CHAPTER 10

REACTOR COOLANTS

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The coolants used for nuclear reactors consist of gaseous coolants such as helium and carbon dioxide; liquid coolants, such as water and deuterium; and liquified coolants, such as sodium, sodium–potassium (NaK) alloys, and polyphenyls. Analytical control of the feed coolants, as well as of the circuit coolants, is important, both from the standpoint of the possible presence of high absorption-cross-section impurities and the radiation stability and chemical compatability of these coolants with other materials in the reactor. The presence of impurities in the coolant that can be activated by capture of thermal neutrons to produce gamma activity are of special interest to the analyst.

Nuclear Coolant Reactions: In a water-cooled reactor the primary coolant is exposed to a high neutron flux as it is circulated. The H^2, O^{16}, O^{17}, and O^{18} nuclides in the water interact with the neutrons to form unstable nuclides that emit beta, gamma, or neutron radiation. The most important recations are $O^{16}(n,p)N^{16}$, $O^{16}(n,\alpha)N^{13}$, $O^{17}(n,p)N^{17}$, $O^{18}(p,n)F^{18}$, $O^{18}(n,\gamma)O^{19}$, and $H^2(n,\gamma)H^3$.

Nitrogen–16 has a 7.35-sec half life and emits beta particles having energies of 3.32, 4.39, and 10.40 Mev and gamma rays of 6.13 and 7.10 Mev. This nuclide has a great effect on reactor-shielding requirements because its radiations are the most intense and penetrating in the system. Nitrogen–17 has a 4.14-sec half life and emits a 3.7-Mev beta particle and a 1-Mev neutron. Its activity and that of O^{19}, which has a 29.4-sec half life, are also important in defining shielding requirements. Tritium has a 12.4-year half life and emits a very weak beta particle. This particle may be absorbed directly through the skin and exchanged with body fluids to form tritiated water. The concentration of the other radionuclides (10-min N^{13} and 1.9-hr F^{18}) limit accessibility to the reactor compartment shortly after shutdown.

The coolant in a gas-cooled reactor is usually helium, carbon dioxide, or nitrogen. The activation of helium is small because only the He^3 isotope (0.00013 per cent abundant in natural helium) is involved: $He^3(n,p)H^3$. In carbon dioxide-cooled reactors, the oxygen undergoes the same reactions as the oxygen in water. In addition, carbon undergoes the reactions $C^{12}(n,\gamma)C^{13}$ and $C^{13}(n,\gamma)C^{14}$. Car-

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bon–13 is stable and carbon–14 is a low-energy beta emitter with a 5600-year half life. Therefore no extra shielding is required for these isotopes.

Primary Coolant Impurities: Although purified to the practical engineering limit for plant usage, primary coolant water contains up to 0.5 ppm of impurities consisting mainly of iron, silica, and sodium. The most important nuclear reaction involved is $Na^{23}(n,\gamma)Na^{24}$. Sodium–24 has a 15-hr half life and is a beta–gamma emitter. Its activity limits accessibility to the system shortly after shutdown.

Make-up water, although deaerated, conveys small amounts of air that consists of 78 per cent nitrogen, 21 per cent oxygen, and 0.9 per cent argon with traces of the other noble gases into the primary system. The oxygen nuclear reactions are discussed above for water. The major reaction in make-up water is $N^{14}(n,p)C^{14}$. The predominant activated gaseous impurity is Ar^{41} produced by the reaction $Ar^{40}(n,\gamma)Ar^{41}$. Argon–41 is a 1.8-hr beta–gamma emitter and is a radiological health hazard if it escapes into the reactor-compartment air. The most probable escape of this isotope would be primary-to-secondary leakage into the steam system.

The impurities in high-purity helium used in gas-cooled reactors are about 0.006 per cent nitrogen, 0.002 per cent oxygen, 0.005 per cent water, and 0.005 per cent hydrogen. Nuclear reactions involving these elements are discussed above. A carbon dioxide coolant contains, in general, impurities of nitrogen, oxygen, and argon. A nitrogen coolant contains small amounts of oxygen and hydrogen, which may undergo the nuclear reactions mentioned above for these nuclides.

Corrosion: In a water-cooled reactor, corrosion occurs on the surfaces of the primary system. Corrosion products flake off from the metal and are transported through the system. They are generally insoluble and circulate as particulate "crud" through the system. Some cruds, however, exhibit a phase distribution between the soluble and insoluble form. Proper control of the water chemistry may promote the formation of a smooth resistant oxide coating on the metals that will minimize further corrosion.

The activation of corrosion products in the coolant may occur by one or more of three processes:

1. Activation of corrosion products circulated through the core by the coolant flow.
2. Activation of corrosion products formed in the reactor core and redeposited elsewhere in the system.
3. Deposition of corrosion products from elsewhere in the system within the core area, followed by activation and subsequent transport out of the core area.

Even though aluminum or zirconium is present as cladding of fuel elements, most of the activated corrosion products are formed from stainless steel in the primary system. Most activated corrosion products are formed by (n,γ) reactions with a stable isotopic form of the element, e.g., $Mn^{55}(n,\gamma)Mn^{56}$ and $Co^{59}(n,\gamma)Co^{60}$. Other nuclear reactions, such as $Ni^{58}(n, p)Co^{58}$ and $Al^{27}(n, \alpha)Na^{24}$, also may occur.

Because of the deposition phenomenon, complete purification of the primary system with, for example, ion-exchange resins is limited, and the system walls become increasingly contaminated with long-lived activities as operation time increases. Ready access to system components for maintenance becomes difficult because of the radiation. The major long-lived activated corrosion products include 45-day Fe^{59}, 5.2-year Co^{60}, 71-day Co^{58}, 291-day Mn^{54}, 28-day Cr^{51}, 65-day Zr^{95} (for reactors with zirconium components), 45-day Hf^{181} (from hafnium impurities in zirconium or from control rods), and 13-year Eu^{152} and 16-year Eu^{154} (from europium control rods). Activities contributing to radiation hazards at shorter intervals after shutdown include 2.6-hr Mn^{56}, 13-hr Cu^{64}, 15-hr Na^{24} (from aluminum), 24-hr W^{187}, and 9.3-hr Eu^{152} (from europium control rods). Carbon dioxide, nitrogen, and helium coolants used in gas-cooled reactors cause little or no corrosion to the primary system.

Erosion: Erosion is differentiated from corrosion in that erosion is the mechanical disintegration of the interior metal surfaces of the system, whereas corrosion is the chemical disintegration of these surfaces. The activated products from erosion are of the same type as the activated products from corrosion, but they are formed from abrasion in both water- and gas-cooled reactors.

Fission Products: Fission fragments have a kinetic recoil energy that enables them to penetrate cladding 0.1 to 1 mil thick. If the cladding (normally several mils thick) should be reduced to this range by various factors, fission products may enter the coolant. Fission products may also diffuse through the cladding into the coolant. Gaseous nuclides have the highest diffusion rates. Because a finite amount of time is involved in the diffusion of gaseous fission products through the cladding, only fairly long half-lived (of the order of days) products and their daughters escape into the coolant by this mechanism. These two modes bring only relatively low amounts of fission products into the reactor coolant and are of minor concern under normal operating conditions.

The rupture of a fuel element or a cladding defect releases large amounts of fission products into the coolant and may increase activities to a significant level. It is imperative that such occurrences be discovered as soon as possible. Contamination of the surface of a fuel element with even a few parts per million of fissionable nuclides may also cause relatively large amounts of fission products in the coolant. Stringent controls must be taken during fuel fabrication to keep fissionable-nuclide contamination to a minimum. Gross iodine activity indicates total fission products being released since 8.05-day I^{131} is obtained from the products of the fission of U^{235}.

Fission-product activity in the primary coolant (water or gas) should be kept as low as possible, not only to minimize radiation levels, but also to minimize waste-disposal problems caused by long-lived fission products such as Sr^{90}.

Primary-system Debris: The minor amounts of debris that accumulate in the primary system before start-up, after refueling, and when primary-system components are replaced, may be circulated through the system and activated. Cleanliness during fabrication and reactor assembly can prevent most of this debris from entering the system.

Coolant Additives: The materials added to the coolant to maintain proper water conditions may become activated. An example is the activation of the lithium hydroxide that is used in coolants for pH control. Tritium may be formed by the reaction $Li^6(n,\alpha)H^3$. In a gas-cooled reactor, impurities in the moderator may enter the coolant by corrosion or erosion and become activated.

10–1 WATER-COOLED REACTORS

By C. J. Rodden

10–1.1 Introduction

Reactors may be cooled with water either by using a once-through system such as is employed in the Hanford reactors or by recirculation of the water as is done in pressurized-water reactors. It is beyond the scope of this book to consider problems relating to water treatment, corrosion, and materials selection. There have been engineering evaluation studies considering these problems.[1] The problems of the once-through coolant are fewer than those of the recirculated coolants.

Design specifications for water purity in the primary systems of nuclear power reactor plants are generally more stringent than those for conventional plants operating at comparable temperatures and pressures because of the problems associated with carrying highly radioactive materials throughout the plant.

The methods of analysis for the initial cooling water are not discussed. The analysis of water has been considered in various reviews that give the necessary references to manuals, books, and journal articles.[2, 3] Standard methods for the examination of water are given in detail in an American Public Health Association publication.[4] In recirculating-water reactors, the greatest number of analyses by far are the so-called "conventional determinations" of pH, chloride content, conductivity, lithium hydroxide content (if this material is used), and isotopic purity (for reactors cooled by heavy water). These analyses are made routinely and are essential for adequate coolant control. Many of the measurements are made automatically. Analyses dealing with radioactive contamination are done only at intervals or after a rupture or similar incident. Indicative of this type of analyses are those performed for reactors such as the ones for the Army nuclear-power plants (SM-1, SM-1A, PM-2A, and PM-3A)[4] and the Shippingport Atomic Power Station.

A description of the Shippingport Pressurized Water Reactor is given in the book of the same title published for the Atoms for Peace Conference in Geneva in 1958 by the Addison-Wesley Publishing Company, Inc., Reading, Mass. Chapter 8 of this book discusses cooling systems.

Examples of the waters used in reactors which are of interest are the primary-system charging water, primary coolant water, canal water, component-cooling water, and neutron-shield-tank water from a pressurized-water reactor. Although turbine and service waters are analyzed, they will not be considered here.

The *charging water* for the primary system is demineralized, deaerated water that is stored under a steam blanket to exclude air. It should contain less than 0.14 ppm of oxygen and 0.1 ppm of chloride and should have a conductivity not exceeding 1.5 μmho/cm and a pH between 6.0 and 8.0 at 25°C.

The *primary-coolant water* is charging water treated with lithium hydroxide to give a pH of 9.5 to 10.5. This pH is maintained by a lithium hydroxide resin in the purification demineralizer. The oxygen concentration is maintained below 0.14 ppm and the hydrogen concentration between 25 to 35 ml per kilogram of water. Analyses are made for conductance, pH, lithium, hydrogen, and oxygen. The 15-min and 120-hr activity measurements are also made. The demineralizer inlet and outlet are analyzed for Kr^{88}, Cs^{138}, Br^{84} and I^{131}. In addition, at one stage or another, Cs^{136}, Cs^{137}, I^{132}, I^{133}, and H^3 are determined. Also the primary-coolant gas activity and Xe^{133} are determined.

The *canal-water* system is initially filled with demineralized non-deaerated water. Make-up water, taken from the primary-coolant charging system, should have a pH between 6 and 8 and should contain less than 2 ppm of solids as SiO_2. The conductivity should not exceed 5 μmho/cm. The radioactivity of the influent and effluent of the demineralizer is monitored.

The initial fill and subsequent makeup for the *component-cooling-water* system and the *neutron-shield-tank water* is made with the primary-system charging water. Potassium chromate is added as a corrosion inhibitor and maintained at a concentration of 500 to 1000 ppm as chromate. Potassium hydroxide is added to adjust the pH to a range of 8.3 to 9.5. Analyses are made for pH, chromate, gross iodine, K^{42}, and gross gamma activity. Continual measurements and recordings are made of pH, electrical conductivity, dissolved oxygen, soluble radioactivity, and insoluble-crud radioactivity.

10–1.2 Analytical Control of Coolant Water

The reliability of the instruments that continually measure and record the concentration of the various constituents given above is checked by taking water samples and analyzing them in the laboratory. Since hydrazine is used to control the oxygen content, it, in addition to hydrogen, is determined. Crud samples from the demineralized influent and effluent are analyzed for iron and total weight of crud. The major radionuclides in the crud include Fe^{59}, Co^{58}, Co^{60}, Ta^{182}, Ta^{183}, Zr^{95}, Hf^{175}, Hf^{181}, Nb^{95}, Mn^{54}, and Mn^{56}. Resin beds are analyzed for fission products and major induced activities. The fission products include Cs^{138}, Cs^{136}, Cs^{137}, I^{131}, Sr^{89}, and Sr^{90}; the major induced activities are Fe^{59}, Co^{58}, Co^{60}, Ta^{182}, Ta^{183}, Hf^{175}, Hf^{181}, Zr^{95}, Cr^{51}, Mn^{54}, and Nb^{95}. In addition, determinations of a number of other radioactive elements that are present are made when required.

A list of the radiochemical determinations that may be made is given in Table 10.1; the half-lives of various nuclides and the types of radiation they emit are given in Table 10.2; and the carriers employed in the radiochemical separations are given in Table 10.3.

Table 10.1—RADIOCHEMICAL DETERMINATIONS

In primary coolant	In crud	In resin bed
Br^{84}	Ba^{140}	Co^{58}
Cs^{136}	Ce^{137}	Co^{60}
Cs^{137}	Ce^{141}	Cr^{51}
Cs^{138}	Ce^{144}	Cs^{136}
Cs^{139}	Co^{58}	Cs^{137}
F^{18}	Co^{60}	Cs^{138}
I^{131}	Fe^{59}	Fe^{59}
I^{132}	Hf^{175}	Hf^{175}
I^{133}	Hf^{181}	Hf^{181}
Kr^{88}	Mn^{54}	I^{131}
N^{13}	Mn^{56}	Mn^{54}
Na^{24}	Nb^{95}	Nb^{95}
H^{3}	Sr^{89}	Sr^{89}
Xe^{133}	Sr^{90}	Sr^{90}
15-min gross gamma activity	Ta^{182}	Ta^{182}
120-hr gross gamma activity	Ta^{183}	Ta^{183}
	Y^{90}	Zr^{95}
	Zr^{95}	

Table 10.2—NUCLIDES*

Nuclide	Half life	Energies, Mev	
		Beta†	Gamma
Ar^{41}	1.83 hr.	1.20 (99%)	1.30 (99%).
Ba^{139}	85.0 min.	2.22 (66%), 2.38 (15%), 0.82 (19%).	1.43.
Ba^{140}	12.8 day	1.02 (60%), 0.49 (25%), 0.60 (10%), 0.89 (5%).	0.53 (25), 0.03 (15), 0.16 (7), 0.42 (5).
Br^{82}	35.9 hr.	0.44	0.77 (10), 0.62 (5), 0.55 (4).
Br^{83}	2.33 hr.	0.94	0.050 (20%).
Br^{84}	31.8 min.	4.21 (3)	0.87 (10), 3.93 (2.5).
Ce^{141}	32.5 day	0.435 (70%), 0.58 (30%)	
Ce^{143}	33 hr.	1.12 (40), 1.40 (37), 0.50 (12).	0.057 (vs), 0.294(s), 0.668(m), 0.351(m).
Ce^{144}	290 day	0.304 (72%), 0.17 (22%), 0.223 (3%).	0.134 (10), 0.08 (5).
Cs^{134}	2.3 year	0.65 (70%)	0.605, 0.797.
Cs^{136}	13.0 day	0 34 (93%), 0.657 (7%)	0.067, 0.153, 0.162, 0.265. 0.335, 0.822, 1.04, 1.24, 1.41, 2.35, 2.49.
Cs^{137}	30 year	0.523 (92%), 1.19 (8%)	
Cs^{138}	32 min.	3.4	1.43 (10), 0.463 (3.6), 1.01 (3.4), 2.21 (2.5), 2.63 (1.2), 0.55 (1.1).
Cs^{139}	9.5 min.	3.17	
Cr^{51}	27.8 day	ϵ	0.323 (10%).
Co^{58}	72.0 day	ϵ; β^+0.475	1.62 (2%), 0.81 (98%.)
Co^{60}	5.27 year	0.309 (100%)	1.173 (100%).
Eu^{152}	13 year	ϵ	0.344, 0.244, 0.72, 0.96, 1.09.
Eu^{154}	16 year	145 (95%), ϵ	0.123, 0.78, 1.12, 1.4.
F^{18}	1.87 hr.	β^+0.649	
Hf^{175}	70 day	ϵ	0.343 (10).
Hf^{181}	46 day	0.410	
I^{131}	8.05 day	0.608 (87%), 0.335 (9%), 0.25 (3%).	0.364 (81%), 0.637 (9%), 0.284 (6.3%), 0.72 (3%).
I^{132}	2.33 hr.	2.12 (18%), 1.5 (24%), 1.2 (23%).	0.67 (10), 0.78 (8), 0.528 (2), 0.96 (2).
I^{133}	20.8 hr.	1.4 (94%), 0.5 (6%)	0.53 (94%), 0.85 (5%).
Fe^{59}	45.1 day	0.462 (54%), 0.27 (46%)	1.10 (57%), 1.29 (43%).
Kr^{88}	2.8 hr.	0.52 (68%), 2.8 (20%), 0.9 (12%).	0.028 (10), 0.191 (10), 2.4 (10), 0.85 (6).
Mo^{99}	67.0 hr.	0.45 (13%), 1.23 (87%)	0.74, 0.18.
Nb^{95}	35 day	0.162	0.764.
N^{13}	9.98 min.	β^+1.19	
K^{42}	12.47 hr.	3.54 (82%), 1.98 (18%)	1.53 (11%).

See footnotes at end of table.

Table 10.2—NUCLIDES—Continued

Nuclide	Half life	Energies, Mev	
		Beta†	Gamma
Pr^{144}	17.5 min	2.98 (97%), 0.8 (2%)	0.695 (10), 2.18 (5).
Rb^{88}	17.8 min	5.3 (75%), 3.6 (15%), 2.5 (10%).	1.85 (10), 0.91 (6), 2.7 (1).
Na^{24}	15.0 hr	1.39 (100%)	1.368 (10), 2.754 (10).
Sr^{89}	50.4 day	1.46	
Sr^{90}	28 year	0.543	
Ta^{182}	112 day	0.51	0.0677 (13), 1.122 (12).
Ta^{183}	5.2 day	0.615 (95%)	0.246 (10), 0.354 (4), 0.1079 (3.5).
Te^{132}	77.7 hr	0.22	0.231.
Tc^{99}	6.04 hr		0.14 (99%).
Xe^{133}	5.27 day	0.345	0.081.
Y^{90}	64.4 hr	2.28 (100%)	1.75.
Zr^{95}	63.3 day	0.364 (54%), 0.40 (43%), 0.88 (2%).	0.754 (54%), 0.722 (43%).
Zr^{97}	17.0 hr	1.91	0.66 (10), 0.75 (9).

*From William H Sullivan, *Trilinear Chart of Nuclides*, U.S. Government Printing Office, Washington, D.C.

†β^- except as indicated by β^+ in column.

(a) *Determinations in Coolant Analysis.* The specific conductance of coolant waters is determined by standard methods[4] as a check on recording instruments. The pH of the various coolant waters is also determined to check recording instruments. Suspended solids in canal water is measured by a turbidimeter. Chromate in component cooling water is determined by titration with 0.025N sodium thiosulfate after the water is acidified and potassium iodide is added. Chloride is determined by titrating with 0.0014N mercuric nitrate using diphenylcarbazone–bromphenol blue indicator. Adjustment of the pH to 3.25 to 3.35 is necessary. Hydrogen is determined by the Blacet–Leighton procedure[5] using a portion of the gas as extracted in the determination of total gas (see below). Iron is determined by a spectrophotometric method using *o*-phenanthroline. Lithium is determined by a flame spectrophotometric method. Hydrazine is determined by a spectrophotometric method using *p*-dimethylaminebenzaldehyde in an acid solution. Dissolved oxygen is determined by the Winkler procedure[4] in which the permanganate, formed by treating the coolant water with manganese hydroxide, reacts with iodide. The iodine produced is titrated with sodium thiosulfate.

The solution of the crud and resin samples are discussed under the radiochemical determinations because the analyses performed on these materials are essentially radiochemical in nature.

Table 10.3—CARRIER SOLUTIONS

Carrier reagent, 10 mg/ml	Material and weight	Dissolve in and/or dilute with
Ammonium	NH_4Cl, 3 g	100 ml of water.
Antimony	Sb_2O_3, 1.20 g	100 ml of dilute HCl.
Arsenic	As_2O_5, 1.53 g	100 ml of dilute HCl.
Barium	$Ba(NO_3)_2$, 1.9 g	100 ml of water.
Bromine	KBr, 1.49 g	100 ml of water.
Cerium	$Ce(NO_3)_3 \cdot 6H_2O$, 3.10 g	100 ml of water.
Cesium	$CsNO_3$, 1.5 g	100 ml of water.
Chromium	$K_2Cr_2O_7$, 2.8 g	100 ml of water.
Cobalt	$CoCl_2 \cdot 6H_2O$, 4 g	10 ml of HCl and 90 ml of water.
Copper	Cu metal, 1 g	25 ml of HNO_3 and 75 ml of water.
Fluoride	NaF, 1.8 g	100 ml of water.
Iodide	KI, 1.3 g	100 ml of water.
Iron	Fe metal powder, 1 g	50 ml of HCl and 50 ml of water.
Lanthanum	La_2O_3, 1.2 g	50 ml of HNO_3 and 50 ml of water.
Manganese	MnO_2, 1.6 g	25 ml of HCl and 75 ml of water.
Nickel	Ni metal powder, 1 g	25 ml of HNO_3 and 75 ml of water.
Niobium	$K_8Nb_6O_{19} \cdot 16H_2O$, 2.6 g	Heat with HNO_3; dissolve oxide in 20 ml of saturated oxalic acid; make to 100 ml with water.
Palladium	$PdCl_2 \cdot 2H_2O$, 2 g	100 ml of water.
Potassium	KCl, 1.9 g	100 ml of water.
Rubidium	RbCl, 1.4 g	100 ml of water.
Sodium	NaCl, 2.542 g	100 ml of water.
Strontium	$Sr(NO_3)_2$, 2.4 g	100 ml of water.
Tantalum	Ta, 1.0 g	100 ml of water containing oxalic acid after dissolving in HNO_3 and HF and precipitating with NH_4OH.
Tellurium	TeO_2, 1.25 g	100 ml 4*N* HCl.
Tungsten	$Na_2WO_4 \cdot 2H_2O$, 1.8 g	100 ml of water.
Yttrium	Y_2O_3, 1.25 g	25 ml of HNO_3 and 75 ml of water.
Zirconium	$ZrO_2Cl_2 \cdot 8H_2O$, 3.54 g	5 ml of HF and 95 ml of water.

Determination of Total Gas (Volumetric). The extraction apparatus consists of a simple gas train employing a Toepler pump to transfer the gas to a measuring buret. The sample system is evacu-

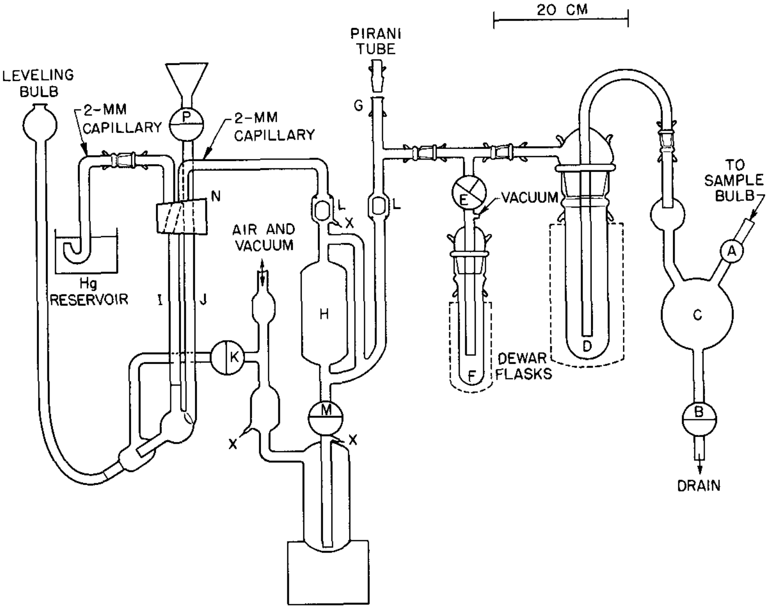

Fig. 10.1—Gas-extraction apparatus, *A*, sample inlet; *B*, stopcock to drain; *C*, water retainer; *D*, cold trap; *E*, *K*, *M*, *N*, *P*, stopcocks; *F*, vacuum cold trap; *G*, Pirani gauge connection; *H*, Toepler pump; *I*, gas buret to contain 5 ml in straight portion; *J*, air leg; *L*, check valves, mercury tight; *X*, Toepler-pump electrical leads.

ated, the sample is introduced, and the evolved gas is transferred and measured in a measuring buret.

Procedure. The Dewar flask around D in Fig. 10.1 is filled with a dry ice–trichloroethylene mixture. The Dewar flask around F is filled with liquid nitrogen. The Toepler pump, H, and the gas buret I are filled with mercury to the point that the tip of the capillary is covered by the mercury in the reservoir. The leveling bulb is in the raised position, with the tube to K filled with mercury. All stopcocks are closed except E, which is opened, and the system is evacuated to below 10^{-2} torr through the vacuum attachment tube below E. The pressure is measured on the Pirani gauge. Stopcock E is then closed.

The sample bomb containing the coolant sample is connected to A, and the system is evacuated by opening E and then slowly opening the sample-inlet cock, A. When pressure is again 10^{-2} torr or less, stopcock E is closed and the Toepler-pump stopcock, M, is opened. The Toepler-pump electrical connections are made. The sample bomb is inverted, and the sample is transferred by opening the sample bomb and allowing the sample to flow into the sample bulb. The sample inlet, A, is now closed. The gas evolves from the sample and the Toepler pump runs until the original pressure is obtained. The leveling bulb is lowered to the bottom, and the gas is transferred to the gas buret I through N, which is then closed as is the Toepler-pump stopcock, M. The leveling

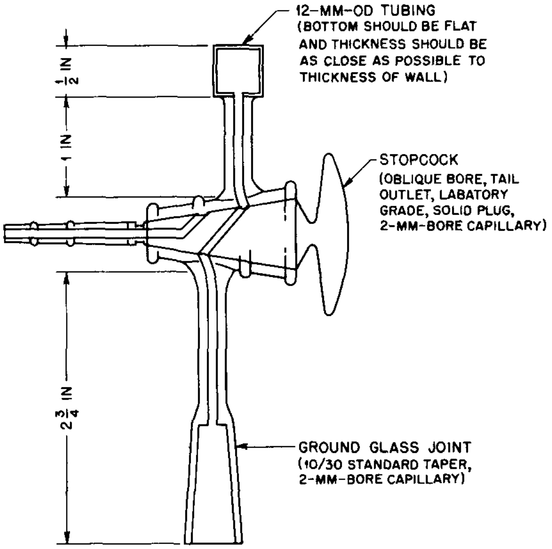

Fig. 10.2—Counting vessel for Ar^{41} and Xe^{133} determination.

bulb is raised to its initial position; and P, the air-leg stopcock, is opened. The leveling bulb is lowered so that the level in J is the same as the level in I, and the volume is measured. The barometric pressure and temperature are measured, and the gas per kilogram of sample is calculated. The gas sample is retained for subsequent analysis. The sample is collected in a Blacet–Leighton gas-analyzer thimble through the 2-mm side arm from the gas buret.

(b) *Radiochemical Analyses.* The radiochemical analyses performed are given below in alphabetical order.

(1) *Argon-41.* Argon-41 and fission gases such as Xe^{133} and Kr^{88} are radiological health hazards with respect to accessibility into the reactor compartment and inhalation. Under normal conditions the predominant gaseous activity will be due to Ar^{41}. The Ar^{41} analysis is performed manually in certain pressurized-water reactors. In the boiling-water reactor, a similar analysis is usually performed with in-line instrumentation.

Argon enters the primary coolant as a component of air, either entrapped in filling, or dissolved in make-up water. The activated Ar^{41} is removed from a water sample along with other gaseous products. Argon-41 has a gamma activity of 1.30 Mev.

Procedure. The gas is stripped from the water sample in a buret as described in Sec. 10-1.2(a). After the gas concentration has been measured, a portion of the gas is transferred to a Blacet–Leighton gas-analyzer thimble,[5] and the volume of the gas is measured. A counting vessel (see Fig. 10.2) is evacuated, and then the ground-glass joint is filled to the cock with mercury by suction applied through the side arm.

The sample in the Blacet-Leighton thimble is transferred to the counting chamber. Argon-41 activity is measured by means of a gamma-ray scintillation detector at a suitable distance to prevent overloading the counting apparatus. A pulse-height analysis is made to determine the count rate at the 1.3-Mev photopeak within 2 hr after sampling. A decay curve is constructed to determine the purity of the Ar^{41} by means of its 110-min half life. In an alternate procedure[6] a sample of the coolant is counted before and after removing gases by bubbling air through the sample.

(2) *Barium.* Barium and strontium occur as fission products. The barium activity is primarily composed of 85-min Ba^{139} and 12.8-day Ba^{140}. Both are beta and gamma emitters. Barium and strontium are precipitated as nitrates from fuming nitric acid, and barium is then separated from strontium by precipitation as barium chromate from an acetate-buffered solution.

Procedure. The sample is added to a centrifuge tube containing 2 ml of barium carrier solution and 2 ml of strontium carrier solution (see Table 10.3). Fuming nitric acid is added, and after digestion the solution is centrifuged. The residue is dissolved in water, and the barium and strontium are again precipitated with fuming nitric acid. The precipitate is dissolved in water; and, after the addition of 8 drops of an iron carrier (Table 10.3), ammonium hydroxide is added. After centrifugation the supernatant is acidified with 6*N* HNO_3 using methyl red as an indicator, and then 1 ml of 6*N* acetic acid and 2 ml of 6*N* ammonium acetate are added. After the resultant solution is heated to boiling, 1.5*M* potassium chromate is added dropwise until precipitation is complete. A couple of drops of Aerosol are added, and the solution is centrifuged. The barium chromate is dissolved in 6*N* HCl, a HCl–ether solution (4+1) is added, and after digestion the solution is centrifuged. The precipitated barium chloride is dissolved in water, and 1 ml of strontium carrier solution (Table 10.3) is added. After the addition of methyl red indicator, the solution is treated with 1 ml of 6*N* acetic acid and then 2 ml of 6*N* ammonium acetate. Potassium chromate is again added to precipitate barium chromate, and the solution is again centrifuged. (This time is noted.) The barium chromate is dissolved in 6*N* HCl and made up to 10 ml with water. Barium sulfate is precipitated from the near-boiling solution with 12*N* H_2SO_4. The barium sulfate is weighed and mounted for beta counting.

The Ba^{139} and Ba^{140} activities are determined with a beta proportional counter. The 85-min Ba^{139} is determined from its decay curve taken over a period of 1.5 hr. The 12.8-day Ba^{140} is determined from its decay curve, taken after the La^{140} has grown to equilibrium between the second and fourth weeks. The Ba^{139} activity must be corrected for the Ba^{140}–La^{140} activity by calculation of their respective degrees of decay and growth at the Ba^{139} counting times.

(3) *Bromine.* Bromine found in coolants after use will be composed principally of Br^{83} and Br^{84} with minor amounts of Br^{82}. Elemental iodine and bromine can be separated from fission elements by extraction into CCl_4. After reduction of these elements to bromide

and iodide, the iodide is oxidized to elemental iodine while the bromide is unaffected. After the iodine is extracted with CCl_4, the bromide is oxidized to elemental bromine with $KMnO_4$ after which it is extracted with CCl_4. Bromine is removed from the CCl_4 with $NH_2OH \cdot HCl$ and finally precipitated as AgBr.

Procedure. The sample is added to a centrifuge tube containing 10 ml of $2M$ Na_2CO_3, and 10 mg of bromide carrier solution and 10 mg of iodide carrier solution (Table 10.3) are added. A stream of H_2S is passed into the solution, and the excess H_2S is removed by boiling. The solution is transferred to a separatory funnel, and 10 ml of CCl_4 is added. After the solution has been acidified with HNO_3, 3 ml of $0.1M$ $NaNO_2$ is added, and the contents are shaken. The CCl_4 layer containing iodine is discarded. The extraction is repeated until the organic layer is colorless. A few drops of $1M$ $KMnO_4$ are added to the aqueous layer to oxidize the bromide, and the elemental bromine is extracted with CCl_4. The bromine is removed from the CCl_4 layer by adding 10 ml of H_2O followed by $1M$ $NaHSO_3$ to decolorize the organic phase. The oxidation and extraction is repeated. The aqueous layer is transferred to a centrifuge tube, and the bromide is precipitated with 2 ml of $0.1M$ $AgNO_3$. Two milliliters of HNO_3 is added, and the suspension is boiled. It is then filtered on a tared filter paper, washed with water and ethanol, dried in a vacuum, and weighed. The paper is then backed with a very thin plastic backing and counted either by beta or gamma counting for Br^{83} and Br^{84} or for Br^{84} by pulse-height analysis.

The bromine isotopes activity can be determined by means of a beta proportional counter. The Br^{84} activity may also be determined with a gamma-ray scintillation detector and a pulse-height analyzer. In the proportional counter the Br^{84} decay is determined by counting through a 440 mg/cm^2 aluminum absorber for a period of 2 hr. The Br^{83} is determined from its decay curve without an absorber for a period of 4 to 8 hr. Based on its decay curve, any Br^{82} is measured after 1 day if required. If a gamma-ray spectrometer is used for the Br^{84}, the decay curve is measured over the 0.87-Mev gamma-ray photopeak. Gamma pulse-height analysis for Br^{84} is made every 0.5 hr for 1.5 hr.

(4) *Cerium.* Cerium and the other rare earths are first separated as insoluble fluorides from the sample. The cerium is then oxidized to the quadrivalent state and extracted with methyl isobutyl ketone from an HNO_3 solution. This effectively separates cerium from the rare earths. After precipitation from alkaline earths with NH_4OH, the cerium is precipitated as oxalate from a nitric acid solution and then converted to oxide for weighing and counting.

Procedure. To the sample are added 20 mg of cerium carrier solution (Table 10.3), 5 ml HNO_3, and 1 ml of saturated $NaBrO_3$ solution. The solution is heated, and 30 per cent peroxide is added until the solution is light brown. The solution is heated to remove bromine, and 5 mg of zirconium carrier solution (Table 10.3) and 0.5 ml of HF are added. After it is centrifuged and washed, the precipitate is stirred with 2 ml of saturated H_3BO_3 and 5 ml of HNO_3; then 2 ml of $2M$ $NaBrO_3$ is added.

The cerium is extracted with 50 ml of methyl isobutyl ketone that has been equilibrated with 50 ml of 9*M* HNO_3 containing 2 ml of 2*M* $NaBrO_3$. The hexone layer is washed with 10 ml of 9*M* HNO_3 containing a few drops of 2*M* $NaBrO_3$. (The water layer is neutralized with NH_4OH and is either discarded or saved for the rare earth determination. This procedure is followed to prevent explosions due to decomposition of hexone in acid.)

The cerium is backwashed from the hexone with 5 ml of water containing a few drops of H_2O_2. The hexone is washed three times with water. The aqueous solution containing the cerium is made basic with NH_4OH. The precipitate is centrifuged down and redissolved by adding 6*N* HNO_3 and boiling the solution. The solution is neutralized, and 1 ml of 2 per cent HNO_3 is added. Saturated $(NH_4)_2C_2O_4$ is then added, and the solution is cooled in ice. The resultant precipitate is centrifuged, washed, and dissolved in 1 ml of 6*N* HNO_3. The solution is diluted to 15 ml, and the cerium is reprecipitated with ammonium oxalate. After centrifugation, the precipitate is transferred to a tared filter disk, washed with ethanol, dried in a vacuum dessicator, weighed, and mounted for beta counting.

The cerium activity is determined with a beta proportional counter. Cerium-144 is determined from an absorption curve of its Pr^{144} daughter, using aluminum absorbers with a density of 100 to 1600 mg/cm^2, at least 5 days after sampling to allow the Ce^{143} to decay to a low level. Cerium-141 may be determined from the difference between the total beta activity at zero absorber and the Ce^{144}–Pr^{144} total activity as estimated by comparison with a pure standard Ce^{144}–Pr^{144} absorption curve.

(5) *Cesium.* Cesium and rubidium are separated from interfering fission-product activity by means of sodium carbonate. The cesium is separated from rubidium as $Cs_2Bi_2I_9$ followed by a Cs_2PtCl_6 precipitation.

Procedure. To the sample are added 20 mg of cesium carrier solution and 5 mg each of rubidium, barium, strontium, and iron carrier solution (Table 10.3). The solution is neutralized with 12*N* NaOH, and 1 ml of 1*M* Na_2CO_3 is added; after this the precipitate formed is centrifuged and discarded. The solution is acidified with glacial acetic acid, keeping the volume to less than 15 ml, and 1 ml of HI–BiI_3 reagent (10 g BiI_3 per 50 ml of 55 per cent HI) is added. The solution is cooled in an ice bath, the precipitate is centrifuged, and the supernatant is discarded. The precipitate is washed with 1 ml of 2*N* HCl and 7 ml of water, and after seperation the supernatant is discarded. The precipitate is dissolved in 2 drops of 12*N* NaOH and 5 ml of water; the mixture is centrifuged and the supernatant is transferred to another centrifuge tube. Five milliliters of HNO_3 is added to the supernatant, and the solution is boiled to expel iodine. After cooling in an ice bath, 10 ml of ethanol and 10 drops of 10 per cent $H_2P_2Cl_6$ are added. After centrifugation, the precipitate is washed with ethanol and transferred to a tared filter paper. It is then vacuum dried, weighed, and counted.

Cesium-138 is resolved from residual Cs^{139} by a decay curve of beta activity measured over a period of 1½ hr through a 300 mg/cm^2 aluminum absorber. The Cs^{139} is determined in a separate procedure.

A beta decay curve of the long-lived isotopes Cs^{136} and Cs^{137} is made without an absorber over a period of a week. A gamma-ray spectrum taken the day following the preparation of the sample is used to determine the ratio of the activity of the Cs^{136} and Cs^{137}. The Cs^{134} is not considered.

The specific activity of Cs^{139} is determined by analyzing for the Ba^{139} daughter activity that grows in. The barium is initially scavanged by precipitation as the carbonate. The cesium is then allowed to decay for a specified time, and the barium that grew in is separated.

Procedure. The sample is added to a centrifuge cone containing 20 mg of barium and 20 mg of cesium carrier solution, (Table 10.3). The barium is precipitated with 2*M* Na_2CO_3, and the time is recorded. The precipitate is centrifuged and discarded, and 20 mg of barium carrier (Table 10.3) is added to the supernatant. The solution is acidified with 6*N* HNO_3 and allowed to stand 35 min. The barium is precipitated with 2*M* Na_2CO_3, and the time for precipitation is recorded. The precipitate is dissolved in 6*N* HNO_3 and water, and the procedure as indicated under barium is followed to complete the determination.

The Ba^{139} activity is measured by means of a beta proportional counter from a decay curve as of the time of the second separation from the Cs^{139}. The Cs^{139} activity is corrected for decay to the original sampling time, taking into account the limited growth of the Ba^{139} and the rapid decay of the Cs^{139} during the 35 min between the first and second separation of the barium.

(6) *Chromium.* Chromium is separated from fission and activation products by a $BaCrO_4$ precipitation and an ether extraction of CrO_5. Radiobarium is separated by a $BaSO_4$ precipitation. The chromium is then precipitated as $BaCrO_4$ for weighing and counting.

Procedure. To an Erlenmeyer flask are added 40 mg of chromium carrier solution (Table 10.3), the sample, and 0.5 ml of HNO_3, after which the solution is evaporated to dryness. After the residue is taken up in 1 ml of HNO_3 and 5 ml of H_2O, 3 ml of saturated $NaBrO_3$ solution is added, and the solution is heated to oxidize the Cr^{3+} to $Cr_2O_7^{-2}$. The solution is then transferred to a centrifuge cone and made basic with NH_4OH. Then 0.1 ml of iron carrier solution is added (Table 10.3), after which the solution is centrifuged. The supernatant is evaporated to one-half its volume and then acidified with HNO_3. To this solution is added 1*M* $NaNO_2$ until the $Cr_2O_7^{+2}$ is reduced to Cr^{+3}. Excess NO_2^- is removed by heating, and NH_4OH is added until $Cr(OH)_3$ precipitates. Excess NH_4OH is removed by heating. The solution is centrifuged, the supernatant is discarded, and the precipitate is washed with H_2O. After dissolution in HCl and reprecipitation with NH_4OH, the $Cr\ (OH)_3$ is dissolved in 5 drops of HNO_3, the solution is diluted to 15 ml, and 3 ml of saturated $NaBrO_3$ solution is added. The chromium is precipitated with a saturated solution of $Ba(NO_3)_2$. To the solution are added 2 ml of 6*M* ammonium acetate and 1 ml of 6*M* acetic acid. The solution is centrifuged, and the supernatant is discarded. The washed precipitate is dissolved in 5 drops of HCl and 10 ml of water. A volume of 1 to 2 ml of saturated $NaBrO_3$ is added. The solution is cooled, a few drops of cold H_2O_2 are added, and the CrO_5 is extracted with 90 ml of cold ethyl ether. The ether layer is washed with 10 ml of H_2O containing 3 ml of HCl per liter. The chromium is back-extracted into water by shaking the ether layer with 15 ml of H_2O containing 3 to 4 drops of NH_4OH. After being transferred to a centrifuge tube, the solution is warmed in a water bath to remove ether; and 2 ml of 6*M* ammonium acetate and 1 ml of 6*M* acetic acid are added. The solution is heated to boiling, and the $BaCrO_4$ is precipitated with saturated $Ba(NO_3)_2$. The solution is centrifuged, the supernatant is discarded, and the precipitate is washed with water. The precipitate is transferred to a weighed filter paper, washed with water and ethanol, and dried at 110°C. It is then weighed and mounted for counting.

The 0.32-Mev gamma ray of Cr^{51} is measured by means of a gamma-ray scintillation spectrometer and the peak-integration method or a spectrum stripping technique.

(7) *Crud and Ion-exchange-resin Solution.* Crud is the jargon applied to the insoluble corrosion products that flake off metal surfaces and are transported through a cooling system. The name, however, has been used to such an extent that its use has become almost universal. In some instances [6] the coolant is removed from the system and filtered to obtain the crud, whereas in others the coolant is passed through a crud probe that filters out the crud in the influent and effluent water of the demineralizer. The major radionuclides in the crud are given in Table 10.1. The resin from the demineralizer contains both crud and resin; and, when the analysis of the resin alone is required, a separation is necessary. This separation is made by taking advantage of the magnetic properties of the crud.

Since the crud consists chiefly of insoluble corrosion products that may be activated by the means indicated in the introduction to this chapter, the chief problem is in the dissolution and separation of the elements found in the crud.

The resin bed contains soluble radioactive elements removed from the coolant in addition to some of the elements found in the crud.

After separation of the resin and crud, they are put into solution and the radio assays of the various isotopes are made as outlined.

Separation of Resin and Crud. The sample of the resin and crud is transferred to a graduated cylinder, the resin is allowed to settle, and its volume is measured. The mixture is then transferred to a beaker with water, stirred with a power stirrer, and a strong magnet is placed near one side of the beaker to attract the crud. The water and crud are decanted through a filter paper in a Büchner funnel. The resin is again wet with water and stirred. More water is added and the procedure above is repeated. Sufficient acetone to cover the resin is added, and it is stirred vigorously to knock the crud off the resin. More acetone is added, and the crud is separated with a magnet as described above except that the crud around the glass near the magnet is separated with a dropper. The crud and acetone are decanted and filtered through the same filter paper as used before.

Dissolution of the Crud. The crud from the crud filter probe or from the resin bed is transferred to a porcelain crucible and ignited over a Meker burner at red heat. A 0.5-g sample of crud is weighed and counted in a platinum planchet after a few drops of 2 per cent Zapon are added to the sample and the planchet is backed with aluminum.

The rest of the crud sample is treated with 50 ml of fuming HNO_3 and 20 ml of $HClO_4$ in a beaker, and the mixture is fumed to a volume of 5 ml. After the cooled solution is taken up in 6*N* HCl, it is filtered and washed, with the filtrate and the washings being collected in a polyethylene bottle. One milliliter of HF is added to the bottle. The beaker is washed with 3*N* HF, and the washings are transferred to a platinum crucible. The residue and filter is again treated with 50 ml of fuming HNO_3 and 20 ml of $HClO_4$ in a beaker. The solution and residue is transferred to a centrifuge tube with 6*N* HCl and is then centrifuged. The supernatant is decanted into the polyethylene bottle, and the residue in the centrifuge tube is transferred to the platinum crucible with 3*N* HF and 2*N* $HClO_4$. The contents of the crucible are evaporated to fumes and cooled; then 3 ml of HF is added, after which the solution is again fumed. After the contents of the crucible is taken up in 6*N* HCl, any residue remaining is retreated as above and finally fused with Na_2CO_3 and dissolved in 6*N* HCl. All solutions are transferred to the original polyethylene bottle and made up to 100 or 200 ml. This combined solution is used for the necessary radioisotopic analysis.

Dissolution of Ion-exchange Resin. The ion-exchange resin may be decomposed by wet combustion or ignition. In the wet ashing method, H_2SO_4 and HNO_3 are used. Any residue is decomposed with HF and H_2SO_4. The final filtered solution is made to 3*M* in HCl. In the ignition method the resin is ignited at a final temperature of 800°C, and the residue is taken up in HNO_3 and $HClO_4$, and the solution is fumed. After the addition of water, any residue is decomposed by fuming with HF, HNO_3, and $HClO_4$. The solution is made up to 3*M* in HCl as above.

(8) *Cobalt.* The reactions $Ni^{58}(n,p)Co^{58}$ and $Co^{59}(n,\gamma)Co^{60}$ are responsible for the radioactive cobalt present in the sample. The precipitation of cobalt as potassium cobaltinitrite has proved satisfactory. Additional decontamination is obtained by the extraction of the cobalt thiocyanate complex into amyl alcohol. Cobalt is precipitated as sulfide, oxidized with HNO_3, and finally reprecipitated with KOH.

Procedure. To the sample in a centrifuge tube are added 20 mg of cobalt carrier solution and 10 mg of nickel carrier solution (Table 10.3), and the solution is treated with 10*N* KOH. The precipitate is centrifuged and washed and the supernatant is discarded. The precipitate is dissolved with 3 ml of 6*N* acetic acid; and, after the solution is diluted to 25 ml, the cobalt is precipitated with 6 ml of KNO_2–acetic acid reagent (3*N* acetic acid saturated with KNO_2). The precipitate is allowed to digest for 20 min, and then it is centrifuged and washed with water. The supernatant is discarded. The precipitate is dissolved in 2 ml of HCl, the solution is boiled to near dryness, and 10 mg of nickel carrier solution is added (Table 10.3). A precipitation is made with 10*N* KOH. The precipitate is centrifuged and washed. After the dissolution and precipitation of the cobaltinitrite is repeated, the $K_3Co(NO_2)_6$ is dissolved in 5 ml of HCl, and the solution is evaporated to near dryness. To the residue are added 5 mg of palladium carrier solution and 5 mg of copper carrier solution (Table 10.3). The solution is diluted to 20 ml with 0.1*N* HCl, heated, and H_2S is passed into it. The sulfide is centrifuged, and the filtrate is collected in a centrifuge cone. Palladium and copper carrier solutions are added as above, and the precipitation is repeated.

The solution is evaporated to near dryness, diluted to 25 ml, and 10 mg of iron carrier solution (Table 10.3) and 0.5 ml of HCl are added. The iron is precipitated with NH_4OH. The solution is centrifuged, and the precipitate is discarded. The supernatant is acidified with HCl, iron carrier solution is added, and the precipitation is repeated. A third iron precipitation also is made. The supernatant is acidified to about 1*N* in HCl and 15 g of ammonium thiocyanate is added. The thiocyanate complex of cobalt is extracted into 50 ml of (1+1) amyl alcohol–ethyl ether mixture. The organic layer is washed with ammonium thiocyanate solution (1 g in 2 ml of H_2O). The cobalt is back-extracted into 20 ml of H_2O containing 6 ml of NH_4OH. The aqueous layer is transferred to a centrifuge cone, and CoS is precipitated with H_2S. The precipitate of CoS is dissolved in 3 ml of HNO_3, the solution is boiled and diluted to 10 ml, and then 1 g of KNO_2 is added, after which the cobalt is precipitated with 10*N* KOH. The precipitate is filtered and ignited in a porcelain crucible at 700°C. The residue is transferred to a tared filter disk, weighed, and mounted for counting.

A gamma-ray scintillation spectrometer is used to measure simultaneously and to resolve the 0.51-Mev positron annihilation radiation from Co^{58} and the 1.17- and 1.33-Mev gamma rays from Co^{60}. A peak-integration technique or a spectrum stripping technique is used to estimate the amount of each isotope.

(9) *Fifteen-minute Activity.* The activity levels of a primary coolant sample or a degassed sample from a pressurized-water reactor and a boiling-water reactor 15 min after sampling indicate the short-lived radioactive level in the coolant and determine accessibility to the reactor compartment shortly after reactor shutdown. In addition, samples taken upstream and downstream of the primary coolant demineralizer determine the efficiency of the ion-exchange resin. The boiling-water-reactor primary coolant samples taken before and after condensation indicate the activity carry-over. The sample is counted

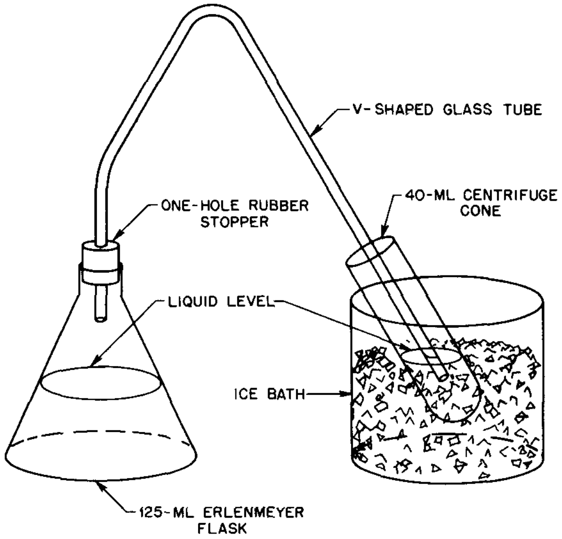

Fig. 10.3—Fluoride distilling apparatus.

in a well counter or is dried and counted in a Geiger–Mueller counter. The level of short-lived activity in the ion-exchange influent and effluent is determined by well-counting a water sample as soon after sampling as is practicable. The sample is counted after each of four successive 15-min intervals.

(10) *Fluorine-18.* Fluorine is separated from halides by the precipitation of the insoluble chlorides, bromides, and iodides with silver. The fluorine is then precipitated as lanthanum fluoride.

Procedure. To the sample are added 10 mg of fluoride carrier solution, 10 mg of iodide carrier solution (Table 10.3), and 0.3*M* $AgNO_3$ to precipitate the iodide. The precipitate is centrifuged down, the supernatant is transferred to the still shown in Fig. 10.3, and 50 ml of H_2SO_4 is added. The distillate formed by heating the solution to fumes is collected in a solution containing 50 mg of lanthanum carrier (Table 10.3). The LaF_3 precipitate is filtered on a weighed glass-fiber filter, washed with alcohol and ether, and weighed. The sample is then counted.

Fluorine–18 activity is measured either with a beta proportional counter or a gamma-ray scintillation spectrometer using the 0.51-Mev annihilation radiation. The activity is followed for 1 hr, and a decay curve is constructed. The curve is extrapolated to sampling time.

(11) *Iodine Activity* (*Gross and* I^{131} *and* I^{133}). The gross-iodine procedure is used to supplement in-line fission-product monitors in the pressurized-water reactor and the boiling-water reactor. The iodine activity levels indicate total fission-products levels. High

levels may limit discharge of primary coolant and may indicate a fuel-element failure. The gross-iodine activity consists chiefly of I^{131} with small amount of I^{133}. The activity of both these nuclides can be determined if desired.

Iodine is effectively separated from other fission products by the extraction of elemental iodine into CCl$_4$. Separation of iodine from bromine is accomplished by reduction of BrO_3^- and IO_3^- to B_r^- and I_2. The elemental iodine is then extracted in CCl$_4$.

Procedure. Into a separatory funnel are placed the sample, 20 mg of iodine carrier solution, and 20 ml of bromine carrier solution (Table 10.3). The solution is made basic with 5 ml of 2*M* Na_2CO_3. To the solution is added 1 ml of a 5 per cent sodium hypochlorite solution. After the solution is acidified with HNO_3, 3 ml of 1*M* hydroxylamine hydrochloride solution is added, and iodine is extracted with CCl_4. The CCl_4 layer is shaken with 10 ml of water containing a few drops of 1*M* $NaHSO_3$. The CCl_4 is discarded. To the aqueous layer is added 1 ml of 6*N* HNO_3 and a few drops of 1*M* $NaNO_2$. The iodine is extracted with 10 ml of CCl_4. The iodine in the CCl_4 layer is extracted into water with 5 ml of water containing a few drops of 1*M* $NaHSO_3$. The water layer is diluted to 50 ml, and 2 ml is placed in a vial for counting. Two milliliters of the remaining solution is transferred to an Erlenmeyer flask, and 10 ml of water and 5 ml of HNO_3 are added. After a known amount (10 ml) of standardized 0.01*M* $AgNO_3$ and 1 ml of saturated ferric alum in 1*N* HNO_3 are added, the excess silver is titrated with 0.01*M* KSCN.

Because, in the determination of iodine in the resin, the ignition of the resin results in loss of iodine, it is necessary to analyze the dried resin. The analysis is done by adding 20 mg of iodine carrier (Table 10.3) and 10 ml of 2*M* Na_2CO_3 followed by 1 ml of a 5 per cent NaClO solution. After the solution is heated in a hot-water bath, it is filtered and the procedure is carried out as described above.

The nuclides I^{131} and I^{133} are measured by means of a gamma-ray scintillation spectrometer and the peak-integration method or the spectrum stripping method. A decay curve of each gamma count rate taken over a period of several days is used to estimate the count rate at sampling time.

(12) *Iron.* Iron is separated from fission products by a sulfide precipitation from a tartrate solution followed by an anion-exchange separation. The iron is finally extracted into isopropyl ether.

Procedure. To the sample are added 10 mg of iron carrier solution (Table 10.3) and 2 ml of saturated tartaric acid solution. The solution is made basic with NH_4OH and saturated with H_2S. The precipitate is centrifuged and then washed with dilute NH_4OH saturated with NH_4NO_3. The sulfide precipitate is dissolved in 0.5 ml of HCl, the H_2S is removed by boiling, and the solution is evaporated to near dryness after the addition of 0.5 ml HNO_3 and 2 ml HCl. The residue is dissolved in 10 ml HCl and poured onto a Dowex-1 anion resin column (1X8, 50 to 100 mesh in a 8-cm by 13-mm tube) previously equilibrated with 10 ml of HCl. The solution is allowed to run through the column, and the resin is washed with 10 ml of HCl followed by 15 ml of 6*N* HCl.

The iron is eluted from the resin with 10 ml of 0.5*N* HCl. To the effluent are added 5 mg of copper carrier solution and a drop each of antimony, arsenic, and tellurium carrier solutions (Table 10.3); and the volume is made to 20 ml with 0.5*N* HCl. The solution is saturated with H_2S; and after centrifugation the supernatant is treated with 2 ml of saturated tartaric acid solution, made basic with 6*N* NH_4OH, and saturated with H_2S. The precipitate is washed again with NH_4OH saturated with NH_4NO_3 as before. The precipitate is dissolved in HCl and then evaporated to dryness. The residue is transferred with 10 ml of 8*N* HCl to a separatory funnel, and 30 ml of isopropyl ether is used to extract the iron. The iron is transferred to the aqueous phase with 10 ml of water. The solution is again precipitated with H_2S from a tartrate solution and reextracted as above. After two more extractions as above, the final sulfide precipitate is washed with acetone and ignited in a porcelain crucible. It is then transferred to a tared filter disk, weighed, mounted, and counted.

The Fe^{59} can be counted by either a beta proportional counter or a gamma-ray scintillation spectrometer. The gamma-ray peaks may be evaluated either by the peak-integration method or the spectrum stripping method.

(13) *Krypton–88.* The activity of the Kr^{88} is determined by measuring the amount of its Rb^{88} daughter that grows in over a 6-hr period. The rubidium is purified by an iron scavenge and precipitated as the chloroplatinate.

Procedure. Six hours after the sample is taken, an aliquot is pipetted into a centrifuge tube, and 20 mg of rubidium carrier solution and 5 mg of iron carrier solution (Table 10.3) are added. The iron is precipitated with 6*N* NaOH. After the solution is centrifuged, the supernatant is acidified with 6*N* HCl, and 1 ml of 0.5*M* H_2PtCl_6 and 10 ml of ethanol are added. The precipitate is washed with ethanol, transferred to a tared filter disk, weighed, mounted, and counted.

The Rb^{88} activity is measured by means of a beta proportional counter and is corrected back to the end of the Rb^{88} growth period by means of a decay curve. The Rb^{88} growth is calculated for the time allowed, and the Kr^{88} is corrected for its decay since the original sampling time.

(14) *Molybdenum.* The radioactive contaminants of concern in the molybdenum determination are those associated with molybdenum in the decay chain strontium–yttrium–zirconium–niobium–molybdenum–technetium. An effective separation from strontium–yttrium–zirconium–niobium is made by an anion-exchange process. Molybdenum is absorbed in the hexavalent state, strontium and yttrium pass through the column, and zirconium is absorbed. Zirconium is eluted with dilute HCl prior to removal of the molybdenum with dilute NH_4OH. α-Benzoin oxime is used to separate the molybdenum from niobium in an oxalate solution.

Procedure. To the sample are added 20 mg of molybdenum carrier solution (Table 10.3) and 5 ml of fuming HNO_3, after which the solution is evaporated to dryness. Two milliliters of HCl is added, and the solution is again evaporated to dryness. This step is repeated. The residue is taken up in ice-cold HCl saturated with HCl gas, and the resultant molybdenum solution is poured onto a Dowex 1 anion resin (1X8, 50 to 100 mesh in a 10-cm by 13-mm tube) that has been converted to the acid form with HCl. The resin column is treated with 15 ml of $4N$ HCl followed by 15 ml of water. The molybdenum is eluted from the column with $3N$ NH_4OH into a centrifuge tube, 5 mg of iron carrier solution (Table 10.3) is added; and, after the solution is centrifuged, the supernatant is acidified with HNO_3 (methyl red end point). One milliliter of saturated oxalic acid, 6 drops of bromine water, and 10 ml of α-benzoin oxime reagent are added. The time of the α-benzoin oxime addition is noted. After it is cooled in an ice bath, the precipitate is removed by centrifugation. The precipitate is transferred to a porcelain crucible, ignited at 500°C, cooled, transferred to a tared filter paper with ethyl alcohol, dried, weighed, and then mounted for counting.

The Mo^{99} activity may be measured using a beta proportional counter and a decay curve taken over a period of 7 days. A gamma scintillation counter may also be used, but a wait of 24 hr is necessary to allow the Tc^{99} activity to grow in.

(15) *Niobium-95.* Niobium is separated from other fission products by extraction of the fluo complex into tributyl phosphate (TBP).

Procedure. To 3 ml of niobium carrier solution (Table 10.3) are added 3 ml of HF, the sample, which should be $4M$ in HCl, 10 mg of zirconium carrier solution (Table 10.3), and saturated $Ba(NO_3)_2$ to precipitate $BaZrF_6$. After centrifugation, the supernatant is treated with an additional 10 mg of zirconium carrier, and the $BaZrF_6$ precipitation is repeated. The precipitate is discarded. The supernatant is treated with 2 ml of saturated H_3BO_3, 20 ml of HNO_3, and 0.5 g of $KBrO_3$, and the solution is heated. Additional $KBrO_3$ in three steps is added with the solution being heated between additions. The solution is evaporated somewhat, centrifuged, and the supernatant is discarded. The precipitate is washed with hot 2 per cent NH_4NO_3. After transferring to a polyethylene centrifuge tube, the precipitate is dissolved in 2 ml of 40 per cent HF and 3 ml of $12M$ H_2SO_4. Five milliliters of TBP is added, the solution is stirred and the organic layer is separated by centrifuging. The TBP layer is treated with 5 ml of petroleum ether and 5 ml of NH_4OH. After centrifugation the aqueous layer is washed with petroleum ether, and the precipitate is centrifuged and washed with hot 2 per cent NH_4NO_3. The precipitate is transferred to a filter paper and ignited at 800°C in a weighed crucible. The residue is transferred to a counting mount. The weight is obtained by reweighing the crucible.

The Nb^{95} activity is measured by means of a gamma-ray scintillation spectrometer, and the peak-integration method or the spectrum stripping method is used on the 0.76-Mev photopeak.

(16) *Nitrogen-13.* Nitrogen-13 is separated by a Kjeldahl distillation procedure followed by a precipitation of ammonium chloroplatinate.

Procedure. To the sample is added 10 mg of ammonium carrier solution (Table 10.3), and the ammonium is distilled from the solution in a micro-Kjeldahl apparatus after the addition of NaOH. The evolved ammonia is collected in a centrifuge tube containing 2 ml of 5 per cent H_2PtCl_6 and 20 ml of ethanol. The precipitate is filtered on a weighed glass-fiber filter, washed with ethanol and ether, weighed, and mounted.

The N^{13} activity is measured either with a beta proportional counter or a gamma-ray scintillation spectrometer using the 0.51-Mev annihilation radiation. The activity is followed for 1 hr, and a decay curve is constructed. The curve is extrapolated to sampling time.

(17) *Potassium-42.* Potassium-42 activity arises from neutron irradiation of the $KrCrO_4$ used as a corrosion inhibitor. Potassium is separated by the precipitation of the tetraphenylboron derivative.

Procedure. To the sample in a centrifuge cone is added sufficient HCl to make the solution 0.2*N* in HCl. Twenty milliliters of 6 per cent sodium tetraphenylboron solution is added; and, after these materials are stirred, the precipitate is separated. The precipitate is dissolved in acetone, the solution is diluted with alcohol, and the potassium is reprecipitated. The precipitate is transferred to a tared filter disk, weighed, mounted, and counted.

The K^{42} activity is determined with a beta proportional counter by means of a decay curve taken over a period of several days.

(18) *One Hundred and Twenty-hour Degassed Activity.* The gross activity or degassed activity of a primary coolant sample from a pressurized-water reactor or a boiling-water reactor 120 hr (5 days) after sampling is from those radionuclides having half lives of the order of days and years. This activity level builds up to an equilibrium value during normal plant operation and is significant in limiting prolonged access to the reactor compartment after shutdown. The method serves as an indication of increases in corrosion product or fission-product activity. The sample from the 15-min activity analysis is allowed to decay for 120 hr and is then counted.

(19) *Rare Earths (Especially Europium).* Europium, which may be present when europium control rods are used, is separated with other rare earths by precipitation with HF in the same manner as is cerium. The rare earths are recovered from the aqueous phase after the extraction of cerium with hexone.

Procedure. The procedure as outlined for cerium is followed to the extraction step. To the aqueous layer and washings is added 10 mg of lanthanum carrier solution (Table 10.3), and the rare earths are precipitated with NH_4OH. The precipitate is washed with 5 per cent NH_4OH containing 5 per cent NH_4NO_3. The washed precipitate is dissolved in HNO_3 and the excess HNO_3 is neutralized with dilute NH_4OH. To the solution is added 10 ml of saturated oxalic solution. The precipitate is washed with water and transferred to a weighed filter disk. Then the precipitate is washed with ethanol and ether and the disk is weighed and counted.

If it is assumed that the predominant activity is due to Eu^{152} and Eu^{154}, the sample activity can be determined by using a gamma-ray scintillation spectrometer and either the peak-integration method or the spectrum stripping method. Visual inspection of the spectrum should indicate if any significant contamination by other rare earths is present.

(20) *Sodium-24.* Sodium is separated as the chloride after scavenging the solution with strontium, lanthanum, and iron carriers.

Procedure. To the sample are added 20 mg of sodium carrier solution, 5 drops each of strontium, lanthanum, and iron carrier solutions (Table 10.3), and a saturated solution of $(NH_4)_2CO_3$. The precipitate is centrifuged down, and the supernatant is treated with 2 ml of HCl and evaporated to dryness. The residue is dissolved in water, 10 ml of HCl and 10 ml of ether are added, and the solution is cooled in an ice bath. The precipitate is centrifuged down and dissolved with water, and HCl and ether are added as above. The final NaCl precipitate is filtered on a weighed glass-fiber filter, washed with ether, and weighed. The sample is then counted.

The activity of Na^{24} can be determined with either a beta proportional counter or a gamma-ray scintillation spectrometer. When using the gamma-ray spectrometer, the peak-integration method is used on the 2.75-Mev photopeak. A decay curve is taken over a period of several hours and extrapolated back to sampling time.

(21) *Strontium-89.* Barium and strontium are the important alkaline-earth fission products. Both are separated by precipitation of the nitrate from fuming HNO_3. An iron scavenge is used to separate yttrium and lanthanum daughters. Barium is separated from strontium by precipitation as the chromate.

Procedure. Into a centrifuge tube are added 20 mg of strontium carrier solution, 20 mg of barium carrier solution (Table 10.3), and the sample. The solution is evaporated to less than 5 ml and cooled; then 50 ml of fuming HNO_3 is added. After the solution is cooled and centrifuged, the precipitate is dissolved in 2 ml of H_2O. After this solution is cooled, 20 ml of fuming HNO_3 is added, the solution is again cooled, and the precipitate formed is centrifuged. The precipitate is dissolved in 10 ml of H_2O; 4 drops of iron carrier solution (Table 10.3) are added: and, after the solution is heated to boiling, CO_2-free NH_4OH is added to the phenolphthalein end point. After centrifugation the supernatant is transferred to another centrifuge cone and the time for zero Y^{90} separation is noted. After the supernatant is acidified with $6M$ HNO_3, 2 ml of $6M$ NH_4OAc and 1 ml $6M$ HOAc are added. The solution is heated to boiling, and 2 ml of $1.5M$ $K_2Cr_2O_7$ is added. After a centrifuging step, the supernatant is transferred to a beaker, and 2 ml NH_4OH is added. After this solution is heated to the boiling point, 20 ml of saturated $(NH_4)_2CO_3$ solution is added. After the solution is cooled the $SrCO_3$ formed is transferred to a weighed filter paper. The precipitate is washed with water and then with ethanol. After the precipitate is dried at 110°C, the paper and its contents are weighed, mounted, and cooled.

Strontium–89 activity is measured with a beta proportional counter. The growth of the Y^{90}, which grows in from Sr^{90}, and the decay of Sr^{89} are followed for a period of 1 week. The decay curve must be corrected for the Sr^{90}–Y^{90} activity by performing a Y^{90} separation at the end of this period as given under Sr^{90}.

(22) *Strontium–90.* The yttrium daughter is separated as the oxalate from a sample of Sr^{90} after a period of 2 weeks.

Procedure. The filter paper from the separation as given in the procedure for Sr^{89} that has aged for 2 or more weeks is ignited and the residue is dissolved in 6*N* HNO_3. After the solution is evaporated to near dryness, 20 mg of yttrium carrier solution (Table 10.3) and 5 ml of fuming HNO_3 are added. The solution is evaporated to near dryness, and 10 ml of saturated Na_2CO_3 and 1 g of solid Na_2CO_3 are added. After this solution is boiled, the precipitate formed is centrifuged and dissolved in 6*N* HNO_3. The solution is diluted to 10 ml and $Y(OH)_3$ is precipitated with NH_4OH. After a centrifuging step, the precipitate is dissolved in 2 ml of 6*N* HCl. This solution is diluted to 15 ml, and 20 ml of saturated $(NH_4)_2C_2O_4$ is added to the hot solution. The $Y_2(C_2O_2)_3$ is centrifuged down, and the precipitate is transferred to a filter paper and washed with alcohol and ether. The filter paper and its contents are ignited in a muffle furnace. The Y_2O_3 is transferred to a tared filter paper with methanol, dried, weighed, and counted.

The activity of Y^{90} is simply measured with a beta proportional counter, and a decay curve is taken over a period of several days.

(23) *Tantalum.* Tantalum and niobium are separated from other fission products by precipitation of the hydrated oxide. The tantalum is then separated from niobium by extraction of the fluo complex into diisopropylketone.

Procedure. The sample is added to 20 mg of tantalum carrier solution (Table 10.3) containing 1 ml of HF. One gram of solid NH_4NO_3 and 5 drops of 1 per cent $Fe(NO_3)_3$ solution are added, and the solution is made basic with NH_4OH. After a centrifuging step, the precipitate is washed by heating with HNO_3. The precipitate is dissolved in a small volume of 12*N* H_2SO_4 which is 0.4*N* in HF. The solution is extracted with 10 ml of diisopropylketone (DIPK), and the DIPK layer is washed with a 2-ml portion of the H_2SO_4–HF mixture. To the organic layer is added 10 ml of H_2O; and the layers are separated by centrifuging after they have been shaken vigorously. The contents of the centrifuge tube are poured into the original separatory funnel, and the aqueous layer is collected in a centrifuge cone. A second extraction with 10 ml of water is made, and this aqueous layer is added to the first one. The aqueous solution is made basic with NH_4OH, and the precipitate is separated by centrifuging. The precipitate is washed with 10 ml of hot HNO_3. The residue is treated twice more with the H_2SO_4–HF mixture, and the extraction with DIPK is repeated.

The final precipitate is transferred to a filter with the aid of 10 ml of absolute methanol and is then ignited at 900°C. The Ta_2O_5 is ground with 1 ml of methanol and transferred to a weighed platinum disk. A couple of drops of HF are added, and the disk is ignited over a Meker burner. It is then cooled, weighed, and counted.

The tantalum activities are counted with a gamma-ray scintillation counter. A decay curve taken over a period of 2 weeks is used to resolve the Ta^{182} and the Ta^{183}. Both are extrapolated back to sampling time, and the amounts of each are calculated.

(24) *Tellurium.* Tellurium is separated as the element after the removal of selenium by volatilization with HBr.

Procedure. To the sample are added 10 mg of tellurium carrier solution (Table 10.3) and then 10 ml of HBr. The beaker is covered with a watch glass and heated on a hot plate to near dryness. The HBr treatment is repeated twice using 5 ml of HBr. The residue is taken up in 5 ml of 3*N* HCl and then transferred to a centrifuge cone. The solution is made basic with 6*N* NaOH, and 2 mg of iron carrier solution (Table 10.3) is added. The solution is centrifuged, and the supernatant is made 3*N* in HCl and heated. Solid sodium bisulfite is added until no more black precipitate forms. A few drops of 1 percent Aerosol solution are added; and, after it is centrifuged and washed with 5 ml of H_2O, the precipitate is dissolved in HCl and HNO_3 and evaporated to dryness. The residue is dissolved in 10 ml of hot H_2O, and 6*N* NaOH is added until a white precipitate appears. Then 10 drops of the NaOH are added in excess. An additional 2 mg of iron carrier solution is added, and the solution is centrifuged. The supernatant is adjusted to 3*N* in HCl and then heated. Solid $NaHSO_3$ is added to precipitate the tellurium. The time of bisufite addition is noted. After it is washed with H_2O and ethanol, the residue is weighed, mounted, and counted.

The Te^{132} and I^{132} activities are measured with a beta proportional counter after a wait of 20 hr for the I^{132} to approach equilibrium. The counting is continued for 2 hr to obtain a decay curve for the Te^{132} and is extrapolated back to sampling time.

(25) *Tritium.* In certain instances the determination of tritium is desired. The sample of coolant water is dropped onto metallic calcium. The evolved hydrogen and tritium are collected in a Geiger–Muller tube, to which subsequently ethylene and argon are added. The sample tube is counted simultaneously with another tube containing inert hydrogen. The detailed procedure is given in Ref. 7.

(26) *Xenon–133.* The radioactive gases xenon, krypton, and argon, as well as inert hydrogen and nitrogen, are stripped from the coolant. The gas mixture is then counted.

Procedure. The gaseous components of the coolant are stripped and collected in the gas buret of the gas-extraction apparatus as given in Sec. 10–1.2(a). A measured amount of gas sample is transferred to the counting chamber as given for the Ar^{41} determination described in Sec. 10–1.2(b)(1). The sample in the counting chamber is stored under water for 1 week to permit decay of short-lived krypton and argon. The sample is then counted.

The Xe^{133} activity is measured by means of a gamma-ray scintillation detector and a pulse-height analyzer, using an NaI(Tl) crystal and a distance combination that gives a reasonable counting rate. A usual combination is a 3- by 3-in. crystal and about a 20-cm distance between the sample and the crystal.

(27) *Zirconium–Hafnium.* The zirconium and hafnium are separated by a barium fluozirconate (fluohafnate) precipitation. After the fluozirconate (fluohafnate) is dissolved, the zirconium-hafnium is separated by a cupferron precipitation. Since there is no simple radiochemical procedure for isolating trace amounts of hafnium from equal or greater amounts of zirconium, the hafnium is not determined. If zirconium is not used as cladding material and if hafnium is used as control rods, the same procedure for zirconium is applied to the hafnium except a hafnium carrier is used in place of zirconium. The zirconium sample may consist of Zr^{95} and Zr^{97}, whereas hafnium samples may contain Hf^{175} and Hf^{181} in addition to the above zirconium radionuclides.

Procedure. To a lusteroid tube are added 50 mg of zirconium carrier solution (Table 10.3) and the sample. The solution is made 4*M* in HNO_3 and 5*M* in HF. To this solution is added 5 ml of saturated $Ba(NO_3)_2$ solution, and the precipitate is centrifuged down. The precipitate is dissolved in 4 ml of saturated H_3BO_3 solution and 2 ml of HNO_3 followed by 10 ml of H_2O. The barium fluozirconate is again precipitated by adding 1 ml of saturated $Ba(NO_3)_2$ solution and 1 ml of HF. The precipitate is redissolved and reprecipitated as above. The final precipitate is dissolved in 4 ml of H_3BO_3, 4ml of HCl, and 10 ml of H_2O. Three drops of H_2SO_4 are added, and the solution is centrifuged. The supernatant is precipitated with NH_4OH (phenolphthalein end point), and the precipitate is dissolved in 2 ml of HCl. After this solution is diluted to 15 ml and cooled, 4 ml of a 6 per cent cupferron solution is added.

The precipitate is centrifuged down and washed with cold 1*M* HCl and then with methanol. The precipitate is transferred to a filter paper and cautiously ignited to 800°C in a porcelain crucible. The ZrO_2 is transferred to a tared 4-ml vial, weighed, and counted.

The zirconium activity, whether it is present alone or as part of a hafnium-zirconium mixture, is measured with a gamma-ray spectrometer by comparison with standards that have been freshly separated from the Nb^{95} daughter (this measurement need be done only once). The hafnium, if present in quantities greater than the zirconium by a factor of 10, can be measured by an integral gamma count above the 30-kev level. Any zirconium activity is then subtracted on the basis of the above gamma-ray spectra. Any 17-hr Zr^{97} present is negligible.

10–2 GAS–COOLED REACTORS

By C. J. Rodden

Of the many reactors now in operation, those of the Calder Hall type, which use carbon dioxide as a coolant, are the best examples of those employing gas coolants. The use of helium as a coolant is limited. Analytical methods using gas-chromatographic techniques for the analysis of impurities in helium when used as a blanket or carrier gas have been described.[8] The analyses performed on carbon dioxide are given as being indicative of gas-cooled reactors. The following discussion is taken from the work of Woodman and coworkers as reported at the Fourth Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., Oct. 12–14, 1960 (Ref. 65).

The gaseous coolant in a reactor must possess a number of characteristics in addition to the important requisite of good heat-transfer properties and this situation is reflected in some of the analytical requirements. Neutron economy considerations dictate that the coolant itself shall have a low absorption cross section and that impurities with high cross sections shall be kept below specified, very low concentrations. It is important that the coolant shall have high radiation stability and that it shall be chemically compatible with other materials in the reactor; analyses throwing light on radiation breakdown and interaction with, say, the graphite moderator, are, therefore, likely to be called for.

10–2.1 Analytical Control of Feed Gas

The gas is delivered to the reactor site in 10-ton-capacity road tankers in the liquid form. Samples are taken from each tanker on arrival and are rapidly examined to determine the percentage of gas not absorbed by a solution of KOH. This examination gives a quick measure of the purity of the gas; it must be made before the gas can be cleared for feeding into the storage tanks. The liquid carbon dioxide is sampled while it flows through a copper spiral immersed in hot water to give continuous gasification under controllable conditions. It is, of course, important to sample the liquid and not the gaseous ullage since fractionation is known to occur. A measured volume of the gas is then collected over brine and absorbed with a KOH solution; the residual gas is measured in a calibrated portion of the absorption vessel and removed, if required, for subsequent analysis by mass spectrometry or gas chromatography.[9]

The analysis of the residual gas includes the determination of argon, hydrogen, nitrogen, methane, ethane, propane, and ethylene. The most important of these is argon since Ar^{40} has a capture cross section of 0.53 barns for thermal neutrons, yielding Ar^{41} with a half life of 1.8 hr. The presence of argon, therefore, has a significant influence on shielding problems when the gas is fed into the circuit as coolant. Initially argon was determined by neutron-activation analysis,[10] but it was soon found more convenient to analyze the residual gas, along with all the other gaseous impurities listed above, by conventional mass-spectrometric techniques.

Another impurity that could have profound effects on the performance of the coolant is boron. Boron in the feed gas is determined by absorption in sodium hydroxide and subsequent distillation as methyl borate followed by absorptiometric estimation of the boron with curcumin.[11]

Moisture is determined on the feed gas by the conventional magnesium perchlorate absorption method.[12]

On occasion, gas-chromatographic analysis of residual-gas samples has been found to be a useful complementary technique to conventional mass spectrometry; for example, the chromatography approach enables one to characterize and estimate traces of dimethyl ether in the parts per million region when it is present as an unexpected impurity. In fact, it is quite feasible to dispense with mass spectrometry as a control technique and use the much cheaper gas-chromatographic method.[13]

Table 10.4 summarizes a typical feed-gas analysis.

Table 10.4—TYPICAL FEED–GAS ANALYSIS [65]

Component determined	Typical result, ppm
Ar	3
H	<1
O	35
N	75
CH_4	1
C_2H_6	<1
C_3H_8	<1
C_2H_4	5
H_2O	40
B	<0.1
Residual gas, vol.%	0.2

10–2.2 Circuit-Gas Analysis

The principal sampling points for the circuit gas of a Calder Hall type reactor are shown in Fig. 10.4.

Sampling of the circuit gas has to be carried out at pressures of the order of 100 psi and at a temperature of about 150°C. These conditions are fairly readily accomplished by using a cylinder fitted with a valve at each end coupled to the sampling point by means of a flexible pressure line incorporating a T-piece and a valve. The line and cylinder are flushed out with the sample gas, and the cylinder is finally filled with gas at the pressure of the system being sampled.[14]

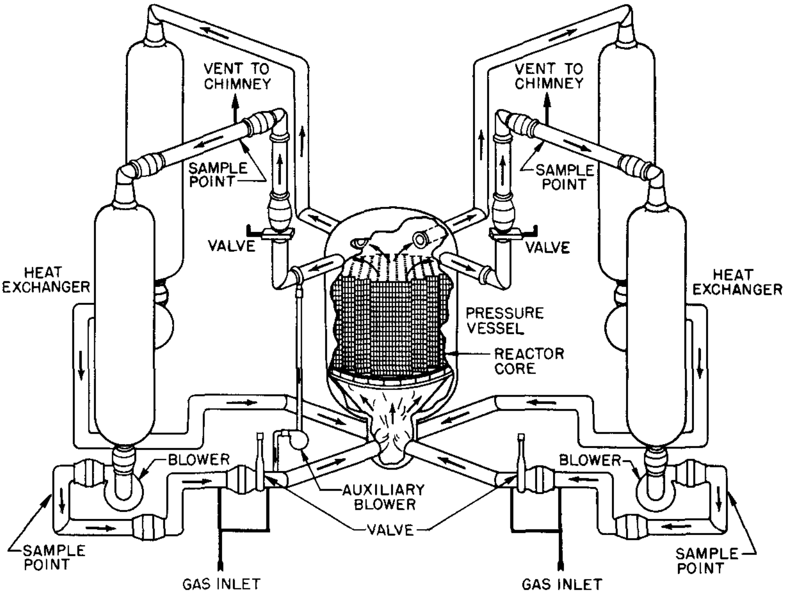

Fig. 10.4—Position of sampling points on a Calder Hall type reactor.

Following a fresh charge of gas to a reactor, a periodic determination of residual gas, i.e., percentage of gas not absorbed in KOH, is usually carried out as supporting evidence of normal satisfactory start-up. Carbon monoxide determinations are made for a similar reason. The method for these determinations is basically the conventional iodine pentoxide procedure. The gas sample is dried by passing it through silica gel and Anhydrone and then through iodine pentoxide at 140°C to 150°C; the resulting iodine is absorbed in potassium iodide and titrated with sodium thiosulphate.[15]

Carbon monoxide can also be determined by infrared monitors installed on a limited scale on the reactors. More important, perhaps, than continuous monitoring of the coolant for carbon monoxide is the application of an infrared analyzer for the detection of combustion. For this purpose the instruments have to be modified to allow differential measurements to be made of gas leaving a channel against the bulk gas entering the bottom duct to the reactor. This technique permits distinction between an ordinary burst without combustion and a burst with combustion. The instrument sensitivity is such that on a background of several thousand parts per million of carbon monoxide an increase of 150 ppm would give full-scale deflection.

Mass-spectrometric analysis of the residual gas enables one to follow the changes in the levels of other gaseous impurities, in particular

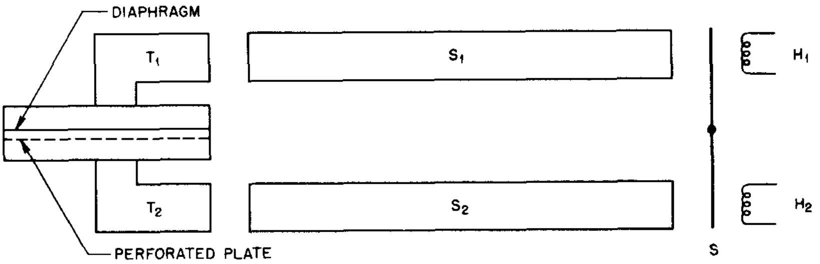

Fig. 10.5—Infrared gas analyzer.

the fall in nitrogen and argon contents soon after start-up. The initial start-up values and the time taken for the levels to fall to those of the feed gas obviously depend on the degree of purging before final pressurizing of the gas circuit and the rate of any leakage of coolant from the reactor.

Moisture determinations are frequently carried out during start-up and under normal operating conditions. A variety of methods for such a determination are available. As a reference method the Anhydrone absorption procedure is preferred.[12] A modification of the Karl Fischer method has been used,[16] but it is subject to interference from some impurities likely to be present in circuit gas. Also this method involves manipulative difficulties and it is rather slow. Therefore it is generally less suitable than other methods. For quick spot checks on moisture, one of the commercially available hygrometers, such as the Alnor hygrometer, has been found quite satisfactory. For continuous monitoring of moisture level, infrared instrumentation has been installed.[65] Their present lower limit of detection is about 20 ppm whereas normal operational levels after start-up fall well below this, usually not exceeding 10 ppm. A diagram of the infrared gas analyzer installed is shown in Fig. 10.5. It is similar to the Perkin–Elmer TRI–NON instrument. The gas to be analyzed is passed continuously through the sample tube, S_1; absorption in S_1 is compared with the absorption in a similar tube, S_2, mounted parallel to S_1 and usually filled with dry air. Energy from two nichrome heaters, H_1 and H_2, is passed through both tubes and the portion transmitted is received by the two chambers, T_1 and T_2, which contain a sample of the gas to be measured.

The chambers T_1 and T_2 are separated by a thin diaphragm that forms one electrode of an electrical condenser. The other electrode is in the form of a closely adjacent insulated, perforated metal plate. Radiation transmitted by S_1 and S_2 is absorbed by the gas in T_1 and T_2 causing a temperature increase with a resultant increase in pressure.

If the transmission through both S_1 and S_2 is identical, the diaphragm remains stationary. When, however, a sample of gas to be analyzed is introduced into S_1, the transmission balance is broken; and the diaphragm is displaced, producing a corresponding change in the capacitance of the condenser. The application of a polarizing potential to the condenser converts the capacity change to a current change that is amplified to provide an indication related to the pressure difference between T_1 and T_2.

To obtain measurements free from zero drift, a rotating shutter S interrupts the radiation from heaters H_1 and H_2 at a frequency of about 6 cycles/sec, allowing pressure changes to be directly related to temperature changes which are themselves related to the differences in absorption of energy S_1 and S_2. Any other gas present in the sample will not affect the result unless it has absorption bands which overlap those of the gas (water vapor) being determined. In this event filter tubes containing the interfering gas or gases can be included in the two optical paths.

The C^{14} content of circuit gas is of interest for two reasons. First, it is necessary to evaluate the activity due to C^{14} prior to the occasional release of the reactor coolant; and, second, it is of interest in the study of coolant–moderator reactions. Carbon monoxide builds up after start-up to a level of the order of 0.3 to 0.4 vol.%, and the C^{14} level in the carbon monoxide is consistently some 20 times higher than it is in the carbon dioxide. This condition presumably follows from the reaction of the fresh coolant carbon dioxide with graphite moderator rich in C^{14} and implies that subsequent exchange is very slow. The result of this observation emphasizes the continuing need for an analytical procedure that can determine C^{14} in the monoxide and dioxide separately; this determination is readily achieved by absorption in KOH (with subsequent regeneration of the carbon dioxide in barium hydroxide) while the residual carbon monoxide is oxidized by iodine pentoxide to the dioxide, which is in turn absorbed in barium hydroxide. The resulting barium carbonate precipitates are gelled with an organic scintillant and the C^{14} content evaluated conventionally in a liquid scintillation counter. A typical figure for the C^{14} content of coolant carbon dioxide is 1 disintegration/min/ml.

One other determination in the circuit gas worth mentioning is that of traces of oil present, e.g., from a faulty seal in the blower. The sampling technique,[17] which perhaps is not ideal, is designed to collect oil in fine droplet form and as vaporized oil; it involves the insertion of a specially designed sampling tube with a $\frac{1}{16}$-in. hole drilled in the side $\frac{1}{8}$ in. from the end. A needle valve leads to a copper cooling spiral and two absorption vessels containing carbon tetrachloride. After a 6-hr sampling time at a rate of 1 liter/min, the tube complete with head is detached and rinsed with carbon tetrachloride. The washings are combined with the main absorbant, and the oil content is assessed by a conventional infrared absorption procedure,[18] making the measurements at 2890 cm^{-1} (3.46 μ) (attributed to the carbon–hydrogen stretching frequency of hydrocarbons) and using as a standard the actual oil used in the blowers. The limit of detection is 5 ppm.

Determination of Radioactive Components of Circuit Gas. It is of great interest and of some importance to determine the radioactive components of circuit gas in prototype power reactors during normal operation for several reasons. First, from the aspect of shielding studies, much valuable guidance can be obtained by characterization of the various active species present. Second, from the health physics standpoint, it is important to have a knowledge of the activities present in circuit gas before a discharge "blow-down" can be authorized. Third, from the point of view of the continuing satisfactory operation of burst-cartridge detection gear, data on activities other than those of fission products is clearly useful. Finally, from the more fundamental aspect of reactor studies, including coolant–moderator interactions and canning-material performance, information on the active species present is important.

Two active components have already been mentioned (Ar^{41} and C^{14}); but, additionally, it would be expected that N^{16} and O^{19} would be present. Preliminary measurements of the activities of the Ar^{41}, N^{16}, and O^{19} in the coolant gas have been made by flowing the gas from a duct sampling point along a delay line and through a flow-through Geiger tube. The separate determination of Ar^{41} in the gas has reached a more advanced stage. The problem is far simpler than that for the shorter lived isotopes since normal gamma-spectrometric techniques can be used. The gas sample is contained in a 4-in.-high 1½-in.-diameter container situated on a 1- by 1½-in. NaI (Tl) crystal. The counting efficiency of this system has been calculated mathematically; and, for gas containing 4 ppm of natural argon, a typical value of Ar^{14} activity of 10 disintegrations/sec/cm^3 (at S.T.P.) is obtained.

This gamma-spectrometric study of the activity of the coolant gas with a 100-channel gamma spectrometer confirms the presence of N^{16}, Ar^{41}, and O^{19} with their energies at 6.13, 1.30, and 0.20 Mev, respectively. Gamma spectra obtained from circuit-gas filter samples are typical of irradiated graphite associated with traces of activated constructional-material corrosion products, e.g., activated iron rust.

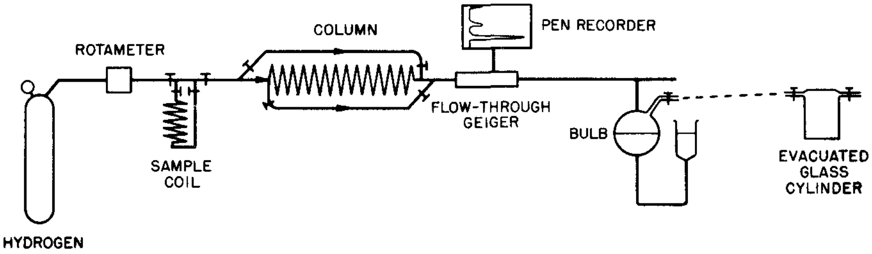

Fig. 10.6—Gas chromatograph.

Some very small contributions to the gas activity come occasionally from fission-product gases released into the coolant from burst cartridges or from cartridge contamination, and some knowledge of these contaminations is very useful in the understanding and improvement of burst-cartridge detection. For one to study the fission-product gases in the coolant without too great a delay, it is necessary to separate the Ar^{41} from the xenon and krypton isotopes by some rapid physical means.

Several techniques have been examined, and the most encouraging method investigated so far is that of passing the gas through a gas-chromatographic column. Figures 10.6 and 10.7 show the more or less conventional apparatus used and the separation achieved.[66] The sample of residual gas is introduced into the gas-chromatographic apparatus by means of the spiral system shown and is flushed through the column (8 ft by ¼-in. ID coiled copper tube filled with $^{36}/_{42}$-mesh 5A molecular sieve) with hydrogen at 150 ml/min.

Detection of the active rare gases is achieved by a flow-through Geiger tube containing a 2-in. plug of activated charcoal. The charcoal serves to hold up the gases inside the counter so that the maximum count can be obtained; this count is shown by a pen recorder. A typical separation is shown in Figure 10.7. Although the activity of Ar^{41} is orders of magnitude greater than the krypton and xenon fractions, it shows only a minimum peak height since it is not held up at all by the charcoal contained in the Geiger detection tube.

The krypton fraction is collected over water, and then the flow of hydrogen through the chromatographic column is reversed. This action quickly elutes the xenon, which is strongly adsorbed at the front of the column. The xenon fraction is also collected over water.

Both rare gases are transferred to evacuated glass cylinders of known dimensions and are then counted on a 3- by 3-in. sodium iodide crystal connected to a 100-channel pulse-height analyzer. Gamma-spectrometric scans of the krypton and xenon fractions are obtained. From these scans the activities of the particular isotopes are calculated and plotted.

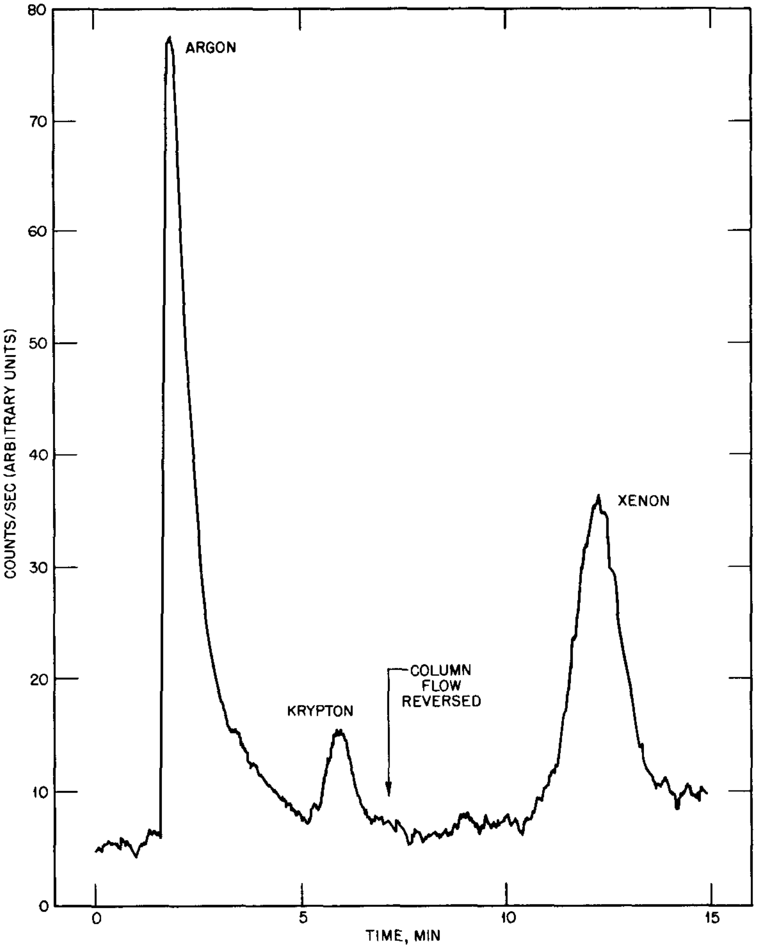

Fig. 10.7—Separation of radioactive gases by gas chromatograph.

10–3 REACTORS COOLED WITH SODIUM OR SODIUM–POTASSIUM ALLOYS

By W. C. Judd and D. Dutina

Metallic sodium contains a wide variety of impurities that are generally of low concentration. Results obtained on typical material are shown in Table 10.5. Of the impurities shown, several are particularly important. Oxygen, for example, must be kept at minimum attainable levels if sodium is to retain its noncorrosive properties. Boron, cadmium, and mercury have extremely high cross sections, and their concentration must be kept in check from the point of view of neutron economy. Indeed, it is for this same reason that the total impurity concentration must be determined and minimized.

There has been concern over the problem of transport of activated nuclides from the structural material of the reactor core to the outer portions of the coolant system. This process takes place through normal corrosion and atom-exchange processes in coolant systems and can lead to excessive radiation levels in system components that may require service. It is necessary, therefore, to try to limit corrosion processes and to perform chemical analyses to assure compliance with necessary specifications of purity.

A variety of analytical methods have been developed to meet this need. Some of the required analyses can be performed after simply testing a standard procedure for applicability to the sample under study; others require some modification of standard procedures to tailor them to the special needs of this system. A few determinations require novel approaches of method and equipment, such as the analyses of oxygen, hydrogen, and carbon.

In the text that follows, a recommended procedure for each of the elements is given in detail. Alternate procedures, when available, are described also but in an abbreviated manner. It should be stated, however, that in many instances the recommended and alternate procedures are of equal suitability and the method chosen for detailed description simply reflects the personal inclinations of the authors of this section.

It is believed that estimations of metallic elements may be made best by spectrographic techniques. These techniques permit the simultaneous observation of a wide variety of contaminants in a single sample of sodium; thus maximum information per dollar spent on analysis is obtained. Spectrographic methods suitable for the analysis of metallic impurities in sodium have been developed by F. P. Landis and coworkers at the Knolls Atomic Power Laboratory [19] and are described in Sec. 10–3.4.

For a few of the elements, e.g., iron and boron, colorimetric methods are presented in addition to the spectrographic ones. These elements are of particular interest and importance in the field. Consequently the colorimetric methods are made available for use in those cases where it is essential to obtain greater precision than that afforded by spectrographic techniques.

10–3.1 Handling and Sampling

A complete description of the physical characteristics of and precautions in handling sodium and sodium–potassium alloy can be found in the book entitled, *Sodium, Its Manufacture, Properties and Uses.*[20]

Table 10.5—IMPURITY CONCENTRATIONS IN SODIUM

Element	Parts per million	Analytical method
Ag	0.3	Spectrographic.
Al	20	Spectrographic.
B	<4	Spectrographic; colorimetric.
Ba	2	Spectrographic.
Be	<1	Spectrographic.
C	50	Manometric.
Ca	15	Spectrographic.
Cd	<1	Spectrographic.
Cl	<20	Volumetric.
Co	<2	Spectrographic.
Cr	<1	Spectrographic, colorimetric.
Cs	<50	Flame photometric.
Cu	4	Spectrographic.
Fe	1	Spectrographic; colorimetric.
H	60	Gasometric.
In	<1	Spectrographic.
Hg	1	Spectrographic.
K	<100	Flame photometric.
Li	15	Flame photometric.
Mg	10	Spectrographic.
Mn	<2	Spectrographic.
Ni	<2	Spectrographic.
O	10	Volumetric.
P	<10	Colorimetric.
Pb	2	Spectrographic.
Pd	<3	Spectrographic.
S	30	Volumetric.
Si	<10	Spectrographic.
Sn	<15	Spectrographic.
Sr	<5	Spectrographic.
Ti	<10	Spectrographic.
Tl	<10	Spectrographic.
U	<0.7	Fluorometric.
V	<2	Spectrographic.

To avoid excessive repetition, the reader is referred to this invaluable work for the various details of sodium technology. Another useful reference is the *Liquid Metals Handbook, Sodium (NaK) Supplement.*[21] Considerable detail concerning the handling and sampling of sodium and sodium–potassium alloy can be found in it. Also the methods used at the Capenhurst Works, United Kingdom Atomic Energy Authority, are presented in Ref. 22.

The casual reader, who is not acquainted with basic properties of sodium, may be helped by the following general observations concerning the properties and technology of sodium. It is a light metal (density, 0.9684 g/cm^3 at 20°C) with a melting point of 97.8°C. It is highly reactive and combines with oxygen, water, etc., in a most violent manner. One product of the reaction with water is hydrogen, which can create a hazardous condition because of its potentially explosive nature in the presence of air. Sodium is a good heat-transfer agent.[23] It can be pumped by means of electromagnetic pumps, thus no moving parts in the coolant system are required. When free of oxygen, it has only slight corrosive action on stainless steel. Finally, pure sodium is commercially available in adequate supply.

When sodium is sampled for analysis, it is quite difficult to obtain a representative fraction. This problem is discussed by Mausteller and Voorhees.[23] In addition, the references to the determination of oxygen also touch on the sampling problems. Probably the most effective method of sampling large systems is by means of the sampler described by Bruggeman et al.[24] When sampling techniques are being devised or selected, due attention must be paid to the problems of homogeneity, differential freeze-out in the sample line, and particulate suspension instead of the true solution. The sodium sample obtained for analysis is generally transferred into an evacuated glass or quartz tube and allowed to cool and solidify. The tubing is then broken, and the sodium is dissolved prior to analysis. There are four dissolution media generally used: alcohol, water, mercury, and organic solvents.

Sodium–potassium alloy, in contrast to sodium, is liquid at room temperature and is violently pyrophoric. Pepkowitz[25] describes a novel and effective method of dissolving sodium–potassium alloy prior to analysis.

10–3.2 Determination of Sodium and Potassium in Sodium–Potassium Alloy

Walters and Miller[26] describe a weighing and titration method to determine the sodium and potassium content of sodium–potassium alloy. These authors also describe a freezing-point determination in the 92 to 100 per cent potassium region.

10–3.3 Chemical Analysis of Impurities in Sodium

When a sample of sodium or sodium–potassium alloy is analyzed, the usual procedure for determining the sample weight is titrating with a standard acid. Flame photometry affords a second way of determining sample weight. A measured aliquot of the solution, resulting from the dissolution step, is analyzed for sodium by a flame photometer. In the case of hydrogen and impurity determinations, the metal sample is weighed directly.

(a) *Hydrogen.* The hydrogen content of sodium or sodium–potassium alloy used as a heat-transfer fluid in a heat-exchange system should be held to a specified minimum because of possible hydriding and subsequent embrittlement of the materials of construction. The determination of an excessive amount of hydrogen in the liquid-metal coolant serves as a warning that a potential danger of hydriding embrittlement exists.

The first description of the determination of hydrogen in sodium was reported by Pepkowitz and Proud.[27] They sealed a sodium sample in an iron capsule and heated it to 700°C in a vacuum system. The hydrogen present diffused through the capsule walls and was measured by the usual vacuum-system techniques. When used to measure the hydrogen content of brick sodium, this technique exhibited a standard deviation of ±15 ppm at concentrations of approximately 60 ppm.

Holt[28] indicated that the above method did not liberate all the hydrogen. He proposed an isotope-dilution method employing a mass spectrometer for measurement of the hydrogen. In Holt's method the rapid exchange of hydrogen and deuterium in sodium and sodium–potassium alloy affords a convenient method for the determination of hydrogen. After a known amount of deuterium has been added, the sample is heated at 500°C for 5 min. The deuterides and hydrides are then decomposed, and the resulting gases are analyzed in a mass spectrometer. Although results derived with sodium were satisfactory, it was found necessary to apply a correction factor with sodium–potassium alloy to compensate for the effect of different rates of formation of the hydrides and deuterides in the cooler zones of the tube during equilibration.

Procedure.[27] This procedure requires the use of iron capsules, welding apparatus, a vacuum system, and an induction heater. This equipment is shown in photographs and in diagrams in the first five figures of Ref. 27. Brief descriptions of this equipment are included below to the extent required for comprehension, but the reader is referred to Ref. 27 for a more complete discourse.

Iron capsules, which are the shells of 6C5 metal radio tubes, and covers, which are press-fit caps stamped from 10-mil sheet iron, are degreased with acetone and oven-dried. The capsules and lids are degassed in the vacuum apparatus by heating them inductively at 700°C while continuously pumping on the system. When the pressure is reduced to 2 or 3×10^{-3} torr, pumping is stopped, the capsules are allowed to cool, and tank helium is bled into the system until atmospheric pressure is attained. The capsules are stored in a desiccator until they are used.

The sodium to be analyzed is stored and sampled in a dry box under a helium atmosphere. In the case of the raw brick metal, a sample from the center of the brick is cut, placed in one of the degassed capsules, and weighed. The lid is pressed into place, and the capsule is removed from the dry box and immediately welded shut. The seal is made with a simple shielded arc-welding technique using a tungsten electrode.

The sealed capsule is next introduced into the vacuum system, which consists of the following parts in sequence: a pyrex furnance tube, a thermocouple gauge, a cold trap cooled with liquid nitrogen, a double McLeod gauge, quartz copper oxide tube with an external heater, and a mechanical pump. The capsule is supported on a molybdenum wire rack positioned in the pyrex furnace tube. Next, the copper oxide is degassed by heating to 400° C while pumping on the system. When the pressure is reduced to 1 to $2\text{X}10^{-3}$ torr, the system is closed to the pump, and the copper oxide is cooled to room temperature with an air blast. During this interval the tightness of the system is verified by means of the thermocouple gauge.

The coil of the induction heater is centered around the portion of the pyrex furnace holding the iron capsule. The temperature is raised to 700°C over a period of 5 min to allow the hydrogen to diffuse through the walls of the capsule as it is generated, thus preventing a build-up of excess pressure in the capsule. Heating is continued until a constant reading, H_T, is attained on the McLeod gauge (usually 15 to 20 min). The induction heater is turned off, and the copper oxide furnace is turned on. The hydrogen is oxidized to water, which is then frozen out in the cold trap, a process normally requiring 35 min. The pressure is read at intervals until a minimum reading, H_R, is reached. The copper oxide furnace is removed, and the system is brought to atmospheric pressure by running in tank helium.

The hydrogen is calculated from the two pressure readings, H_T and H_R, and from a blank, b, obtained by running an empty capsule through the procedure. The equation employed is:

$$\text{Mg of H}_2 = (H_T^2 - H_R^2)K - b$$

where K is an experimentally determined constant for the whole system. It it determined by carrying known amounts of standard sucrose through the procedure using magnesium turnings as the reducing agent.

(b) *Carbon.* When sodium is employed as a coolant in a reactor heat-exchange system made from stainless steel, the carbon content of the sodium must be kept low because stainless steels are subject to grain-boundary carburization and consequent embrittlement.

Stoffer and Phillips[29] determined carbon in sodium–potassium alloy by combustion of the sample in an atmosphere of pure oxygen. The carbon is thus converted to carbon dioxide, which is absorbed and weighed. A temperature of 950°C is necessary to assure complete recovery of the carbon dioxide.

A wet-combustion technique for measurement of the carbon in sodium, after the sodium is converted to hydroxide by contact with moist nitrogen, is reported by Farrington et al.[30] Pepkowitz and Downer[31] also discuss a procedure that involves wet combustion followed by a conductometric determination of the carbon dioxide. A manometric method of carbon dioxide measurement following a wet-combustion procedure is reported by Pepkowitz and Porter.[32] This method is designed to measure carbon concentrations in the 0.01 per cent range in sodium. The method has a standard deviation of ±0.001 per cent. A modification of the latter method, usable in the 10 to 300 ppm concentration range, is included in the Capenhurst compilation.[22]

Procedure.[22] The apparatus is comprised, in sequence, of a conventional gas-purifying train, a reaction tube, a system of cold traps, a manometric system, and a vacuum pump. The purifying train for the oxygen sweep gas consists of a copper oxide preheater (600°C), a sulfuric acid bubble counter, and an Anhydrone–Carbsorb adsorber. The reaction tube is fitted with a dropping funnel. The three cold traps, in order, are cooled with a dry-ice–acetone mixture, liquid nitrogen, and again liquid nitrogen. The manometer is connected by means of a 3-way stopcock in the line between the first trap and the second trap. The manometer pressure is indicated by the level of oil in the capillary tube; contact between oil and carbon dioxide is prevented by a mercury seal. The method for filling the manometer is described in Ref. 22.

Approximately 1 g of sample is weighed and transferred to the dry reaction tube, which is disconnected from the apparatus. With the funnel head attached and closed, the vessel is purged with nitrogen. Five milliliters of water are added dropwise through the funnel; nitrogen flow is continued until the sodium has dissolved. The solution is neutralized with 3.6*M* sulfuric acid, and a few milliliters in excess are added. The solution is evaporated to dryness by suspending the tube between two vertical infrared heaters while the nitrogen flow is maintained to speed up the dehydration. The reaction tube is attached to the manometric system. The cold traps and manometer are evacuated to the limit of the vacuum pump while the rest of the system is isolated. During this period the first trap, which removes water, is cooled, as is the third trap, which is designed to guard the pump. The stopcock connecting the traps to the rest of system is gradually opened.

Next, oxygen is drawn into the manometer at a sufficient rate (about 20 ml/min) to produce a 2-cm rise. After the entire system has been purged for 10 min, a flask of liquid nitrogen is placed under the second trap and the CO_2 is frozen out; the oxygen purge is continued. Through the dropping funnel, 5 ml of the oxidizing solution is added. (To form this solution, combine 13 g of chromic acid, 85 ml of orthophosphoric acid, and 165 ml of fuming sulfuric acid. This solution is gradually warmed to 140°C and then cooled to 80°C. Suction is applied during the remainder of the cooling time to remove dissolved CO_2.) The mixture is heated at incipient boiling for 5 min; oxygen is drawn through the system for an additional 5 min. Again the reaction vessel and gas train are isolated, and the remainder of the system is evacuated. Next, the third cold trap and the pump are isolated, and the connection between the manometer and the second cold trap is made by means of a stopcock. The pressure P_1 is read, the liquid-nitrogen flask is removed, the trap is warmed to room temperature, and the pressure P_2 is read. A reagent blank is handled in the same way as the sample was handled. The carbon content of the sample is calculated from the following expression:

$$\text{Carbon (ppm)} = \frac{(P_2 - P_1) - (B - P_3)F}{W}$$

where P_1 and P_2 = pressure readings taken above the sample
B = room-temperature pressure reading of the blank
P_3 = manometer reading for the blank with the liquid-nitrogen trap in place
W = weight of sample in grams
F = calibration factor for the system

The calibration factor is determined by adding 1 ml of sucrose solution (1 mg/ml) to the reaction tube and carrying out the procedure detailed above. This procedure is repeated with successively larger aliquots until the limit of the manometric system is reached. A graph of micrograms of carbon vs. pressure is plotted. The factor F for the apparatus is calculated as

$$F = \frac{\text{Sum of micrograms of carbon added}}{\text{Sum of pressures in millimeters produced}}$$

(c) *Nitrogen.* The determination of nitrogen in sodium has not assumed the importance of the determinations of oxygen or hydrogen, but a knowledge of the nitride nitrogen concentration permits a useful estimation of the possible extent of nitriding of structural materials in the system. The nitride level has been measured by the Nessler technique.[33]

The sample is decomposed with alcohol followed by steam, and the nitride is allowed to react with water, forming ammonia. This procedure is done in a flask fitted with a delivery tube immersed in a dilute acid solution. The remainder of the ammonia is distilled into the dilute acid, the distillate is evaporated to remove alcohol, and the ammonia is determined by the Nessler method.[4, 34] The useful range of this method is 5 to 400 ppm with a standard deviation of ±10 per cent.

Procedure. The steam-distillation apparatus employed in this determination is a conventional one. It consists of a steam-generating flask closed with a one-hole stopper in which is inserted a vent tube with a stopcock. The steam leaves the flask through a side arm, which holds a stopcock and which terminates in a standard-taper joint. This joint connects with a matching joint on the reaction flask. The flask is fitted on top with a dropping funnel and is connected by means of a standard-taper joint to a water-cooled condenser. The receiver for the condensate is a 150-ml beaker. Heating of the steam generator is accomplished by an electrical heating mantle.

The complete apparatus is assembled, and the water in the steam generator is heated to a vigorous boil. Steam is passed through the apparatus for 30 min with the condenser water not running. After this steaming-out period, the receiver is removed and the steam is vented to the atmosphere. The stopcock on the steam-flask side arm is closed, the reaction flask is removed, and the tip of the side arm is dried carefully. Twenty milliliters of 0.02N hydrochloric acid is placed in the receiving beaker. The beaker is placed in such a manner that the condenser tube presses against the flat bottom; this arrangement serves to break up the gas bubbles. Water flow through the condenser is started. The sodium sample (1 to 2 g) is placed in the dry reaction flask, which is then attached to the distillation assembly. By means of the dropping funnel, 15 to 20 ml of ethyl alcohol (95 per cent) is added slowly to the sample. Near the end of the dissolving period, 2 to 3 ml of water is added to speed up the reaction. The reaction rate, controlled by the rate of alcohol addition, should be such that a rapid stream of bubbles is caused to evolve from the condenser tip. The rate, however, should not be so rapid that contact of the gas and receiver solution are not maintained. If necessary, the reaction rate can be reduced by raising an ice bath around the reaction flask.

When the reaction is complete, the side arm of stopcock is opened, and the vent on the steam flask is closed. The receiving flask is lowered momentarily while steam sweeps air out of the apparatus. It is raised again so that the condenser tip is just immersed, and the steam flow is continued until a total of 50 ml of distillate has been collected. The receiver is lowered, the distillate is allowed to drip for 30 sec, and the condenser tip is rinsed with water into the receiver solution. The heat is removed, and the steam generator is vented.

The receiver solution is boiled down to a volume of 25 ml, cooled, and transferred to a 50-ml volumetric flask. One milliliter of Nessler's reagent is added. (To make this reagent add to a solution containing 61.75 g of potassium iodide dissolved in 250 ml of water sufficient saturated mercuric chloride to just make it bright red. The red precipitate is dissolved with 0.75 g of potassium iodide, and a solution of 150 g of potassium hydroxide in 250 ml of water is added. The volume is then brought up to 1 liter.) After this volume is diluted to the mark, the absorbance is measured at 410 mμ in 1-cm cells with water as a reference solution. The nitrogen concentration is obtained from a reference curve made by measuring the absorbance of solutions containing known amounts of ammonium chloride to which Nessler's reagent has been added. Blanks are run on triply distilled sodium carried through the entire procedure.

The weight of the sodium sample taken may be determined by titrating the solution remaining in the reaction flask with standard acid.

(d) *Oxygen.* When sodium or sodium–potassium alloy is used as a heat-transfer medium in a nuclear power plant, the determination and control of the oxygen content is of considerable importance. High oxygen levels lead to excessive corrosion rates and also may cause plugging of constricted passages in the system.

The first method reported for the determination of oxygen (sodium monoxide) in sodium was that of Pepkowitz and Judd.[35] This method is based upon the principle of extraction of the metallic sodium with mercury, leaving sodium monoxide as a residue in the extraction vessel. The sodium monoxide can then be dissolved in distilled water and titrated with standard acid or determined with a flame photometer. The sodium sample weight is determined by dissolving the sodium from the mercury alloy and titrating with standard acid.

The original procedure was modified by Williams and Miller[36] and by Pepkowitz, Judd and Downer.[37] Williams and Miller were able to obtain a mean deviation of ±0.002 per cent with their refined procedure. All the authors cited in Refs. 35 to 37 describe the difficulties encountered when attempting to obtain a truly valid sample from a liquid-metal system. Bruggeman and Billuris[24] described a system for sampling sodium and performing the analysis in an argon-filled chamber attached to the heat-exchange system. This ingenious apparatus gave results with a standard deviation of ±0.001 per cent.

Another technique for determining the sodium monoxide content of sodium makes use of the Wurtz reaction.[38] Sodium metal reacts with excess alkyl halide in xylene. The products formed are sodium halide and hydrocarbon. The sodium halide and sodium monoxide are dissolved in water. An acid titration measures the amount of sodium monoxide originally present. The amount of sodium originally present can be determined by performing a halide analysis. The standard deviation of this method is ±0.005 per cent according to White, Ross, and Cowan.[38] A method for obtaining an improved acidimetric end point, which is necessary when the sample has a small oxygen content, is presented by Smythe and deBruin.[39] Silverman and Shideler[40] report a modification in the method used to dry the alkyl halide reagent and claim an improvement thereby, but the authors present no direct comparison of results obtained by the modified and the original methods. A modified version of the alkyl halide method is also reported by the Ethyl Corporation.[41] Their version describes a novel sample preparation involving the use of a blanket of hot white oil (Primol D) and isopropyl alcohol to prevent oxidation. Since the alcohol film so produced might lead to high results, it is removed prior to analysis by rinsing in a warm (70°C) mixture of white oil, *n*-butyl bromide, and *n*-hexane. Other modifications suggested are the use of a closed reaction vessel to prevent moisture absorption by the alkyl bromide reagent and the drying of the reagent over warm, powdered calcium metal. A standard deviation of ±0.0006 per cent is reported for the method.

A third type of method for the estimation of oxygen in sodium consists of distillation of the metal away from the oxide.[42, 43] The oxide is dissolved and determined by titration. This method requires more elaborate equipment and techniques than the methods discussed above.

Procedure.[41] The reactor employed is fabricated from 35-mm glass tubing. It is approximately 12 in. long and is sealed closed at one end and fitted with a standard-taper 40/50 glass joint at the open end. The top for this reactor vessel consists of a male 40/50 joint fitted with a three-way stopcock, the arms of which are made of 9-mm tubing. Nitrogen gas, used for purging, is purified by passage through a glass tower filled with Dehydrite.

The three-way stopcock and the glass joint of the reaction vessel are lubricated with a minimum of Dow–Corning high-vacuum grease. The entire assembly is heated in an oven at 500°C for 30 min. The apparatus is then cooled just sufficiently so that it can be connected to a vacuum line and a dry nitrogen tube. The vessel is alternately evacuated and then filled with dry nitrogen several times by means of the three-way stopcock. The vacuum is maintained for approximately 30 min while the vessel cools to approximately 80 to 60°C. A Glass-Col heater, under the reactor, serves to maintain the temperature.

The reactor is filled with dry nitrogen, the head is removed, and approximately 75 ml of *n*-butyl bromide–hexane solution is filtered into it. (Four parts of *n*-butyl bromide are mixed with five parts of *n*-hexane.) Oxygen compounds are removed by extracting in a separatory funnel with successive 25-ml portions of sulfuric acid until the acid layer remains colorless. The entrained acid in the organic layer is neutralized by mixing the organic solution with solid sodium bicarbonate. The organic solution is filtered and kept stoppered in a flask that has a drying tube filled with Dehydrite attached to the stopper. The reagent is dried by boiling it gently (70°C) with ground calcium metal. The reactor is again alternately evacuated and purged with nitrogen.

The sodium sample is dropped into a 250-ml large-mouth Erlenmeyer flask containing 100 ml of white oil [dry Primol D mixed with a small volume (5 per cent) of dry xylene and boiled to expel moisture] and 1 ml of isopropyl alcohol (dried by refluxing with molten sodium and distilling). The oily solution is heated until the sodium melts, and the flask is rotated to slough off any oxide film from the molten sodium. The ball of molten sodium is split in two by squeezing the middle of the sphere with a dry pair of tweezers. The oil is cooled with a blast of air, and one ball of sodium is quickly transferred to a second flask containing white oil and isopropyl alcohol. Again the solution is heated until the sodium melts, and then it is immediately cooled. The sodium is rapidly transferred to a stoppered Erlenmeyer flask containing 50 ml of dry white oil and 50 ml of the *n*-butyl bromide–hexane solution heated to 70°C. The sodium is permitted to react with the reagent for 3 to 5 min, and some of the blue-black crust of sodium bromide is sloughed off. The sample is then transferred to the reaction vessel, which is alternately evacuated and purged with dry nitrogen until the reaction subsides. A stirring rod (12-in.-long 7-mm-diameter glass rod flattened at one end) is used to pulverize the sodium bromide mass, and the vessel is heated gently at 70°C for 30 min to ensure complete conversion of sodium to sodium bromide.

The hot solution is hydrolyzed with approximately 50 ml of distilled water and stirred to extract all the alkali-metal oxides from the two-phase system. The mixture is transferred to a 250-ml separatory funnel, and the aqueous layer is drained into an Erlenmeyer flask. The reaction flask and separatory funnel are washed with an additional 25-ml portion of distilled water, which is combined with the first aqueous extract. The solution is titrated with standard 0.01*N* hydrochloric acid to the phenolphthalein end point. The weight of the combined oxygen is equal to the milliequivalents of acid required times 0.008.

The weight of the sodium sample may be determined on the neutral aqueous extract by means of a Volhard titration for bromide. The extract is diluted to 1 liter, and a 25-ml aliquot is placed in a 250-ml flask. Twenty milliliters of dilute nitric acid (1+9), 5 ml of benzyl alcohol, and 3 to 5 ml of ferric alum indicator are added. From a buret is added 0.2 to 0.3 ml of standard 0.1*N* potassium thiocyanate solution. Next, the solution is titrated to the disappearance of the red-brown color with standard 0.1*N* silver nitrate solution.

(e) *Lithium and Potassium.* The determination of the alkali elements in sodium has not attracted much attention, with perhaps the exception of potassium. Traces of lithium and cesium are hardly deleterious to the performance of sodium as a heat-exchange medium; hence little concern over their absolute levels is shown. Natural potassium levels in sodium are not of great concern, but because of certain developments in the technology, there is usually a need to know the potassium content of sodium.

Lithium and potassium are usually determined by flame photometer techniques.[44] The sodium sample is dissolved in water by dropping very small pieces of it into about 2 ml of water in an Erlenmeyer flask or beaker into which a stream of nitrogen gas is rapidly flowing. As more and more sodium reacts with the water, the resulting hydroxide solution becomes quite concentrated, and the sodium–water reaction then slows down. Slightly larger pieces of sodium can now be added, and a small amount of water can be added to speed up the dissolution. In this way, a 1-g sodium sample can be dissolved in about 15 min. The sodium hydroxide formed is titrated with standard hydrochloric acid; the titration neutralizes the solution and gives an estimate of the amount of sodium in the sample. The solution is evaporated and transferred to a volumetric flask and diluted to volume (10 ml for each gram of sodium).

The line intensity of an aliquot of the solution is read on the flame photometer using a didymium filter to reduce the intensity of the sodium light. Standards can be prepared easily by dissolving the appropriate amount of pure sodium chloride and adding measured amounts of alkali-metal standard solutions. The line intensities of the standards are compared with the line intensities of the sample. It is important to have identical sodium chloride concentrations in the standard and sample solutions since the aspiration rate of the solution is affected by the salt content when the solution is moderately concentrated.

An alternate method for estimating the lithium or potassium content of the sample solution is given by the method of standard addition. After the inital line intensities are observed, a measured aliquot, V_1, of a concentrated standard solution is added to a measured aliquot, V_2, of the sample solution and mixed well. The resulting line intensity is again observed; the increase in intensity is proportional to the mass of standard added. With this information it is possible to calculate the original concentration of the element in the sample solution.

Table 10.6.—WAVE LENGTHS AND SENSITIVITIES OF ALKALI METALS DETERMINED BY FLAME SPECTROPHOTOMETRY

Element	Wave length, mμ	Sensitivity, ppm
Lithium	671	15
Potassium	767	100
Cesium	852	50

Listed in Table 10.6 are the wave lengths and sensitivities for the estimations of the alkali metals in sodium by a flame-photometer technique.

(f) *Cesium.* The determination of cesium[45] in sodium can be accomplished by precipitating ammonium chloroplatinate from a chloride solution and allowing the cesium chloroplatinate to coprecipitate with it. The chloroplatinate is then dissolved in hydrochloric acid, diluted to volume, and determined with the flame photometer.

(g) *Boron.* The boron content of sodium has been measured at the 0.5-ppm level using a 2-g sample. The method utilizes the chromogenic properties of the curcumin–boron complex. Sodium is dissolved in a boron-free container and evaporated to dryness as the chloride salt. The boron is separated from the salt by extracting into acidified ethanol. The boron is estimated colorimetrically in the ethanol extract with curcumin as a reagent. The details of extraction and color development as described by Rynasiewicz et al.,[46] are given in the following procedure.

Procedure. Approximately 2 g of sodium are dissolved in 50 ml of water in a quartz Erlenmeyer flask purged with a continuous stream of nitrogen. The solution is cooled in an ice bath and nearly neutralized to the methyl red end point with the standard 4.5*N* hydrochloric acid. The volume of acid required is a measure of the sample weight. The solution is transferred to a 3¾-in. platinum dish and evaporated just to dryness under a heat lamp. The aggregated sodium chloride is broken up, and 10 per cent hydrochloric acid is added dropwise until the salt is just acid to methyl red. The boron is extracted with 15 ml of 95 per cent ethanol and decanted into a 50-ml centrifuge tube; the extraction is repeated with two more portions of alcohol made acid with 1 drop of 10 per cent hydrochloric acid. The combined extracts are centrifuged for 5 min, transferred to a 2¾-in. platinum dish, and neutralized with 0.1*N* sodium hydroxide. Five milliliters of 0.1*N* sodium hydroxide and 2 ml of 3 per cent glycerol in methanol solution are added, and the mixture is evaporated to dryness under a heat lamp. Heating is continued for several minutes, after which the residue is charred gently over a Meker burner. Ignition is completed with the full heat of the burner. The platinum dish is cooled in a tray of crushed dry ice, and 2 ml of 0.1 per cent curcumin in ethanol is added down the sides of the dish. One milliliter of oxalic–hydrochloric acid reagent is added. (To make this reagent, mix 6 g of oxalic acid and 20 ml of hydrochloric acid and dilute to 100 ml with water.) The reagent is added dropwise allowing each drop to freeze before adding the next one. The dish is removed from the ice and heated in the palm of the hand, and the viscous mixture is rotated around the inside walls of the dish until most of the salt dissolves. The dish is then floated on a water bath maintained at 60±1°C. After evaporation has occurred, the dish is heated for an additional 10 min. The residue is extracted with 70 per cent ethanol, transferred to a 25-ml volumetric flask, and made to volume with 70 per cent ethanol. The suspension is shaken well, and a portion is transferred to a 15-ml centrifuge tube in which it is centrifuged at 1500 rpm for 10 min. The supernatant is decanted into a 20-mm cuvette, and the absorbance is measured at 550 mμ in a spectrophotometer using air as 100 per cent transmission. The blank on the reagents should read about 80 per cent transmission. A standard curve (boron concentration in the 0.02- to 0.32-ppm range vs. absorbance) is prepared by treating standard boron samples in the same manner as the unknown samples except for the alcohol extraction from sodium chloride. The boron in the unknown is determined from the standard curve, which is prepared with each new batch of curcumin reagent.

It should be noted that throughout the procedure, including reagent preparation, the usual laboratory glassware that contains boron is avoided because of the danger of contamination. Details on the precautions used in this regard may be found in the original paper.[46]

(h) *Sulfur.* An Ethyl Corporation procedure[47] describes a nephelometric determination of sulfur in sodium in the 30- to 300-ppm range. This procedure involves measurement of the turbidity produced by the precipitation of barium sulfate. Sulfur also has been determined at concentration levels greater than 30 ppm in sodium by a procedure that entails a reduction to hydrogen sulfide, distillation of the gas, and determination of sulfide by an iodimetric titration.[48, 49]

Procedure. A 3-g sample is dissolved in distilled water, and the sample weight is determined by titration with standard 3*N* hydrochloric acid to the phenolphthalein end point. The sample is evaporated to a volume of 2 ml. Twenty-five milliliters of a reducing mixture (4 parts of hydriodic acid, 4 parts of hydrochloric acid, and 1 part of hypophosphorous acid by volume) is boiled for 20 min in a distillation flask attached to a still. An apparatus of the type shown in Fig. 8.4 of Ref. 49 is suitable for this purpose. During this preboiling a stream of nitrogen purified through Ascarite is bubbled through the solution at the rate of one bubble per second. The flask containing the reducing mixture is detached and cooled. The sample is added, and the flask is reattached to the still. Twenty milliliters of 0.01*N* sodium hypochlorite in 2*N* sodium hydroxide is introduced into an absorption tube that is attached to the outlet of the still. The flask is heated sufficiently to maintain a steady gentle boil for a period of 20 min, during which time the nitrogen sweep is maintained as during the preboiling of the reducing mixture. Rapid boiling must be avoided to ensure that all the evolved gas condenses. The sodium hypochlorite solution is transferred to a 500-ml iodine flask, 3 g of potassium iodide are added, and the solution is acidified with 6*N* sulfuric acid. After the solution is mixed well, it is allowed to stand 5 min; and then it is titrated with standard 0.01*N* sodium thiosulfate to a starch end point. A reagent blank is carried through the procedure.

(i) *Chloride.* Chloride may be determined turbidimetrically[47] at concentrations of 50 to 500 ppm in a 1-g sample of sodium. Turbidity is produced by the addition of silver nitrate to the sample dissolved in a water–methanol mixture.

Chloride also may be determined by a modification of the mercurimetric titration commonly employed in water analyses.[50, 51] The chloride in the dissolved sample is determined by titration with a standardized solution of mercuric ion. The end point of the reaction is signaled by the formation of a blue-violet complex cation between the excess mercuric ion and the diphenylcarbazone added as an indicator. The procedure is applicable down to a concentration range of 50 ppm in a 1-g sample.

Procedure. Approximately 1 g of sodium is dissolved in water under a stream of nitrogen. The solution is titrated with standard 3*N* nitric acid to the equivalence point as determined with a pH meter. The volume of nitric acid required is a measure of the sample weight. The solution is transferred to a porcelain evaporating dish, and 10 drops of a mixed indicator [diphenyl carbazone (0.5 g) and bromphenol blue (0.05 g) in 100 ml of 95 per cent ethyl alcohol] are added. The pH is adjusted with 0.05*N* sodium hydroxide and 0.05*N* nitric acid until a yellow color is just attained. The solution is then titrated with standard 0.01*N* mercuric nitrate until a blue-violet color just persists. This stage marks the equivalence point for the titration. A reagent blank is titrated in an identical manner. The mercuric nitrate is standardized by titrating aliquots of a standard sodium chloride solution to the same end point.

(j) *Chromium.* Chromium in sodium is determined colorimetrically using diphenylcarbazide as the chromogenic agent. In one procedure[52] the chromium is oxidized to the hexavalent state with potassium permanganate in a sulfuric acid medium. Sodium azide is added to destroy the permanganate color, and the chromium diphenyl carbazide color is developed. The chromium can be estimated at concentrations of 1 ppm in a 1-g sample.

Mann and White[53] describe a method for determining chromium in sodium at a concentration level of 0.5 ppm using a 4-g sample of sodium. The chromium in the hexavalent state is complexed with tri-*n*-octylphosphine and extracted into benzene. Oxidation is accomplished either with bromine water in a hydrochloric acid solution or with argentic oxide in a sulfuric acid solution. The chromium is then determined directly in the benzene phase by spectrophotometric measurement of the chromium–diphenylcarbazide complex.

Procedure.[53] Sufficient sodium is dissolved in water to yield 1 to 10 μg of chromium. However, no more than 4 g of metal should be dissolved in any case. The solution is titrated to a pH of 7 with standardized 6*N* hydrochloric acid, and the weight of the sample is obtained from the volume of acid required. Sulfuric acid is added in sufficient quantity to produce a final solution that is 5 vol.% in sulfuric acid and has a total volume less than 80 ml. Next, 3 ml of sulfuric acid and 100 mg of argentic oxide are added. The solution is stirred well and then boiled vigorously for 5 min. The solution is cooled, diluted with water to 50 ml if necessary, and transferred to a 125-ml separatory funnel. Sulfuric acid (5*M*) is added to make the solution 1*M*. Five milliliters of 0.2*M* tri-*n*-octylphosphine oxide in benzene is added, and the flask is shaken for 2 min. The phases are allowed to separate, and the organic phase is collected in a test tube containing nonindicating silica gel. Two milliliters of diphenylcarbazide solution (0.25 per cent in absolute alcohol) are transferred to a 10-ml volumetric flask. Next, a 3-ml aliquot of the organic extract is added, and the sample is diluted to volume with ethanol. The procedure for color development just described should be carried out in the sequence given and without interruption. The absorbance of the solution is measured within 1 hr. The measurement is made at 550 mμ against a reference solution that contains only the reagents that have been taken throughout the entire procedure. The chromium concentration is obtained by comparing the absorbance with that of standard solutions of chromium that have been carried through the same procedure.

(k) *Iron.* Rodgers et al.[54] describe a procedure for the analysis of iron in sodium. A large sample is dissolved in methyl alcohol; the resultant solution is neutralized with hydrochloric acid and then evaporated. The salts are dissolved in water, and tartaric acid is added. Ferric sulfide is precipitated with hydrogen sulfide water from an ammoniacal solution. The sulfide is dissolved, the iron is oxidized to the ferric state, and the absorbance of the ferric thiocyanate complex is measured.

Iron also may be estimated colorimetrically at the 1-ppm concentration level on a 1-g sodium sample by means of the standard 2,2′-dipyridyl method.[55] Iron in the dissolved sample is reduced to the ferrous state, the reagent solution containing acetic acid–sodium acetate as a buffer is added, and the absorbance of the pink ferrous complex is measured. The procedure is not sensitive below about 1 ppm.

The ferrous color is measured in the presence of sodium chloride, the solubility of which is equivalent to approximately 1 g of sodium in 10 ml of solution. This factor limits concentrating the sample to improve the sensitivity. Cobalt, nickel, and copper, which may interfere with the iron determination, are not normally present at sufficient concentration levels to warrant separation.

Procedure. Approximately 1 g of sodium is dissolved in water under a blanket of nitrogen. Glass spatulas are used to cut the sodium to prevent contamination of the sample. The solution is titrated to the phenolphthalein end point with standardized 3*N* hydrochloric acid. The volume of hydrochloric acid required is a measure of the sample weight. Three additional drops of hydrochloric acid are added, and the solution is boiled to dissolve iron. The heating is continued until the solution volume is reduced to approximately 20 ml; than the sample is transferred to a 25-ml volumetric flask. Two milliliters of the reagent (1.5 g of 2,2′-dipyridyl, 200 ml of glacial acetic acid, 30 g of sodium acetate, and 50 g of hydroxylamine hydrochloride are dissolved in 500 ml of water) is added. The solution is brought to a 25-ml volume, mixed well, and allowed to stand for 0.5 hr. The absorbance is measured at 522 mμ using 1-cm cells against a reagent blank in the reference cell. A standard curve is prepared by adding known amounts of iron to solutions of dissolved triply distilled sodium and treating the solutions as described above for the actual sample.

(1) *Uranium.* If sodium or sodium–potassium alloy are to be used as a nuclear reactor primary coolant, it is usually desirable to establish the uranium impurity level so that one can be assured of a low initial level of fission-product activity in the system. The analysis may be accomplished by first separating the uranium via an extraction of the tetrapropylammonium uranyl trinitrate with methyl isobutyl ketone from an acid-deficient aluminum nitrate solution.[56] Uranium may be determined in the extract by fluorimetry[57] (see Chap. 1, Sec. 1–3.4). The sensitivity of the method is <0.01 ppm in sodium.

Only the separation procedure is given in detail below.

Procedure. A 1-g sample of sodium is dissolved in water and titrated with standard 6*N* nitric acid to the phenolphthalein end point. A slight excess of nitric acid is added, and the solution is boiled to ensure the dissolution of hydrated uranium oxide. The solution is evaporated to a point just prior to the salting out of sodium nitrate. The solution is transferred quantitatively to a 125-ml separatory funnel with two 25-ml washings of acid-deficient aluminum nitrate containing tetrapropylammonium hydroxide. (In the preparation of this reagent, sufficient water is added to 1050 g of aluminum nitrate hydrate to give a volume of 900 ml. After the salts are dissolved by warming, 67.5 ml of ammonium hydroxide is added, and the solution is stirred until the hydroxide precipitate dissolves. The solution is cooled to less than 50°C, 10 ml of 10 percent tetrapropylammonium hydroxide reagent is added, and the solution is stirred until dissolution is complete. The solution is diluted to 1 liter with water. The reagent is purified by extracting with methyl isobutyl ketone, and an additional 10 ml of 10 percent tetrapropylammonium hydroxide reagent is added.) The first washing is heated slightly for a few minutes. The solution is extracted with 25 ml of distilled hexone for 10 min. The phases are allowed to separate. The lower, aqueous, phase is discarded, and the uranium in the hexone layer is determined fluorimetrically.

(m) *Other Elements.* Methods for other elements have appeared in the literature, including methods for nickel,[58] cobalt,[59] and calcium.[60]

10–3.4 Spectrographic Determination of Metallic Impurities in Sodium

Unless high accuracy is required, the method of choice for the determination of impurities in sodium would be a spectrographic technique. It is possible to estimate the concentration of many impurities in sodium utilizing only one or two samples instead of individual sample treatment. The time saved is thus an overriding factor when considering the analytical program to support a liquid-metal engineering facility.

Because the determination of a large number of metallic impurity elements is required, it is necessary to employ several different techniques for the complete spectrographic analysis of sodium. These separate spectrographic methods are discussed in (a), (b), (c), and (d) of this section.

Prior to spectrographic analysis, the sodium, when received in the metallic form, must be dissolved and converted to the appropriate salt. In all the methods the sample is dissolved by dropping small bits of the metal into 2 or 3 ml of water contained in a stainless-steel beaker. While the sodium is dissolving, a rapid stream of clean nitrogen is blown into the beaker to prevent ignition of the evolved hydrogen. As the solution becomes concentrated, the reaction rate decreases and may be controlled by small additions of water from time to time. Sodium–potassium alloy samples also are dissolved directly. However, this alloy is extremely reactive and must be dissolved in a mixture of dry ice and ethyl alcohol by a procedure similar to that described by Pepkowitz.[25] In this procedure the tube containing the sodium–potassium alloy is frozen in a dish setting on dry ice. The tube is then shattered. Small pieces of the frozen alloy are then carefully dropped into a slurry of ethyl alcohol and dry ice in an Erlenmeyer flask. The rate of the reaction is controlled by heating or cooling the flask.

When sodium is dissolved in this manner, there is always some contamination by iron, nickel, and chromium if a stainless-steel container is used. Therefore, if these elements are to be determined, the sodium sample must be dissolved in water in a polyethylene or Teflon beaker.

The procedure is identical to that described above, except that when using polyethylene more care must be taken to prevent overheating and damage to the beaker.

For the determination of most of the impurities [Sec. 10–3.4(a)], the dissolved samples are converted to sulfates by titration with 5*N* sulfuric acid. Avoidance of excess acid not only serves to measure the amount of sample taken but also facilitates the evaporation of the solution and drying of the sulfate salt. Similarly, for the determinations of barium and calcium [Sec. 10–3.4(b)] and for mercury [Sec. 10–3.4(c)], the sample solution is titrated with 5*N* hydrochloric acid as the first step in the preparation described below.

Standards are prepared for the determination of most of the impurity elements by the addition of oxides or sulfates of the elements to pure sodium sulfate powder. When standards that will include a large number of impurity elements are being prepared, it is advisable to separate the elements into three or four groups. These groups should be selected to avoid combinations of common groups of elements, such as alkalis and alkaline earths. Three or four high-impurity master standards are then prepared, each of which contains high concentrations of the impurities included in one of the preselected groups. Mixtures of these standards with each other are then made to obtain various concentrations of each of the impurity elements. The standards are mixed in such proportions that no final standard has an appreciably higher total impurity content than the others. When standards are prepared in this manner, there will be no general trend of concentration or composition, and interelement effects are minimized. A discussion of the effects of changing sample composition on element line intensities is given by Ahrens.[61]

No internal-standard element is added to these standards or to the sodium samples. Instead, at least one impurity standard is run in triplicate on each sample analysis plate. Revisions of sample estimates are made to conform to the apparent values for the impurities in this standard.

(a) *Determination of 27 Common Impurities.* The general method for the determination of most of the common metallic impurities in sodium begins with the conversion of the dissolved sample to the sulfate by titration with 5*N* sulfuric acid. The solution is then evaporated, and the dry salt is ground to a fine powder. A spectrograph with a dispersion of 5 to 7 A per millimeter is satisfactory. Normal photographic developing and processing procedures are employed. Other spectrographic conditions used for the analysis are listed in Table 10.7.

Table 10.7—SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF GENERAL IMPURITIES IN SODIUM

Wave-length range	2200 to 3600 A
Photographic plate	Eastman spectrum analysis No. 1
Upper electrode	Cathode ($\frac{3}{16}$- by $1\frac{1}{2}$-in. pure graphite, hemispherical tip)
Lower electrode	Anode ($\frac{1}{4}$- by $1\frac{1}{2}$-in. pure graphite, drilled with a 0.196-in.-diameter 0.120-in.-deep hole)
Sample charge	Salt sample ($\sim$75 mg) packed tightly into the anode crater
Excitation	15-amp d-c arc with 2-mm arc gap
Exposure	About 2 min (until the final disappearance of sodium color in the arc)

After the development of the plate, the line intensities of the 27 elements are observed and compared with the impurity lines on a plate of standard samples prepared in the same manner. The lines used and the approximate limits of detection are listed in Table 10.8. Since the method is semiquantitative, the comparison is accomplished by visual means using a projection comparator. Sample estimates are corrected by reference to the observed values for impurities in the standard sample. If these observed values are greater than 50 relative per cent different from the known values for the standard sample, the analysis plate is rejected and the samples are reanalyzed.

Table 10.8—ANALYSIS LINES FOR GENERAL IMPURITIES IN SODIUM

Element	Line, A	Limit of detection, ppm	Element	Line, A	Limit of detection, ppm
Al	3082.2	4	Li	3232.6	20
Sb	2598.1	20	Mg	2795.5	0.2
As	2349.8	50	Mn	2794.8	1
Be	2348.6	0.2	Mo	3132.6	2
Bi	3067.7	1	Ni	3414.8	1
B	2497.7	2	Pd	3242.7	2
Cd	2288.0	1	Si	2881.6	2
Cr	2835.6	20	Ag	3280.7	0.1
Co	3453.5	2	Tl	2767.9	1
Cu	3247.6	0.2	Sn	2840.0	10
Ge	3039.1	5	Ti	3349.0	5
In	3256.1	1	V	3184.0	2
Fe	3020.6	1	Zn	3345.0	20
Pb	2833.1	1			

Table 10.9—SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF BARIUM AND CALCIUM IN SODIUM

Wave-length range	3760 to 5120 A
Photographic plate	Eastman IV F spectroscopic plate
Upper electrode	Cathode (3/16- by 1½-in. pure graphite, hemispherical tip)
Lower electrode	Anode (¼- by 1½-in. pure graphite drilled with a 0.196-in.-diameter 0.100-in.-deep hole)
Sample charge	Salt sample (~60 mg) packed tightly into the anode crater
Excitation	15-amp d-c arc with 2-mm arc gap
Exposure	About 100 sec (until the final disappearance of the sodium color in the arc)

(b) *Determination of Barium and Calcium.* For this procedure the dissolved sample is neutralized with 5*N* hydrochloric acid. At this point a strontium chloride internal-standard solution is added to the sample in the ratio of 100 μg of strontium per gram of sodium dissolved. The sample is then evaporated and the residue is ground to a fine powder. A spectrograph with a dispersion of 5 to 7 A per millimeter is satisfactory. Normal photographic developing and processing procedures are employed. Other spectrographic conditions used are listed in Table 10.9.

Since this determination is an internal-standard method, the analysis line Sr: 4811.9 is measured, as well as the lines Ca: 4226.7 and Ba: 4554.0. Line intensities are read from a calibration curve prepared from two-step data by the preliminary-curve technique.[62] The standard curve is plotted as log I(analysis line)/log I(internal-standard line) vs. log concentration, and data for the curve are run in triplicate.

(c) *Determination of Mercury.* This determination is performed by a concentration technique in which a hydrochloric acid solution of the sample is stirred with copper powder. In a matter of a few minutes, all the mercury in any form in the solution is amalgamated with the copper. The copper powder is washed, dried, and arced in boiler cap electrodes for the detection of mercury at concentrations above 1.0 ppm in the sodium sample. The method has been described in detail by Landis and Pelrine [63] and appears to give a precision of approximately 20 relative per cent. Further work has extended the limit of detectability to as low as 0.1 ppm in sodium.

(d) *Determination of Some Rare-earth Elements.* The determination of the rare-earth elements is accomplished by a separation technique using yttrium as both a carrier and an internal standard. Forty milligrams of yttrium in a nitrate solution are added directly to the dissolved sodium sample. The solution is neutralized with HF, and

Table 10.10—SPECTROGRAPHIC CONDITIONS FOR THE DETERMINATION OF RARE EARTHS IN SODIUM USING YTTRIUM CARRIER

Wave-length range	2350 to 4600 A
Photographic plate	Eastman Spectrum Analysis No. 1
Upper electrode	Cathode (3/16- by 1½-in. pure graphite, hemispherical tip)
Lower electrode	Anode (¼- by 1½-in. pure graphite, center-post type with an annular cavity of 0.190- and 0.080-in. diameters and a 0.060-in. depth, UCP type 5986)
Sample charge	~40 mg Y_2O_3 and graphite (1:1 mixture packed into annular cavity)
Excitation	12-amp d-c arc with 2.4-mm arc gap

an excess of 20 ml of concentrated acid is added to precipitate all rare-earth fluorides with the yttrium fluoride. The precipitate is washed thoroughly with 5 vol.% HF, filtered, and ignited to the oxide for spectrographic examination. A spectrograph with a dispersion of approximately 4 A per millimeter which is capable of covering the necessary wave-length range is satisfactory. Normal photographic developing and processing procedures are used. Other spectrographic conditions for the analysis are listed in Table 10.10.

After development of the spectrographic plate, the lines listed in Table 10.11 are read and converted to relative intensities. Intensity ratios of analysis lines to internal-standard lines as concentrations of the elements are read from the standard curves. The ranges of the individual standard curves are listed in Table 10.11. It should be noted that normally a 1-g sodium sample is taken, to which 40 mg of carrier is added. Therefore the concentration factor to be used is approximately 1/25 to convert percentages of rare earths from yttrium to sodium. The precision of this method varies from 10 to 20 relative per cent for the different elements determined.

Table 10.11—ANALYSIS LINES AND RANGES FOR RARE-EARTH ELEMENTS IN YTTRIUM CARRIER

Element line, A	Internal standard line for yttrium, A	Range, %
Ce 4012.39	4291. 03	0. 005–0. 5
Dy 3407.80	3450. 95	0. 005–1. 0
Eu 4435.60	4291. 03	0. 03 –1. 0
Gd 4327.10	4291. 03	0. 05 –1. 0
Sm 4334.14	4291. 03	0. 10 –2. 0

Table 10.12.—SUMMARY OF ANALYTICAL METHODS

Component or property	Method	Accuracy	Precision	Time required, hr
Biphenyl and σ-, m-, and p-terphenyls.	Infrared spectroscopy*	σ = ±0.5% absolute	σ = ±0.5 wt.% absolute	3
	Gas chromatography†	σ = ±0.5% absolute	σ = ±0.4 wt.% absolute	4
Triphenylene	Ultraviolet spectroscopy‡	Variable	σ = ±0.6%	4
Low boilers (benzene toluene, ethyl benzene, and others).	Gas chromotography	5 to 10 wt.% relative	5 to 10 wt.% relative	8
High-boiler components (group type analysis)	Mass spectroscopy (low voltage)¶			
High-boiler content	Microdistillation	?	σ = ±0.6 wt.% absolute	3
	Macrodistillation	?	σ = ±0.23 wt.% absolute	3
Molecular weight§	Signer method**	5 to 10%	5%	3
	Cryoscopic in benzene	5 to 10%	5%	2
	Cryoscopic in camphor	5 to 10%	5%	2
Carbon and hydrogen	Macrocombustion	%C ±0.06% absolute		
		%H ±0.03% absolute	Same	2
Olefin content	Ozone absorption	σ = ±0.0303% absolute 2 to 10% relative.	σ = ±0.030% absolute 2 to 10% relative.	4

*Applicable mainly to virgin coolants. Radiolysis products or other components that absorb at designated wave lengths interfere.

†*Applicable to samples containing up to 40 per cent high boilers.*

‡Accuracy depends on composition, especially presence of other condensed-ring hydrocarbons and substituted triphenylenes. Limit of detection is about 0.4 per cent as triphenylene.

¶This method can be considered routine only when examining similar materials. Time required depends mainly on difficulty of interpretation of data and is variable. *Minimum time is about 8 hrs.*

§Accuracy and precision are estimates. Duplicate determinations usually agree within 5 per cent, but differences between methods may be 10 per cent or more.

**Two or three weeks may be required for equilibrium to be established.

10.4 POLYPHENYL REACTOR COOLANTS

By C. J. Rodden

The use of organic materials for moderating and cooling reactors required that methods be developed for the determination of the organic coolants as well as their pyrolytic–radiolytic decomposition products.[64] The coolants are of the polyphenyl type and consist of biphenyl and ortho-, meta-, and para-terphenyls. Composition of the initial coolants is determined by gas chromatography or by an infrared absorption method.

The pyrolytic–radiolytic decomposition products of the polyphenyl coolants are grouped according to their boiling points. The low boilers have a higher boiling point than biphenyl and a lower one than terphenyl. High boilers have a higher boiling point than terphenyl. Because of the volatility of the low boilers, the total vapor pressure of the coolant mixture may depend to a considerable extent upon their presence. The low boilers are determined by gas chromatography.

Intermediate boilers may make up 6 to 10 per cent of the decomposition products, but their determination is not routine.

High boilers are usually determined by a mass-spectrometric procedure although triphenylene, a high-boiling decomposition product of terphenyl, is determined by a differential ultraviolet absorption method.

Other methods for the determination of individual compounds as well as for certain properties, such as high-boiler content of coolants, average molecular weight, carbon and hydrogen content, and olefin content, have been described in detail in Ref. 64. This report should be consulted for procedural details. The various methods used are summarized in Table 10.12.

REFERENCES

1. Sargent and Lundy Engineers, Chicago, USAEC Report TID–11918, January 1961.
2. M. W. Skovgstad and M. J. Fishman, *Anal. Chem.*, **33**: 138R (1961).
3. L. L. Thatcher and R. T. Kiser, *Anal. Chem.*, **31**: 776 (1959).
4. American Public Health Association, *Standard Methods for the Examination of Water and Sewage*, 10th ed., p. 240, New York, 1955.
5. F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**: 266 (1931).
6. R. L. Hoover, E. T. Borawski, G. S. Golden, R. L. Hancock, and R. L. Layfield, USAEC Report IDO–19014 (Vols. I and II), Combusion Engineering, Inc., 1960.
7. J. McClelland (Comp.), USAEC Report LA–1858, Los Alamos Scientific Laboratory, December 1954.
8. J. Malgialio, E. A. Limoncelli, and R. E. Cleary, USAEC Report TID–7606, p. 140, Oak Ridge National Laboratory, 1961.

9. B. S. Dunn, W. G. Harrison, and R. C. Williams, British Report IGO–AM/W–63, April 1957.
10. J. C. Dalton, British Report Windscale Tech. Memo. 289, September 1954.
11. British Report IGO–AM/W–176, 1958.
12. British Report IGO–AM/W–76, Feb. 14, 1957.
13. D. G. Timms, H. J. Konrath, and R. C. Chirnside, *Analyst*, **83**: 600 (1958).
14. B. S. Dunn, British Report IGO–AM/W–62, Apr. 8, 1957.
15. J. C. Dalton, British Report IGO–AM/W–83, Apr. 18, 1957.
16. D. G. Boase and R. C. Williams, British Report IGO–AM/W–80, Mar. 23, 1957.
17. W. G. Harrison and H. A. Wright, British Report IGO–AM/W–77, Mar. 8, 1957.
18. E. Hughes, British Report IGO–AM/W–78, Mar. 7, 1957.
19. F. P. Landis *et al.*, Knolls Atomic Power Laboratory, unpublished data, 1954.
20. M. Sittig, *Sodium, Its Manufacture, Properties and Uses*, Reinhold Publishing Corporation, New York, 1956.
21. C. B. Jackson (Ed.), USAEC Report TID–5277, July 1955.
22. British Report IGO–AM/CA–110, March 1958.
23. R. N. Lyon, (Ed.) *Liquid Metals Handbook* [Report NAVEXOS–P–733 (Rev.)] U.S. Government Printing Office, Washington, D.C., 1952.
24. W. H. Bruggenman and G. Billuris, USAEC Report KAPL–P–777, Knolls Atomic Power Laboratory, 1953.
25. L. P. Pepkowitz, *Anal. Chem.*, **26**: 574 (1954).
26. S. L. Walters and R. R. Miller, *Ind. Eng. Chem., Anal. Ed.*, **18**: 468 (1946).
27. L. P. Pepkowitz and E. R. Proud, *Anal. Chem.*, **21**: 1000 (1949).
28. B. D. Holt, *Anal. Chem.*, **31**: 51 (1959).
29. K. C. Stoffer and J. H. Phillips, *Anal. Chem.*, **27**: 773 (1955).
30. P. S. Farrington, C. Niemann, and E. Swift, *Anal. Chem.*, **21**: 1423 (1949).
31. L. P. Pepkowitz and R. J. Downer, *The Determination of Carbon in Sodium and Sodium–Potassium Alloy*, paper presented before Pittsburgh Conference on Analytical Chemistry, March 1953. Abstracts in *Anal. Chem.*, **25**: 520 (1953).
32. L. P. Pepkowitz and J. T. Porter II, *Anal. Chem.*, **28**: 1606 (1956).
33. R. J. Downer, Knolls Atomic Power Laboratory, unpublished data, 1954.
34. Ethyl Corporation Analytical Procedure Number 111, *Colorimetric Determination of Nitride Nitrogen in Sodium*, Ethyl Corporation, Baton Rouge, La., 1954.
35. L. P. Pepkowitz and W. C. Judd, *Anal. Chem.*, **22**: 1283 (1950).
36. D. D. Williams and R. R. Miller, *Anal. Chem.*, **23**: 1865 (1951).
37. L. P. Pepkowitz, W. C. Judd, and R. J. Downer, *Anal. Chem.*, **26**: 246 (1954).
38. J. C. White, W. J. Ross, and R. Rowan, Jr., *Anal. Chem.*, **26**: 210 (1954).
39. L. E. Smythe and H. J. deBruin, Australian Report AAEC/E–22, June 1958.
40. L. Silverman and M. Shideler, USAEC Report NAA–SR–1509, Atomics International Division, North American Aviation, Inc., June 15, 1956.
41. Ethyl Corporation, *The Determination of Trace Amounts of Oxide in Sodium*, Ethyl Corporation, Baton Rouge, La., 1954.
42. J. C. White, USAEC Report CF–56–4–31, Oak Ridge National Laboratory, Apr. 5, 1956.
43. R. D. Peak, USAEC Report CF–57–4–115, Oak Ridge National Laboratory, Apr. 30, 1957.

44. W. C. Judd and D. Dutina, Knolls Atomic Power Laboratory, unpublished data, 1954.
45. W. C. Judd, Knolls Atomic Power Laboratory, unpublished data, 1954.
46. J. Rynasiewicz, M. P. Sleeper, and J. W. Ryan, *Anal. Chem.*, **26**: 935 (1954).
47. Ethyl Corporation Analytical Procedure 109, *The Determination of Sulfate and Chloride in Sodium*, Ethyl Corporation, Baton Rouge, La., 1954.
48. E. L. Shirley, Knolls Atomic Power Laboratory, unpublished data, 1954.
49. F. E. McKenna and D. H. Templeton, in *Analytical Chemistry of the Manhattan Project*, C. J. Rodden (Ed.), p. 309, National Nuclear Energy Series, Div. VIII, Vol. 1, McGraw-Hill Book Company, Inc., New York, 1950.
50. F. E. Clarke, *Anal. Chem.*, **22**: 553 (1950).
51. D. Dutina, Knolls Atomic Power Laboratory, unpublished data, 1954.
52. W. C. Judd, Knolls Atomic Power Laboratory, unpublished data, 1954.
53. C. K. Mann and J. C. White, *Anal. Chem.*, **30**: 989 (1958).
54. S. J. Rodgers, J. W. Mausteller, and E. F. Batutis, Mine Safety Technical Report 27, Report NP-5247, Mine Safety Appliances Co., June 1954.
55. E. R. Proud, Knolls Atomic Power Laboratory, unpublished data, 1954.
56. W. J. Maeck, G. L. Booman, M. C. Elliot, and J. E. Rein, *Anal. Chem.*, **30**: 1902 (1958).
57. F. A. Centanni, A. M. Ross, and M. A. DeSesa, *Anal. Chem.*, **28**: 1651 (1956).
58. T. M. Florence, *Anal. Chim. Acta*, **19**: 548 (1958).
59. L. Silverman and R. L. Seitz, *Anal. Chim. Acta*, **20**: 340 (1959).
60. J. Rynasiewicz and M. E. Polley, *Anal. Chem.*, **21**: 1398 (1949).
61. L. H. Ahrens, *Spectrochemical Analysis of Minerals and Rocks*, Addison-Wesley Publishing Company, Cambridge, Mass., 1950.
62. J. R. Churchill, *Ind. Eng. Chem., Anal. Ed.*, **16**: 653 (1944).
63. F. P. Landis and J. P. Pelrine, USAEC Report KAPL-674, Knolls Atomic Power Laboratory, Jan. 31, 1952.
64. R. T. Keen, R. A. Baxter, L. J. Miller, M. A. Rotheram, and R. H. J. Gercke, USAEC Report NAA-SR-4356, Atomics International Division, North American Aviation, Inc., Jan. 30, 1961.
65. R. W. Dickinson, E. Hughes, A. R. Newcombe, R. C. Williams, and F. J. Woodman, British Report PG-Report-173(W) (Rev.), 1961.
66. D. W. Ockenden, R. W. Dickinson, B. Bradley, and R. L. O. French, United Kingdom Atomic Energy Authority, Risley, Warrington, Lancs, England, unpublished data.