful tracer species. In some cases, elements present as cooling-water contaminants could be used as separated isotopes because of the higher possible concentration of the more desirable isotopes. For example, tungsten-186 normally has a 28.7 per cent abundance. If it were present with 100 per cent abundance as a separated isotope, the yield of the 24-hr tungsten-187 activity would be increased by almost a factor of 4. This increased activity might allow its use even though natural tungsten is present as a cooling-water contaminant.

The use of gallium and terbium as tracer elements proved possible despite the fact that they are also formed as fission products. Gallium-72, for instance, was readily found in the activated specimen to which gallium had been added, but it could not be found in specimens to which no gallium had been added. The fission yield, of course, is only of the order of 10^{-5} per cent, and calculations indicate that it is unlikely that any fission product with yield greater than 10^{-3} per cent would be usable. On this basis, these two are practically the only fission-product elements suitable for use as tracers.
Chemical Separations

The methods for separating the tracer elements from the coolant are primarily methods which were described previously in the literature. The only exception to this was the iridium method. The procedure described in the literature was found to be very difficult to reproduce, gave very low yields, and had an insufficient decontamination from fission products. The ion-exchange method described in the Appendix was developed in this laboratory.

All of the analytical methods could be improved significantly with a moderate amount of research. It should be possible to make them shorter, easier to perform, and more reproducible. Higher yields and decontamination factors may be achieved by adapting the more recently developed techniques of cation and anion exchange and solvent extraction. Greater use of the gamma-ray spectrometer in conjunction with group separation might also increase the sensitivity of identification while shortening the chemical procedure.

Decontamination From Fission Products and Cooling-Water Contaminants

The fission products used in the decontamination studies were a synthetic mixture. Long-decayed solutions were mixed with fresh solutions and the resultant half life was measured. The actual fission-product spectrum which will be encountered in the use of a tracer system will depend upon the history of the reactor operating cycle. Any synthetic mixture will be only an approximation.

The sample of reactor cooling water had a period of 3 to 5 days of decay before use. This allowed the short-lived activities to decay and, for this reason, was not an entirely accurate test. A more reliable measure of the presence of the tracer elements as cooling-water contaminants could be made with an in-pile test where the analytical facilities are in a closer proximity to the reactor.

Identification of Tracer Elements

Following the chemical separation of the tracer elements from the cooling water, they must be identified by their nuclear properties. These are half life and energies of beta and gamma radiation. On the basis of
Literature values and the gamma-ray-spectrometer scans of the irradiated standards, the following characteristics appear best for identification purposes.

Erbium

The erbium-171 isotope has a very short half life, 7.5 hr, which aids in its identification. Also, the 0.33-mev beta from erbium-169 should be easily distinguished from the higher energy betas of erbium-171 by absorption measurements. The gamma-spectrometer scan indicates many poorly defined gamma rays, none of which are suitable for identification.

Gallium

The single gallium-72 isotope must be identified in this case. The 14-hr half life is a characteristic, as is the well-defined gamma-spectrometer peak at 0.84 mev.

Holmium

The single isotope holmium-166 possesses a 27-hr half life, which is easily identified. Should additional proof be required, the gammas at 0.08 and 1.44 mev are easily identified. The beta at 1.84 mev should be readily characterized by absorption measurements.

Iridium

The primary activity produced in the irradiation was iridium-192, whose nuclear properties have not been fully characterized. The gamma spectrometer shows a well-defined peak at about 0.32 mev, which is due to a number of gamma rays. This peak is the most convenient for identification.

Osmium

The 16-day osmium-191 and the 31-hr osmium-193 may be found in irradiated osmium specimens. For identification purposes, the gamma-spectrometer scan shows well-defined peaks at 0.65 and 0.13 mev. The 0.143-mev beta from osmium-191 and the osmium-193 beta of 1.1 mev should be easily resolved by absorption measurements.
Platinum

The 18-hr platinum-197 is sufficiently short lived to be used in characterization. Also, its 0.67-mev beta is the only beta radiation from the separated platinum activities. Spectrometer scans taken shortly after irradiation show well-defined peaks at 0.14 and 0.19 mev for identification. The 0.14-mev peak is particularly suitable.

Rhenium

The gamma-spectrometer scans taken shortly after irradiation show peaks at 0.13, 0.48, 0.65, and 1.37 mev. As a later scan shows, the 0.13-mev gamma is best for identification. The peak at 0.055 mev may be an X-ray resulting from electron capture. The short half lives of 92 hr for rhenium-186 and 18 hr for rhenium-188 are also easily determined.

Scandium

The 85 day half life of scandium-46 is readily identified by its gamma-ray spectrum. The peaks at 0.9 and 1.12 mev are readily resolved and identified. The 0.36-mev beta should also be readily characterized by absorption measurements.

Terbium

Because of its 73-day half life, terbium-160 must be identified by gamma-spectrometer measurements or beta absorption curves. The spectrometer scan shows a well-defined gamma peak at 0.087 mev and fairly well defined groups at 0.21 and 0.31 mev. The 0.86- and 0.52-mev betas would be difficult to resolve.

Thulium

The half life of 129 days for thulium-170 is too long to aid in identification. However the well-defined gamma-spectrometer peak at 0.084 mev and the 0.97-mev beta should be sufficient to characterize it.

Ytterbium

For identification purposes, the gamma-ray scan indicates that gamma rays at 0.05 and 0.11 mev may be used. The weak beta at 0.5 mev should
also prove characteristic, since it is the only beta radiation produced in irradiated ytterbium.

Preparation of Alloys

As was indicated in the section on metallurgical factors, difficulty was experienced in alloying scandium, thulium, and ytterbium. Ultimately, scandium was successfully alloyed, and thulium and ytterbium apparently still remained unalloyed. Radiochemical analysis of the activated specimens, however, proved the presence of an unknown quantity of thulium. Thus, ytterbium is the only tracer element which has not been alloyed or detected.

Considering the scale on which the alloy specimens were prepared, it is quite obvious that considerable development will have to be carried out before production-scale procedures may be specified. Should such a program be initiated, it would be desirable to include thulium and ytterbium in the investigation.

Tracer-Element Combinations

The proposed reactor system consists of 19 individual subassemblies. To tag each subassembly with a specific element would require 19 tracer elements. Since only 11 elements possess the necessary chemical and nuclear properties, and only 9 have been proven to be metallurgically compatible, it is necessary to use combinations of the available elements. The scheme shown in Table 8 is one example of a system of combinations in

<table>
<thead>
<tr>
<th>Table 8. TRACER COMBINATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Gallium</td>
</tr>
<tr>
<td>Platinum</td>
</tr>
<tr>
<td>Erbium</td>
</tr>
<tr>
<td>Holmium</td>
</tr>
<tr>
<td>Terbium</td>
</tr>
</tbody>
</table>
which 20 unique combinations are available using only 9 elements. Each element in the first horizontal row is used in combination with each element beneath it. The availability of 20 combinations would allow one to be used as a replacement. Such a combination system will identify the location of a failure implicitly so long as failure occurs in only one subassembly at a time. In case of failures in two subassemblies, a degree of ambiguity results. If three tracer elements are identified following a failure, the two subassemblies in which failure occurred may still be identified implicitly. However, if four different tracer elements are identified following a failure, as many as four or as few as two individual subassemblies may be faulty. This ambiguity will, of course, increase if even larger numbers of tracer elements are found in the coolant. At the least, however, the possible subassemblies in which failure has occurred will be indicated. Knowing this, a system for pin-pointing the actual subassemblies in which failure has occurred may be established. Such a system may be based on a series of reactor operations and shutdowns with one or more of the suspected subassemblies inoperative in each cycle. Analysis of a coolant sample after each operation should serve to locate the subassemblies in which failure has occurred.

RECOMMENDATIONS FOR FUTURE STUDY

The objective of this investigation was to determine the feasibility of a tracer system for locating subassemblies in reactors in which fuel-element failure had occurred. It is believed that the results have established that such a system is feasible. Before the system can be considered practical, however, certain areas remain to be investigated.

Metallurgical Development

The metallurgical investigation of the proposed tracer-containing alloys was carried out on a very small scale. From the viewpoint of the effect of tracer addition on the physical and corrosion properties of the fuel alloy, however, it is believed that the results are reliable. No noticeable effect was observed. Very little was learned, though, which might help in prescribing manufacturing and control procedures for these alloys.

Development of such procedures, and more precise evaluation of the cost of these tracer fuel alloys, remains to be worked out. This will require an experimental program on a much larger scale than the 50-g laboratory melts used in this study.
In such a program, it would also be desirable to re-evaluate the preparation of thulium- and ytterbium-containing fuel alloys. Considering that three other rare earths have been alloyed, more or less readily, there seems to be no apparent reason why thulium and ytterbium should not do so.

In-Pile Studies

The laboratory experiments in which the separation and identification of the tracer elements was proven still leave several important questions unanswered. A major one is the form in which the tracer elements will appear in the coolant.

For the laboratory studies, all specimens were dissolved in acid and generally existed in solution as well-known ionic species. Just how they will exist in the actual reactor coolant can only be conjectured. It is known that the ion-exchange bed in the coolant system does an excellent cleanup job. It is also believed that, at the very small concentrations being considered, it is very unlikely that the elements will exist as metallic aggregates. Certainly, most of the elements being considered as tracers are likely to be most reactive with water under the conditions of the system.

These factors all point toward a homogeneous distribution of the elements in the coolant, if not actual solution. It seems likely that a representative sample will be obtained from the coolant. There is a possibility of plating out or some other form of concentration of some of the tracer elements in the coolant systems. The platinum metals are particularly suspect.

For this reason, it will be desirable to incorporate representative intentionally defected fuel elements, containing the tracer, or perhaps a single element containing all the tracers, in an operating reactor prototype subassembly. Such an experiment will, of course, represent the ultimate in a complete test of the proposed system. If information is desired sooner, a suitable substitute would be an in-pile loop experiment, again with a fuel-element specimen containing all the tracer elements. Such an experiment would also permit a test to be made of the possibility of concentrating the tracer element on an ion-exchange column, as well as provide a means for studying removal of the tracers from the column.

Separation and Identification Techniques

Because of the short time available for this study, existing separation procedures were adapted and checked out for the proposed tracer
elements. These are basically well-established methods with high decontamination efficiency. They are, however, relatively long and tedious.

It seems quite likely that easier, faster, more sensitive methods could be developed with no sacrifice in decontamination factor. Newer techniques such as anion exchange, solvent extraction, or specific precipitation might be utilized. These techniques, coupled with precise gamma-ray spectrometry, hold the promise of achieving the desired improvement in separation and identification of the tracer elements.
APPENDIX

ANALYTICAL METHODS

Platinum

Introduction

Platinum is separated from the tracer osmium, and the fission products ruthenium and iodine by distillation of these contaminants. Decontamination from tracer gold is effected by extraction with butyl acetate. Fission-product palladium and corrosion-contaminant nickel are precipitated by dimethylglyoxime. Platinum is then reduced with stannous chloride and the chloride extracted with butyl acetate. The aqueous layer may be used for determining iridium. The platinum is washed from the aqueous layer and precipitated as sulfide. Further decontamination is given by lanthanum hydroxide and 8-hydroxyquinoline precipitations. Platinum is then reduced to the metal, filtered, dried, and weighed. The chemical yield is about 50 per cent with an over-all decontamination factor of $10^6$ from fission products. Eight hours is required for performing duplicate analyses.

Reagents

Platinum carrier: 5.7 mg platinum per ml (25 ml 5 per cent $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ diluted to 100 ml)

Ruthenium carrier: 5.9 mg ruthenium per ml (1 g $\text{RuCl}_3$ dissolved in water and diluted to 100 ml)

Palladium carrier: 6.0 mg palladium per ml (1 g $\text{PdCl}_2$ dissolved in water and diluted to 100 ml)

Molybdenum carrier: 10 mg molybdenum per ml (1.85 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in water and diluted to 100 ml)

Lanthanum carrier: 10 mg lanthanum per ml (3.12 g $\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$ dissolved in water and diluted to 100 ml)

KI: 1 per cent aqueous solution

RECLASSIFIED
KIO₃: 1 per cent aqueous solution
HClO₄: Concentrated (60 per cent)
HC₂H₃O₂: Concentrated (glacial)
HNO₃: Concentrated
HCl: Concentrated
NH₄OH: Concentrated
H₂O₂: 30 per cent
NaOH: 6 N

Butyl acetate: Reagent grade
SnCl₂: (15 g SnCl₂·2H₂O dissolved in 25 ml of 10 per cent HCl)
Dimethylglyoxime: 1 per cent (1 g dissolved in 100 ml ethyl alcohol)
NaOAc buffer: (3.8 ml acetic acid plus 29.5 g NaOAc diluted to 100 ml)
Mg metal: Powdered
H₂S: Gas
8-hydroxyquinoline: 5 per cent (5 g 8-hydroxyquinoline dissolved in 100 ml of 2 M glacial acetic acid)

Aqua regia: (3 volumes HCl and 1 volume HNO₃)

Equipment

Drying oven
Block for holding centrifuge tubes
Assorted sizes of pipettes
Filter chimney
250-ml Erlenmeyer flask
50-ml ruthenium still
Electric stirrer
Microburner
100-ml beakers
pH indicator paper
Centrifuge
Forceps
Ground-off Hirsch funnel
1-in. -diameter filter circles
40-ml glass centrifuge cones
50-ml extraction funnels
Stirring rods
Hot plate
Wash bottle

**Procedure**

**Step 1.** Pipette an aliquot of the sample into a distillation flask and add 5 ml of platinum carrier, 4 ml of ruthenium carrier, and 2 ml each of concentrated HNO₃ and 60 per cent HClO₄. Distill by heating with a micro-burner until copious white fumes of HClO₄ are observed. Catch the distillate in a 250-ml Erlenmeyer flask containing 6 N NaOH. Allow the distillation flask to cool, and rinse the neck of the flask with water. Add 2 ml of ruthenium carrier, 2 ml of concentrated HNO₃, and 10 drops of 60 per cent HClO₄, and repeat the distillation until the appearance of HClO₄ fumes. Cool the distilling flask, and rinse the neck with water.

**Step 2.** Add 1 ml each of KI and KIO₃ solutions, and redistill until the appearance of fumes of HClO₄. Repeat the addition of KI and KIO₃ solutions and distill to fumes of HClO₄.

**Step 3.** Wash the solution from the distilling flask into a 50-ml extraction funnel. Keep the volume down to about 6 ml. Add 10 drops of concentrated HCl and 6 ml of butyl acetate. Mix thoroughly for 5 min with an electric stirrer and allow the phases to separate. Remove the upper organic layer and add 6 ml of fresh butyl acetate, and again mix for 5 min and allow the phases to separate. Transfer the lower aqueous layer to a 100-ml beaker.

**Step 4.** To the solution in the beaker add 40 ml of water, 1.5 ml of palladium carrier, and 5 ml of 1 per cent dimethylglyoxime. Stir the solution and divide it equally in two 40-ml centrifuge cones. Add 5 drops of aerosol solution to each cone and heat on the steam bath for 2 min to coagulate the precipitate. Centrifuge at top speed for 5 min. Transfer the supernates to a single 100-ml beaker and discard the precipitates.
Step 5. Evaporate the supernate from the palladium separation to about 5 ml and transfer it to a 50-ml extraction funnel. Add 5 ml of concentrated HCl and dilute to 10 ml. Add SnCl₂ dropwise until the solution turns cherry-red. Add 10 ml of butyl acetate, mix mechanically for 5 min, and allow the phases to separate. Transfer the lower aqueous portion to a clean extraction funnel, leaving the butyl acetate portion in the first funnel.

Step 6. Add 2 ml of concentrated HCl to the aqueous portion and add SnCl₂ dropwise, until the solution turns cherry-red. Extract any remaining platinum with another 10-ml portion of butyl acetate. Discard the lower aqueous layer and combine the two butyl acetate portions in one extraction funnel.

Step 7. Add 5 ml of 6 N NaOH and mix thoroughly for 5 min. Allow the phases to separate. Transfer the lower aqueous layer to a 40-ml centrifuge cone. Repeat the addition of 5 ml of 6 N NaOH, mix, allow to separate, and discard the organic layer, transferring the aqueous layer to the 40-ml cone.

Step 8. Boil the aqueous portion in the cone for 1 min to remove any remaining butyl acetate. Slowly add 10 ml of concentrated HCl plus 3 drops of 30 per cent H₂O₂. Heat until the solution becomes clear, and then boil for 1 min to drive off all the H₂O₂.

Step 9. Transfer the clear solution to an extraction funnel, add SnCl₂, dropwise, until the solution is cherry-red. Add 10 ml of butyl acetate and mix thoroughly for 5 min and allow the phases to separate. Transfer the lower aqueous portion to a clean extraction funnel, leaving the butyl acetate portion in the first funnel.

Step 10. Repeat Steps 7, 8, and 9. Finally transfer the aqueous portion to a 40-ml centrifuge cone.

Step 11. Precipitate PtS by passing H₂S gas into the clear solution for 1 min. Centrifuge for 5 min at top speed and discard the supernate. Dissolve the sulfide in a 5-ml aqua regia solution.

Step 12. Dilute the solution to 20 ml with water, add 10 drops of lanthanum carrier and concentrated NH₄OH until the solution is ammoniacal as shown by indicator paper. Centrifuge for 5 min.
Step 13. To the cone containing both residue and solution, add 10 more drops of lanthanum carrier, stir without disturbing the original precipitate, and centrifuge for 5 min. Transfer the supernate to a clean 40-ml centrifuge cone, and discard the precipitate.

Step 14. Add glacial acetic acid to the supernate until it is slightly acid. Then add 10 ml of NaOAc buffer, 2 drops each of molybdenum and palladium carriers, and 10 drops 5 per cent 8-hydroxyquinoline. Heat on the steam bath for 2 min, and centrifuge for 5 min.

Step 15. To the cone containing both residue and solution, add 2 more drops of molybdenum and palladium carriers. Stir without disturbing the original precipitate, and centrifuge for 5 min.

Step 16. Repeat Step 15.

Step 17. Transfer the supernate from Step 16 to a 100-ml beaker. Add 5 ml of concentrated HNO₃, 1 ml of concentrated H₂SO₄, and take to SO₃ fumes over a microburner to destroy all organic matter.

Step 18. Add powdered magnesium slowly until all the acid is destroyed and an excess of unreacted magnesium is seen in the beaker. Add concentrated HCl dropwise with stirring and heating until no magnesium metal remains. This will precipitate the platinum as the metal. Boil gently for 5 min to coagulate the metal. Filter the platinum metal through a weighed filter circle of Whatman 42 paper contained in a ground-off Hirsch funnel-filter chimney apparatus. Wash two times with 10 per cent HCl, then with water and acetone. Dry the precipitate in an oven for 30 min at 110 C. Cool for 20 min and weigh as platinum metal. Measure the activity of the precipitate with a thin-end-window Geiger-Müller tube and scaler.

Iridium

Introduction

Radioiridium is decontaminated from fission products by passing the oxidized solution through an anion-exchange column. Tetravalent iridium remains on the column while the fission products are washed through. The iridium is reduced and washed off the column with 1 M FeSO₄ in 10 per cent
HCl. The iridium is reoxidized and the procedure is repeated three ad­ditional times. Iridium is finally reduced to the metal, filtered, dried, and weighed. The chemical yield is about 30 per cent, with an over-all decon­tamination factor of $10^6$ from fission products.

Four hours is required for a single analysis.

Reagents

Iridium carrier: 4.6 mg iridium per ml (1 g IrCl$_3$ dissolved in water and diluted to 100 ml)

FeSO$_4$: 1 M (278 g dissolved in 1000 ml of 10 per cent HCl)

HCl: Concentrated

HCl: 1:1

HNO$_3$: Concentrated

Powdered magnesium

Anion-exchange resin: Dowex 1, obtained pretreated from Bio-Rad Laboratories

Equipment

Drying oven
Bunsen burner
100-ml beakers
Ion-exchange columns
Forceps
Assorted sizes of pipettes
Ground-off Hirsch funnel
Filter chimney
1-in. -diameter filter circles
Wash bottle

Procedure

Step 1. Pipette an aliquot of the sample into a 100-ml beaker. Add 2 ml of iridium carrier, 10 drops of concentrated HCl, and 5 drops of
concentrated HNO₃. Heat the beaker over a Bunsen burner until it is almost dry. Add 5 more drops of concentrated HNO₃, and reheat until brown NO₂ fumes are evolved.

Step 2. Transfer the solution to the top of a freshly prepared anion-exchange column, using a minimum amount of water, and wash the column with 30 ml of 10 per cent HCl. Air pressure is used to force the solution through the column at the rate of 1 drop per sec. Tetravalent iridium will remain at the top of the column. Discard the eluate.

Step 3. Reduce the tetravalent iridium to the trivalent state by eluting the column with a 1 M FeSO₄-10 per cent HCl solution. Pass the 1 M FeSO₄-10 per cent HCl through the column for 20 min at a rate of 1 drop every 7.5 sec. Collect the eluate in a clean 100-ml beaker. Wash the column by eluting with 8 ml of 1:1 HCl. Combine the washings with the main fraction. (If the color of the column remains reddish-brown, elute with more 1 M FeSO₄-10 per cent HCl.)

Step 4. Evaporate the solution to about 5 ml and add 5 drops of concentrated HNO₃. Continue evaporating the solution until almost dry, and then add 5 more drops of HNO₃ and evaporate almost to dryness.

Step 5. Repeat Steps 2 through 4 two times.

Step 6. Repeat Steps 2 and 3.

Step 7. Add powdered magnesium slowly to the final eluate. Continue adding magnesium until all the acid is destroyed and an excess of unreacted magnesium is seen in the beaker. Add concentrated HCl dropwise with stirring and heating until no magnesium metal remains. This will precipitate the iridium as the metal. Boil gently for 5 min to coagulate the metal. Filter the iridium metal through a weighed filter circle of Whatman 42 paper contained in a ground-off Hirsch funnel-filter chimney apparatus. Wash two times with 10 per cent HCl, then with water and acetone. Dry the precipitate in an oven for 30 min at 110 C. Cool for 20 min and weigh as iridium metal. Measure the activity of the precipitate with a thin-end-window Geiger-Müller tube and scaler.
Osmium

Introduction

Radio-osmium is distilled from a HNO$_3$ solution and the distillate is caught in 6 N NaOH. After precipitating the osmium as the sulfide, the distillation and sulfide precipitation are repeated. This is followed by a double distillation from HClO$_4$. The osmium is finally reduced to the metal with powdered magnesium, weighed, and counted. The chemical yield is about 30 per cent and the decontamination factor about 10$^6$.

Six hours is required for duplicate analyses.

Reagents

Osmium carrier (a): 10 mg osmium per ml (1 g OsO$_4$ dissolved in 0.1 M H$_2$SO$_4$ and diluted to 75 ml)

Molybdenum carrier: 10 mg molybdenum per ml (1.85 g (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O dissolved in water and diluted to 100 ml)

HCl: Concentrated

HClO$_4$: 60 per cent

H$_3$PO$_4$: 85 per cent

HNO$_3$: Concentrated

NaOH: 6 N

NaOH: 3 N

Magnesium metal: Powdered

H$_2$S: Gas

Crushed ice

(a) Extremely hazardous.
Apparatus

Centrifuge
40-ml glass centrifuge cones
Block for holding centrifuge cones
50-ml ruthenium still
Stirring rods
Microburner
Assorted sizes of pipettes
Wash bottle
100-ml beaker

Procedure

Step 1. Pipette an aliquot of the sample into a 50-ml distillation flask. For the receiver, use a clean 40-ml centrifuge cone containing 20 ml 3 N NaOH. Surround the centrifuge cone with crushed ice. Add 2 ml of osmium carrier and 5 ml of concentrated HNO₃ to the distilling flask, and distill for 10 min.

Step 2. Heat the distillate to boiling, and precipitate osmium sulfide by passing H₂S gas into the solution for 1 min. Allow the precipitate to settle for 5 min and centrifuge at top speed for 5 min. Discard the supernate and wash the precipitate into a clean distilling flask with a minimum amount of water.

Step 3. Repeat Steps 1 and 2 without adding any additional osmium carrier or sample.

Step 4. Replace the receiver with a clean 40-ml centrifuge cone, packed in ice, and containing 10 ml of 6 N NaOH. Add 2 ml of molybdenum carrier, 2 ml of 85 per cent H₃PO₄, and 3 ml of 60 per cent HClO₄ to the distilling flask, and distill until the appearance of HClO₄ fumes.

Step 5. Repeat Steps 2 and 4.

Step 6. Transfer the distillate to a clean 100-ml beaker and add powdered magnesium until all the acid is destroyed and an excess of unreacted magnesium is seen in the beaker. Add concentrated HCl dropwise
with stirring and heating until no magnesium metal remains. This will precipitate osmium as the metal. Boil gently for 5 min to coagulate the osmium precipitate. Filter the osmium metal through a weighed filter circle of Whatman 42 paper contained in a ground-off Hirsch funnel-filter chimney apparatus. Wash two times with 10 per cent HCl, then with water and acetone. Dry the precipitate in an oven for 30 min at 110°C. Cool for 20 min, and weigh as osmium metal. Measure the activity of the precipitate with a thin-end-window Geiger-Müller tube and scaler.

**Scandium**

**Introduction**

Radio-scandium is decontaminated by the sixfold repetition of the following cycle:

1. Lanthanum fluoride scavenging in a medium which is slightly acidic and contains a large excess of fluoride ion
2. Iron hydroxide scavenging
3. Destruction of ScF$_4$-complex by the addition of 60 per cent HClO$_4$ and precipitation of scandium as ScF$_3$.

At the end of the final cycle, ScF$_3$ is dissolved and converted to the hydroxide. Scandium is finally precipitated as K$_3$ScF$_6$, weighed, and counted. The chemical yield is about 40 per cent, with a decontamination factor of about $10^6$ from gross fission products.

Sixteen hours is required for quadruplicate analyses.

**Reagents**

Scandium carrier: 6.52 mg scandium per ml (1 g Sc$_2$O$_3$ dissolved in a minimum of concentrated HCl and diluted to 100 ml)

Iron carrier: 10 mg iron per ml (4.84 g FeCl$_3$·6H$_2$O dissolved in dilute HCl and diluted to 100 ml)

Lanthanum carrier: 10 mg lanthanum per ml (3.12 g La(NO$_3$)$_3$·6H$_2$O dissolved in water and diluted to 100 ml)
HCl: 6 M
HNO₃: Concentrated
HClO₄: 60 per cent
NH₄OH: Concentrated
H₃BO₃: Saturated aqueous solution
NH₄HF₂: Mixture of two volumes of 6 M NH₄OH and one volume of 27 M HF
NH₄NO₃: 2 per cent aqueous solution
KF: Saturated aqueous solution
Aerosol: 1 per cent aqueous solution
Methanol: Absolute

Equipment

Drying oven
Centrifuge
Block for holding centrifuge cones
Forceps
Assorted sizes of pipettes
Ground-off Hirsch funnel
Filter chimney
1-in. -diameter filter circles
40-ml glass centrifuge cones
40-ml Lusteroid centrifuge tubes
Steam bath
Stirring rods
Wash bottle
pH indicator paper

Procedure

Step 1. Pipette an aliquot of the sample into a 40-ml glass centrifuge cone and add exactly 2 ml of scandium carrier, 4 drops of lanthanum carrier and dilute to 20 ml. Add concentrated NH₄OH to precipitate scandium
hydroxide. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of 2 per cent NH₄NO₃ and discard the washings.

Step 2. Dissolve the precipitate in 10 drops 6 M HClO₄. Add 3 ml of NH₄HF₂ solution and concentrated NH₄OH until the solution is just slightly acidic to pH paper. Dilute the solution to 12 ml with water, centrifuge, transfer the supernate to a 40-ml Lusteroid tube, and discard the precipitate.

Step 3. To the solution, add 4 drops of lanthanum carrier, 5 drops of iron carrier, and 30 drops of concentrated NH₄OH. Dilute to 20 ml with water and heat on the steam bath for 2 min to coagulate the iron hydroxide precipitate. Centrifuge, transfer the supernate to a clean 40-ml Lusteroid tube and discard the precipitate.

Step 4. Add 6 ml of 60 per cent HClO₄ and 4 drops of aerosol to the supernate. Heat for 5 min on the steam bath. Allow to cool for 10 min, centrifuge, and discard the supernate.

Step 5. Dissolve the precipitate with 3 ml of NH₄HF₂ solution. Make the solution just acidic to pH paper with concentrated NH₄OH, and add 4 drops of lanthanum carrier. Dilute the solution to 12 ml with water, centrifuge, transfer the supernate to a clean 40-ml Lusteroid tube, and discard the precipitate.

Step 6. Repeat Steps 3, 4, and 5 four additional times and then repeat Steps 3 and 4.

Step 7. Dissolve the scandium fluoride precipitate in 2 ml of saturated H₃BO₃ solution and 3 ml of concentrated HNO₃. Dilute the solution to 20 ml with water and centrifuge. Transfer the supernate to a clean Lusteroid tube. Add 10 ml of concentrated NH₄OH and four drops aerosol to precipitate scandium hydroxide. Centrifuge and discard the supernate. Wash the precipitate with 20 ml of water and discard the washings.

Step 8. Dissolve the scandium hydroxide in a minimum of 6 M HCl, add 5 ml of saturated KF solution, dilute to 12 ml with water, and heat on a steam bath for 20 min. Allow to cool for 30 min. Swirl the mixture and transfer it to a 40-ml glass centrifuge cone. Wash the Lusteroid tube with 5 ml of saturated KF solution and add the washings to the glass centrifuge cone. Centrifuge and discard the supernate.
Step 9. Add 10 ml of absolute methanol to the precipitate, stir, and transfer the slurry onto a weighed filter circle contained in a ground-off Hirsch funnel-filter chimney setup. Rinse the centrifuge cone with two 10-ml portions of methanol and pour the washings through the filter. Dry the precipitate in an oven for 10 min at 110°C. Cool for 20 min and weigh as K\(_2\)ScF\(_6\). Measure the radioactivity of the precipitate with a thin-end-window Geiger-Müller tube and scaler.

Rhenium

Introduction

Radiorhenium is separated from solution by precipitation with tetr phenylarsonium chloride. The impure tetr phenylarsonium rhenate is dissolved in H\(_2\)SO\(_4\) and distilled. Radiorhenium is decontaminated by an acid sulfide precipitation and an iron hydroxide scavenger. Further purification is accomplished by reprecipitating the rhenium with tetr phenylarsonium chloride and repetition of the distillation, acid sulfide, and iron hydroxide scavenging steps. Rhenium is finally precipitated as the tetr phenylarsonium rhenate, weighed, and counted. The chemical yield is about 10 per cent, with a decontamination factor of about 10\(^6\) from gross fission products.

Eight hours is required for duplicate analyses.

Reagents

Rhenium carrier: 10 mg rhenium per ml (1.30 g Re\(_2\)O\(_7\) dissolved in water and diluted to 100 ml)

Iron carrier: 10 mg iron per ml (4.84 g FeCl\(_3\) \cdot 6H\(_2\)O dissolved in dilute HCl and diluted to 100 ml)

Tetr phenylarsonium chloride: 1 per cent solution in water

HCl: Concentrated

H\(_2\)SO\(_4\): Concentrated

NH\(_4\)OH: Concentrated

HCl: 3 N

HCl: 10 per cent
Aerosol: 1 per cent aqueous solution
H₂S: Gas
H₂O₂: 30 per cent

Equipment
- Drying oven
- Centrifuge
- 40-ml centrifuge cones
- Block for holding centrifuge cones
- Forceps
- Assorted sizes of pipettes
- Ground-off Hirsch funnel
- Filter chimney
- 1-in.-diameter filter circles
- Fisher burner
- Microburner
- Steam bath
- Ruthenium distilling flask
- 125-ml Erlenmeyer flask
- Red and blue litmus paper

Procedure

Step 1. Pipette an aliquot of the sample, free from nitrate and perchlorate ions, into a 40-ml centrifuge cone. Add exactly 1 ml of rhenium carrier and dilute to 15 ml with water. Heat the solution to boiling and slowly add 15 ml of 1 per cent tetraphenylarsonium chloride. Add 3 drops of aerosol, stir and digest on the steam bath for 5 min. Centrifuge for 5 min, and discard the supernate. Add 10 ml of 10 per cent HCl to the precipitate, stir well, allow the precipitate to settle, and centrifuge for 5 min. Discard the supernate.

Step 2. Dissolve the tetraphenylarsonium rhenate precipitate with 10 ml of concentrated H₂SO₄ and transfer the solution to a 50-ml ruthenium distilling flask. Wash the centrifuge cone with 5 ml of concentrated H₂SO₄ and add the washings to the solution in the distilling flask. Distill by heating with a Fisher burner until 2 ml of H₂SO₄ is left in the distilling flask. Catch the distillate in a 125-ml Erlenmeyer flask containing 20 ml of water and surrounded by crushed ice.
Step 3. Divide the distillate equally into two 40-ml centrifuge cones and add 5 ml of concentrated HCl to each. Bubble H₂S gas into both solutions for 2 min and then allow the rhenium sulfide precipitates to settle. Centrifuge for 5 min and discard the supernates. Add 10 ml of 3 N HCl to each centrifuge cone, stir well and combine the solutions in one cone. Allow the precipitate to settle and centrifuge for 5 min. Discard the supernate.

Step 4. Add 10 ml of concentrated NH₄OH and 10 drops of 30 per cent H₂O₂ to the rhenium sulfide precipitate. Heat over a microburner until the precipitate is dissolved and the H₂O₂ is decomposed. Dilute the solution to 15 ml with water and add concentrated HCl to the solution until a drop of solution turns blue litmus paper red. Add 10 drops of iron carrier, stir well, and add concentrated NH₄OH, dropwise, until a drop of the solution turns red litmus paper blue. Add 3 drops concentrated NH₄OH in excess, 3 drops aerosol, stir well, and allow the precipitate to settle. Centrifuge for 5 min and transfer the supernate to a clean 40-ml centrifuge cone. Discard the precipitate.

Step 5. Add 10 ml of concentrated HCl to the solution and heat the solution to boiling. Slowly add 15 ml of 1 per cent tetraphenylarsenium chloride and 3 drops of aerosol. Stir well, allow the precipitate to settle and centrifuge for 5 min. Discard the supernate.

Step 6. Repeat Steps 2 through 5.

Step 7. Add 10 ml of ice water to the final tetraphenylarsenium rhenate precipitate, stir well, and centrifuge for 5 min. Discard the supernate and repeat the washing with another 10 ml of ice water.

Step 8. To the washed precipitate add 10 ml of ice water, stir well, and transfer the precipitate onto a weighed filter circle contained in a ground-off Hirsch funnel-filter chimney setup. Rinse the centrifuge cone with ice water, and pour the washings through the filter. Wash the precipitate once with acetone, and dry it in an oven for 10 min at 110 C. Cool for 20 min and weigh as (C₆H₅)₄AsReO₄. Measure the radioactivity of the precipitate with a thin-end-window Geiger-Müller tube and scaler.
Erbium, Holmium, Thulium, Terbium, and Ytterbium

Introduction

The combined rare earths are separated as a group and purified by preforming each of the following steps twice:

1. Fluoride precipitation of lanthanum carrier in the presence of dichromate
2. Barium sulfate scavenge in dilute acid solution
3. Precipitation of the rare-earth hydroxides with NH$_4$OH
4. Passage of the rare-earth group through a small Dowex A-1 anion-exchange column in concentrated HCl
5. Zirconium phosphate scavenge in 4 N HCl.

The filtrate after the final zirconium phosphate scavenge contains the purified rare earths. The rare earths are precipitated with NH$_4$OH, dissolved in HCl, and the pH is adjusted to 3.19.

The mixed rare earths are passed through a heated cation-exchange column and are eluted with an ammonium lactate eluting agent whose pH is changing at a constant rate. Fractions are collected every 3 min and are identified for a specific rare-earth activity either by decay characteristics or by use of a gamma-ray spectrometer. The chemical yield is about 90 per cent, with an over-all decontamination factor of at least $10^5$ from fission products.

Sixteen hours is required for purifying and separating erbium, holmium, thulium, terbium, and ytterbium.

Reagents

- Lanthanum carrier: 10 mg lanthanum per ml (3.12 g La(NO$_3$)$_3$ dissolved in water and diluted to 100 ml)
- Barium carrier: 10 mg barium per ml (1.78 g BaCl$_2$ dissolved in hot water and diluted to 100 ml)
Zirconium carrier: 10 mg zirconium per ml (3.53 g ZrO\(_2\cdot8\)H\(_2\)O dissolved in dilute HCl and diluted to 100 ml)

Cesium carrier: 10 mg cesium per ml (1.27 g CsCl dissolved in water and diluted to 100 ml)

Strontium carrier: 10 mg strontium per ml (3.04 g SrCl\(_2\cdot6\)H\(_2\)O dissolved in hot water and diluted to 100 ml)

Molybdenum carrier: 10 mg molybdenum per ml (1.85 g (NH\(_4\))\(_6\)Mo\(_7\)O\(_24\)\cdot4\)H\(_2\)O dissolved in water and diluted to 100 ml)

Ruthenium carrier: 4.88 mg ruthenium per ml (1 g RuCl\(_3\) dissolved in water and diluted to 100 ml)

Rhodium carrier: 3.56 mg rhodium per ml (1 g Rh(NO\(_3\))\(_3\) dissolved in water and diluted to 100 ml)

Palladium carrier: 6.02 mg palladium per ml (1 g PdCl\(_2\) dissolved in water and diluted to 100 ml)

Tin carrier: 10 mg tin per ml (2.96 g SnCl\(_4\cdot5\)H\(_2\)O dissolved in 35 ml concentrated HCl and diluted to 100 ml with water)

Tellurium carrier: 10 mg tellurium per ml (2.14 g Na\(_2\)TeO\(_4\cdot2\)H\(_2\)O dissolved in hot dilute HNO\(_3\) and diluted to 100 ml)

Antimony carrier: 10 mg antimony per ml (1.88 g SbCl\(_3\) dissolved in dilute HCl and diluted to 100 ml)

HCl: Concentrated
HCl: 6 N
HF: 13 N
K\(_2\)Cr\(_2\)O\(_7\): Saturated solution
Boric acid: Saturated solution
H\(_2\)SO\(_4\): 10 per cent solution
Aerosol: 1 per cent eolation

\( \text{NH}_4\text{OH} \): Concentrated

\( \text{H}_2\text{SO}_4 \): 16 N

\( (\text{NH}_4)_2\text{HPO}_4 \): 10 per cent solution

Anion-exchange resin: 200-400 mesh

Cation-exchange resin: Dowex-50 "Minus" 400 mesh, 12X

Lactic acid: 85 per cent

pH 3.19, 1 M lactate: (83.7 ml of 85 per cent lactic acid plus 1 g phenol diluted to 1 liter with water and adjusted to pH 3.19 with concentrated \( \text{NH}_4\text{OH} \))

pH 7, 1 M lactate: (83.7 ml of 85 per cent lactic acid plus 1 g phenol diluted to 1 liter with water and adjusted to pH 7.00 with concentrated \( \text{NH}_4\text{OH} \))

\( \text{AgNO}_3 \): 1 M

\( \text{NH}_4\text{CNS} \): 6 M

Ammonium lactate: 1 M

**Apparatus**

Centrifuge

40-ml centrifuge cones

Block for holding centrifuge cones

Culture tubes

Forceps

Assorted sizes of pipettes

Platinum stirring rod

Microburner

Wash bottle

Ion-exchange column

Pressure regulator

Electrothermal heating tape

pH meter

Variac variable transformer

Magnetic stirrer
The ion-exchange-column apparatus and associated equipment is described in the article by Nervic*.

Procedure

Step 1. Pipette an aliquot of the sample into a 40-ml centrifuge cone. Add 5 mg of lanthanum carrier, 10 mg each of barium and zirconium carriers, plus 1 mg each of antimony, cesium, molybdenum, rhodium, strontium, tellurium, and tin carriers. Add 1.5 ml concentrated HCl and saturated K₂Cr₂O₇ dropwise until the solution is yellow, and add 1 mg each of palladium and ruthenium carriers. Dilute the solution to 20 ml with water and add 25 drops of 13 N HF. Stir the solution well with a platinum stirring rod and allow to settle for 5 min. Centrifuge at top speed for 5 min and discard the supernate.

Step 2. Add 1 ml of saturated boric acid to the lanthanum fluoride residue and heat over a microburner until the precipitate is dissolved. Add 1.5 ml of concentrated HCl and reheat the solution. Dilute the solution to 20 ml with water and add saturated K₂Cr₂O₇ dropwise until the solution is yellow. Add 25 drops of 13 N HF, stir well and allow the precipitate to settle for 5 min. Centrifuge at top speed for 5 min and discard the supernate.

Step 3. Add 1 ml of saturated boric acid to the residue, and heat over a microburner until in solution. Add 5 drops of concentrated HCl and bring the solution to a boil. Dilute the solution to 20 ml with water and add 1 ml of barium carrier. Stir the solution and add 2 ml of 10 per cent H₂SO₄ and 4 drops of 1 per cent aerosol. Stir the solution and allow the precipitate to settle for 5 min. Centrifuge at top speed for 5 min.

Step 4. To the centrifuge the cone above, containing the barium sulfate precipitate and the supernate liquor, add an additional 1 ml of barium carrier and 4 drops of 1 per cent aerosol. Stir the solution without disturbing the original precipitate. Allow the precipitate to settle for 5 min and centrifuge, at top speed, for 5 min. Transfer the supernate to a clean 40-ml centrifuge cone and discard the precipitate.

*Reference (14) at end of text.
Step 5. Add concentrated NH₄OH dropwise to the solution until lanthanum hydroxide precipitates and then add 5 drops NH₄OH excess. Stir well and allow the precipitate to settle for 5 min. Centrifuge at top speed for 5 min and discard the supernate.

Step 6. Dissolve the residue by slowly adding concentrated HCl, about 4 drops, dilute the solution to 20 ml with water and repeat Step 5.

Step 7. Dissolve the residue by slowly adding concentrated HCl, about 4 drops. Transfer the solution to the top of a small anion-exchange column and elute with 5 ml of 6 N HCl. Catch the eluate in a clean 40-ml centrifuge cone.

Step 8. Dilute the eluate to 20 ml with water and repeat Step 5.

Step 9. Dissolve the residue with about 4 drops of concentrated HCl and dilute the solution to 15 ml with water. Add 4 ml of 18 N H₂SO₄ and 1 ml of zirconium carrier. Stir the solution and add 1 ml of 10 per cent (NH₄)₂HPO₄. Stir the solution and allow the precipitate to settle for 5 min. Centrifuge at top speed for 5 min.

Step 10. To the centrifuge cone above, containing both residue and supernate, add an additional 1 ml of zirconium carrier, and stir without disturbing the original precipitate. Allow the precipitate to settle for 5 min and centrifuge at top speed for 5 min. Transfer the supernate to a clean 40-ml centrifuge cone.

Step 11. Repeat Step 5 and then dissolve the purified rare-earth hydroxide precipitate with about 4 drops of concentrated HCl.

Step 12. Transfer the solution to a clean culture tube and add a small amount of prepared cation-exchange resin. Stir well and allow the resin to settle for 5 min. Centrifuge at top speed for 5 min and decant the supernate.

*See procedure for preparing the cation-exchange resin and loading the ion-exchange column.
Step 13. Add 3 ml of boiling water to the resin, stir well, and allow to settle for 2 min. Centrifuge at top speed for 2 min and transfer the washings to a clean culture tube. Test for the presence of chloride ions by adding 1 M AgNO₃ to the washings contained in a clean culture tube. A white silver chloride precipitate indicates the presence of chloride ions. Repeat with additional 3-ml portions of hot water until all chloride ions are removed.

Step 14. Transfer the resin containing the rare-earth activities to the top of the hot-resin bed and pass pH 3.19, 1 M lactate through the column. Adjust the flow of the solution through the column to about 3 drops per min. Continue to elute the column with pH 3.19, 1 M lactate for 6 min.

Step 15. Start the pH 7, 1 M lactate dropping into the lower reservoir at a rate of 3 drops per min. Change the collecting tube every 3 min. The desired rare-earth activities (holmium, terbium, thulium, and ytterbium) are eluted in approximately 4 hr.

Step 16. Identify the active fractions for specific rare earths by taking a gamma- or beta-decay curve or gamma-spectrometer scans.

Procedure for Preparing the Resin and Loading the Ion-Exchange Column

Step 1. Grade the 12 per cent cross-linked Dowex 50 cation-exchange resin to obtain the portion which settles between 1.0 and 1.5 cm per min in distilled water.

Step 2. Wash the resin into a 40-ml centrifuge cone and centrifuge at top speed for 2 min. Discard the supernate.

Step 3. Add 20 ml of 6 M NH₄CNS to the resin and stir well. Centrifuge at top speed for 2 min and discard the supernate. Continue washing with 6 M NH₄CNS until the red ferric thiocyanate color is no longer visible.

Step 4. Add 20 ml of distilled water to the resin, stir well, and centrifuge at top speed for 2 min. Discard the supernate.
Step 5. Add 20 ml 6 N HCl to the resin, stir well, and centrifuge at top speed for 2 min. Discard the supernate.


Step 7. Add 20 ml 1 M ammonium lactate to the resin, stir well, and centrifuge at top speed for 2 min. Discard the supernate.

Step 8. Add 20 ml of water to the resin and transfer the mixture to a 250-ml beaker. Boil the mixture to remove any dissolved gases and transfer to the column unit while hot.

Step 9. Assemble the ion-exchange apparatus as shown in the diagram in the article by Nervic* and heat the column to 90 C. Pass approximately 100 ml of pH 3.19, 1 M lactate through the column before adding the resin containing the combined rare earths.

Gallium

Introduction

Radiogallium is initially extracted with di-isopropyl ether from a 7 N HCl medium. Molybdenum is separated by an α-bensoinoxime precipitation which is followed by an acid sulfide scavenger and a series of iron hydroxide and barium carbonate scavengers. After extracting again with HCl and di-isopropyl ether, the radiogallium is re-extracted into water and precipitated with 8-hydroxyquinoline. The radiogallium is weighed as gallium-8 hydroxyquinolate and counted. The chemical yield is about 50 per cent, with a decontamination factor of about 10^5 from gross fission products.

Four hours is required for duplicate analyses.

Reagents

Gallium carrier: 10 mg gallium per ml (1 g gallium metal dissolved in concentrated HCl and diluted to 100 ml)

*Reference (14) at end of text.
Zirconium carrier: 10 mg zirconium per ml (2.76 g ZnCl₂ dissolved in water and diluted to 100 ml)

Molybdenum carrier: 10 mg molybdenum per ml (1.85 g (NH₄)₆Mo₇O₂₄·4H₂O dissolved in water and diluted to 100 ml)

Bismuth carrier: 10 mg bismuth per ml (1.51 g BiCl₃ dissolved in water and diluted to 100 ml)

Iron carrier: 10 mg iron per ml (4.85 g FeCl₃·6H₂O dissolved in dilute HCl and diluted to 100 ml)

Strontium carrier: 10 mg strontium per ml (3.04 g SrCl₂·6H₂O dissolved in warm water and diluted to 100 ml)

Barium carrier: 10 mg barium per ml (1.78 g BaCl₂·2H₂O dissolved in warm water and diluted to 100 ml)

Di-isopropyl ether: Reagent grade

HCl: Concentrated

HCl: 7 N

KBrO₃: Saturated solution

α-Benzoinoxime: 2 per cent solution in ethyl alcohol

Aerosol: 0.1 per cent aqueous solution

KI: 2 per cent solution

H₂S: Gas

NaOH: 5 N

K₂CO₃: 1 M

8-Hydroxyquinoline: 5 per cent (5 g 8-hydroxyquinoline dissolved in 100 ml of 2 M glacial acetic acid)

NH₄C₂H₃O₂: 6 M
**Equipment**

Drying oven  
Centrifuge  
Block for holding centrifuge cones  
Forceps  
Assorted sizes of pipettes  
Ground-off Hirsch funnel  
Filter chimney  
1-in. -diameter filter circlets  
50-ml funnels  
Assorted sizes of graduates  
Stirring rods  
Wash bottle  
Ice bath  
Electric stirrer  
Lead acetate indicator paper  
Microburner

**Procedure**

**Step 1.** Pipette an aliquot of the sample into a 50-ml extraction funnel. Add exactly 2 ml of gallium carrier and 2 ml of zinc carrier. Dilute to 8 ml with water and add 12 ml of concentrated HCl and 20 ml of di-isopropyl ether. Mix thoroughly for 5 min with an electric stirrer and allow the phases to separate. Discard the lower aqueous layer.

**Step 2.** Add 10 ml of 7 N HCl and 5 drops of a saturated KBrO₃ solution to the ether layer. Mix thoroughly for 5 min with an electric stirrer and allow the layers to separate. Discard the lower aqueous layer. Repeat the above procedure two times with 10-ml portions of HCl, omitting the saturated KBrO₃.

**Step 3.** Add 5 ml of water to the ether layer and mix thoroughly for 5 min with an electric stirrer. Allow the layers to separate and collect the lower aqueous layer in a 40-ml centrifuge cone.

**Step 4.** Repeat Step 3.
Step 5. Dilute the combined aqueous extracts to 20 ml with water and add 10 drops of concentrated HCl, 10 drops of molybdenum carrier, 2 ml of 2 per cent α-benzenoxime and 4 drops of aerosol. Stir well, and allow the precipitate to settle. Centrifuge for 5 min, transfer the supernate to a clean 40-ml centrifuge cone, and discard the precipitate.

Step 6. To the solution add 10 drops of bismuth carrier and heat to near boiling with a microburner. Add 1 ml of 2 per cent KI solution and bubble H₂S gas into the solution for 2 min. Allow the precipitate to settle, and centrifuge for 5 min. Transfer the supernate to a clean 40-ml centrifuge cone, and discard the precipitate.

Step 7. Heat the solution with a microburner until lead acetate paper does not turn black when held at the top of the cone. Add 10 drops of iron carrier and 4 ml of 5 N NaOH. Stir, allow the precipitate to settle, and centrifuge for 5 min. Transfer the supernate to a clean 40-ml centrifuge cone and discard the precipitate.

Step 8. Add 5 drops of barium carrier, 5 drops of strontium carrier, 2 ml of 1 M K₂CO₃ solution, and 4 drops of aerosol to the solution. Stir, allow the precipitate to settle, and centrifuge for 5 min. Transfer the supernate to a clean 40-ml centrifuge cone and discard the precipitate.

Step 9. Add concentrated HCl to the solution until a drop of solutions turns universal indicator paper yellow. Heat the solution slightly with a microburner, and readjust the acidity with concentrated HCl. Add 4 drops of aerosol and cool in an ice bath for 10 min to aid coagulation of the gallium hydroxide precipitate. Centrifuge for 5 min and discard the supernate. Dissolve the gallium hydroxide with 10 ml of 7 N HCl, and transfer the solution to a 50-ml extraction funnel.

Step 10. Add 20 ml of di-isopropyl ether to the solution, and mix thoroughly for 5 min with an electric stirrer. Allow the phases to separate, and discard the lower aqueous phase. Wash the ether layer three times with 10-ml portions of 7 N HCl, discarding the aqueous layer after each washing.

Step 11. Add 5 ml of water to the ether layer, mix thoroughly for 5 min and allow the phases to separate. Draw off the lower aqueous phase into a clean extraction funnel. Repeat with two additional 5-ml portions of water, and combine the aqueous layers.
Step 12. Add 15 ml of concentrated HCl to the aqueous layer, and repeat Steps 10 and 11.

Step 13. Extract the ether layer with an additional 10 ml of water, and combine the aqueous layers in a clean 40-ml centrifuge cone.

Step 14. Heat the solution with a microburner to drive off any entrapped ether. Add 3 ml of 5 per cent 8-hydroxyquinoline and 6 M NH₄C₂H₃O₂ dropwise until a permanent yellow precipitate forms. Add 1 ml excess of 6 M NH₄C₂H₃O₂, 4 drops of aerosol, and stir well. Transfer the precipitate onto a weighed filter circle contained in a ground-off Hirsch funnel-filter chimney setup. Rinse the centrifuge cone with two 10-ml portions of water and pour the washings through the filter. Wash the precipitate once with acetone and dry it in an oven for 10 min at 110 °C. Cool for 20 min, and weigh as gallium 8-hydroxyquinolate. Measure the radioactivity of the precipitate with a thin-end-window Geiger-Müller tube and scaler.