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CHAPTER 7

PREPARATION OF SAMPLES AND STANDARDS

The preparation of samples and standards is of great practical importance. If possible, the analyst himself should carry out all processing of material under controlled conditions, or at least be aware of the detailed history of the sample, so that he can take any necessary steps to remove surface contamination before or after activation is carried out.

Commensurate with availability, sensitivity requirements, dimensions of the container, matrix activity and macroscopic cross section, sample weights are usually maximized.

If the impurity content of the sample is approximately known, the sample size can be estimated for a given irradiation condition (flux, irradiation time, . . .).

In most cases the problem of the standard is not so difficult as in other physical methods of analysis, such as emission spectrography, X-ray fluorescence, etc., since matrix or third-element effects are less important. However, neutron shielding is possible (see Chapter 10), and should be eliminated or at least kept equal for standards and samples. Absorption of emitted radiation in the sample must also be taken into account.

The irradiation time for a given flux is mostly chosen considering the saturation factor for the radionuclide of interest, $[1 - \exp(-\lambda t)]$.

For 14 MeV neutron activation, the irradiation time is kept as short as possible to prevent untimely exhaustion of the tritium target.

I. Preparation of Samples

(A) SAMPLING OF SOLID SAMPLES

Massive solids can be wrapped in aluminium foil and packed in standard aluminium cans for irradiation.

Solid samples may be too large for direct irradiation so that it may be necessary to reduce the sample size by grinding, cutting, drilling, etc. before packing. Hard steel tools, used for this purpose or for cleaning

metal samples, contain a number of elements, which can contaminate the sample, so that the latter must obviously be etched before (dissolving and/or) counting.

Comparing the analysis of 0.5 g filings, obtained by filing tin with a stainless steel file with that of the etched sample itself, yielded the following results: (1)

	Filings	Sample (etched)
tungsten (^{187}W)	40 ppb	n.d.
chromium (^{51}Cr)	300 ppb	n.d.
silver ($^{110\text{m}}\text{Ag}$)	800 ppb	20 ppb
iron (^{59}Fe)	2800 ppb	n.d.
cobalt (^{60}Co)	40 ppb	4 ppb
zinc (^{65}Zn)	detected	n.d.

For copper also positive results were found (^{64}Cu).

Etching a sample before or after irradiation does not always eliminate all the contaminants, particularly if they are more electropositive than the matrix. During the etching, elements such as gold and copper—from the sample itself or from contamination on the sample surface—were found to be deposited to a certain extent on the residual lump. This phenomenon has been observed for tin and zinc matrices. Etching several times in fresh solutions can eliminate this problem.

It should be borne in mind that chemical etching often preferentially attacks some parts of the surface of the solid lump. Therefore, "mechanical etching" has been proposed by some authors.

Sometimes, solid samples may melt during activation in high fluxes (e.g. 10^{14} n cm $^{-2}$ s $^{-1}$) as is the case for cadmium (see Chapter 4, Section I, A). It is obvious that etching after irradiation has then no sense. Considerable heating from the reaction $^{10}\text{B}(n, \alpha)^7\text{Li}$ also occurs in samples, irradiated under a boron shield (2).

Contamination is also possible by automatic mills and by mortars and pestles made of boron nitride, agate, diamonite, etc. Grinding high purity germanium in a diamonite mortar increased the apparent As-content from 5 to 50 ppb. Bowen (3) has described a mill made entirely of Perspex for grinding dry biological materials; here the contamination is restricted to perspex dust, which has a low metal content. Such a mill can grind thin bones, but probably not mollusc shells, for instance. Other workers have used silica knives to carve up fresh biological tissue.

Polythene screens and nylon nets are available which avoid contamination associated with the use of brass or steel sieves.

In the case of accelerator activation, solid samples, which are sufficiently "unbreakable" can be machined in the dimensions of the pneumatic tube (disk, rod, pin . . .) and irradiated without container. It is obvious that the surface oxidation for a number of metals must be eliminated when determining oxygen. Hoste *et al.* (4) removed the oxide layer from aluminium, tantalum, niobium, chromium, lead and zinc by means of silicon carbide paper, rinsing with perchlorethylene and drying prior to activation. The surface can be protected with a thin layer of vaseline of low oxygen content. Fujii *et al.* (5) recommend cleaning aluminium by immersing the sample in 5% NaOH solution for 2 m, and then in HCl solution (2:1) for 2 m, thereafter washing with water, ethanol and chloroform, or by dipping the sample in a mixture of phosphoric acid (35 ml) + chromic acid (20 g) + water (95 ml) at 80°C, then washing with water, ethanol and chloroform. Another method is "electropolishing": the sample is dipped into 100 ml HClO $_4$ + 700 ml ethanol, applying a 1.5 A current with 10 V bias at <40°C for 2 m, followed by washings with ethanol, chloroform and drying. K. R. Blake *et al.* (6) determined oxygen in vacuum-melted and extruded beryllium and found that the total apparent oxygen content was reduced by a factor of 10 after cleaning the surface with acids. It is significant that the specimen after five months storage did not pick up any oxygen contamination: the surface contamination of vacuum melted and extruded beryllium apparently takes place during the machining process. For vacuum melted beryllium, which is not extruded, the total oxygen content increased, however, after acid treatment. The acid treatment seems to form oxygen containing substances in the crystal boundaries of the sample; cracks were formed by the sudden impacts in the pneumatic transfer system.

Accurate oxygen determinations are difficult with samples in the form of turnings unless the machining and packaging are carried out in an inert atmosphere.

Special precautions are required with reactive materials, such as cesium (7). A container—low oxygen content polyethylene—is obviously needed in this case and the packaging must be carried out in a nitrogen dry box. For the transfer between the nitrogen dry box and the nitrogen tent over the sending station of the pneumatic system, the cesium containing vials were kept in nitrogen purged and sealed

screw-cap glass bottles in order to minimize oxygen diffusion through the polyethylene into the vials. When preserved in this way, no increase in oxygen content was observed in samples stored for a week after the initial analysis.

(B) POWDERS

Powders are usually weighed in a suitable box or vial and directly irradiated in the reactor or at the accelerator. If the powder has been prepared from a solid sample, it is certainly more or less contaminated, as described above. On the other hand, very pure chemicals are produced in powder form by precipitation, recrystallization or sublimation. Contamination by laboratory dust should be avoided by sealing the powders in suitable containers immediately after preparation.

Whereas in the reactor the neutron flux is relatively uniform, flux gradients are very steep at the target of a neutron generator. Consequently it is necessary to press the powder as a pellet or at least to compact the powder uniformly with a levered pestle in a suitable container in order to obtain a reproducible irradiation (and counting) geometry. The combined effect of density and geometry can be noticed, e.g. when the second and third determination of oxygen in many samples are consistently higher than the first, independent of the time elapsed between the determinations (8). This effect is caused by the sudden impacts of the sample vials at the arrestor pins or bumpers of the pneumatic system, so that powdered materials are packed densely at, e.g. the bottom of the vial, while the top portions are more loosely packed. Loosely packed and only partly filled samples also give considerably different results when compared to properly prepared standards.

When determining oxygen in powders of substances with high oxygen content, such as TiO_2 , oxalic acid, benzoic acid, sucrose, calcium phosphate, etc. surface contamination is obviously of little importance. The situation is different for metal powders, for instance. The following procedure is described by Girardi *et al.* (9) for SAP (sintered aluminium powder): the sample is agglomerated by means of polystyrene and dissolved in benzene. The solution is stored over metallic sodium in order to eliminate possible traces of humidity. The weighed samples are mixed with a few ml of this solution and the obtained suspension poured on a thin aluminium foil; after evaporation of benzene, the

foil with the powder can be detached. The oxygen content of the polystyrene foil is negligible compared with that of the SAP sample.

(C) LIQUID SAMPLES

Liquid samples are mostly irradiated in quartz ampoules or polythene vessels. Liquids are assumed to be mostly homogeneous. However, it should be remembered that the composition of sea water, for instance, depends on many variables such as depth, time of year, proximity to land and to large rivers (3). Even if great care is taken to prevent contamination during collection, trace elements may be lost by precipitation or adsorption on planktonic debris, particularly if the sample is not analyzed soon after collection. Such debris should be centrifuged off in the stoppered container as soon as possible. Filtration is not recommended as it can introduce further loss and/or contamination.

Biological liquids, such as blood, urine, ... also vary in trace element composition as a function of time, certain pathological conditions and peculiarities of diet or drugs.

A second important problem is the possibility of loss of trace elements by adsorption on the walls of containers and of contamination by dissolution of traces of materials from the container walls or by desorption of previously adsorbed ions. An excellent review of these phenomena has been given by Thiers (10). Leutwein (11) found that the concentration of a 10 ppm solution of Ni, Mn, Mo, V, Au, Pt, Ru and Ti decreased by a factor of 10 in 75 days when stored in 6% mineral acids in glass. When fused quartz was used, only Ni, Au, Pt and Ru decreased in concentration. No substantial losses were observed for $10^{-3}\%$ solutions of Ir and Os in 6N HCl, stored in pyrex for one year (12) and for cobalt (13 ng/ml as cobalt chloride at pH = 3.0 in a pyrex bottle) (10). A solution of Mn and V (1 and 7 ppm respectively) in 6% mineral acid had not changed its concentration after 250 days, when stored in polythene.

The adsorption and desorption of gold traces on glass as a function of the gold concentration, the pH and the composition of the solution has been described by Beneš (13). The observations were explained on the basis of an ion exchange mechanism, the adsorbed species being the positively charged hydrolyzed forms of gold. Gold deposition from a 10^{-2}M solution was less than 5% over the whole pH scale. For more

dilute gold solutions the adsorption is only negligible in acid medium ($\text{pH} \approx 0$) or $< 5\%$ at $\text{pH} > 6$. Complete desorption is achieved by means of concentrated hydrochloric acid.

The effect of pH and time on the loss of Ag^+ on brown borosilicate glass is discussed by Dyck (14). The adsorption is appreciable at low concentrations (~ 0.02 ppm Ag^+) ml. $\sim 20\%$ after 50 days at $\text{pH} = 3.8$ and $\sim 5\%$ after 50 days at $\text{pH} = 1.5$ (HNO_3). The lowest adsorption was observed on borosilicate glass, treated with an organo-silicon product used to produce hydrophobic glass surfaces; this surface is easy to clean. Molded plastic surfaces adsorb less strongly than glass surfaces during short intervals (1-2 days), but they are more difficult to clean; over a period of several months, however, they adsorbed appreciably more than glass.

The adsorption of a large number of tracers (Ag , Au , Cu , Fe , In , Na , Rb , Sb , Zn) on quartz, silicon and germanium was studied by Sotnikov *et al.* (15,16) in the presence of various etching agents, such as KOH , H_2O_2 , a mixture of hydrofluoric and nitric acids and acetone. It was shown that with a content of these impurities in the etching agents from 10^{-5} – $10^{-1}\%$, the amounts of adsorption lie in the range from 10^{11} – 10^{16} atoms/cm².

Heavy metal contamination of acid ($\text{pH} = 2$, HNO_3) and alkaline (0.1N NaOH) solutions is less serious in high pressure polythene than in glass, pyrex or wax. Indeed, the metal content is much higher in glass (pyrex: Si , B , Na , Al , K , Fe , Ca , Mn , Mg : 0.01–40%) than in polythene (ppb-ppm). Polythene proved to be purer by orders of magnitude than other readily available bottle material, including polystyrene and methyl methacrylate.

Contamination of liquid samples by activities originating from polyethylene and quartz containers transferred to the container surface due to recoil effect in the thermal neutron capture process was found to be negligible (17). However, when the containers are rinsed with hydrochloric acid, activities are extracted from depths of the order of 10^{-3} and 10^{-4} cm in the polyethylene and the quartz materials respectively, which in some cases necessitates corrections. The extracted amounts of Cu , Mn , Na and Sb , expressed in μg per cm² container area, are given in Table 7.1.

The concentration of Sb in quartz was 0.2 ppm and that of Cu and Mn in polyethylene 3.5 and 0.065 ppm respectively.

The interference of nuclides from the container wall can be avoided

by freezing the sample during the irradiation (18). Before the samples are transferred to containers for chemical processing or measurement, they are allowed to melt for a short time. This removes a thin ice layer which may have carried impurities from the container walls.

TABLE 7.1
Extracted amounts of some elements from irradiated containers
($\mu\text{g. cm}^{-2}$) (17)

Element	Polyethylene container	Quartz container
Cu	0.004–0.008	0.001
Mn	0.00006–0.00008	0.00002–0.00003
Na	0.002	0.03
Sb	0.00008	0.0001

The freezing technique may also be applied to biological samples by freezing them in their extra- and intra-cellular fluids. The freezing of the samples during activation also offers other advantages: the pressure in the ampoules caused by radiolysis of water is considerably reduced. Losses of activities due to vaporization as well as adsorption of activities on container walls are strongly suppressed.

A special application has been described by Brocas and Picciotto (19) for the determination of nickel in antarctic snow at the ppb level. The 500-gram samples were cored with a plastic tube in the center of large blocks of firn, and kept in the frozen state during the irradiation (2–3 h at 10^{12} n cm⁻² s⁻¹) by wrapping them in a thick layer of polystyrene foam. The whole package was cooled at liquid air temperature before irradiation. After irradiation the ice was melted for a short time, and then completely melted in the presence of nickel carrier. This procedure excludes all contamination and losses.

Many water-moderated and high-flux reactors have understandably been reluctant to accept liquid samples at all because of spread of contamination and chemical reactions with reactor internals, especially if halogens are present. Sometimes, small volumes (~ 0.1 ml) are allowed on condition that the ampoule is surrounded with a sufficient amount of absorbing paper. One can thus be obliged to evaporate a known volume of the liquid to dryness in a quartz vial before irradiation.

tion. But even at moderate temperatures this evaporation can lead to losses of some elements. This should be checked by radioactive tracer techniques. Contamination by air dust can be minimized when the evaporation is carried out as presented in Figure 7.1 (10). Some laboratories have installed clean rooms to exclude air dust contamination (20). The clean room described has met a specification of less than 100 particles ($\leq 0.3 \mu$ diameter) per cubic meter of air.

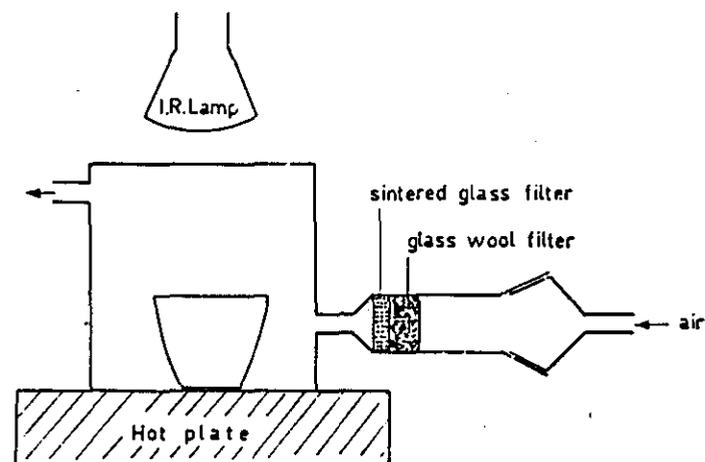


Fig. 7.1. Apparatus to avoid contamination by air during dissolution or evaporation (10).

(D) GELS

Biological material often occurs as a gel, so that it can be cut. To avoid contamination, a quartz or perspex knife is recommended (3). If direct activation is not possible (high temperature reactors) it may need drying or even ashing (see further). Surface contamination can be removed as described for massive solids.

(E) PASTES

Girardi (9) describes the determination of oxygen in terphenyl, using polypropylene containers (Figure 7.2(a)). These are filled by the system

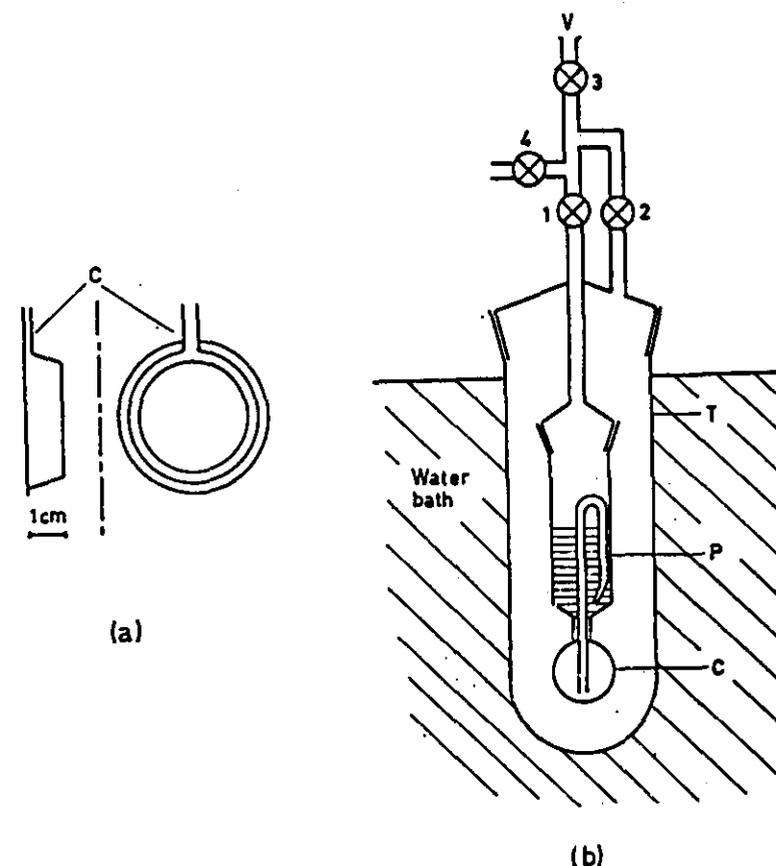


Fig. 7.2. Sampling of pastes (9).

a) polypropylene container

b) filling system

C: container; P: pipette; T: glass tube; V: to vacuum pump; 1, 2, 3 and 4: stopcocks.

shown in Figure 7.2(b). It is placed in a large glass tube *T*, which is heated in a water bath and evacuated by aspiration at *V*, keeping cocks 1, 2 and 3 open. After the organic material is fused and degassed in order to eliminate dissolved oxygen, 2 and 3 are closed, and 4 is opened to admit a small amount of air (or another gas) so that the fused liquid enters in the container *C* via the pipette *P*. Then the introduc-

tion channel (c) is squeezed with a pair of tweezers and sealed, e.g. by warming in a cigar lighter.

(F) SAMPLING OF GASES

Gaseous samples and standards are usually irradiated in quartz tubes. Diebolt (21) uses a quartz tube of 5 mm internal diameter; the wall thickness is 1 mm. One end is closed, whereas the other is drawn to obtain a capillary with a bore of 1 mm and a minimum length of 10 cm (see Figure 7.3). The extremity *A* is connected with a vacuum

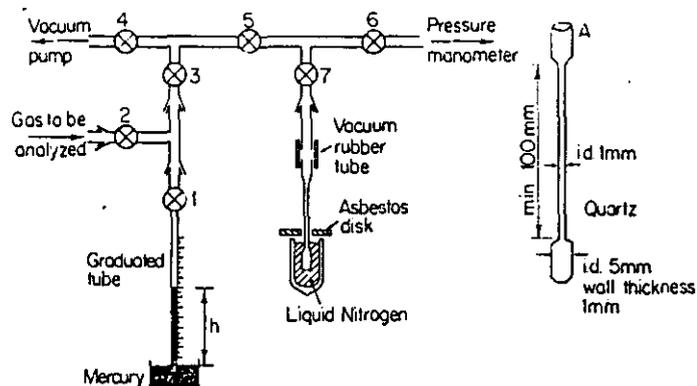


Fig. 7.3. Sampling of gases (21).

manifold by means of a short rubber vacuum tube, which allows one to obtain a good vacuum in the quartz tube. The gas is introduced into the ampoule by immersing the latter in liquid nitrogen. No gas is lost when sealing off the ampoule, since the capillary tube can instantaneously be closed by means of a burner.

The exact volume of gas is measured before irradiation. A tracer study by Diebolt (21), using ^{41}A , has shown that no losses occur when proceeding as follows:

1. Make a vacuum of 5×10^{-4} to 1×10^{-5} mm Hg in the apparatus between 1, 2, 6 and the ampoule. Heating the quartz ampoule from time to time with a burner is recommended.
2. Close cock 7 to isolate the ampoule.

3. Draw the mercury into the graduated tube by opening 1; close cock 1, taking care that a drop of mercury remains upon the cock. Make again a good vacuum (10^{-5} mm Hg) (3, 4 and 5 open) to prevent contamination of the gas to be analyzed by the air from the graduated tube. Close 3 and open 1 and 2 carefully. If a sufficient amount of gas is collected in the graduated tube, 1 is closed.
4. The pressure in the graduated tube is given by

$$h_s = h_a - h \quad (7.1)$$

where h_a = atmospheric pressure

h = height of the mercury column.

The volume of gas under standard conditions (0°C and 760 mm Hg) is calculated as follows:

$$V_0 = \frac{V_s h_s}{760(1 + \alpha t)} \quad (7.2)$$

where V_s is the measured volume in the graduated tube, and t the temperature. In the case of perfect gases, $\alpha = 1/273 = 0.00367$; for exact data, reference is made to tables of physical constants.

5. Cock 2 is closed, 3 is opened and the vacuum reestablished (cocks 1, 2 and 7 closed).
6. The ampoule is immersed in liquid nitrogen and the gas is collected in the ampoule (cocks 1, 3, 5 and 7 open, cocks 2, 4 and 6 closed). The graduated tube is empty, if a mercury drop can be formed upon cock 1.
7. The ampoule is sealed just above the asbestos disk (Figure 7.3), which protects the liquid nitrogen from excessive evaporation. The above formula is valid for a dry gas. For gases saturated with water equation (7.2) is replaced by

$$V_0 = \frac{V_s(h_s - h_0)}{760(1 + \alpha t)} \quad (7.3)$$

where h_0 is the saturation pressure of water vapour at temperature t . The ampoules with sample and standard are packed in a standard aluminium can, which is cold welded.

The ampoules are opened by means of a "magnetic hammer"

(Figure 7.4) and the radioactive gas adsorbed on active coal (e.g. particle size 0.5–0.75 mm) at the temperature of liquid nitrogen in an apparatus similar to that shown in Figure 7.3.

In practice, direct irradiation of gases is only necessary in the case of noble gases. Other gases can often be converted into solids. An example is the determination of ^{18}O by the nuclear reaction $^{18}\text{O}(n, \gamma)^{19}\text{O}$ ($T_{1/2} = 29.4$ s), involving a separation of oxygen from other sample constituents by conversion of the oxygen into carbon dioxide and subsequently into solid ammonium carbamate prior to neutron irradiation (22). The samples of CO_2 are collected by distillation in either polyethylene or polystyrene tubes, which are attached to the vacuum manifold with Apiezon *W* wax and held at liquid nitrogen temperature.

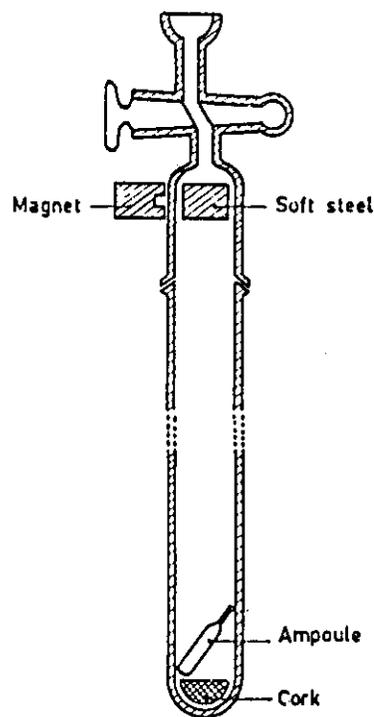


Fig. 7.4. Magnetic hammer for opening silica ampoules, containing irradiated gas samples (21).

The solid ammonium carbamate samples were prepared by adding ammonia gas in excess by distillation to the labelled carbon dioxide. After the reaction had taken place, the tube was cut away with a razor blade (a hot razor blade was required for cutting the polystyrene tubes). The tubes were brought to room temperature and sealed off using either a hot soldering iron or a small gas flame.

After irradiation, the sample tubes were opened with a razor blade and the tube contents transferred by flushing with water into radioactively clean counting vials and counted.

(G) SAMPLING OF AEROSOLS

Millipore type EA 1.0 μ cellulose acetate filters can be used to collect aerosol particles by impaction, probably down to a particle radius of $\sim 0.1 \mu$ (23). One should indicate: height of the filter above ground level, air speed, type of pump, location of sampling (distance from sea coast, distance from street with heavy traffic, etc.). Contamination of the samples by particles of, e.g. blowing snow can be guarded against by extending the opening of the Millipore open-type filter folder with a cylindrical plastic baffle and by hanging the opening vertically downward during collection.

Aerosols have been collected by aircraft, with a four-stage cascade impactor based on a design by May (24) and described in the manufacturer's literature (25). The relative humidity affects both the particle size and the sticking probability. To minimize contamination from the ground, the collector should be covered with plastic until a few seconds before take off and again be covered immediately after landing. One should indicate height and speed of the airplane.

(H) CONCENTRATION AND SEPARATION PRIOR TO ACTIVATION

Direct irradiation of a sample can be difficult if its volume is too large or if it contains elements which will give rise to very high activities and hot chemistry facilities are often not available. If the matrix forms interfering activities, systematic errors are possible, as described in Chapter 10. Dissolution of the sample and chemical separations after irradiation may be too time-consuming for some short-lived radio-nuclides.

Liquid samples can be concentrated by evaporation. Possible losses of volatile elements should be checked by radioactive tracer techniques and air dust contamination avoided, as pointed out above.

Jaskólska *et al.* (26) compared the results of gold and arsenic determinations in semiconductor grade nitric acid previously concentrated 20 times and not concentrated. The results were 8×10^{-10} – 2×10^{-9} and 1×10^{-9} respectively for arsenic (same order of magnitude); 1×10^{-11} – 7×10^{-11} and 2×10^{-10} respectively for gold, indicating that the concentration process can lead to serious errors.

Biological samples should be dried, preferably just under 100°C, in order to avoid losses of iodine and possibly of mercury. The determination of Na, K and P in human muscles after simply drying the samples at 100°C for 20 hours is described by Stone (27). A similar technique has been employed for the determination of Rb and Cs in marine organisms and of As in grain (28). The effect of drying kale powder (slightly hygroscopic) is described by Bowen (29). Van den Winkel *et al.* (30) described the determination of a number of elements in this biological standard powder after simple drying, by irradiating 50 mg amounts for 15 h at a flux of 10^{14} n cm⁻² s⁻¹ and decomposing the organic material after irradiation by a Schöniger combustion in an Erlenmeyer flask of 0.5 liter.

A simple technique for collecting residues from large amounts of solution is the freeze drying technique (31): the sample is frozen quickly at about -15°C in a rotary evaporator and the water then removed by sublimation. The residue is collected as a finely divided powder, ideally suited for encapsulation and irradiation. The technique of freeze drying can also be applied to pharmaceutical products, blood plasma, vaccines, sera and even to rocks, minerals and fossils. Laboratory freeze dryers are manufactured, which are suitable for drying a number of specimens simultaneously.

Several chemical separations before irradiation have been described, to isolate a number of elements from their matrix, such as ion-exchange, paper chromatography, precipitation, solvent extraction, electro-deposition, electrolysis. Two major advantages of activation analysis can be lost by such procedures, the risk of losing a part of the element to be determined and the possibility of contamination. The behaviour of micro- and submicrogram quantities of the elements of interest during such procedures must therefore be checked by radiotracer techniques in the same experimental conditions. If the recovery of the element of

interest is not quantitative, the chemical yield of the prepreparation can be determined using a carrier-free isotopic tracer (32,33).

It can be difficult to distinguish the activity induced by irradiation and that added to determine the chemical yield. This problem can be solved by several means: (32)

- (i) Choosing a short-lived radioactive tracer and performing the activation analysis after its decay;
- (ii) The radiotracer used is different from that formed by (n, γ) reaction. The use of selective counting techniques, such as gamma spectrometry, allows us to distinguish between the two different radionuclides. If only a long-lived radiotracer is available and if the activation analysis can be done using a short-lived radionuclide, one can subtract the long-lived activity after counting the two radionuclides, in order to obtain the net induced activity of interest.
- (iii) If for the element to be determined, there exists only one long-lived radioisotope which is convenient as radiotracer and which must be used for its determination by activation analysis, it is still possible to make the difference of the activities before and after irradiation.

If the radiotracer is not carrier-free, one must obviously take the mass of the element added into account (isotope dilution).

Such techniques have been used by Pauly *et al.* (32) for the determination of Mo, Ru, La and Ce in uranium alloys. U is separated from Mo by precipitation with ammonia, and from La and Ce by extraction from 4M HCl with TNOA into benzene and cyclohexane. Ru is distilled from perchloric acid.

Towell *et al.* (33) used a group separation of the rare earths from standard rocks with a mixture of perchloric and hydrofluoric acid, and carrier-free ¹³⁹Ce and ⁸⁸Y were added. Following precipitation by ammonia, the rare earths were isolated as a group by ion exchange and chemical yields were determined at this stage by measuring the tracer radioactivities. The rare earth group was irradiated as an aqueous solution, together with a similar solution of rare earths in known concentrations. The irradiated sample and standard solutions were chromatographed by gradient elution and the isolated fractions measured. This procedure is claimed to be less time-consuming than others and selfshielding errors, particularly if rare earth minerals are

present in the sample, are minimized by irradiation of samples and standards as aqueous solutions.

Ion-exchange has also been used to concentrate elements such as Pb, Cs, Sr, Ba, Au, Bi, Cd, Hg from sea water, urine, etc. After adsorption of the element on the resin, the latter can either be irradiated as such or ashed.

Paper chromatography can more easily introduce some contaminants (Na, Cl, Mn, Ca, Cu, Mo . . .). Washing the chromatography paper with triply distilled water can sometimes be recommended. Ördögh *et al.* have used Whatman-1 and Schleicher-Schüll 2043a papers to separate 100 mg amounts of uranium from its impurities (Ag, Cd, Co, Ni, Fe, Cr, P, Cu, Mo, Mn, Si) before activation (34).

The use of precipitations and solvent extractions has been mentioned already. Typical examples include the separation of gallium from germanium by coprecipitation on aluminium oxalate in order to avoid errors by the interfering reaction $^{72}\text{Ge}(n, p) ^{72}\text{Ga}$ (35), the separation of vanadium from aluminium and of vanadium, aluminium and magnesium from iron and zirconium by coprecipitation on iron hydroxide in order to allow activation analysis using short-lived radionuclides. The aluminium matrix was first separated by crystallization of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in concentrated hydrochloric acid; the iron matrix by extraction in ether and the zirconium matrix by precipitation as zirconium mandelate (36). Coprecipitation on iron hydroxide has also been used for the pre-separation of rhodium from industrial concentrates, consisting mainly of lead, antimony, copper, silicon, . . . and traces of platinum metals. Lead, silver and antimony were first separated as chlorides, respectively oxychloride in hydrochloric acid (37).

Another simple technique is the spontaneous electrodeposition of noble elements such as Au, Ag, Pt, Pd and Rh from weakly acid solution (<0.1N HCl for instance) on amalgamated copper foil or powder; base metals and iridium are not reduced. This method has been used for the trace analysis of complex materials, containing lead, copper, silicon, antimony, arsenic, tellurium (37). Without pre-separation, one has to work with very high activities, mainly of ^{122}Sb and ^{124}Sb . However, one should be aware of the presence of gold even in high-purity copper.

Several publications have proposed the use of pyrolytic graphite as an electrodeposition matrix at controlled potential for preconcentration in neutron activation analysis (38-40) which is a technique

that shows promise. Its usefulness is limited by the purity of the graphite matrix. Impurity levels in pyrolytic graphite are given in Table 7.2 (41).

TABLE 7.2
Impurity levels in pyrolytic graphite (ppm) (41)

Element	Uncleaned	Cleaned
Na	13	0.0016
Cl	4.2	n.d.
Mn	0.023	0.0091
W	90	9.1

After short waiting times, ^{28}Al is found (2.3 m), which would be very detrimental to short-lived activation analysis. Other activities, found after irradiation, are ^{52}V and ^{64}Cu .

This technique can be used for the determination of Cu, Mn, Ag and Au in sea water, and for the analysis of trace metal ions in biological fluids, such as blood. In these systems the large amounts of organic material present pose a problem for the electrodeposition step, as they will adsorb and/or undergo redox reactions themselves to form polymeric films on the electrode, with consequent passivation of the latter. This problem can be avoided, however, by employing a dialysis membrane placed between the electrode surface and the biological fluid. This membrane is permeable to the metal ions but not to the large organic molecules (see also Chapter 6, section III, C, 1).

When using pre-separation techniques, blank determinations should obviously be included. To reduce blank values to a minimum, chemicals of ultra purity can be used. Some maximum impurity concentrations in a number of commonly used reagents are given in Table 7.3. Actual impurity concentrations, as determined by neutron activation analysis, are given between brackets (26,41).

In purified water, preliminary analyses by neutron activation analysis gave the following impurity concentrations (in ppb): Au: 0.014, Mn: 0.14 and Na: 105-170 (41). Correction for pre-separation does not exist in practice for a number of elements (rare elements) because they are unlikely to be present in significant amount in any of the reagents

TABLE 7.3
Maximum impurity concentrations in ultra-pure analytical reagents (ppb)

	Ammonia solution	Bromine	Hydrogen peroxide	Hydrochloric acid	Hydrofluoric acid	Hydroiodic acid	Nitric acid	Perchloric acid	Sulfuric acid
Ag					0.1			see Hg	
Al	1-5	5	5	10		50	5	5	5
As	10	5	5	5			1-5	5	5-10
Au			(0.001)	(0.0004; <0.001)			(0.002- 0.006)		
B									100
Ba	2000						1000	1000	
Br				1000 (+I) (2.6)			(7)		
Ca	10-500	20-300	500	50		300	50-200	50-1000	300
Cd		5-10	10				5		5
Cl	100-500	10.000	2500	—	100-1000		200-500	—	200
Co	1-5	5	5	5		10	1	5-10	5
Cu	1-5	5-20	10(<0.1)	5 (<0.01-2)	10	10	5(<0.1-7)	5	5-10
F							500		
Fe	5-10	10-15	250	20-200	20-500	50	10-200	20-100	20-50
Ga			(n.d.)	(0.0002)			(n.d.)		
Hg	100			100				20 (+Ag)	
I		100		see Br					
In			(n. d.)	(0.01)			(n. d.)		
K	50	20	200	50		5000	50	50	500
Li	5					500		10	
Mg	5		500	50	10	10	200	1000	5
Mn		5	10			50	5	5-50	5
Mo			(<0.1)	(1-2)			(0.01-0.1)		
Na	50-500	50	5000	50(4)		1000	500 (170)	200-1000	500
Ni	1-5	1-10	10	5	20	10	5	2-10	5
Pb	1	1-20	10	1-5	10-20	20	1-5	5-20	5
PO ₄	100	50	2500		500	50	10-100	100-1000	10
S	50								—
SO ₄	500	500-5000	3000	250	1000		500	25,000	—
SO ₃	500			500	4000				—
Sb			(n. d.)				(0.002)		
Se									100
SiO ₂	100	100	2000		50,000			1000	
Sn			20(n. d.)				(n. d.)		
Sr	50						50		
Tl						10	1	5	5
Zn	5-10	10-20	40(0.4)	5-20(0.05)		50	5(0.4)	5-40	5

normally used either for dissolution of the sample or for the separations, or in the glass ware, crucibles, etc.

(I) DRY ASHING AND WET COMBUSTION

One of the most important problems concerning the analysis of trace elements in biological samples is how to decompose a large quantity of organic substances in the course of sample preparation.

As impurities in reagents can produce a significant problem in wet combustion (see however Table 7.3), dry ashing is generally recommended for trace element analysis before irradiation, the more so as the powder obtained is very suitable for irradiation. During dry ashing, which normally requires heating the specimen to temperatures above 400°C, elements from the container and the atmosphere may be introduced into the sample. Certain classes of biological material tend to froth and char and particles may be driven out by decrepitation. Some substances may ignite upon heating, others are converted into difficultly soluble compounds or will be found in the container's surface, so that recovery is only possible by sufficiently drastic treatment. According to Smales (42) the need for this latter step can often be avoided by adding an "ashing agent", such as magnesium nitrate, to provide a large inorganic surface area competing for retention of the trace elements with the container surface. When used before irradiation this coating can, however, introduce contaminants, and blank values must obviously be determined. Retention on crucible walls has been described for Ag, Al, Cd, Cu, Cr, Cs, Fe, K, Mn, Na, Rb, Pb and Sb.

Serious losses are caused by diffusion and volatilization for elements such as Br, Cl, I, Ge, Hg, Se, As, etc. (Table 7.5) and Cd, Ga, In, Ni, Os, P, Re, Ru, Sn, Te, Tl, V though contradictory statements are found in the literature (e.g. 43). As volatility depends on the composition of the substrate (Table 7.4), on the temperature and on the oxidation state of the element (Table 7.5, iodine), one cannot accurately predict which elements will be lost in a specific sample. Besides, it appears that it is difficult to control precisely the temperature of the substances being destroyed, as was shown by Oosting (44). During the destruction of powdered grass, for instance, at an oven temperature of 530°C, the organic material itself reached a temperature of 710°C.

Gorsuch (45) determined the losses of trace elements by volatilization

during oxidation at 600°C for 16 hours, in the presence of inorganic chlorides, by counting the tracer activity in a silica or porcelain crucible before and after heating, to avoid the confusion that might arise from the incomplete extraction of the trace elements from the crucible, see Table 7.4. The free-energy changes for the postulated reactions ($MO + 2 NaCl = MCl_2 + Na_2O$ or $MO + 2 HCl = MCl_2 + H_2O$) are in agreement with the experimental findings. The results indicate that with NaCl no loss occurs for any of the elements investigated. This is interesting as NaCl is of such widespread occurrence in biological materials.

TABLE 7.4
Recovery of trace elements after heating at 600°C for 16 hour,
in the presence of inorganic chlorides (45)

Element	Compound added	Recovery %	Element	Compound added	Recovery %
Sb	NaCl	100	Pb	NaCl	95
	NH ₄ Cl	6-19		NH ₄ Cl	69-75
Cr	NaCl	95-97	Zn	NaCl	100
	NH ₄ Cl	97-100		NH ₄ Cl	6-9
Fe(III)	NaCl	98-100	MgCl ₂	52-53	
	NH ₄ Cl	93-97	CaCl ₂	4	
			BaCl ₂	99-100	

An alternate method (46) employs a high frequency electromagnetic field (power ~250 watts) to produce a stream of active oxygen, which decomposes organic substances, such as muscle tissue, fat, fecal matter, ion exchange resin, cellulose and polyvinylchloride filter paper, activated charcoal, a 40-g rat, etc. Superficially, the apparatus is similar to high temperature dry-ashing in an induction furnace. Both methods employ a closed system to minimize the introduction of atmospheric impurities. However, induction heating units incorporate a metallic substance into the sample or combustion boat to heat the sample to high temperature and provide the requisite activation energy. In the radio frequency discharge method, electrical energy is transferred directly to a stream of low pressure gas (flow rate ~70 ml/m, pressure ~1 mm Hg), producing highly excited states of oxygen. Because the

sample temperature is low, volatility and diffusion losses are substantially decreased. Non-volatile mineral constituents remain in the sample container. The authors claim that the ash is completely soluble in mineral acid.

The oxygen tank must be separated from the borosilicate glass or quartz reactor section by a liquid nitrogen trap and glass wool filter to prevent contaminants in the oxygen tank or valves from reaching the specimens. Two dry ice-acetone traps in series separate the reaction chamber from the exhaust pump (general purpose mechanical vacuum pump) and prevent contamination of the sample by back diffusion of oil from the pump.

Dry ashing allows a considerable reduction of the original bulk weight of biological samples. The ratio of ash to bulk weight varies, for instance, from approximately 0.5 to 2% for meat (edible matter of chicken, beef, pork, ham, . . .) (48).

Wet combustion, used extensively with mixtures of hot mineral acids, results in quantitative recovery for most elements, excepting As, Au, Fe, Hg and Sb (Table 7.5). Quantitative recovery of these elements can, however, be achieved with the proposed destruction mixture (1 vol. H_2SO_4 98% + 1 vol. $HClO_4$ 70% + 3 vols. HNO_3 66%) when use is made of a reflux condenser.

Guinn (49) describes a carefully conducted pre-irradiation wet combustion of milk powder and hair with transistor-grade sulfuric acid. The process is carried out to dryness (700°C) and the residue is activated for the determination of vanadium via $3.7 m$ ^{52}V .

In Table 7.5 some experimental results are summarized (43,46,47).

General considerations concerning the application of neutron activation analysis upon biological and medical problems are given by Kwan Hsu (50). A method, which has not yet been mentioned here, is the Schöniger combustion. This method is limited to small samples to achieve complete oxidation, e.g. 50–100 mg when using a $\frac{1}{2}$ liter Erlenmeyer flask and can be used successfully after neutron irradiation of dried samples (30). Note that elements such as gold and silver can be deposited on the platinum wire.

(J) DISSOLUTION OF SAMPLES PRIOR TO ACTIVATION

In neutron activation analysis, irradiation of samples and standards as aqueous solutions is often preferable to solids. It allows the elimina-

tion of selfshielding errors if the solid sample and standard are not identical in form. It also avoids the difficulty of measuring small size standards as solids, together with the radiation hazard, time and expense in dissolving the solid samples after irradiation and performing all radiochemical separations, particularly if short-lived radionuclides are to be measured. The addition method of analysis (see further, section II, E of this chapter) can most ideally be applied to liquid samples.

As already stated above, many water-moderated reactors do not accept liquid samples. Winchester *et al.* (51) have, however, irradiated

TABLE 7.5
Recovery of radioactive tracers in dry ashing and wet combustion
(Tabulated values are percent recovered from vessel) (43,46,47)

Nuclide	Sample	Wet combustion (a)	Muffle furnace Dry ashing 24 h, 400°C	Muffle furnace Dry ashing 3 h, 900°C	R.F. dis-
					dry ashing (~100°C)
^{114}Sb	$SbCl_3$ + blood	99; 101*	67	9	99
^{74}As	$HAsO_3$ + blood	93; 101*	23	0	100
^{137}Cs	$CsCl$ + blood				100
^{60}Co	$CoCl_2$ + blood	100	98	30	102
^{64}Cu	$CuCl_2$ + blood	102	100	58	101
^{51}Cr	$CrCl_3$ + blood	100	99	56	100
^{51}Cr	Na_2CrO_4 + blood		100		
^{198}Au	$AuCl_3$ + blood	77; 100*	19	0	70+
^{131}I	NaI + filter paper				31+
^{131}I	$NaIO_3$ + filter paper				100
^{59}Fe	$FeCl_3$ + blood	98; 100*	83	27	101
^{210}Pb	$Pb(NO_3)_2$ + blood	100	103	13	100
^{54}Mn	$MnCl_2$ + blood	99	99	79	99
^{203}Hg	$Hg(NO_3)_2$ + blood	24; 100*	< 1	0	92+
^{99}Mo	$(NH_4)_2MoO_4$ + blood	101	100	83	100
^{75}Se	Alfalfa				99
^{110m}Ag	$AgCl$ + blood	100	66	21	72+
^{22}Na	$NaCl$ + blood				100
^{65}Zn	$ZnCl_2$ + blood	99	100	30	99

* Reflux condenser.

+ Rest volatilized.

(a) 1 vol. H_2SO_4 98% + 1 vol. $HClO_4$ 70% + 3 vols. HNO_3 66% for 1.5 h.

several hundred aqueous samples up to 7 ml in volume and for periods of up to 18 hours at a neutron flux of 10^{13} neutrons $\text{cm}^{-2} \text{s}^{-1}$ in the M.I.T. reactor for activation analysis of atmospheric precipitation samples for halogens, of solutions of rare earths separated from silicate rocks and of solutions for calcium isotopic analysis. In all of these cases the authors regard irradiation of samples and standards in aqueous solution not only a convenience but a necessity and in none of the irradiations did leakage out of the sample container occur.

A solid sample can often be dissolved by several methods: acid, mixture of acids, bisulfate fusion, peroxide fusion, etc. Fusion increases the risk of contamination and introduces a number of ions, which can interfere in subsequent chemical separations. Dissolution in pressure tubes can often be recommended, as it is a "clean" method. Due to the increased efficiency of hydrochloric and similar acids at higher temperatures and pressures a large number of elements and oxides can easily be dissolved in pressure tubes (glass, pyrex, vycor, quartz); the pressure developed at 250 to 300°C by 48% hydrochloric acid is about 4000 psi.

The oxides of aluminium, beryllium, tin, cerium, chromium and plutonium which have been ignited at 1500°C are completely dissolved at 250–300°C within 15–24 hours. All the oxides of the elements of the second, third and fourth groups of the periodic system, with the exception of silicon, titanium, zirconium and hafnium respond to this treatment; some ceramic materials of zirconium oxide and silica can be decomposed. Many silicate minerals are readily dissolved (52).

If hydrochloric acid plus an oxidizing agent (Cl_2 , NaClO_3 , HClO_4 , HNO_3) is used, even osmium, ruthenium, rhodium, iridium and iridosmine can be dissolved. The use of perchloric acid as an oxidizing agent is desirable if the reaction is to be conducted above 250°C; perchloric acid has the advantage of not reacting with hydrochloric acid at room temperature, so that it is not necessary to chill the tube before sealing.

The great advantage of the method described is that a convenient acid solution is obtained directly and that contamination is a minimum (Table 7.3). Bromine is a typical contaminant and, of course, chlorine. For many working details the original papers should be consulted.

For activation analysis, it is possible to weigh the samples directly in small quartz tubes; after addition of 0.1 ml of conc. hydrochloric acid and, if necessary, a few drops of nitric acid, the contents of the

tube are frozen in liquid nitrogen and sealed. After leak testing with an indicator paper, the tube is introduced in a sealed steel shell and heated in a Carius oven at a temperature of 150–250°C. The Carius oven has normally six openings. Quartz tubes 5 cm in length, 0.4 cm internal diameter and 0.1 cm wall thickness withstand 24 hour of heating at 220–250°C. At higher temperature, explosion is possible; it is then recommended to add solid carbon dioxide before closing the steel shell, in an amount calculated to give the desired pressure at the operating temperature. After cooling to room temperature, the ampoules are packed for irradiation. This method has successfully been used for trace analysis in osmium, ruthenium, rhodium and platinum (5–100 mg amounts) (53–55).

After irradiation, the ampoules are again immersed in liquid nitrogen to reduce internal pressure, before opening. Note that the method allows a sample to dissolve without losses of volatile impurities. It can easily be coupled to an addition method of analysis (see section II, E of this chapter).

If a silica ampoule withstood the oven temperature, it will normally not explode in the reactor and will withstand the impacts at the arrestor pins of the pneumatic system, on condition that it is carefully wrapped in absorbent paper.

(K) STANDARD MATERIALS FOR INTERLABORATORY COMPARISON

Interlaboratory comparison of a standard material is a good method for assessing the accuracy and, incidentally, the precision of analytical techniques. A number of metallurgical standards are available from the National Bureau of Standards and the British Standards Institution; in some of them up to 28 elements have been determined. For geochemical applications, one can use, for instance, the G-1 and W-1 standard rocks (56) or the sulfide and syenite standard rocks, distributed by the Canadian Society for Applied Spectroscopy (57). Comparative analyses for 40 elements in a standard plant material by 29 laboratories are discussed by Bowen (58).

Another possibility of revealing systematic errors is the application of two or more independent techniques, for instance wet combustion and dry ashing of organic material before and after irradiation, analyses with and without separation prior to activation, etc. If several methods are all reliable, one can choose the simplest one for routine analysis.

If possible, the activation analysis should be checked by another analytical method, such as colorimetry, flame photometry, spectrometry, although the latter is significantly less precise (58).

Before applying a procedure, it should obviously be checked by a number of good radiotracer experiments.

II. Preparation of Standards

(A) SPECIFIC ACTIVITY OF THE STANDARD

A good standard must fulfill the requirement that - after irradiation - its measured specific activity equals that of the element to be determined in a given matrix. For that reason, the activity is measured in the same geometry, with the same radiation detection system, using the same absorbers, etc. The measurement of low-energy β , γ or X-rays may require special precautions, as pointed out in Chapter 10, section II, D and Chapter 6, section III, C, 1. In the case of heavy samples, errors are even possible for high energy γ -rays.

Moreover, during activation, the standard must receive the same neutron dose as the sample. This requirement is normally easy to fulfill, except in the case of accelerator activation.

In order to illustrate some of the above problems, the calibration of an oxygen standard for the determination of oxygen in steel with 14 MeV neutrons will be described (59). The samples have the form of a disk of 9 mm thickness, with a diameter of 26 mm; they are pneumatically transferred and irradiated without container in an aluminium tube of rectangular section (9.5 mm \times 26.5 mm). The standard consists of 4.92 g of a mixture of 26.62% Fe_2O_3 + 73.33% graphite, i.e. 394 mg of oxygen, pressed in a steel box with the same external dimensions as the samples. The blank value of box plus graphite is 4 mg of oxygen. The internal diameter of the box is 22.00 ± 0.02 mm and the internal thickness 7.00 ± 0.02 mm (Figure 7.5). The standard is irradiated simultaneously with the sample, in an aluminium tube which is placed directly behind the sample tube, as appears from Figure 7.5. Several problems now occur:

1. Due to the steep flux gradient in the neighbourhood of the target (see Figure 10.2), the average dose in position 2 is approximately 3 times smaller than in position 1.

2. The standard (position 2) is screened by the sample (removal of neutrons by absorption and scattering).
3. The neutron absorption in sample and standard is not equal; the same remark holds for the emitted 6 MeV γ -ray of ^{16}N in sample and standard (different "transmission factor").
4. Due to the different distribution of the oxygen in sample (26 mm \varnothing , 9 mm thickness) and standard (oxygen concentrated in 22 mm \varnothing , 7 mm thickness), the specific ^{16}N counting rates would not be equal even if they were irradiated at the same place and if neutron and γ -ray absorption were negligible.
5. The ^{16}N activities from sample and standard are counted simultaneously with two separate but similar detection systems; hence one must take into account the different detection efficiency for both counters (different geometry, different discriminator setting, etc.).

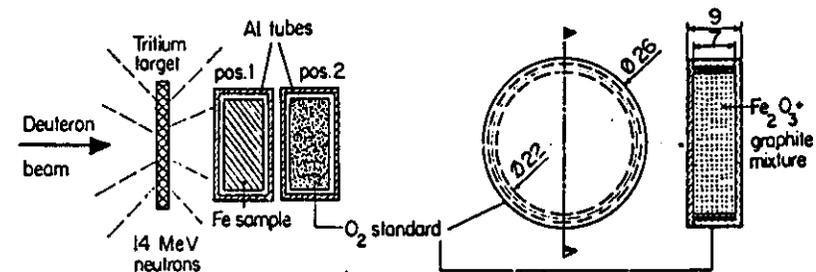


Fig. 7.5. Positioning of steel sample and oxygen standard for irradiation with 14 MeV neutrons (59). All dimensions in mm.

The above problems were solved as follows:

1. Two identical standards are prepared, the boxes having identical dimensions (tolerance ± 0.01 mm). Irradiating a standard in position 1 yields a measured ^{16}N activity:

$$R_{n1}(1) = z_{16} z_1 \sigma [F_1] w_{st} \theta N_A S / A \quad (\text{cps}) \quad (7.4)$$

at the end of irradiation. Here:

- σ = $\sigma_{14 \text{ MeV}}$ for the reaction $^{16}\text{O}(n, p)^{16}\text{N}$;
- w_{st} = weight of oxygen in the standard (394 mg);
- θ = isotopic abundance of ^{16}O ;
- N_A = Avogadro's number;

- S = saturation factor = $1 - \exp(-\lambda_b)$;
 A = atomic weight of oxygen;
 $[\bar{F}_1]$ = average neutron flux in the box at position 1;
 z_1 = the detection efficiency of the counter 1 for 6 MeV γ -rays (depends on the geometry, absorber thickness, discriminator setting, . . .);
 z_{st} = transmission factor for 14 MeV neutrons and 6 MeV γ -rays in a standard (i.e. in 2×1 mm steel plus 7 mm standard mixture), taking into account that the front is more active than the back.

Simultaneous irradiation of a standard in position 2 yields a ^{16}N activity at the end of activation:

$$R_{st}(2) = z_{st} z_2 \sigma [\bar{F}_2] w_{st} \theta N_A S \exp(-\Sigma_{st} d) / A \quad (7.5)$$

where $\exp(-\Sigma_{st} d)$ represents the screening effect of a standard in position 1 upon the activity, induced in a standard in position 2.

From equations (7.4) and (7.5) follows:

$$\frac{R_{st}(1)}{R_{st}(2)} = k = \frac{z_1 [\bar{F}_1]}{z_2 [\bar{F}_2] \exp(-\Sigma_{st} d)} \quad \text{or} \quad \frac{z_1 [\bar{F}_1]}{z_2 [\bar{F}_2]} = k \exp(-\Sigma_{st} d) \quad (7.6)$$

2. In the case of an analysis, a steel sample is irradiated in position 1 and a standard in position 2. Then the measured ^{16}N activity is given by:

$$R_{Fe}(1) = z_{Fe} z_1 \sigma \bar{F}_1 w_x \theta N_A S / A \quad (7.7)$$

for the steel sample, and by

$$R_{st}(2) = z_{st} z_2 \sigma [\bar{F}_2] w_{st} \theta N_A S \exp(-\Sigma_{Fe} d) / A \quad (7.8)$$

for the standard, where \bar{F}_1 = average neutron flux in the sample at position 1; z_{Fe} represents the transmission factor for a steel sample. Hence,

$$\begin{aligned} \frac{R_{Fe}(1)}{R_{st}(2)} &= \frac{w_x z_1 \bar{F}_1 z_{Fe}}{w_{st} z_2 [\bar{F}_2] \exp(-\Sigma_{Fe} d) z_{st}} \\ &= \frac{w_x z_{Fe} \bar{F}_1 z_1 [\bar{F}_1]}{w_{st} z_{st} [\bar{F}_1] z_2 [\bar{F}_2] \exp(-\Sigma_{Fe} d)} \end{aligned} \quad (7.9)$$

From equations (7.6) and (7.9) it follows that the unknown weight of oxygen is given by:

$$w_x = \frac{w_{st}}{k} \cdot \frac{R_{Fe}(1)}{R_{st}(2)} \cdot \frac{\exp(-\Sigma_{Fe} d)}{\exp(-\Sigma_{st} d)} \cdot \frac{z_{st}}{z_{Fe}} \cdot \frac{[\bar{F}_1]}{\bar{F}_1} \quad (7.10)$$

where k takes into account the flux gradient and differences in the detection efficiency (ca. 3);

$\exp(-\Sigma_{Fe} d) / \exp(-\Sigma_{st} d)$: the different screening effect in the case of a steel sample or a standard (0.949 ± 0.006);

z_{st} / z_{Fe} : the "transmission" factor for standard and steel sample (1.065 ± 0.005);

$[\bar{F}_1] / \bar{F}_1$: the average flux (in position 1) over the contents of a box and over the whole sample (1.042 ± 0.005).

The experimental determination of these correction factors is described in ref. (59) for a tritium target with an effective diameter of ca. 16 mm, if the front sides of sample and standard are at a distance of approximately 9 and 22 mm from the target. The total correction factor is thus 1.053 ($\pm 1\%$), plus a 4.5 mg oxygen blank. In other words, although the standard contains 394 mg of oxygen, it can be considered to contain an apparent weight of

$$\frac{(394 \times 1.053) + 4.5}{k} \quad \text{or} \quad \frac{419.2}{k} \text{ mg.}$$

Preisler and Stärk (60) investigated the feasibility of several standards for the determination of tantalum in niobium by reactor activation: (a) compact Ta metal (one piece); (b) finely powdered Ta; (c) finely powdered Ta_2O_5 , 5–40 μ ; (d) finely powdered Ta_2O_5 mixed with spectroscopically pure carbon 1/20; (e) Ta_2O_5 produced from Ta-fluoride solution and precipitated on carbon powder, 1/50; (f) Ta-fluoride solution, 0.8 mg/ml; (g) Ta_2O_5 mixed with Nb_2O_5 , precipitated from the fluoride solution with ammonia. The specific activity of standard (e) was considerably less than that of standards (f) and (g), whereas standard (a) was even smaller (factor of 2). Note that (g) can be considered as an addition method of analysis.

(B) SECONDARY STANDARDS

The problems described above can also occur in reactor activation analysis. The elimination of systematic errors, due to flux gradients,

different absorption of thermal and/or epithermal neutrons or of emitted β -particles and γ - or X-rays is discussed in Chapter 10.

Sometimes interfering activities are produced by the matrix or other constituents in the sample. In that case, the samples should be irradiated together with primary and secondary standards. An important example of interference occurs in the analysis for phosphorus in biological materials.

Reaction: $^{31}\text{P}(n, \gamma)^{32}\text{P}$; $T_{1/2} = 14.2$ d; 1.707 MeV β^-

Interfering reactions: $^{32}\text{S}(n, p)^{32}\text{P}$; $^{35}\text{Cl}(n, \alpha)^{32}\text{P}$.

The relative importance of interference can be found by the method, described by Koch and Roesmer (48). This method requires the knowledge of the Cl and the S concentration in the sample; this can be found by determining the ^{35}Cl activity (from $^{35}\text{Cl}(n, \gamma)$) in the sample and in a secondary Cl-standard, and the ^{35}S activity (from $^{34}\text{S}(n, \gamma)$) in the sample and in a secondary S-standard. After the determination of the ^{32}P production in the secondary Cl- and S-standards, this allows calculation of the ^{32}P activity due to chlorine and sulfur in the sample. If these ^{32}P activities are subtracted from the total ^{32}P activity in the sample, the net contribution of the reaction $^{31}\text{P}(n, \gamma)^{32}\text{P}$ is obtained; by comparison with the ^{32}P activity in the "primary" P-standard, the phosphorus concentration in the sample can be calculated.

A simpler correction method is possible by irradiating the sample with and without cadmium cover. Subtracting the first value (due to (n, p) and (n, α) reactions with fast neutrons) from the second (due to (n, p), (n, α) and (n, γ) reactions) leaves only the activity induced by thermal neutrons (< 0.5 eV).

Irradiation with and without cadmium allows the simultaneous determination of phosphorus and of sulfur via the radionuclide ^{32}P , which is easily counted, on condition that the chlorine content of the sample is sufficiently low.

$$^{32}\text{P activity from bare sample: } A_0 = A(n, \gamma) + A(n, p) \quad (7.11)$$

$$^{32}\text{P activity from covered sample: } A_c = \frac{A(n, \gamma)}{CR_p} + \frac{A(n, p)}{CR_s} \quad (7.12)$$

CR_p is the cadmium ratio of phosphorus, as determined by means of a phosphorus standard:

$$CR_p = \frac{\text{specific } ^{32}\text{P activity without Cd}}{\text{specific } ^{32}\text{P activity with Cd}} \quad (7.13)$$

and depends on the φ_e/φ_{th} ratio.

CR_s is the cadmium ratio for sulfur, determined by the counting of ^{32}P , i.e. from the $^{32}\text{S}(n, p)$ reaction. Since the cadmium cover does not influence the fast neutron reaction rate, $CR_s \approx 1$. Hence the solution of the above equations is

determination of phosphorus:

$$A(n, \gamma) = (A_0 - A_c) \frac{CR_p}{CR_p - 1} \approx A_0 - A_c \quad (7.14)$$

if $CR_p \gg 1$.

determination of sulfur:

$$A(n, p) = A_c - \frac{(A_0 - A_c)}{CR_p} \approx A_c \quad (7.15)$$

if $CR_p \gg 1$.

The simultaneous determination of phosphorus and sulfur is easy if

$$0.1 < \frac{A(n, \gamma)}{A(n, p)} < 10$$

The concentration of Cl in the sample must be determined, e.g. via the reaction $^{37}\text{Cl}(n, \gamma)^{38}\text{Cl}$, and the corresponding ^{32}P activity from the reaction $^{35}\text{Cl}(n, \alpha)^{32}\text{P}$ subtracted from A_0 and A_c . In any case, two secondary standards (S and Cl) are required for the determination of phosphorus.

(C) PHYSICAL AND CHEMICAL FORM OF THE STANDARDS

The standards or comparators can be prepared from known amounts of the respective elements or compounds. If a compound is used, it should exhibit stoichiometric and radiolytic stability. Some examples: arsenic As_2O_3 ; antimony Sb_2O_3 ; barium $\text{Ba}(\text{NO}_3)_2$; cesium CsNO_3 ; chlorine NaCl ; copper Cu ; hafnium Hf ; cobalt Co-Al alloy ; iron Fe ; indium In ; mercury HgO ; molybdenum MoO_3 ; phosphorus $\text{Mg}_2\text{P}_2\text{O}_7$; rubidium Rb ; scandium $\text{Sc}(\text{NO}_3)_3$; selenium Se , SeO_2 ; silver AgNO_3 ; strontium $\text{Sr}(\text{NO}_3)_2$; sulfur S , $(\text{NH}_4)_2\text{SO}_4$, Li_2SO_4 ; tellurium Te ; tin

Sn; zinc Zn, ZnO; zirconium $ZrO(NO_3)_2 \cdot 2H_2O$; uranium natural U_3O_8 , . . . The weights must be chosen to limit the attenuation of the neutron flux to 1 or 3% (see equations (10.11)–(10.13) and (10.18)–(10.20), Chapter 10).

Some elements have such high absorption cross sections for thermal and/or epithermal neutrons, that it becomes very difficult to weigh the required amount accurately (rhodium, gold, iridium, indium, . . .). As stated in Chapter 10, this problem can be solved by using a known amount of dilute standard solution.

A pipetting device for volumes of 10^{-4} – 10^{-9} ml has been described by Farlow *et al.* (61). As already stated above, the problem of losses by adsorption on the glass, pyrex or polythene walls must be considered for dilute solutions.

The percentage adsorption depends on the concentration of the element, on the acidity of the solution and on the nature of the element and of the container. In general, it is recommended to start from relatively concentrated stock solutions and to prepare the necessary dilutions just before use. The adsorption can also occur in the irradiation capsule and even be enhanced by the intense radiation in the reactor.

Approximately 30–40% of the activity was adsorbed on a polythene capsule for 10^{-7} g NH_4I after an irradiation of 30 minutes at a flux of 6.10^{12} n cm^{-2} s^{-1} (62). In the case of mercury (10 ppm in aqueous solution), up to 90% was adsorbed on polythene or quartz. After irradiation of a gold solution in a quartz capsule at high neutron fluxes, it may be necessary to remove the adsorbed activity by boiling in aqua regia.

Contamination of the standard solution by the container wall is unlikely to be troublesome.

If irradiation of liquids in the reactor is forbidden, the solution can be evaporated before sealing the tube. Such standards can be used for high integrated neutron fluxes.

For short irradiations or low integrated neutron fluxes, the standard solution can be transferred to a disk of chromatography paper (Whatman no. 3, 12 mm in diameter) by means of a micropipette or by turning the calibrated micrometer head of a modified microburette assembly ($\pm 2 \times 10^{-4}$ cm^3). The disk is covered with a solution of polystyrene; after evaporation of the solvent, it is packed in a thin polyethylene foil and sealed with a soldering iron. The reproducibility is

better than 1% (63). The problem of neutron shielding in the standards is obviously eliminated. If the samples are counted after precipitation and filtration upon a similar disk of filter paper, the geometry is practically the same as for the standards.

Whatman No. 1 paper has even been used for irradiation at a neutron flux of 4×10^{11} n cm^{-2} s^{-1} for 11 days (64); the paper then becomes brittle, although it can still be used.

Gibbons and Lawson (65) prepared indium standards by absorbing a standard indium solution on pure cellulose to give a physical size similar to that of the zinc samples to be analyzed. When no chemical separations are performed, one will count ^{41}Ar activity shortly after the end of irradiation ($E_\gamma = 1.28$ MeV, $T_{1/2} = 1.8$ h) from air enclosed with the sample or standard. When the irradiation can and container are opened, this activity will mostly disappear. According to Anders (66) one can also get ^{41}Ar activity from recoil of the air, surrounding the vials during activation. If, for short irradiation and waiting times, chemical separations are carried out upon the sample and not upon the standards, this could give rise to low results.

The most desirable mechanical form of the standards may be dictated to a considerable extent by the environment in which they are to be activated. Long irradiation times, high neutron fluxes and/or high temperatures impose several restrictions: the standard material must be present in very small quantities in order to avoid severe handling problems after activation and/or must be capable of withstanding high temperatures. The latter requirement is met and dilution of the standard material achieved by alloying with high-purity aluminium. A wire diameter of 0.5 mm, for instance, requires no large corrections for local flux depressions; the quantity of the standard material to be activated should be held at or below a level such that no neutron, of any energy, would have greater than 1% probability of capture during a traverse through the wire in a direction perpendicular to its axis (see Chapter 10, section II, B 4c(2)). This specification leads to the following typical compositions (weight % of natural element in aluminium): (67)

Lu (5.9); Eu (0.17); Ir (0.26); In (0.037); Au (0.065); W (0.067); Se (2.5); As (0.30); La (0.61); Cd (0.17); Cu (0.51); Co (0.1).

Most of the above elements have been successfully combined with high purity aluminium, swaged into slender rods, and drawn into wires.

Mostly a true alloy is formed; in other cases (tungsten) a dispersion of finely divided particles is obtained by mixing the element of interest as a fine powder into the molten aluminium (67). Difficulties have been encountered for achieving a mixture of aluminium with arsenic, selenium, and cadmium.

At the Central Bureau for Nuclear Measurements of Euratom (Geel, Belgium), a number of alloys are made, in the form of disks, wires and tubes (Table 7.6). Details concerning the preparation of homogeneous Al-alloys by levitation melting in argon are described in ref. (68).

TABLE 7.6
Homogeneous alloys (68)
Between brackets: weight %

Al-Ag (0-2)	Al-Eu (0-5)	Al-Lu (0-5)	Al-W (0-10)
Al-Au (0-5)	Al-Gd (0-5)	Al-Mn (0-4)	
Al-B (0-1)	Al-Ho (0-5)	Al-Rh (0-5)	} any composition
Al-Cd (0-2)	Al-In (0-1)	Al-Sm (0-2)	
Al-Co (0-5)	Al-Ir (0-5)	Al-Th (0-20)	
Al-Dy (0-10)	Al-Li (0-1)	Al-U (0-24)	Zr-Co (0-1)

The homogeneity can be checked by standard methods of chemical analysis. For Co-Al alloy a homogeneity of $\pm 2-3\%$ has been reported (63); the Co-Al alloy prepared at the C.B.N.M. of Euratom (Geel, Belgium) has a homogeneity of $\pm 0.3\%$.

Impurities from aluminium give rise to negligible activities, so that, in most cases, a chemical separation is not necessary. Aluminium itself is a favourable base material from the nuclear standpoint as well as the mechanical. The cross section is small for radiative capture, yielding $2.3 \text{ m}^2 \text{ }^{26}\text{Al}$ which can be permitted to decay before counting begins. The $^{27}\text{Al}(n, p)^{26}\text{Mg}$ reaction is scarcely more troublesome, in view of the 9.5 m half-life of the product. The 15-hour ^{24}Na from the (n, α) reaction is a potential source of trouble, the high threshold and small cross section for the reaction are favourable, however.

Recke and Sorantin (69) determined silver in lead and prepared standards by melting a known amount of high quality lead with pure silver after removing the oxide layers. Melting was performed in an inert atmosphere and an alloy of 1% was produced.

(D) LARGE NUMBER OF STANDARDS

If a large number of elements are determined simultaneously, it becomes a problem to irradiate a standard for each element in the same irradiation can. One can then irradiate a solution, containing all the elements of interest in known concentrations and separate them chemically just as for the sample. The work of Towell *et al.* (33) about the determination of rare earths in rocks has already been mentioned in section I, H of this chapter.

A chemical separation of such a complex standard solution can be avoided, e.g. by measuring the activities with a Ge(Li) detector. Such a method has been used by Ballaux (70) for the determination of Na, K, Sc, Cr, Fe, Co, Cu, Zn, Ga, Cd, La, Pt, Tl, Ag and W in selenium. The HCl solution, containing known amounts of suitable compounds of these elements ($0.03-1400 \mu\text{g}/100 \mu\text{l}$) was freshly prepared. Silver and tungsten were added after evaporation of HCl. After dilution, aliquots of $100 \mu\text{l}$ were directly pipetted into a number of quartz ampoules, evaporated to dryness and sealed. For each analysis, such a standard ampoule was taken. After irradiation at a flux of $6 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, the selenium matrix was distilled and the gamma spectrum of the residue compared with that of the standard solution. For the determination of gold a separate standard was used, to avoid misinterpretation of the analysis (^{199}Au from the reaction $^{197}\text{Au}(n, \gamma)^{198}\text{Au}(n, \gamma)^{199}\text{Au}$ could introduce positive errors in the determination of platinum via the reaction $^{198}\text{Pt}(n, \gamma)^{199}\text{Pt} \xrightarrow{\beta^-} ^{199}\text{Au}$). It is obvious that the elements in the standard solution must be present in suitable proportions, so that their activities will be of the same order of magnitude.

The standards can also be irradiated in several groups, e.g. an ampoule containing elements, soluble in HCl (such as Cr, Cu, Au, Ge, Zn, . . .) another ampoule containing elements soluble in ammonia plus ammonium tartrate (such as Sb, As, W, etc.). This method is used by Maenhout (71) and by Neirinckx (72) for the determination of impurities in tin and titanium respectively. After irradiation, the gamma spectrum of the impurities in tin (after distillation of the matrix) or in titanium (after separation of the scandium activity by ion exchange) is compared with that of the standard solutions, using a Ge(Li) detector.

If the activation is performed at a relatively low integrated neutron flux, a large number of standard solutions can be spotted on a paper

strip (2 cm × 20 cm) which can first be washed with triple distilled water, if necessary. After covering with a cellophane or an aluminium foil (to avoid contact between different parts of the paper), the strip is rolled up and irradiated with the samples. If exposed to high neutron doses, the paper decomposes, and adheres to the aluminium foil.

A similar method is described by Barthomeuf *et al.* (73). The pieces of paper, on which the standard solution is spotted, are placed next to each other on a sufficiently long polyethylene belt and covered with polyethylene; by means of a suitable heat-sealing iron, a ring is sealed around each standard. Finally, the ribbon is folded like the bellows of an accordion and placed in the irradiation can. One can easily irradiate 70 such standards in the same container.

A large number of standards can be irradiated in a small volume, if capillary capsules are used. Up to 100 of these capillaries fit into a standard irradiation can. The possibility of bursting in the reactor, owing to the formation of volatile radiolysis products, is negligible because of the great relative strength of these small silica containers.

De Corte and Van den Winkel (74) proposed to replace standard solutions by ion exchange beads, on which a known amount of element had been adsorbed in a suitable medium. It has been found that the element was homogeneously distributed over the ion exchanger. It is easier to weigh accurately such a powder than a liquid. Amounts of 20–50 mg were sealed in fused silica capillaries. After irradiation, the element was desorbed in a suitable solution and counted. Note that the resin contains impurities such as Na, Cl, Zn. A large number of such "standards" fit in the irradiation container. In Table 7.7, the conditions for adsorption and desorption of a number of elements are summarized. Fe(III), Sn(IV) and Tl(III) can easily be weighed in capillary quartz tubes, hence no K_D values were determined.

Girardi *et al.* (75) considered the possibility of eliminating the comparators by using an absolute method. As could be expected, this procedure cannot compete in accuracy with the relative method, due to the uncertainties in the knowledge of nuclear constants required for the calculations, especially cross sections and γ -ray abundances of radionuclides (see Chapter 10, section I).

The method of a single comparator for different elements has been critically evaluated by Girardi *et al.* (76). In the relative method the unknown weight of the element in the sample is calculated from the equation

$$w_x = \frac{R_x}{R_s} w_s \quad (7.16)$$

where R is the count rate, w the weight, the subscript x refers to the sample and s to the standard (see Chapter 10, equation (10.1)); in the single comparator method this equation is replaced by

$$w_x = k \frac{R_x S_x f(t)_s}{R_s S_s f(t)_x} w_s \quad (7.17)$$

where $S = 1 - \exp(-\lambda t)$ (saturation factor) and $f(t) = \exp(-\lambda t)$ (decay factor).

If the half-lives of the radionuclide of interest and of the comparator

TABLE 7.7
Adsorption and desorption of some elements on Dowex
ion exchange resins (74)

Element	Adsorption in	K_D	Desorption in	K_D	Resin form
As(III)	HA $\bar{5}$, 17.5M adsorption on column	16	HCl, 1M	0.9	1X8/A $\bar{5}$ ⁻
Au(III)	HCl, 2M	7×10^4	Thiourea, 7.5%	0.3	1X8/Cl ⁻
Co(II)	H ₂ O ₂ , 10 ⁻² M	1500	HNO ₃ , 8M	0.3	1X8/O ₂ ²⁻
Cr(III)	H ₂ O ₂ , 10 ⁻² M	200	HCl, 9M	1	1X8/O ₂ ²⁻
		(2d shaking)			
Cu(II)	HA $\bar{5}$, 17M	960	HA $\bar{5}$, 6M	0.7	1X8/Cl ⁻
Eu(III)	H ₂ O ₂ , 10 ⁻² M	1.5×10^5	HCl, 6M	1	1X8/O ₂ ²⁻
Ga(III)	HCl, 8M	10 ⁵	HCl, 0.5M	0.5	1X8/Cl ⁻
In(III)	H ₂ O ₂ , 10 ⁻² M	10 ⁵	HNO ₃ , 1M	1	1X8/O ₂ ²⁻
K(I)	H ₂ O	3×10^4	HCl, 9M	5	50X4/H ⁺
La(III)	HCl, 0.1M	9×10^4	HCl, 6M	9.5	50X4/H ⁺
Mo(VI)	HCl, 6M	225	H ₂ SO ₄ , 98%	9.3	1X8/Cl ⁻
Na(I)	H ₂ O	5460	HCl, 9M	3	50X4/H ⁺
Sb(III)	HCl, 2M	500	NaOH, 1M	6	1X8/Cl ⁻
Sc(III)	H ₂ O ₂ , 5×10^{-2} M	10 ⁵	HCl, 2M	1.3	1X8/O ₂ ²⁻
Ta(V)	HF, 5M	10 ⁵	NH ₄ F, 4%	1	1X8/F ⁻
			NH ₄ Cl, 14%		
W(VI)	HF, 8M	335	HF, 1M	2.5	1X8/F ⁻
			H ₂ BO ₃ , 2%		
Zn(II)	HCl, 2M	960	HA $\bar{5}$, 6M	0.7	1X8/Cl ⁻

are not equal $\neq S_s$ and $f(t)_x \neq f(t)_s$. Hence, the irradiation and waiting time as well as the half-lives must be exactly known.

As can be seen from equations (7.17) and (10.1), the factor k is given by

$$k = \frac{\left(\sigma_0 + \frac{\varphi_s I}{\varphi_{th}}\right)_s}{\left(\sigma_0 + \frac{\varphi_s I}{\varphi_{th}}\right)_x} \cdot \frac{\theta_s}{\theta_x} \cdot \frac{z_s}{z_x} \cdot \frac{A_x}{A_s} \quad (7.18)$$

The factor k is determined by measuring the activity (e.g. the photopeak counting rate) of a known amount of the elements of interest (x_1, x_2, \dots) and of the comparator (s). This k value must obviously be the same when performing the actual analysis; i.e. z_s/z_x must remain constant (constant counting geometry with the same detection system, identical evaluation of the photopeak, counting rate, etc.) and

$$\left(\sigma_0 + \frac{\varphi_s I}{\varphi_{th}}\right)_s / \left(\sigma_0 + \frac{\varphi_s I}{\varphi_{th}}\right)_x$$

must remain constant. If $(I/\sigma_0)_s \neq (I/\sigma_0)_x$ this means that φ_s/φ_{th} must be constant. When the irradiation position is well thermalized so that the cadmium ratio for the nuclide of interest is ≥ 50 , variations in the epithermal contribution have a negligible effect (cf. Chapter 10, II, B, 4b). When the epithermal component of the reactor flux increases, the number of elements to which the method can be applied decreases. The elements which can still be determined are those having I/σ_0 values within a certain range from that of the single comparator.

The applicability of the method can be increased by an appropriate choice of the neutron flux monitor, in relation to the neutron spectrum available and the nature of the problem under study. Cobalt is a good single comparator for elements such as Nb, ^{235}U , Eu, Hf, Ga, Zn, Cu, Pr, Mn, . . . Other elements, such as Ta, Sb, I, In, Br, Sm, Tl, W, Ir, Ag, Re, Th, As, have I/σ_0 values between 8 and 26, for which gold is a better single comparator than cobalt.

The method can find useful applications in automated analysis, or when a large number of elements are determined in one sample. According to Girardi *et al.* (76) the accuracy and precision are similar to those of the relative method. Applications include non destructive determination of trace elements giving short-lived isotopes (Mn, Cl,

Na and Cu in terphenyls, Mn in biological materials) and destructive analysis of trace elements giving both short-lived and long-lived isotopes (Rb, Cs, Sr, Fe, Co, Zn, U, Th, Sc, Cr, Hg, . . . in biological specimens), determination of Cr in iron, chlorine in lake water (76), As, Sb, Cu and Au in lead (77) and of rare earth elements in minerals, such as gadolinite and tantalocolumbite (78). This method is not recommended if only a reactor with a high epithermal flux and non-steady operation is available. In this case one can expect better results from dual comparator monitoring as described in Chapter 3, section VI, A. A large variety of elements to be determined in a small series of samples may not warrant the preliminary assessment of k values and continuous control of the constancy of the experimental parameters.

To obtain a large number of uniformly activated samples and standards, a rotary specimen rack (lazy Susan), can be used. It is enclosed in a water tight aluminium case and fits into a well in the graphite reflector of a Triga reactor. This specimen rack has forty aluminium cups, each of which can hold two standard specimen containers. Rotating is performed at one rev per min (79). The samples and standards should be fixed at the same radius from the disk axis. Using cobalt wire monitors, it has been found that the fluctuations in neutron flux did not exceed $\pm 1\%$ (60). (See also Chapter 4, section II).

(E) THE ADDITION METHOD IN TRACE ANALYSIS BY NEUTRON ACTIVATION

The method of known additions allows the detection and/or elimination of relative systematic errors. These errors can be due to a poor reproducibility of the experimental conditions (e.g. unstable counting equipment, local flux differences during the irradiation of the samples, etc.) or to the influence of foreign substances (matrix effect, neutron shielding differences between samples and comparators, influence of the density of the radioactive source on the detection efficiency, etc).

Absolute systematic errors cannot be eliminated by the addition method of analysis. Hence, interferences due to a systematically insufficient radiochemical purity remain unknown by this method. Such interferences can, however, be detected in many cases by gamma ray spectrometry. Even then, absolute systematic errors are possible if a foreign radionuclide is present, which emits a gamma ray of the same

energy, or the case of two positron emitters. This problem can be solved by measuring more than one photopeak or by repeating the measurements at different times after the end of the irradiation, i.e. by checking the results by a quasi-independent method.

Partial decrease of the induced activity in samples and comparators (by different neutron shielding) or concentration dependent variations in the finally recorded signal (such as coincidence losses during the counting, e.g. due to the poor quality of the live timer of the multichannel spectrometer, or when counting short-lived radionuclides with the multichannel analyzer) arise normally as relative systematic errors.

The elimination of relative systematic errors must, however, be paid for with a decreased precision or reproducibility, i.e. with larger random deviations (80). The numerical exactness of a result is, however, undoubtedly more important than the extent of the scatter.

The application of the addition method must be limited to linear functions. This condition is normally fulfilled in activation analysis: activity = experimental constant \times weight. The experimental constant is identical with the specific measured activity. It can be shown that the best precision and accuracy are obtained if the amount of the element added equals approximately the amount originally present in the sample. The addition method of analysis is also discussed in Chapter 11, section I, F and Chapter 10, II, B, 4c(3). In Chapter 10, II, B, 4c(4) the combination of the addition method of analysis and of the internal standard method is described. Statistical considerations and a numerical example can be found in section V, C of Chapter 11.

Practical addition method in activation analysis. The finely powdered samples (10–100 mg) are weighed and sealed in silica tubes. Standards are prepared by addition of a known volume (50–100 μ l) or weight of a suitable standard solution of the element to the same weight (10–100 mg) of sample powder. After carefully evaporating to dryness, the silica tubes are sealed. All weights should preferably be the same within $\pm 1\%$. This procedure is applicable to materials which are soluble in a liquid (water, acid, . . .) after irradiation. It must be borne in mind that there is no absolute certitude that the added material is homogeneously distributed in the standard, i.e. samples and standards are possibly not identically irradiated. Spiking is also possible on clean, solid blocks (sandwich mounting), although, in that case, the added material is obviously not homogeneously distributed.

For the determination of silver in lead, Adams *et al.* (81) added a

standardized solution of AgNO_3 to the lead powder. Tracer experiments showed that 99% of the silver was deposited on the lead powder after 48 h, and that the homogeneity of the sample was better than 2% for a silver concentration of 100 ppm.

Recke *et al.* (69) melted lead and added a known amount of silver to produce an alloy with 1% Ag, from which filings were used as the standard. Such a procedure eliminates different detection efficiencies for the radionuclide of interest by different absorption in samples and standards. These authors measured the 2.87 MeV beta radiation of ^{24}Ag , taking care that the sample thickness was 2.1 g cm^{-2} , which is slightly more than needed to reach the infinite thickness for the 2.87 MeV beta rays (see Chapter 6, section III, C, 1).

When samples and standards (i.e. samples + known additions) are irradiated in solution, the added element is, of course, homogeneously distributed and there are no neutron shielding differences.

An example is the determination of mercury in bismuth (82): 12 g of a bismuth sample was dissolved in 7N nitric acid and made up to 50 ml. From this solution 0.5 ml was transferred to a quartz ampoule. In this way a number of samples were prepared to which 0.2 to 2 μ g of mercury were added. To the remaining samples no mercury was added. Two blank solutions of the same volume were prepared. The result of this addition method was in good agreement with that obtained by comparison with a mercury standard.

This method is even applicable to many refractory materials, if Wichers' method is followed, as described in section I, J of this chapter.

In some cases the samples must be dissolved by a peroxide fusion after the irradiation. The addition method can then be carried out as follows: 20–100 μ l of a suitable standard solution of the element is spotted on a small filter paper (ca. 15 mg) and dried. The sample is weighed in cellophane or Mylar foil (also ca. 15 mg), wrapped in the spiked filter paper and irradiated in an aluminium saucer. The complete contents of the saucers are fused with sodium peroxide in a nickel crucible after which chemical separations are carried out. There is, of course, no homogeneous distribution of the element in the sample, but in most cases there is no substantial difference in received flux between the sample and the added element (53,64).

Preisler and Stärk (80) determined tantalum in niobium and prepared standards by precipitation of Nb_2O_5 + Ta_2O_5 from fluoride solution with ammonia (see section II, A of this chapter).

Anders and Briden (7) used an addition method for the determination of oxygen in cesium metal with 14 MeV neutrons.

III. Containers and Canning Material

The most commonly used canning materials are aluminium, silica and polyethylene. These materials can be made very pure, have a low cross section for thermal neutrons, give little or no long-lived activity by activation and are resistant to radiation. Some properties and impurities are indicated in Table 7.8. Each material has some disadvantages: aluminium gives rise to ^{24}Na by (n, α) reaction and is not always very pure; Cornelis (83) found the following long-lived impurities: Fe 2.5 ppm, Cr 50 ppm, Co 0.25 ppm, Sc 0.75 ppm and Zn 460 ppm. Silica becomes relatively active after irradiation and polyethylene becomes brittle after exposure to relatively low integrated neutron fluxes. Ultra pure quartz is available, which contains a total impurity level of less than 1 ppm, except for chlorine (~ 37 ppm) (84).

(A) POLYETHYLENE

Suitable polyethylene containers can be constructed for powders or solid samples and for liquids.

1. Polyethylene Containers for Powders

Powders can be packed in small snap-cap polyethylene vials. For short irradiations oblong gelatine capsules have been used.

Satisfactory sealed pockets are prepared by placing a weighed sample on a square of 25 μ polyethylene and covering this with a second square. The assembly, on a sheet of paper, is then transferred to a heat-sealing iron and a ring is sealed around the sample by pressing a 1 cm vial cap on the polyethylene for a few seconds. If the manipulations are carried out with tongs and gloves, contamination of the polyethylene with sodium is very small. Together with standards and samples, several blank polyethylene packets are prepared. Individual specimens can be numbered with ink or by paper tabs fastened with tape, such that the labels, which become radioactive during neutron irradiation, can be clipped off before counting. This method has been

TABLE 7.8
Extra-pure canning materials for neutron activation analysis (3)

	Aluminium		SiO_2 high purity	$(\text{CH}_2)_n$ commercial polyethylene
	refined	zone refined		
n. cross-section		0.23 b	0.13 b	0.33 b
activation products	$\left\{ \begin{array}{l} 2.3 \text{ m } ^{24}\text{Al} \\ 15 \text{ h } ^{24}\text{Na} \\ 9.5 \text{ m } ^{27}\text{Mg} \end{array} \right.$		2.6 h ^{28}Si	
n. cm^{-2} for breakdown		$> 10^{20}$	$> 10^{20}$	5.10^{17}

ppm Al			< 0.02	0.3
As	1.5	0.001	< 0.0002	
B		< 0.5	< 0.01	0.09
Ca		< 0.5	< 0.1	0.2
Cd		0.07		
Cr		< 0.01	< 0.1	0.3
Cu	1.9	0.08	< 0.0002	0.004-4 (a)
Fe	3	< 0.2	< 0.1	0.6
Ga	0.3			
Mg		10		0.08
Mn	0.3	0.15	< 0.001	0.08 (a)
Pb		< 0.1		0.2
Sb	1.2	0.002	0.0001-0.2 (a)	
Sc	0.5	0.2		
Zn		0.6		
U	0.002			

(a) D. Bruns (17)				

presented by Schroeder and Winchester (85) for the determination of sodium in silicates and rocks.

The problem of numbering can be avoided by placing all the samples next to each other on a large polyethylene ribbon, having a thickness of 0.1 mm, a width of 20 mm and the desired length as described by Barthelemy *et al.* (73). The foil is prepared by making cavities for the powders, using a small press equipped with a soldering iron. The samples weighing ca. 20 mg are placed in these cavities and covered with a piece of polyethylene. A ring is sealed around each sample as described above. The belt is then folded like the bellows of an accordion

and placed in the standard irradiation can. One can easily irradiate an accordion with 40 samples. In order to avoid systematic errors, due to neutron flux gradients, one can for instance irradiate 30 samples and 10 standards, spaced at identical intervals.

2. Construction of Polyethylene Vials for Liquids

Pieces of tubing can be sealed by warming in a bunsen or cigar lighter flame until opalescence disappears and then squeezing with forceps. Such vials occasionally develop leaks on impact in the pneumatic tube of the reactor, and can thus not be recommended for packing liquid samples.

A much stronger heat seal can be made using a special glass tubing device, as described by Winchester and Hashimoto (51). A 2 cm length of glass tubing of inner diameter equal to the polyethylene outer diameter is fused to a handle of capillary glass tubing. A short length of polyethylene tubing, previously cleaned with nitric acid, is slipped into the device which has been made wet with water. The device is warmed in a flame at the point of attachment of the capillary handle, and as the polyethylene is warmed it is pushed in and becomes molded into a strong seal. The device is cooled in water and the sealed polyethylene is removed easily as air can pass into the capillary. Prior cleaning of the glass device in hot concentrated nitric acid is recommended to prevent sticking to the polyethylene.

The vial can be filled with the sample solution leaving a small air space at the top. The top is then sealed in the same way. These vials can also be used for solid samples.

After irradiation, the vial can be opened by supporting it in a one hole rubber stopper and slicing off one end.

Instead of constructing vials from polyethylene tubing, one can obviously also use commercially available vials. For irradiation of liquid samples, they must be sealed hermetically. Two methods of sealing polyethylene vials are described by Hislop (86).

The apparatus consists of a bar of stainless steel 2 cm in diameter and 13 cm long which replaces the copper bit of a 300 watt soldering iron. In the bottom of this bar a hole 1.25 cm in diameter is drilled to enable the insertion of the top of the polyethylene vial. Unless considerable precautions are taken, the steel tends to overheat, causing the molten polyethylene to adhere to it. This can be overcome by wrapping

the top of the vial tightly with aluminium foil before insertion. The foil acts as a heat transfer medium, forms a mold for the molten polyethylene and prevents it from adhering to the steel. After cooling, the foil can easily be removed from the polyethylene.

The method requires little skill and is claimed to be especially suitable for sealing inflammable samples such as benzene. A disadvantage is the use of aluminium due to an increased danger of vial contamination by small aluminium particles.

It has been found that a miniature welding torch using a mixture of oxygen and acetylene and capable of producing an intense, pin-point flame, is ideally suited for sealing polyethylene vials. The extremely small size of the flame enables very localized heating of the polyethylene around the junction of the lid and the vial itself. No difficulties are said to occur by surface tension effects in the molten polyethylene, which may result in a separation between the polyethylene comprising the lid and that of the vial.

The risk of contamination in the case of leakage can be considerably reduced by placing the sealed polyethylene vial in one or even two other sealed vials of appropriate dimensions.

Low oxygen content polyethylene can be prepared as described by Anders and Briden (7) and can be used for packing samples for oxygen determinations with 14 MeV neutrons. The only way the oxygen content of the polyethylene in a molded product can increase over that of the molding material is by oxidation of the hot molten polymer during the molding process and the use of a mold-release agent containing oxygen. Avoiding the need for a release agent, keeping the molding temperature low, and excluding air from the melt should reduce oxygen pickup. Optimum conditions are described by Anders (7).

Marking polyethylene vials can be done by scoring with hot metal and rubbing the wax from a china marking pencil into the depressions. Neat alphabetic and number marks can be made with a set of metal punches which are warmed in a flame.

(B) ALUMINIUM

Aluminium foil can be used for packing dry solid samples. For powders, aluminium saucers with covers can be used. Sufficient sealing is obtained by squeezing the edge of the cover. If the sample must be dissolved by a peroxide fusion after irradiation, it is convenient to

wrap it first in a Mylar or cellophane foil so that it is easily quantitatively removed from the aluminium saucer; the peroxide fusion is not hampered by the presence of ca. 10–20 mg of Mylar or cellophane.

After irradiation of salts in aluminium, one often observes particles which are projected against the container walls. For that reason several authors prefer to dissolve the aluminium envelope together with its contents in the case of powdered standards (several mg), since the probability for contamination can be kept negligible when high-purity aluminium is used.

Aluminium containers can be marked by scoring with a pin or a glass marker.

(C) SILICA

The preparation of vials from silica tubing with an oxygen–hydrogen flame causes no special difficulties to a glass blower. Such vials are suitable for activation of solid samples, powders, liquids, gases, . . . , as described above. To facilitate a quick sealing of the vials by means of a high temperature burner ($>1700^{\circ}\text{C}$), they are often provided with a narrowing. This is particularly important for liquids and gases. If a gas is developed from the liquid by heating (e.g. mixture of hydrochloric and nitric acid), it is recommended to chill the vial in liquid nitrogen before sealing.

Westermarck and Sjöstrand (87) described the sealing of quartz tubes after placing them in a small water-filled can with a hole in the cover, fitting the tube. The can is mounted vertically and rotated slowly (20–30 rpm) by means of a small motor. The tube is inserted in the can ($4/5$ of the tube under water) and is then ready for sealing. This method is recommended by the authors (87) in the case of mercury-containing materials. The size of the ampoule should be at least 40 mm to ensure no radiant heat damage on the sample; the latter should be placed only in the lower part of the tube.

After irradiation of liquid samples, the content of the silica vials can be frozen before opening, to reduce the internal pressure and to avoid losses by foaming, etc. The ampoules can be washed with nitric acid and distilled water.

Silica ampoules can be opened with a glass-cutter or a diamond saw. The diamond saw must be mounted in a special glove-box to avoid spreading of radioactive particles. For irradiated liquids it is recom-

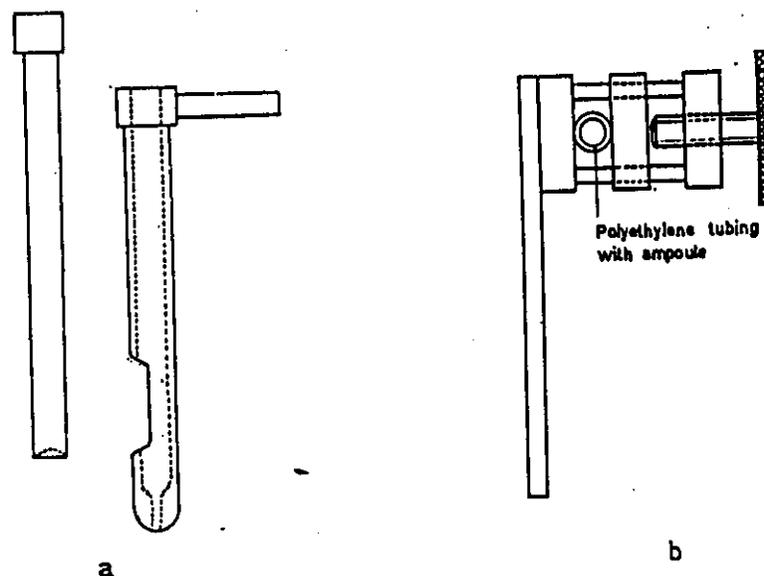


Fig. 7.6. Devices for crushing silica ampoules
(a): taken from ref. 88.

mended to freeze them first in dry ice or liquid nitrogen. Several authors prefer crushing the ampoules, e.g. in a special device (Figure 7.6a) made of acid-resistant steel, which is inserted in the vessel where the subsequent dissolution and chemical manipulations will take place (88). Another device is represented in Figure 7.6b. It can be used to crush silica ampoules in which a solution has been evaporated prior to activation. The irradiated ampoule is inserted in a piece of polyethylene tubing, which is sealed at one end. By turning the screw, the ampoule is crushed and falls into a beaker. The polyethylene tube is rinsed and the rinsing liquid transferred to the beaker. After irradiation of gases, a magnetic hammer can be used (see Figure 7.4).

The use of small samples can be very interesting because it permits many samples to be irradiated at the same time as a set of standards and greatly reduces the cost of irradiation per sample (89). This can be done using small fused silica capillaries as mentioned already in section II, D of this chapter.

Silica ampoules are usually marked with chinese ink or a glass marker.

Note: Some compounds are not heat resistant so that they melt or decompose when sealing the ampoule (e.g. cerium oxalate). If polyethylene vials cannot be used (long irradiation times and/or high neutron flux) it is sometimes possible to close the silica ampoules by means of a conical aluminium stop.

(D) STANDARDIZED CANNING MATERIAL FOR REACTOR IRRADIATION

In general, standard cans and rabbits must meet the following requirements:

- give rise to low activities only and/or from short-lived radionuclides only;
- resist high neutron and gamma fluxes;
- be easy to machine and be mechanically strong.

The final volume of a sample is determined by the dimensions of the standard canning material used in the reactor. The useful diameter is mostly 16–25 mm; the useful height 50–70 mm. In most cases aluminium containers are used, which are sealed by cold welding. After irradiation they can be opened using an automatic lathe.

Polyethylene or nylon rabbits are used to transport samples in and out of the reactor via pneumatic tubes. Due to radiation damage, these rabbits have obviously a limited life. Swelling can cause blocking of the rabbit in the pneumatic tube. Nylon rabbits can be used for irradiations of one day at a flux of 10^{13} n cm⁻² s⁻¹. At higher fluxes, aluminium is mostly used. Whereas 99.5% aluminium is sufficiently pure for normal working conditions, a purity of 99.95% is required for irradiations at very high neutron fluxes (10^{14} n cm⁻² s⁻¹) in order to keep the activity due to long-lived radionuclides as low as possible. The use of beryllium is not recommended, due to the toxicity of the dust; moreover, it must contain 1–3% of copper to be machinable. Girardi (90) successfully uses Magnox 80 rabbits (magnesium, containing 0.8% of aluminium). For long irradiations at very high neutron fluxes, high-purity graphite can be recommended; a typical long-lived radioisotope, found in such graphite, is ⁴⁶Sc.

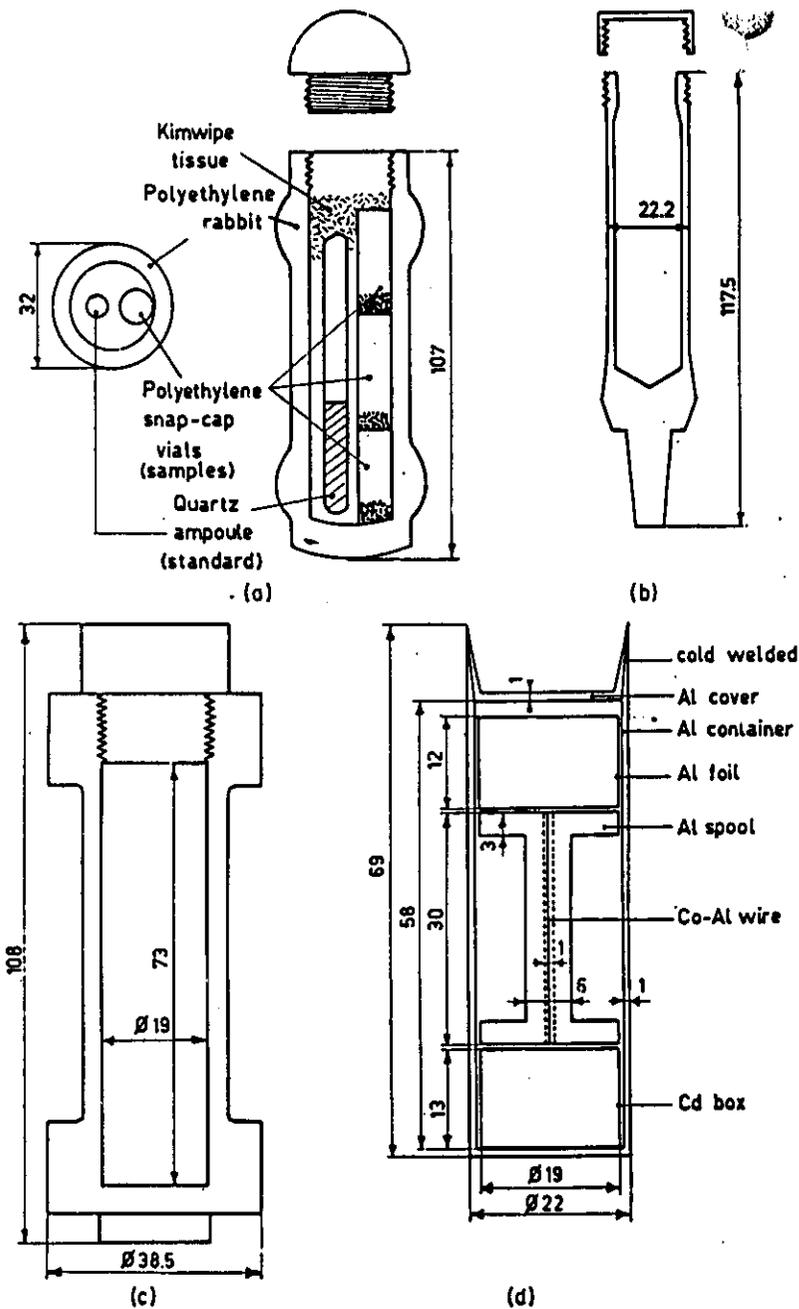


Fig. 7.7. (a) and (b): polyethylene rabbits (91, 92).
 (c): nylon rabbit
 (d): standard aluminium can for irradiation at high neutron fluxes: the container is hermetically sealed by electron beam welding.

Samples larger than the dimensions of the standard canning material can sometimes be irradiated by packing them in watertight containers and hanging them over the side of the pool on strings.

Some practical arrangements are shown in Figure 7.7. The standards and samples are wrapped in absorbing material such as absorbing paper, cotton wool or quartz wool (for high flux irradiations). Systematic errors are possible due to flux gradients (see Chapter 10, section II, B, 2). Figure 10.1 shows a method to correct for lateral flux gradients. A Co-Al alloy wire, placed along the axis of the containers allows one to detect longitudinal flux gradients, after cutting it in 0.5 cm pieces and counting (cf. Figure 7.7d). Alternatively one can place Co-Al alloy disks at the bottom and at the top of the container. In Figure 7.7d, a typical arrangement is shown, which can be used for irradiations of samples and standards with and without cadmium, e.g. in order to evaluate a cadmium ratio or an interfering reaction with fast neutrons. The cadmium box must be placed at a distance of ca. 3 cm from the bare samples in order to avoid flux depression in the latter as appears from ^{60}Co activity measurements of the Co-Al wire.

(E) RABBITS FOR 14 MeV NEUTRON ACTIVATION

In practice, short-lived radionuclides are mostly used when performing activation analysis by means of a small accelerator. Hence, a rapid pneumatic system is required. The most important application is undoubtedly the determination of oxygen via the reaction $^{16}\text{O}(n, p)^{16}\text{N}$, $T_{1/2} = 7.35$ s.

One of the major difficulties in determining trace amounts of oxygen is finding a suitable container material having a sufficiently low oxygen content, or a rapid decapsulation system. Various techniques have been proposed to solve this problem.

Coleman (94) essentially eliminated the interfering ^{16}N activity by using a 6 in. capsule in which the sample was supported by a catch near the upper end. After irradiation the catch was released dropping the sample to the lower end of the capsule. The lower part of the container having been well away from the neutron source during irradiation had very little activity.

Containers fabricated from specially-treated copper tubing, having an oxygen content of ~ 5 ppm have been proposed. Even if free from oxygen, copper and also aluminium containers provide a sufficient

number of high-energy pulses due to pile-up of lower-energy pulses, which cause severe interferences.

Broadhead *et al.* (95) circumvent the container problem. The metal sample is cut to size, filed clean or acid-etched to remove surface contamination, and placed in a plastic sample container for irradiation. Upon return to the counting room, the container is ejected from the shuttle system and caught by hand. The cap is quickly removed and the sample dumped into the test tube in the well crystal (delay 4.5 s). A similar method is used by Girardi (9). Wood *et al.* (96) also use a piston, which ejects the sample (plus polyethylene container) on impact at the counting station, so that it falls immediately into the detector.

Blake *et al.* (97) determined oxygen in high-purity beryllium metal. The samples were in the form of disks and were transferred via a rectangular shaped pneumatic tube. The samples were contained in a polyethylene ring of known oxygen content.

Hoste *et al.* (98) used rectangular samples which were transferred with neither container nor rabbit. Later on, cylindrical samples were used via a rectangular-shaped pneumatic tube also without container (59).

When analyzing reactive materials, such as cesium, a container cannot be avoided. Anders and Briden (7) described the preparation of

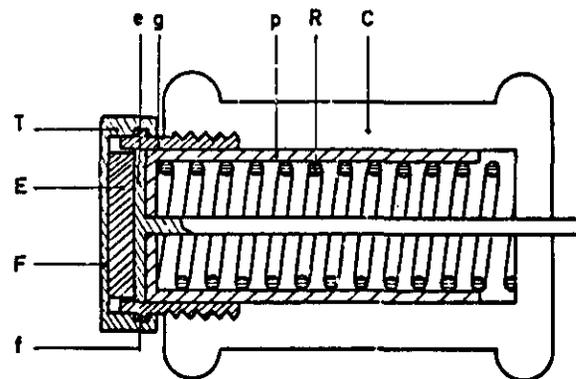


Fig. 7.8. Rabbit for 14 MeV neutron activation (9). E: sample; T: stainless steel cover; g: stainless steel tube; f: bayonet lock; F: stainless steel window of 1 mm thickness; p: polyethylene piston; e: foam rubber; R: spring; C: polyethylene rabbit.

low-cost, low oxygen content polyethylene vials (<0.01 mg per gram). Commercial polyethylene may contain 0.25–0.5 mg of oxygen per gram. A typical rabbit is shown in Figure 7.8. They are usually in polyethylene.

When analyzing powders, it is very important to fill the containers completely as discussed above (see section I, B of this chapter).

(F) ROTATING ASSEMBLIES

Due to flux inhomogeneities and deuteron beam instabilities, several authors prefer to spin samples and/or standards at the irradiation position. Anders and Briden (8) observed an improvement in precision and accuracy when a single sample is axially rotated and when appropriate corrections are made for neutron and gamma attenuation in the sample. Further enhancement has been demonstrated in subsequent work (99), where both sample and standard rotated about two independent and perpendicularly oriented axes. An improved design of a dual sample-biaxial rotating assembly is used at the National Bureau of Standards (100). More details are given in Chapter 4, section II, D.

IV. Choice of a Suitable Irradiation Facility

(A) WELL-THERMALIZED NEUTRONS

As discussed in detail in section II, C of Chapter 10, primary interference from the matrix or a major constituent in the sample by (n, p) or (n, α) reactions can be suppressed by irradiation in a well thermalized neutron spectrum. The determination of manganese in steel via the reaction $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ should thus be carried out in the reflector of the reactor. The same irradiation place can also eliminate resonance self-shielding. It should be borne in mind, that in the reflector steep flux gradients occur. An internal standard method can be used to correct for such a nonuniformity of the neutron flux (see Chapter 10, section II, B, 4c(4)).

(B) UTILIZATION OF FAST NEUTRONS

By means of (n, p), (n, α), (n, 2n) and (n, n') reactions (cf. Chapter 3, section V, C, 3b) activation products different from thermal neutron activation are generated which may be of interest in situations where

thermal neutron activation techniques are not satisfactory or may be complicated (92).

1. A number of elements yield little or no gamma ray activity when bombarded for moderate periods of time even with high fluxes of thermal neutrons, e.g. H, He, Li, Be, B, C, N, O, Si, P, S, Cr, Fe, Pb and Bi.

2. Fast neutron activation of the matrix may yield the same radionuclide as thermal neutron activation of the element being determined and interfere even for very favourable $\phi_{th}/\bar{\phi}$ ratios. For low contents it may be worthwhile to consider another reaction. Example: determination of low levels of vanadium in a chromium-rich matrix.

Reaction $^{51}\text{V}(n, \gamma)^{52}\text{V}$, $T_{1/2} = 3.77$ m; interfering reaction $^{52}\text{Cr}(n, p)^{52}\text{V}$.

Alternative solution: fast neutron activation yields another radionuclide $^{51}\text{V}(n, p)^{51}\text{Ti}$, $T_{1/2} = 5.79$ m (gamma energies: mainly 320 keV).

3. Similar energy gamma rays from thermal neutron activation of a matrix element and of the desired component may make thermal neutron activation ambiguous or complicated.

Example: the determination of titanium in a chromium-rich matrix.

Reactions: $^{50}\text{Ti}(n, \gamma)^{51}\text{Ti}$, $T_{1/2} = 5.80$ m, $E_{\gamma} = 320.0$ keV

$^{50}\text{Cr}(n, \gamma)^{51}\text{Cr}$, $T_{1/2} = 27.8$ d, $E_{\gamma} = 320.0$ keV.

The large difference in half lives, of course, simplifies this case, but the presence of large amounts of Cr still limits the amount of Ti detectable.

Alternative reactions $^{47}\text{Ti}(n, p)^{47}\text{Sc}$, $T_{1/2} = 3.43$ d, $E_{\gamma} = 160.0$ keV

$^{52}\text{Cr}(n, p)^{52}\text{V}$, $T_{1/2} = 3.77$ m, $E_{\gamma} = 320.0$ keV.

The (n, p) reaction on ^{47}Ti has the additional advantage of yielding a long lived radionuclide, which allows a titanium determination in laboratories which do not have their own reactor.

4. Matrix activation may be too intense to allow the sample to be counted at a reasonable geometry. Fast neutron activation analysis, coupled with suppression of (n, γ) matrix activation may satisfactorily overcome this problem. A thermal neutron absorber may be required to eliminate interference from the matrix. Strain and Lyon covered soil samples with cadmium to suppress the interference from the reaction $^{27}\text{Al}(n, \gamma)^{28}\text{Al}$ with the reaction

$^{28}\text{Si}(n, p)$ ^{27}Si , which was used for the determination of silicon in soil samples with an isotopic neutron source (101).

Considerable fast neutron fluxes may be available in reactor cores. Thermal neutrons can be filtered by surrounding the samples with a cadmium foil, or by placing them in rabbits having a slow neutron absorbing liner of elemental boron or enriched in ^{10}B . Yule *et al.* (92) describe

TABLE 7.9
Variable energy neutron activation analysis, indicating the most important reactions* (102)

Element	Reaction with 14 MeV neutrons	Reactions with 10-11 MeV neutrons
Vanadium	$^{51}\text{V}(n, p)^{50}\text{V}$ (1.7 MeV, 4.4 MeV)	$^{51}\text{V}(n, p)^{50}\text{V}$
Copper	$^{63}\text{Cu}(n, 2n)^{62}\text{Cu}$ (10.75 MeV)	—
Chromium	$^{52}\text{Cr}(n, p)^{51}\text{Cr}$ (3.1 MeV, 4.3 MeV)	$^{52}\text{Cr}(n, p)^{51}\text{Cr}$
Manganese	$^{55}\text{Mn}(n, \alpha)^{52}\text{V}$ (0.6 MeV, 3.6 MeV) [$^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$]	— [$^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$]
Iron	$^{56}\text{Fe}(n, p)^{55}\text{Fe}$ (2.9 MeV, 4.65 MeV) $^{56}\text{Fe}(n, 2n)^{55}\text{Fe}$ (13.8 MeV)	$^{56}\text{Fe}(n, p)^{55}\text{Fe}$
Cobalt	$^{60}\text{Co}(n, \alpha)^{57}\text{Ni}$ (-0.4 MeV, 3.35 MeV)	—
Fluorine	$^{19}\text{F}(n, \alpha)^{16}\text{O}$ (1.6 MeV, 3.1 MeV) $^{19}\text{F}(n, p)^{18}\text{F}$ (4.2 MeV) $^{19}\text{F}(n, 2n)^{18}\text{F}$ (10.95 MeV)	$^{19}\text{F}(n, \alpha)^{16}\text{O}$ $^{19}\text{F}(n, p)^{18}\text{F}$
Oxygen	$^{16}\text{O}(n, p)^{15}\text{N}$ (10.2 MeV)	—

* Between brackets: Threshold (MeV) or Coulomb barrier (MeV); cf. Chapter 3, section III, B.

epoxy rabbits containing 30% by weight B_4C or ^{10}B (90% enriched); the walls of these rabbits contain about 170 mg cm^{-2} of B_4C or ^{10}B . Plugs of the same materials cover the top of the sample.

Fast neutron sensitivities are better than thermal neutron sensitivities for O, Si, P, Fe, Y and Pb; they are in the same range but less than thermal neutron sensitivities for F, Mg, Al, S, K, Ti, Cr, Co, Ni, Zn, Ge, Se, Br, Nb and W (for Se and W: combined reaction yields

$Z^{A-1}(n, \gamma) + Z^A(n, n') + Z^{A+1}(n, 2n)$). For seven elements (Ga, Re, Eu, Ho, Ta, Cs) no fast neutron products were observed (92).

Another source of fast neutrons is a small deuteron accelerator, which has the advantage that there is no epithermal flux which yields (n, γ) reactions. An accelerator is most suitable for the production of short-lived radionuclides.

With a small accelerator (150 kV, 1 mA deuteron beam), variable energy neutron activation is possible when using different targets, e.g. loaded with tritium, giving 14 MeV neutrons, or loaded with deuterium, giving ~2.6 MeV neutrons (102). A variable-energy cyclotron has been used as a source of 12 MeV ^3He -ions and 7 MeV deuterons. Stacked-foil techniques allow the energies of the positive ions to degrade below these values; typical beam currents are 1-100 μA . Bombarding a thick D_2O or a beryllium metal target with 7 MeV deuterons yields ~10 MeV neutrons, and allows the determination of vanadium in copper, of fluorine in the presence of oxygen, of chromium in the presence of manganese, of phosphorus in the presence of copper and of iron in the presence of cobalt (Table 7.9). Whether a reaction occurs or not, depends on the threshold energy and on the Coulomb barrier for the emitted charged particle.

(C) SELECTIVE ACTIVATION BY MEANS OF EPITHERMAL OR RESONANCE NEUTRONS

A quantitative treatment of the advantage of applying resonance neutrons in activation analysis has been given by Borg *et al.* (2) and Brune and Jirlow (103). The resonance effect is utilized after removing thermal neutrons by means of a thin cadmium shield surrounding the sample. The lower limit of the epithermal region, 0.5 eV, coincides practically with the effective cut-off energy for cadmium foil thicknesses of about 0.5-1 mm (see Chapter 3, section V, C, 2).

Without neutron filter, the reaction rate is given by

$$R_{\text{tot}} = \varphi_{\text{th}}\sigma_0 + \varphi_e I \quad (7.19)$$

as is described in Chapter 3, section V, C, 2c. In a well-thermalized reactor this expression reduces to

$$R_{\text{tot}} \approx R_{\text{th}} = \varphi_{\text{th}}\sigma_0 \quad (7.20)$$

Irradiation of cadmium however yields:

$$R_e = \varphi_e I \quad (7.21)$$

It is obvious that the determination of an element in a given matrix is easier to perform, if the element of interest has a nuclide with a prominent resonance activation peak, whereas the matrix (interfering nuclide(s)) has not.

Example: determination of molybdenum in steel (103):

	σ_0	I	$T_{1/2}$
$^{98}\text{Mo}(n, \gamma)$	0.14	6.4	67 h
$^{56}\text{Fe}(n, \gamma)$	1.2	0.66	45 d

Neglecting effects of isotopic abundance, of irradiation and waiting time and of detection efficiency, one can calculate, in a well-thermalized neutron spectrum

$$\frac{R_{th}(\text{Mo})}{R_{th}(\text{Fe})} = \frac{0.14}{1.2} = 0.117$$

Under a cadmium filter:

$$\frac{R_e(\text{Mo})}{R_e(\text{Fe})} = \frac{6.4}{0.66} = 9.70$$

The advantage factor is thus $9.70/0.117 \approx 83$ when using a cadmium absorber. The ^{56}Mn activity from the reaction $^{56}\text{Fe}(n, p)^{56}\text{Mn}$ is short-lived (2.58 h) and is allowed to decay before counting.

The absolute amount of ^{98}Mo which can be detected increases obviously when irradiating the covered sample at a position where the resonance flux is as high as possible, e.g. in the neighbourhood of the reactor core.

Another example is the determination of antimony in selenium (106).

An advantage factor of 10–20 may be considered as favourable (103).

Brunfelt and Steinnes (104) found that the instrumental determination of rubidium, cesium, barium, hafnium, tantalum and antimony in rocks is much easier by epithermal neutron activation than by thermal neutron activation (105). It is even possible to determine strontium and uranium without chemical separations. Determination of rare earth abundances, on the other hand, is probably better performed by the use of thermal neutron activation.

The determination of impurities in cadmium is discussed in Chapter 10, section II, B, 4c (6). The use of epithermal activation should also

be considered for the determinations of elements such as Au, Cu, Ag, Hf, Ir, which possess high resonance activation integrals compared to their thermal neutron cross sections.

The advantage factor for Mn/Na, using a cadmium cover, is ca. 2 only, as appears from the nuclear data. When using a ^{10}B $1/\nu$ -absorber, all neutrons up to an energy E_1 , well above thermal, will be screened, where E_1 depends on the absorber thickness.

A quantitative treatment is given by Borg *et al.* (2). Consider the simple case, wherein both the thermal neutron cross section and the resonance integral are dominated by one single resonance at an energy E_r . Using a $1/\nu$ -absorber (cut off at E_1) and assuming $\Gamma \ll E_r$, $E_1 \ll \Gamma$ one can show that the number of captures per unit time is given by

$$N_{cap} = \frac{Kg\Gamma_n\Gamma_\gamma}{-2E_r^2} \left[\frac{1}{\sqrt{(E_r E_1)} + \frac{\pi}{\Gamma}} \right] \quad (7.22)$$

where K is a numerical factor

g a statistical weighting factor

Γ_n , Γ_γ partial level widths of the resonance for emission of a neutron or a γ -ray respectively.

Γ = total level width (*cf.* Chapter 3, section V, B, 2).

This means that there are two contributions to the resonance capture from a single resonance

- (i) the "normal" integral over the resonance, $n(E_r) (\pi/2) \sigma_r(E_r) \Gamma$, where $\sigma_r(E_r)$ is the peak cross section and $n(E_r)$ is the number of neutrons at energy E_r (second term in equation (7.22)).
- (ii) An additional contribution from the low-energy wing of the resonance, particularly because the number of captures is weighted by the neutron spectrum of $1/E$ (see Chapter 3, section V, C, 2). This contribution is significant only if $E_r E_1 \lesssim \Gamma^2$ or if $E_1 \lesssim \Gamma^2/E_r$.

The resonance parameters of ^{55}Mn and ^{23}Na are given in Table 10.2. One calculates $\Gamma^2/E_r = 1.4$ eV (^{55}Mn) and 5.8 eV (^{23}Na). Thus it can be seen that the contribution to capture from low-energy neutrons is relatively greater for sodium than for manganese. Therefore in attempting to suppress activation of sodium relative to capture in ^{55}Mn , it pays to thicken the ^{10}B neutron absorber until $E_1 \approx 6$ eV. The ultimate calculated ratio of capture in ^{55}Mn to that in ^{23}Na is approximately 6.5–7 in agreement with experimental results (2), *cf.* Figure 9.2.

The above equation can be generalized to include more than one resonance, e.g. ^{37}Cl (2). A ^{10}B neutron filter, having a cut off at about 100 eV, gives an advantage factor of 14, for the Mn/Cl activity ratio.

Note: When using cadmium foils, it is recommended to pack the samples first in a thin aluminium foil (e.g. 60 μ , purity 99.999%) or in a quartz ampoule, in order to prevent Cd-recoil nuclei with long half-lives from penetrating the samples.

When using a boron shield (e.g. metallic ^{10}B powder, enriched to $\sim 93\%$ ^{10}B in the hollow walls of an aluminium container, or other systems - see above), the heating from the $^{10}\text{B}(n, \alpha)^7\text{Li}$ reaction can present a serious problem by thermal destruction of biological samples. By enclosing the capsule in a cadmium foil, this effect markedly diminishes. With ashed or thermoresistant materials the cadmium outer can may, however, be omitted, thus simplifying the handling of the sample container by avoiding the intense cadmium radioactivity otherwise induced in it (2).

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CHAPTER 8

ACTIVATION ANALYSIS WITH POST-IRRADIATION RADIOCHEMICAL SEPARATIONS

The most simple way of performing an activation analysis is by means of an instrumental method, without any chemical treatment. A number of analyses can be performed in this way by gamma spectrometry, particularly with selective detectors such as Ge(Li) and/or using coincidence set-ups, computer calculation of photopeak areas, etc.; in other cases, decay curve analysis is required. Examples can be found in Chapter 9. Such procedures can easily be applied if the matrix activity is low or short-lived, e.g. in the case of lead, silicon, iron.

It is often possible to determine a number of impurities in a sample without further chemical separations, on condition that the bulk of the matrix activity is eliminated, i.e. a single radiochemical separation may be sufficient.

I. Removal of Matrix Activity

(A) PURE ELEMENTS

After distillation of the selenium matrix as the bromide, one can detect the following impurities (1): sodium, potassium, scandium, chromium, iron, cobalt, copper, zinc, gallium, silver, cadmium, lanthanum, tungsten and gold as appears from Figure 8.1. One gram of tin can be distilled for more than 99.999(9)% as tetrabromide (2). The gamma spectrum of the residue of 1 g of irradiated tin is shown in Figure 8.2. Note the interference from the radioactive indium daughters of tin with the detection of some impurities. If irradiated titanium is brought on a Dowex 1-X8 column in 1M HF-9M HCl, most of the impurities remain on the resin (As, Sb, W, Cu, Ta, Zn, Co, Fe, Au, Sn, Mo) whereas the matrix activity, mainly ^{46}Sc , ^{47}Sc and ^{48}Sc from (n, p) reactions, is eluted (> 99.5%) together with Cr, Na, Ag (3). If the eluate is passed through a column in 1M HF, Ti and Sc are retained