CHAPTER 9

HEAVY WATER

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Heavy water (D_2O) as a reactor moderator must be maintained in an extremely pure state to ensure efficient and successful reactor operation. Hence analytical control of heavy water requires accurate and precise determinations not only of deuterium oxide but also of specific impurities, some of which may be present in concentrations as low as a few parts per billion.

There are many excellent references dealing with the determination of deuterium oxide and its impurities which cover in detail the theoretical aspects of the particular analyses, the techniques, and the equipment required. Therefore this chapter will only review the analytical methods that are employed in the routine control of heavy-water moderator.

9–1 LABORATORY TECHNIQUES

Most equipment used in the analysis of heavy water is not unique; it is usually found in any well-equipped laboratory. However, because the exchange of deuterium with protium (H^1) is very serious when the D_2O concentration approaches 100 mole %, it is imperative that equipment and techniques be employed which will minimize, and, whenever practical, prevent the exposure of heavy water to sources of protium contamination. Many inaccuracies in analyses arise from improper treatment of the sample and equipment.

9–1.1 Equipment Conditioning

Laboratory equipment for transferring and containing heavy water must be scrupulously cleaned to eliminate any traces of grease or protium-containing compounds and then conditioned to eliminate any traces of light water. The conditioning can be accomplished by rinsing the equipment with $\geqq 99$ mole % D_2O, drying it in a 150°F oven, and then storing it in a dry box or desiccator until it is to be used. In some instances, drying under vacuum may be in order.

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9–1.2 Transferring and Storing Samples

Heavy water should be transferred in a dry box or by means of a semiclosed system whenever practical. One satisfactory method for transferring small samples is by means of a hypodermic syringe. A siphon arrangement is sometimes used for large quantities. Whenever a transfer that exposes the material to the atmosphere must be made, a blanket of a dry inert gas, usually helium, is maintained over the heavy water throughout the transfer.

Containers for storage of samples should be completely filled with the sample, or a dry inert gas should be introduced to replace the air above the sample. For storing small quantities of heavy water for an extended period of time, a pyrex glass ampoule is the preferred receptacle. The ampoule should be flame sealed after receiving the heavy water. Polyethylene, glass, or metal containers can be used for transporting heavy water from an operating facility to the laboratory and for short-term storage if the container has been properly conditioned. A comparison of the storage stability of 50 ml of heavy water in sealed pyrex ampoules, screw-cap glass bottles, and polyethylene bottles is shown in Fig. 9.1.

9–2 DETERMINATION OF ISOTOPIC CONCENTRATION

There are many methods for the isotopic analysis of heavy water. Most of these are applicable, with some modification, over the entire concentration range from normal abundance (0.0147 mole % D_2O) to 100 mole % D_2O. The selection of an analytical method for routine use is usually based on three factors: the availability of equipment, the frequency and urgency of analysis, and the precision required.

Heavy-water analysis methods can be divided into two main categories: analysis by determination of a physical property of D_2O (e.g., density methods) and analysis by instrumental means (e.g., mass spectrometer). Some methods have been well established and are used routinely; these include the pycnometer and the float temperature, among the density methods, and the mass spectrometer and infrared spectrometer, among the instrument methods. Other methods, although not so well known or so frequently used, are available; some of these (emission spectroscopy, nuclear magnetic resonance, cryoscopy, and refractometry) are described briefly in this chapter.

9–2.1 Density Methods

Three density methods are discussed: the gravimetric method (pycnometer), the float temperature method, and the displacement method (Westphal balance).

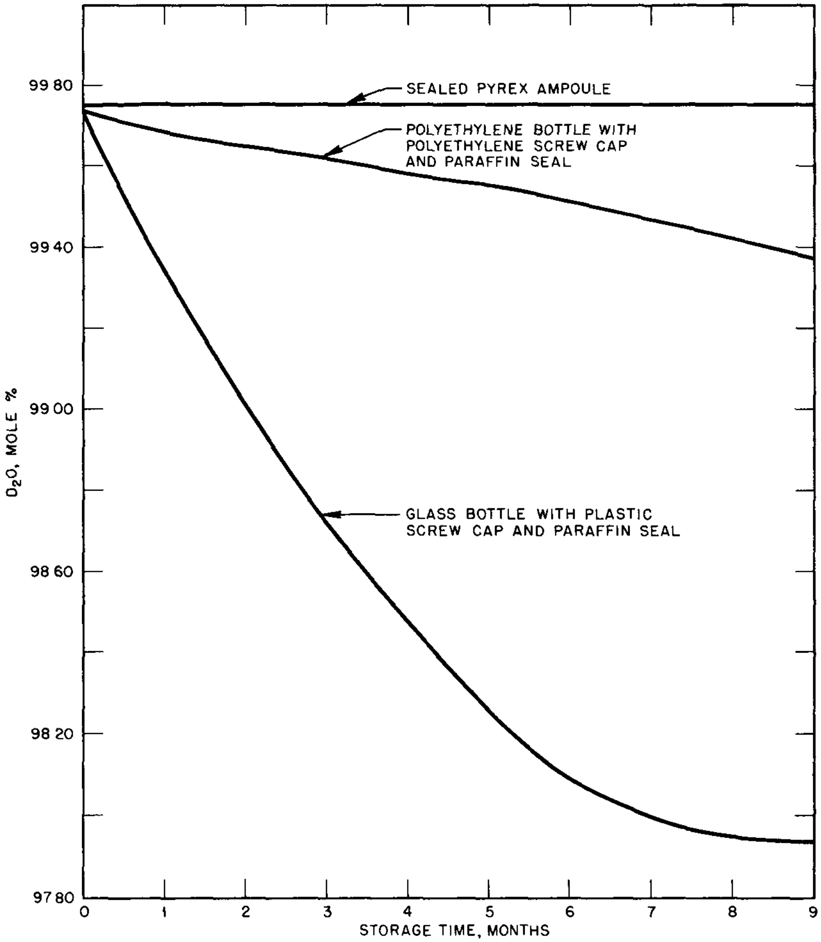

Fig. 9.1—Storage stability of heavy water in 50-ml containers. (Normalized curves, based on mass spectrometric data.)

(a) *Gravimetric Method* (*Pycnometer*). This is one of the classical methods for determining D_2O content, and it is still useful for very precise work, such as establishing standard samples and confirming results obtained by other methods. The method is time consuming and requires a fair degree of skill for highest accuracy; but the equipment is relatively simple and inexpensive, and, if only a few analyses are required, the pycnometer method is ideal. Routinely, a precision of ± 0.02 mole % D_2O is obtainable at concentrations of $\geqq 95$ mole % D_2O, and, with care, a precision of ± 0.01 mole % can be attained.

One of the most important considerations in the pycnometer method, as in any density method, is the purity of the sample. The sample

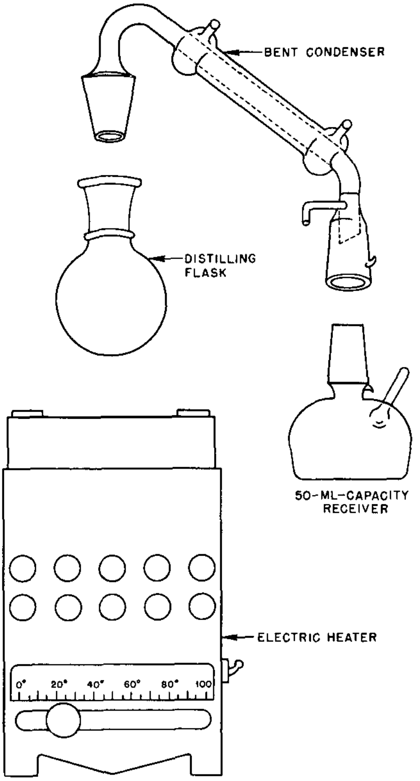

Fig. 9.2—Distillation assembly.

must be free of dissolved and particulate matter. An error of 0.0001 in specific gravity introduces an error of approximately 0.1 mole % in the analysis results. One of the more common ways of purifying the sample is by digestion with an oxidizing agent (such as a peroxide or alkaline permanganate), followed by distillation. Depending upon the condition of the sample, a more vigorous purification may be in order. Three important aspects of any cleanup procedure are: (1) particular care must be exercised to ensure complete distillation since light water–heavy water mixtures fractionate readily; (2) all vessels and chemicals used in purifying the samples must be free of any protium-containing compounds; and (3) contamination by exposure to atmospheric moisture must be avoided.

Procedure.[1] About 50 mg each of dry potassium permanganate and sodium peroxide are added to a 300-ml distilling flask (Fig. 9.2). A hypodermic syringe and needle are used to transfer approximately 35 ml of product from the sample container to the flask. A few chips of dry carborundum are added to the flask, and the sample is distilled to dryness. (Flaming of the flask may be necessary to transfer the last portions of sample to the receiver.) The distillation equipment is vented through a silica gel drying tube to prevent dilution by atmospheric moisture. Contamination of the sample with grease from the ground-glass joints is to be avoided; serious contamination of samples has resulted from careless use of lubricants. A minimum amount of a good silicone grease is recommended.

After distillation the sample is transferred, by means of a hypodermic needle inserted in the side arm of the receiving flask, to a 25-ml Reischauer pycnometer (which has been calibrated and weighed, taking all standard weighing corrections). The pycnometer is stoppered and placed in a nominal 25.00°C±0.001°C constant-temperature bath, and the meniscus is adjusted to the calibration mark. The pycnometer is then removed from the bath, dried, allowed to reach room temperature, and weighed against a tare pycnometer (which has been filled with freshly boiled and cooled normal water, sealed, and weighed, taking all standard weighing corrections). The mole % D_2O, uncorrected for O^{18}, is calculated from the density of the sample, as follows:

$$A=B-C \tag{9.1}$$

$$d=A/E \tag{9.2}$$

$$\Delta d=d-d_1 \tag{9.3}$$

$$\text{Mole \% } D_2O=\frac{(927.35)(\Delta d)}{1-[(0.0329)(\Delta d)]} \tag{9.4}$$

where

A=true weight of sample in grams
B=total of tare and brass weights
C=true weight of sample pycnometer
d=density of sample at 25°C in grams per milliliter
E=true volume of sample pycnometer in milliliters
Δd=difference between density of sample and density of protium oxide
d_1=density of protium oxide at 25°C in grams per milliliter (lighter in density than ordinary water by 1.6×10^{-5} g/ml)

In any determination of D_2O content by density and by most other methods involving a physical property, the abundance of the O^{18} isotope must be considered since, in a number of the processes used for extracting D_2O (e.g., distillation), the product is enriched in the heavier isotopes of oxygen as well as in deuterium. The natural abundance of O^{18} is reported[1] as 0.198 mole % and that of O^{17} as 0.042 mole %. For routine work the change in the abundance of O^{17} has a negligible effect on the determination of the D_2O concentration; but any change in the O^{18} content is usually significant, and any D_2O determination must include the appropriate O^{18} correction. For work of highest precision, the O^{18} correction should be applied in the calculation[1] of sample density (0.0000012 specific gravity units per 0.001 mole % O^{18}).

Two general approaches used to determine the O^{18} content are (1) determination of O^{18} as it exists in the sample and application of a correction to the D_2O results, and (2) reduction of the O^{18} content to normal abundance. The most convenient method is to determine the O^{18} by equilibration with CO_2; this is accomplished by determining the mass 46 to mass 44 ratio of the CO_2 by a mass spectrometer after equilibration with the D_2O sample. The equilibrium constants[1] for the carbon dioxide–heavy water reaction have been established, and the formula generally used is:

$$\text{Mole \% } (0^{18})_{\text{water}} = \frac{100\ R_x}{(K_aK_b)^{1/2} + R_x} \tag{9.5}$$

where

$$(K_aK_b)^{1/2} = 2.088$$

$$R_x = \frac{C^{12}O^{16}O^{18}}{C^{12}O^{16}O^{18}} = \frac{m/e\ 44}{m/e\ 46}$$

Briefly, the equilibration procedure consists in shaking 5 ml of purified sample with approximately 20 cm^3 of CO_2 at atmospheric pressure for 5 hr at 25°C. No catalyst is required. The equipment preparation and sample purification are similar to those used in other heavy-water procedures. It is especially desirable that nitrogen dioxide or any compound containing NO_2 be absent.

The other, and usually less desirable, approach to the oxygen isotope problem is to normalize the O^{18} content of both the sample and a standard by bubbling anhydrous sulfur dioxide through the sample and standard. The time necessary to normalize is determined experimentally; in most cases it will be several hours at a gas flow of 15 to 20 liters/hr. Obviously, with this much gas any traces of moisture in the SO_2 (commercial anhydrous SO_2 usually contains some water) must be eliminated by use of a trap or drying tube. Also, the effluent gas from the sample container must be trapped to recover any sample vapor carried over.

(b) *Float Temperature Method* (*Float Bath*). Determining density by a float is an old technique. The particular adaptation of this principle which has been used for determining heavy water is quite simple; however, it requires well-trained personnel, a great deal of patience, and extremely clean equipment. For routine control it has been largely replaced by other methods, but it is still useful in establishing standards at concentrations of less than 1 mole % D_2O.

In principle the float method works as follows: the temperature at which a small quartz float has the same density as a sample, i.e., when the float is suspended below the surface of the sample, neither rising nor falling, is compared with the temperature at which the same float has the same density as a standard sample. The temperature difference (corrected for the coefficient of expansion of water, quartz, and heavy water) is then used to calculate the difference in density of the sample and the standard; this density difference is then used to calculate the mole % of heavy water in the sample.

Although this method has been used primarily in determining concentrations of D_2O of less than 5 mole %, it can be used over the entire concentration range if the proper precautions are taken for maintaining standards free of protium contamination. For best

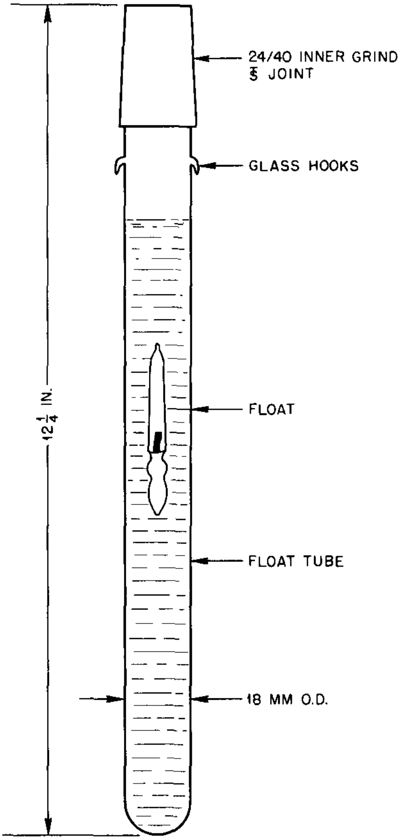

Fig 9.3—Float and float tube.

results the D_2O concentration of the standard should be as close as possible to that of the sample.

As in all density methods, the sample must be extremely pure, and the cleanliness of the equipment must be rigidly controlled. This is particularly true of the floats themselves. They must be cleaned and conditioned to the D_2O concentrations being analyzed; this is done by soaking them and then properly storing them in comparable material. In the very low D_2O concentration range (near normal abundance), dilution with moisture from the atmosphere is not important; however, above 0.05 mole % D_2O, atmospheric dilution becomes a factor and must be controlled.

The float must be so designed that it has approximately the same density as the sample and standard at normal temperatures. Figure 9.3 shows one successful design in which fused quartz is used. The distillation apparatus required is similar to that used in the pycnometer method (Fig. 9.2), except that the receiving vessel is the tube used for floating the sample (Fig. 9.3).

A precision of ±0.01 mole % at the 95 per cent confidence interval is attainable at concentrations in the $\geqq$90 mole % D_2O range, and a precision of ±0.0002 mole % is attainable at 0.015 mole % D_2O.

Procedure. Gases and other impurities are removed from the sample by completely distilling it directly into the float tube in exactly the same manner as in the pycnometer method. The float tube is then immersed in a water bath controlled at ±0.001°C by a thermostat. The float is very carefully placed in the sample, and the temperature of the sample is adjusted until the float remains motionless for 200 sec. The position and movement of the float are observed with a cathetometer or telescope. The float is then removed, rinsed in a portion of standard D_2O, and then placed in another float tube containing a standard of approximately the same D_2O concentration as the sample. Again, the temperature is adjusted until the float becomes motionless. Sufficient time must be allowed for the water bath and standard to reach equilibrium. Assuming that the sample and standard are very close in D_2O concentration and the same float is used, the equation for calculating the mole % of heavy water becomes

$$\text{Mole \% } D_2O = 927.35 \times [(\Delta T \times d_3) + K] \tag{9.6}$$

where

ΔT = difference in temperature between standard and sample

d_3 = average change in density per degree for reference water at 25.9°C ($=262.6 \times 10^{-6}$)

K = difference in density of normal water and pure protium oxide ($=16 \times 10^{-6}$)

(c) *Displacement Method.* The density of heavy-water samples can be determined by displacement (with, for example, the Westphal balance). Although not so accurate as the pycnometer or float bath methods, this is an excellent method when time is a factor and precise measurements are not required. This method utilizes less expensive equipment than the pycnometer or float bath and requires less skill on the part of the operator. The precision of the method is ±0.10 mole % at $\geqq$90 mole % D_2O.

The procedure consists simply in suspending a sinker in a heavy-water standard and then in the sample. At a particular temperature, the buoyant force exerted on the sinker by the sample is compared with the buoyant force exerted by the standard. Once again, the sample must be free of dissolved and suspended impurities. Although the precision of the method normally does not warrant it, corrections for the O^{18} content of the sample and for the surface-tension effect on the wire suspension should be considered for highest accuracy. A simplified formula that can be used to calculate the mole % of heavy water is

$$\text{Mole \% } D_2O = (A-B) \times 927.35 \qquad (9.7)$$

where

A = density of the sample
B = density of normal water at the temperature at which the sample was measured

9–2.2 Mass Spectrometer

Mass spectrometry will not be discussed here except as it applies to the control of heavy water. For a discussion of the theory and general operation of mass spectrometers, see Chap. 13.

(a) *General.* The determination of the isotopic distribution of hydrogen by mass spectrometer was one of the original techniques used in the study of hydrogen isotopes. One of the earlier types of mass spectrometers used extensively for heavy-water control was the Nier instrument.[1] This instrument measures the ratio of the HD to D_2 mass peaks or the HD to H_2 mass peaks; therefore the problem of preparing a representative hydrogen gas product from the sample must be resolved. Two general methods are available: (1) the sample of water can be decomposed chemically if care is taken to decompose the entire sample to prevent fractionation of the D_2-H_2 mixture, or (2) the liquid sample can be equilibrated with a standard deuterium gas (or with hydrogen gas if the sample contains only traces of D_2O), and the equilibrated gas can be analyzed for D_2 content. Although these methods of sample preparation and this type of mass spectrometer are still employed, they have been largely replaced by other mass-spectrometric procedures and equipment that are more adaptable for rapid routine control work. The precision of these gas mass spectrometers is ±0.02 mole % at the ≥ 98 mole % D_2O range.

(b) *Heavy-water Mass Spectrometer.* One of the mass spectrometers[2, 3] now being used most successfully for the routine control of heavy water is the Consolidated Electrodynamics Corporation model 21–330. This instrument is a continuous-recording isotope-ratio mass spectrometer specifically designed to measure the relative abundance of hydrogen isotopes in water vapor. Its greatest advantage is its ability to accept a sample of water vapor, thus eliminating the need for converting the sample to a gaseous product. This mass spectrometer is designed to collect, simultaneously and separately, ions having mass to charge ratios of 19 and 20 (representing HDO^+ and D_2O^+) or 18 and 19 (representing H_2O^+ and HDO^+). These two ion-beam signals are sent to a direct-reading ratio recorder that records the mole % D_2O. Since the ratios recorded are not an absolute measure of the relative abundance of the respective molecules, standards must be used whose values have been determined by other methods, such as pycnometer. Results obtained by pycnometer, Nier ratio (3/4) spectrometer, and the CEC 21–330 instrument are compared in Table 9.1.

Table 9.1—COMPARISON OF RESULTS BY DIFFERENT METHODS

Sample No.	Heavy water, mole %		
	Pycnometer	CEC 21–330 mass spectrometer	Nier ratio (3/4) mass spectrometer
1	99. 73	99. 74	99. 72
2	99. 75	99. 75	99. 75
3	99. 75	99. 76	99. 75
4	99. 76	99. 76	99. 75
5	99. 67	99. 68	99. 68

The precision of measurements on the CEC 21–330 instrument varies with the concentration. Some typical precision data on routine control analyses are shown in Table 9.2.

Table 9.2—PRECISION OF CEC 21–330 MASS SPECTROMETER

Concentration range, mole % D_2O	Number of determinations	Precision (95% confidence interval), mole % D_2O
0.05 to 0.15	45	0. 0046
0.50 to 2.00	60	0. 028
13.0 to 17.0	40	0. 10
Above 99	150	0. 02

The CEC 21–330 instrument, mainly because it is subjected to water vapor, has an appreciable "memory" owing to the retention of trace amounts of the last material analyzed on the internal surfaces of the sample-introduction system and ionization chamber of the spectrometer. When the next sample is introduced, a small portion of this retained material is released from the internal surfaces and contaminates the material being analyzed. With samples of similar concentration, the effect is negligible. Therefore it is desirable to limit the samples being analyzed by one instrument to a narrow D_2O concentration range. If this is not possible, frequent flushing with standards of known D_2O concentration is required.

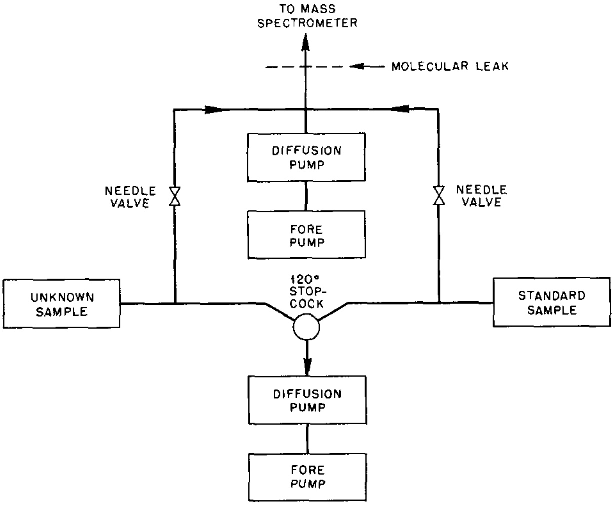

Fig. 9.4—Continuous-flow introduction system.

One modification of the CEC 21–330 mass spectrometer introduction system has been made which has minimized the memory effect, particularly at high concentrations of D_2O, and has substantially reduced the time of analysis, enabling an operator to analyze a sample in 2 to 3 min. In the original design of the introduction system, a small sample (less than 0.1 ml) was introduced into the instrument with a capillary dipper and mercury seal. With the modified arrangement a much larger quantity (several milliliters) is continuously vaporized and allowed to pass through the introduction system into a separate pumping system, with only a small side stream of vaporized sample being introduced into the ionization chamber by means of a molecular leak. The pressure is controlled at 100 μ or less by a needle valve. Isotopic separation does occur when the sample and standard are vaporized, but the effect is canceled if the concentrations of sample and standard are similar. A block diagram of the continuous-flow introduction system is shown in Fig. 9.4.

In the analysis of D_2O by a mass spectrometer, as in all other methods of heavy-water analysis, contamination of the sample with light water is always possible, and even probable, unless the necessary handling precautions are taken. However, one big advantage over the gravimetric and density methods is that no extensive cleanup of the sample is necessary. A specially designed sample boat (Fig. 9.5), which is essentially a hollow two-way stopcock, is used for presenting the sample to the instrument. Approximately 3 to 4 ml of sample is transferred from the sample bottle to the outer bulb of the boat by a

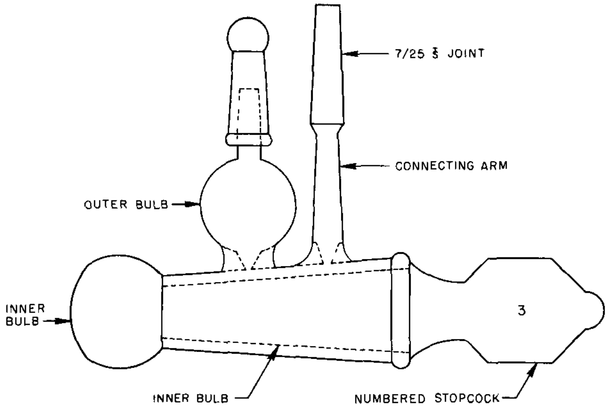

Fig. 9.5—High-range mass-spectrometer sample boat.

hypodermic syringe and then admitted to the inner bulb, which has been previously evacuated. Enough sample is left in the outer bulb to form a seal from the atmosphere. The sample boat is then connected to the mass spectrometer introduction system (Fig. 9.4) and the sample of standard is introduced into the instrument as required.

> *Procedure.* From a set of previously prepared standards, the one nearest the estimated D_2O value of the sample is selected. The sample is transferred, by means of a hypodermic syringe or in a closed dry box, to special sample boats (Fig. 9.5), which are then connected to the introduction system (Fig. 9.4). After evacuation of the introduction system manifold, the standard is introduced into the system. The sample flow is controlled at a pressure consistent with good mass-spectrometer operation, nominally 100 μ. When the recorder has maintained a constant value for 30 sec, the sample flow is stopped, the instrument is evacuated, and the unknown sample is introduced at the same pressure. After 30 sec of steady output as indicated by the recorder, the unknown sample is evacuated from the instrument, and the standard is introduced again. An average value for the standard is calculated, and, by comparison of this value with the true value of the standard, a correction factor is determined. This correction factor is applied to the unknown sample reading to obtain the corrected value for the unknown.

There are numerous variations to this general scheme, depending on the range of concentrations being determined, the memory effect to be overcome, the concentration spread between standard and sample, and other factors. In some laboratories where the D_2O concentration of the samples varies very little, as many as 10 samples have been run between introductions of the standard.

Of course, any results by this method are only as good as the standard values. Since some slight fractionation occurs as the standard samples vaporize and since the handling that standards experience in daily use tends to contaminate them, rigid control of the standards, including frequent verification of their true values, is necessary if reliable results are to be obtained.

9–2.3 Infrared Spectroscopy

The analysis of heavy water by infrared spectroscopy is a comparatively recent development, but one which promises to become one of the more important methods, particularly for "in-line" monitoring of heavy water at the $\geqq 99$ mole % concentration.

The precision of the method is excellent at $\geqq 99.7$ mole % and at less than 0.3 mole %, but it rapidly becomes worse as the mixture approaches equal parts of light and heavy water. The infrared measurements are made on the HDO absorption band, usually at 2.95 μ. This is the region of greatest sensitivity with samples of greater than 99 or less than 1 mole % D_2O since the equilibrium reaction for heavy water–light water mixtures is such that, at these concentrations, essentially all the lesser hydrogen isotope[4, 5] is present as HDO.

The advantages of the infrared spectrometer as a laboratory batch analyzer compared with the mass spectrometer are (1) lower instrument cost, (2) no memory effect, and (3) better precision (± 0.002 mole % at the $\geqq 99.7$ mole % D_2O range).[4, 5] Its advantages over the pycnometer method are (1) less analysis time, (2) less demand on operator skill, and (3) less rigorous purification of the sample.

Automatic infrared in-line monitoring has the additional advantages of (1) eliminating the light-water contamination problem experienced with batch sampling, (2) monitoring the heavy-water concentration continuously rather than intermittently, and (3) substantially reducing attention time. Unlike the mass spectrometer, the infrared spectrometer is temperature sensitive, i.e., the temperature of the sample being analyzed is critical and should be controlled for maximum precision. Also, the sample should be free of any contaminants that might interfere with the infrared wave transmission.

Although the sensitivity of the method is ± 0.002 mole % at the 99.7 mole % concentration range, standardization of the instrument with standard samples is required, and the accuracy of the measurement is limited by the accuracy of the standards, usually ± 0.01 mole % as determined by pycnometer. In most procedures a double-beam differential absorption technique[4] is used. The sample cell, which usually has a capacity of less than 1 ml, is flushed several times by repeatedly introducing a small amount of sample with a hypodermic syringe or in a dry atmosphere. The reference cell is filled with H_2O

or is replaced by an optical absorber, such as soda glass, with the proper absorption characteristics. The analytical results are obtained either from a recording device calibrated to read directly in mole % D_2O or from a recorder whose reading can be converted to mole % from a calibration curve. Calibration is accomplished by analyzing known standards introduced in the same manner as an unknown sample. Frequency of calibration depends upon operating experience with the particular instrument being used and upon the degree of precision required.

9–2.4 Other Methods

Four other methods, emission spectroscopy, nuclear magnetic resonance, cryoscopy, and refractometry are briefly described in this section.

(a) *Emission Spectroscopy.* Development work on a spectrographic method of analysis for hydrogen isotopes has been conducted by Tomkins and Fred [6] and more recently by Broida and associates.[7] The method is discussed in the chapter on spectrochemical methods (Chap. 12). In the work of Broida et al., the vapor from an aqueous sample containing light water–heavy water is pumped at a nominal pressure of 400 μ through a glass tube in which a high-frequency electrodeless discharge is maintained. The light emitted from the discharge tube contains lines of the Balmer series of hydrogen and deuterium. The emitted light is dispersed by a monochromator, and the relative intensities of the beta lines of the Balmer series are measured. The ratio of intensities of the hydrogen and deuterium lines is a function of the relative concentration of the isotopes. Standardization against known standards is required.

A precision of 0.1 to 3.0 per cent has been obtained under different conditions of experimentation. The method has the advantages of using a small sample (less than 1 ml) and of not requiring sample purification (since the water vapor is analyzed). The method is sensitive to sample flow rate, pressure, temperature, and discharge-tube temperature. Some memory effect is present, and some fractionation takes place when the sample vaporizes.

(b) *Nuclear Magnetic Resonance.* Nuclear magnetic resonance [8] can be used for the determination of heavy-water purity, although the accuracy with presently available equipment and techniques is considerably less than that of most of the better-known methods. Most of the work of adapting this technique to D_2O analysis is in the development stage, and no established routine methods or precision data exist. Since the technique is intrinsically more sensitive to the proton than to the deutron, by a factor of approximately 200, and since the minor component is measured, less precise measurements are experienced at low concentrations of D_2O than at high concentrations.

(c) *Cryoscopy.* Although the difference in the freezing points of heavy water and light water (heavy water freezes at 3.802°C) has been evaluated as a means of determining heavy water,[9] only in recent years have techniques been developed that make the method comparable in precision to other procedures, and then only in the 0 to 5 mole % D_2O range.[10] This recent work, in which the Fiske osmometer was used, is based on the principle that slightly supercooled solutions can be rapidly frozen, by agitation, and that the temperature of the ice crystals will remain constant long enough to make an accurate reading. A thermistor was used, and a precision of ±0.014 mole % D_2O was obtained at the 0 to 5 mole % D_2O range.

(d) *Refractometry.* A significant difference (0.0048 at a wave length of 5461 A at 20°C) exists between the index of refraction of ordinary water and that of heavy water. This difference, which can be measured by either a refractometer or an interferometer, can form the basis for the isotopic analysis of water. A higher accuracy is more easily obtainable with the interferometer than with the refractometer since the refraction of one liquid is compared with that of another having nearly the same composition and temperature coefficient at that refractive index. The temperature must be controlled within ±0.01°C for accurate refractometer measurements.[1] For precise results all impurities must be removed. Any of the purification methods mentioned previously can be applied here.

(e) *Miscellaneous.* Several other methods for determining deuterium have been developed and used to a limited extent. As in the better-known methods, advantage is taken of the differences in some particular physical property of light and heavy water or hydrogen and deuterium gas. Thermal conductivities, viscosities, and vapor pressures, for example, have all been used with some success.[1]

9–3 DETERMINATION OF IMPURITIES

In a heavy-water-moderated reactor the efficiency of the reactor operation and the maintenance of the reactor system, as well as the control of any moderator purification equipment, require a knowledge and quantitative determination of the moderator impurities. Since heavy water is normally free of contaminants before its use as a reactor moderator, the impurities present, except for light water, are corrosion or radiation products resulting from exposure to the reactor complex.

The analytical methods used can be grouped in three major categories: (1) determination of individual cationic and anionic impurities, (2) determination of the radioactive species present, and (3) determination of changes in the physical properties of the moderator which are indicative of the level of contamination. The methods employed are standard analytical techniques and are therefore only briefly described in this chapter to indicate the specific methods that have been used successfully. Because the concentrations of the contaminants are normally in the parts per million or parts per billion range, methods of highest sensitivity must be used, and extreme care must be exercised in handling the samples to prevent contamination.

9–3.1 Cationic and Anionic Impurities

As a rule, ionic impurities are determined by chemical methods; however, emission spectroscopy is preferred in some specific situations.

(a) *Emission Spectroscopy.* The emission spectrograph is used for determining cations in the parts per billion range when extreme precision is not required or when no adequate chemical methods exist. The ability to detect cations in this concentration range is made possible by a 50 to 100 volume concentration of an acidified sample in quartz equipment. Quartz ware is recommended to prevent contamination from the impurities found in conventional glassware, and acidification is recommended to prevent the loss of cations due to deposition on the evaporation equipment. The method has been used for the determination of boron, cadmium, manganese, iron, magnesium, chromium, nickel, aluminum, copper, cobalt, calcium, uranium, sodium, and lithium.

Procedure. Approximately 1 liter of sample is introduced into a round-bottom quartz flask. Two to three drops of hydrofluoric acid (1+100) are added to the sample, and the sample is carefully evaporated just to dryness. The "soft" residue is redissolved in 10 ml of 6*N* spectrographically pure hydrochloric acid; then 200 μl of the concentrate is evaporated on a paraffin-coated graphite electrode (in some applications, copper or silver electrodes have been used[11]). The impurity-element spectra are excited and recorded by the use of a conventional spark source and spectrograph. Conventional spectrograph techniques are used throughout the procedure. The concentrations of the impurity elements are estimated by comparison with standard films. The precision of the method is a factor of 2 (+100 per cent to −50 per cent).

(b) *Chemical Methods.* Since most of the impurities in heavy water occur in trace quantities, very little preliminary separation or pretreatment is required. Interference found in individual methods are usually eliminated by minor adjustments of a particular method. Spectrophotometric, nephelometric, and flame photometric methods are particularly adaptable to the determination of such ions as sodium, lithium, aluminum, iron, chromium, cadmium, nickel, copper, mercury, peroxide, chloride, nitrate, sulfate, and silica, when present in the parts per million range. All working curves are made from pure chemicals.

(1) *Sodium-Lithium.*[12, 13] Flame photometry is a rapid, accurate method for the determination of sodium or lithium. In dilute solutions, interfering ions that normally inhibit the lithium-flame excitation (such as calcium and strontium) become negligible; however, for best lithium results the free-acid concentration must be no greater than 0.12 equivalents per liter of solution, and the sodium content should not exceed 25 mg/liter. No interfering ions have been encountered with this method in determining sodium. For best accuracy and sensitivity a photomultiplier attachment used with the phototube is recommended.

Procedure. As required by the flame photometer, the appropriate amount of sample (usually several milliliters) containing approximately 2.5 mg of lithium or sodium per liter is placed in the atomizer. The sample is excited in a hydrogen-oxygen flame, and the percentage of transmission is noted at a wave length of 671 mμ for lithium and 590 mμ for sodium.

(2) *Aluminum.*[14] Heavy water samples are treated with an acid dye (sold under the trade name Pontachrome Blue-Black R) which produces a red fluorescence with aluminum at a pH of 4.9. The fluorescence, which is proportional to the concentration of aluminum, is measured with a fluorophotometer, such as the Lumetron, model, 402–EF.[15] The method is sensitive to 0.001 to 0.025 mg of aluminum. Iron in concentrations of less than 0.3 ppm in the final volume will not interfere.

Procedure. An aliquot of sample containing 0.001 to 0.025 mg of aluminum and not more than 0.015 mg of iron is placed in a 50 ml beaker, and the volume is adjusted to approximately 30 ml by distilled water and 5 ml of 10 per cent ammonium acetate. The pH of the solution is adjusted to 4.9±0.1 with 6*N* ammonium hydroxide or 6*N* sulfuric acid. The solution is transferred quantitatively to a 50-ml volumetric flask, and 1.5 ml of 0.1 wt.% Pontachrome Blue-Black R dye is added. The solution is diluted to 50 ml, mixed, and allowed to stand for at least 1 hr and not more than 2 hr. The percentage of fluorescence is measured using a fluorophotometer.

(3) *Iron.*[16, 17] Ammonium thioglycolate reacts with ferrous and ferric iron in a solution having a pH of 6 to 11 to give a reddish-purple color proportional to the iron concentration when it is between 0.005 and 0.5 mg. The color developed is stable for about 2 hr. More than 10 mg of copper in the final volume causes a loss in the color of the iron complex, but this can be corrected by the addition of excess ammonium thioglycolate. Cyanide and mercurous ions interfere.

Procedure. An aliquot of sample containing at least 0.01 mg of iron is pipetted into a 50-ml volumetric flask, and the volume is brought to about 30 ml with distilled water. To the flask are added 5 ml of 1 vol.%

neutral thioglycolic acid and enough 6*N* ammonium hydroxide to make the solution basic, plus a 2 ml excess of 6*N* ammonium hydroxide. The solution is diluted to 50 ml with distilled water and mixed. The absorbancy of the sample is measured in a spectrophotometer at a wave length of 530 mμ by absorption cells with a 50-mm light path.

(4) *Chromium.*[18] Hexavalent chromium in an acid solution reacts with diphenylcarbazide to form a soluble red-violet colored complex. Interference by molybdenum and mercury is minimized by proper adjustment of the acidity of the solution with sulfuric acid. Ferric iron is also an interfering element but is removed by the addition of ammonium hydroxide. Potassium bromate in the presence of a small amount of manganese as a catalyst is used to oxidize chromium to a valence of six. After oxidation of the chromium, any bromine remaining in the solution is removed by boiling the solution with ammonium sulfate and adding hydrochloric acid. As little as 0.001 mg of chromium can be detected by this method, but the preferred concentration range is 0.005 to 0.010 mg.

Procedure. An aliquot of sample containing approximately 0.005 mg of chromium is placed in a 125-ml Erlenmeyer flask and diluted to about 20 ml with distilled water. To the flask are added 3 ml of 60 g/liter potassium bromate, 0.5 ml of 0.1 mg/ml manganese, and 2 ml of 5*N* sulfuric acid. The solution is boiled for 5 min. While the solution is boiling, 1 ml of 20 wt.% ammonium sulfate and 1 ml of 10 wt.% hydrochloric acid are added slowly. Thirty seconds after the solution becomes colorless, it is allowed to cool; then 5 ml of concentrated ammonium hydroxide is added. The solution is again boiled for 2 to 3 min to remove the excess ammonia, and it is then filtered quantitatively into a 50-ml volumetric flask. To this flask are added 2 ml of 5*N* sulfuric acid and 0.5 ml of 4 g/liter diphenylcarbazide in 95 vol.% ethyl alcohol. The solution is diluted to 50 ml with distilled water and allowed to stand for 15 min to develop maximum color. The absorbancy of the sample is measured in a spectrophotometer at 540 mμ with a 50-mm light path.

(5) *Cadmium.*[16, 17, 19] Dithizone in chloroform will extract cadmium from a strongly basic solution (pH 12.5). The reddish-pink cadmium dithizone complex formed in the chloroform layer is stable for at least 2 hr. Improved separation from interferences is achieved through the use of potassium cyanide and tartaric acid. Loss from decomposition is controlled by using hydroxylamine hydrochloride and reducing the time of contact of the chloroform with the alkali. A maximum of 5 mg of cobalt, copper, iron, manganese, and nickel can be tolerated without serious effect on color development. The range of the method is 0.001 to 0.005 mg of cadmium.

Procedure. An aliquot of sample containing approximately 0.002 mg of cadmium is placed in a 125-ml separatory funnel, and enough distilled water is added to bring the volume to 25 ml. Then, with mixing after each addition, 1 ml of 20 per cent potassium tartrate, 5 ml of 10 per cent sodium hydroxide–1 per cent potassium cyanide, and 1 ml of 20 per cent hydroxylamine chloride are added. Next, 15 ml of chloroform containing 80 mg/liter of dithizone is added, and the two phases are shaken together for 1 min. The chloroform layer is drained into a second separatory funnel containing 25 ml of cold 20 g/liter tartaric acid solution. The aqueous solution remaining in the first separatory funnel is washed with 10 ml of chloroform, and this chloroform wash is then added to the second separatory funnel. The contents of the second separatory funnel are shaken for 2 min, and the chloroform-dithizone layer is discarded. To the aqueous layer remaining are added 0.25 ml of 20 per cent hydroxylamine chloride, 15 ml of chloroform containing 8 mg/liter of dithizone, and 5 ml of 10 per cent sodium hydroxide–0.05 per cent potassium cyanide solution. The funnel is shaken for 1 min, and the chloroform layer is filtered through a glass-wool plug into a dry 20-mm absorption cell. The absorbancy of the developed color is measured in a spectrophotometer at 520 mμ.

(6) *Nickel.*[16, 17] In an alkaline solution, dimethylglyoxime reacts with nickel in the presence of an oxidizing agent to give a pink-colored slightly soluble complex that is proportional to the nickel concentration when it is between 0.01 and 0.1 mg. Aluminum and cobalt will interfere if present. Iron interference is prevented by the addition of citric acid.

Procedure. An aliquot of sample containing at least 0.01 mg of nickel is pipetted into a 50-ml volumetric flask and diluted to approximately 35 ml with distilled water. In sequence, with thorough mixing after each addition, 5 ml of 10 per cent citric acid solution and 2.5 ml of saturated bromine water are added, and the pH is adjusted by adding concentrated ammonium hydroxide until the solution is basic. To the basic solution, 1 ml of 10 g/liter dimethylglyoxime in 95 per cent ethyl alcohol is added. The volume is increased to 50 ml with distilled water, and the solution is mixed thoroughly. The absorbancy of the sample is measured in a spectrophotometer at 535 mμ with a 50-mm light path.

(7) *Copper.* Sodium diethyldithiocarbamate reacts with small amounts of copper to produce a golden-brown suspension in acidic, ammoniacal, or neutral solution. Since the colored compound is a colloidal suspension, gum arabic has a stabilizing effect. Iron causes no interferences when present in amounts of 2 ppm or less. The method is sensitive over the range of 0.01 to 0.1 mg of copper.

Procedure. An aliquot of sample containing approximately 0.02 mg of copper is pipetted into a 50-ml volumetric flask and diluted to approximately 30 ml with distilled water. To the flask, with mixing after every addition, are added 0.5 ml of a 50 g/liter gum arabic solution, 5 ml of concentrated ammonium hydroxide, and 5 ml of 0.1 percent sodium diethyldithiocarbamate. The volume is increased to 50 ml with distilled water, and the solution is mixed thoroughly. The absorbancy of the sample is measured in a spectrophotometer at 440 mμ with a 50-mm light path.

(8) *Mercury.*[16, 17] Dithizone dissolved in carbon tetrachloride will extract mercury from an aqueous solution, forming an orange-colored complex. The colored complex is stabilized by the addition of acetic acid, and the extraction is more efficient in a sulfuric acid solution. In an acidic solution, silver, copper, gold, and palladium will also react with dithizone. The green color of the dithizone reagent exhibits maximum light absorption at a wave length of 620 mμ. For greatest sensitivity the decrease in the intensity of the green-colored dithizone reagent, due to the formation of the mercury complex, is measured, rather than the orange color of the mercury complex itself.

Procedure. To 480 ml of previously neutralized sample in a 2-liter separatory funnel are added 20 ml of 25*N* sulfuric acid and 5 ml of 6*N* acetic acid. The mercury is extracted by shaking the sample solution for 10 min with 10 ml of 0.005 per cent dithizone in carbon tetrechloride. The absorbancy of the dithizone solution is immediately measured in a spectrophotometer at 620 mμ with a 10-mm light path.

(9) *Peroxide.* At temperatures between 60 and 70°C, hydrogen peroxide reacts rapidly with acidified ferrous sulfate, oxidizing the ferrous ion to ferric. With the pH of the solution held between 4 and 6 by an acetate buffer, orthophenanthroline forms a colored complex with unreacted ferrous ion. A comparison of the intensity of the colored complex of unreacted ferrous ion in the sample with a blank containing no peroxide determines the amount of peroxide.

Procedure. An aliquot of sample containing approximately 0.01 mg of hydrogen peroxide is pipetted into a 50-ml volumetric flask containing 3 ml of 4 μg/ml ferrous sulfate solution. The contents of the volumetric flask are heated to 60 to 70°C for 10 min; then 2 ml of acetate buffer solution is added, and the pH of the solution is adjusted to 4 to 6 by either 0.1*N* ammonium hydroxide or 0.1*N* sulfuric acid. Next, 1 ml of 5 g/liter orthophenanthroline is added. The solution is diluted to 50 ml with distilled water and mixed thoroughly. The absorbancy of the sample is measured in a spectrophotometer at 510 mμ with a 50-mm light path.

(10) *Chloride.* The addition of silver nitrate to an aqueous sample containing chloride to which has been added methyl alcohol, nitric acid, and sodium sulfate produces a turbidity that is proportional to the amount of chloride in the sample. The preferred concentration range is 0.005 to 0.10 mg of chloride per 50 ml of solution. The particles of silver chloride form agglomerates and settle out on standing, particularly at the higher concentrations.

Procedure. An aliquot of sample containing an estimated 0.01 to 0.1 mg of chloride is pipetted into a 50-ml volumetric flask and diluted to approximately 35 ml with distilled water. To the flask are added 5 ml of methyl alcohol, 5 ml of 0.35M sodium sulfate–2.3M nitric acid solution, and 1 ml of 0.075N silver nitrate. The solution is diluted to 50 ml with distilled water, mixed, and allowed to stand for at least 10 min but not more than 1 hr. The absorbancy of the sample is measured in a spectrophotometer at 450 mμ with a 50-mm light path.

(11) *Nitrate.* Phenoldisulfonic acid reacts with nitrates, producing a yellow color proportional to the nitrate concentration. The color formed with the phenoldisulfonic acid is intensified by the addition of ammonium hydroxide. Chlorides up to 30 ppm can be tolerated. The method is usually used in the range of 0.01 to 0.1 mg of nitrate but is sensitive to 0.001 mg of nitrate.

Procedure. An aliquot of sample containing approximately 0.05 mg of nitrate is pipetted into a 3-in. evaporating dish, and 2.5 ml of 0.1N sodium hydroxide is added to the dish. The solution is evaporated to dryness on a steam bath. After the residue has cooled, 1 ml of phenoldisulfonic acid is added, and the solution is allowed to stand for 10 min. Then 7.5 ml of distilled water is added and the mixture is heated on a steam bath until any remaining residue is dissolved. The solution is transferred to a 50-ml volumetric flask containing 25 ml of distilled water, and 7.5 ml of 6N ammonium hydroxide is added. The solution is diluted to 50 ml with distilled water and mixed. The absorbancy of the sample is measured in a spectrophotometer at 410 mμ with a 50-mm light path.

(12) *Sulfate.*[20] This method depends upon the formation of highly insoluble barium sulfate, which is precipitated in the presence of excess salt and acid and is held in suspension by glycerol. The percentage of light transmitted through the suspension, as measured in a spectrophotometer, is inversely proportional to the sulfate concentration. In some procedures the amount of scattered light is measured. The nominal concentration range is 0.05 to 0.7 mg of sulfate per 50 ml of volume.

Procedure. An aliquot of sample containing approximately 0.3 mg of sulfate is pipetted into a 50-ml volumetric flask and diluted to approximately 30 ml with distilled water. Then, with mixing after each addition, 5 ml of 16 g/liter sodium chloride–8.7 g/liter hydrochloric acid solution, 5 ml of 33 vol.% glycerol solution, and approximately 0.3 g of barium chloride crystals are added. The contents of the flask are diluted to 50 ml with distilled water, mixed, and allowed to stand for 10 to 15 min. The absorbancy of the sample is measured in a spectrophotometer at 450 mμ with a 50-mm light path.

(13) *Silica.*[21] Soluble silica reacts with ammonium molybdate in an acid solution to form a yellow ammonium silico-molybdate complex.

This yellow complex is reduced with 1-amino-2-naphthol-4-sulfonic acid reagent to form molybdenum blue. The intensity of the color is proportional to the amount of dissolved silica present. Tartaric acid prevents interferences from phosphates.

Procedure. To a 100-ml volumetric flask, 50 ml of sample and 1 ml of 7.5 per cent ammonium molybdate in sulfuric acid are introduced. The contents of the flask are mixed thoroughly and allowed to stand for 5 min. Then, 4 ml of 10 per cent tartaric acid solution is added, the solution is mixed, and immediately 1 ml of a 0.15 per cent 1-amino-2-naphthol-4-sulfonic acid solution in a 10 per cent sodium bisulfite–7 per cent sodium sulfite solution is introduced. The flask contents are diluted to 100 ml with distilled water, mixed, and allowed to stand for 20 min for color development. The absorbancy of the sample is measured in a spectrophotometer at 700 mμ with a 50-mm light path.

9–3.2 Radioactive Contaminants

Since heavy water as a reactor moderator is exposed to an intense field of radiation, it is natural to expect that a significant amount of the impurities present will be converted to radioactive species and that some degradation of the heavy water itself will occur. In addition, any reactor fuel failures will, in most reactor designs, contribute fission-product activity to the heavy water. Quantitative identification and control of these radioactive impurities are important, not only for the reasons stated previously concerning all impurities but also because of the associated radiation hazards to personnel. Table 9.3 lists the radioactive nuclides that have been detected and identified in heavy-water moderator used in a reactor complex in which the materials of construction are primarily stainless steels and aluminum and in which fuel failures have occurred with the release of fission products.

Methods for determining individual radioactive isotopes include radiochemical separation and gamma scintillation spectrometry. Methods for determining tritium are discussed separately; these are generally based upon measurement of tritium beta activity.

(a) *Radiochemical Separation.* One means of determining the individual nuclides is by chemical separation, followed by gamma or beta counting. Although accurate and precise results are possible, this technique requires extreme care to obtain effective separation since the concentrations of the individual nuclides are usually very low. The method is also time consuming if several nuclides are to be separated, a consideration of particular importance if short-lived isotopes are involved. Obviously, it is impossible to list a universally adaptable

Table 9.3—RADIOACTIVE NUCLIDES OCCURRING AS IMPURITIES IN HEAVY-WATER MODERATOR

Isotope	Half life
From Structural Materials	
Na^{24}	15 hr.
Mn^{56}	2.6 hr.
Co^{60}	5.3 years.
Cr^{51}	26.5 days.
Fe^{59}	45 days.
Ni^{65}	2.5 hr.
Cu^{64}	12.8 hr.
Al^{28}	2.3 min.
From Fuel Failure	
Zr^{95}	65 days.
Nb^{95}	35 days.
Ru^{103}	40 days.
From Heavy Water	
H^3	12.3 years.

separations scheme. Dissolved and suspended contaminants, elemental groupings, individual concentrations, and many other factors must be considered. Figure 9.6 shows a sequential scheme of separation that has been used routinely when fission-product activity is absent.[22] Although theoretically this scheme or similar schemes should isolate the various nuclides, particularly with the use of inactive carriers, separation is seldom quantitative; therefore the purity of the separate radioactive precipitates or solutions should be confirmed by gamma spectrometry or by analysis of decay curves.

(b) *Gamma Spectrometry.* Of the several approaches to the quantitative or qualitative determination of individual radioactive isotopes in heavy-water moderator, probably the most versatile, efficient, and accurate method is gamma scintillation spectrometry.[23, 24] This method has gained wide acceptance and is now being used routinely in many laboratories. Spectrometers are being manufactured in a sufficient variety of designs to fit almost any requirements.

In brief, a gamma scintillation spectrometer consists of (1) a scintillator, usually a sodium iodide (thallium-activated) crystal that emits light when struck by a gamma photon, (2) a phototube that converts the light energy into electrical energy and provides some amplification.

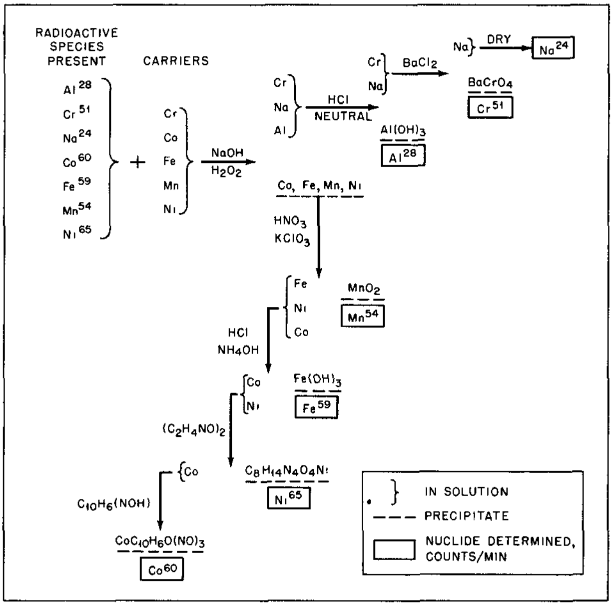

Fig. 9.6—Typical radiochemical analysis.

and (3) a pulse-height analyzer that further amplifies the electrical signal and sorts the electrical pulses according to their amplitude. Since the pulse heights are very nearly proportional to the energies of the different gamma photons, the gamma energy spectrum can be analyzed from the pulse-height distribution.

Pulse-height analyzers are designed with a single channel or with a number of channels. With a single-channel analyzer, only one pulse height can be examined at a time; whereas the multichannel instruments allow the simultaneous examination of several pulse heights. If the interest is in only one or two particular nuclides, the single-channel analyzer will suffice. Usually, however, the activity present in heavy-water moderator comes from many different radioactive isotopes, and for efficiency and accuracy the multichannel analyzers are preferred.

A 3- by 3-in. crystal has been found to be ideal for the detector. For the best resolution and for a minimum of interference from light leakage, the crystal should be mounted as an integral part of the phototube. Spurious scattered radiation arising from interaction with surrounding material must be controlled; graded shielding of the detector is suggested to reduce secondary and background radiation to the lowest possible level.

Although tedious chemical separations are not usually required in preparing heavy-water samples for pulse-height analyses, some preliminary separation is occasionally needed if gamma energies cannot be resolved by the analyzer or if high-energy gammas in relatively large abundance mask the low-energy spectrum. In some instances, differences in half lives can be used to advantage in eliminating interferences. In complex mixtures the contribution of secondary energy peaks of one nuclide to the primary peaks of other nuclides can be resolved by suitable calibration and the proper mathematical treatment. The time required to perform final computations can be substantially reduced through the use of high-speed computers. In one instance calculations that required two days with a desk calculator were completed in 30 min by electronic computers.

(c) *Tritium.* In heavy-water-moderated reactor systems, tritium is formed from deuterium by neutron capture. Since the tritium concentration is a function of the neutron flux, it is subject to wide variations; hence methods must be available to detect a wide range of concentrations. Most of the tritium is present as tritiated heavy water, but a small amount exists as the gas. Generally, the analytical methods are based upon the measurement of tritium beta activity.

(1) *Tritium Oxide: Ionization Chamber.* In this method the sample of heavy water is decomposed by metallic calcium, the gaseous decomposition products are transferred to an evacuated ion chamber, and the ionizing current produced by the beta radiation from the tritium decay is measured by a vibrating-reed electrometer (Fig. 9.7). Since the rates of reaction of calcium with the different hydrogen isotopes vary, either the entire sample must be decomposed and all the gaseous product introduced into the ion chamber, or the standards used in calibrating the electrometer must be similar in composition to the material being analyzed. The current produced is a linear function of the tritium concentration in heavy water. The lower limit of sensitivity is approximately 0.1 μc/ml.

Procedure. About 3 g of calcium metal and 3 or 4 granules of calcium chloride are placed in a 125-ml acetylating flask. After the electrometer background on air at atmospheric pressure is determined, the entire system is evacuated, and approximately 5 ml of sample is added to the sample buret. The sample is introduced to the system dropwise until the pressure in the system returns to 1 atm. Then the ion chamber is isolated from the rest of the apparatus, the current produced by the beta radiation is measured, and the concentration of tritium is determined from a standard calibration curve.

(2) *Tritium Oxide: Scintillation Counting.* In recent years the technique of measuring low-energy beta emitters in liquid scintillators has been adapted for the determination of tritium in water.

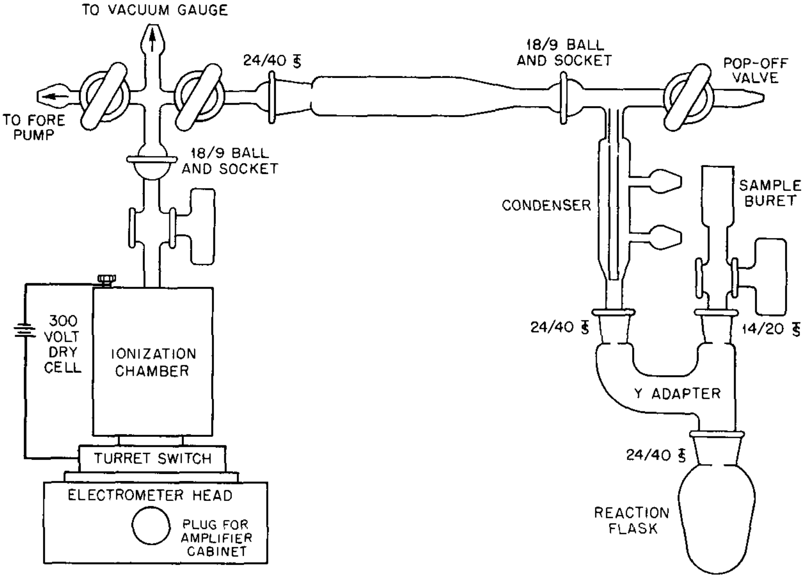

Fig. 9.7—Vibrating-reed electrometer and associated equipment.

The liquid scintillator–phototube system is combined with a pulse-height analyzer to provide discrimination of the tritium-decay-activated pulses from other radioactive contaminants. This is an extremely sensitive method; tritium oxide below 0.00005 μc/ml can be detected. The thermal noise produced by the photomultiplier must be controlled to obtain this low limit of sensitivity. This is accomplished by cooling the samples and phototube and by using a coincidence arrangement of two photomultipliers to screen out the thermal noise pulses originating from the individual phototubes.

Procedure. A scintillation solution is prepared by dissolving 50 g of naphthalene, 4 g of 2,5-diphenyloxazole, and 0.1 g of *p*-bis 2-(5-phenyloxazole)-benzene in 1 liter of 2,4-dioxane. Twelve milliliters of this scintillation solution and three milliliters of sample are mixed in a 16-ml polyethylene vial, placed in the refrigerated detection compartment of the spectrometer, cooled for 30 min to approximately 5 to 10°C, and counted.

(3) *Tritium Gas.* Ion-chamber techniques can be used to determine gaseous tritium. The current produced by the beta radiation is measured by an electrometer and converted to tritium concentration by comparison with a standard calibration curve.

9–4 DETERMINATION OF PHYSICAL PROPERTIES

Because heavy-water moderator must be maintained in a high state of purity for efficient reactor operation, the equipment and methods used for determining its physical properties must be capable of accurately detecting extremely small changes; good, reliable equipment of the highest sensitivity should therefore be used. Usually, pH (or pD), conductivity, and turbidity are determined. If turbidity is high, the size of the particulate matter may be of interest.

9–4.1 pH

Because heavy water as a moderator is usually a highly unbuffered pure material and hence readily absorbs atmospheric gases and other contaminants, accurate pH values are difficult to obtain. In-line analyses are preferable but, if a bench type pH meter is used, consideration must be given to providing proper grounding for the meter and adequate shielding to protect the sample from atmospheric contamination. A low-resistance large-surface-area glass electrode is recommended in all applications. A sensitivity of 0.02 pH unit is desirable.

9–4.2 Conductivity

Since heavy water as a moderator is very pure, its specific conductance is very low and can be used as a means of measuring dissolved ionic impurities. A conductivity cell and bridge capable of measuring values in the 0- to 50-micromho range are desirable.

9–4.3 Turbidity[15]

Turbidity can be determined visually by comparing the sample against turbidity standards with the use of Nessler tubes or instrumentally by passing a beam of light through the sample and measuring the scattered or absorbed light. Although it is known that the particle size of suspended matter and the color of the sample have a very pronounced effect on the absorption and scattering of light, it is believed that the photoelectric method is as good as, or better than, other methods for routine control. The concentration range of interest is usually 0 to 100 ppm as silica, based on American Public Health Association turbidity units. For highest sensitivity, nephelometric measurements are usually employed. With this technique a precision of 0.1 ppm in the 0- to 5-ppm range is possible.

9–4.4 Particle Size

Information concerning the size of particulate matter is important in designing equipment for turbidity removal or control. There are many techniques for determining particle size, but unfortunately the diameter of the particles found in moderator is quite often in the 0.1- to 10-μ range, and particles in this size range and in concentrations of 0 to 100 ppm can be characterized by only a few of the standard techniques. The optical microscope can be used; the electron microscope is suitable but is expensive and requires considerable skill for proper operation.

Light scattering,[25, 26] although not quantitative, provides information concerning the particle-size range and the average particle size. With this method the intensity of scattered light is measured over an angular range, and the measurements are converted to a special graphical form, forming a composite curve in which the individual particle-size groups appear as steps in the change of intensity with angle. This procedure is effective in the 0.2- to 50-μ-diameter range.

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