Procedures for Accurately Diluting Dispensing Radioactive Solutions

1st edition

1975

**Bureau International
des Poids et Mesures**

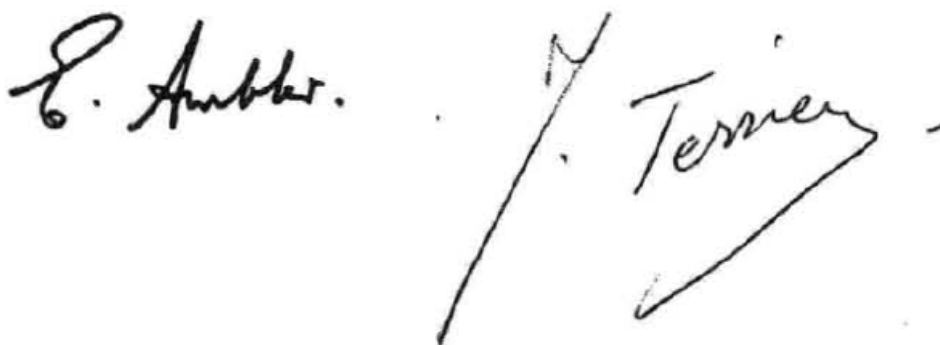1st edition   1975

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Foreword

This monograph is one of several to be published by the Bureau International des Poids et Mesures (B.I.P.M.) on behalf of the Comité Consultotif pour les Etalons de Mesure des Rayonnements Ionisants (C.C.E.M.R.I.). The aim of this series of publications is to review various topics which are of importance for the measurement of ionizing radiation and radioactivity, in particular, those techniques normally used by participants in international comparisons. It is hoped that these publications will prove to be useful reference volumes both for those who are already engaged in this field and for those who are approaching such measurements for the first time.

This volume is concerned with a particular aspect of radionuclide metrology and was prepared for publication by P.J. Campion.

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Procedures for Accurately Diluting and Dispensing Radioactive Solutions   Contents

1.   Introduction

Advances in metrology are usually made by concentrating on the reduction of the magnitude of the most significant source of potential error in a measurement to a value which is small compared with those of other sources; the process is then repeated with the next most significant source and so on. Thus, a particular technique which may be good enough within a measuring system which is capable of an accuracy of, say, $\pm 2\%$ may not be acceptable when all the other techniques in that system have been improved to a level of accuracy of $\pm 0.2\%$. Hence techniques and procedures, which may be found satisfactory at a given time, must be examined periodically in the light of advances made in the rest of the system. With the present state-of-the-art of radioactivity metrology the two stages in the determination of radioactive concentration where errors are perhaps most likely to occur (apart from the disintegration rate measurement of the individual sources) are (1) the dilution of a concentrated solution and (2) the dispensing of small quantities of the diluted solution in the preparation of sources for counting. Techniques for the satisfactory accomplishment of both these manipulations have been described in the literature although a considerable amount of additional and detailed knowledge remains unpublished and is vested in many laboratories throughout the world. This monograph represents an attempt to provide a guide to what might be called "good laboratory practice" in this area. Because not all laboratories agree on the best practice at every point, an attempt has been made to record variant procedures where these have been made known to the author. It follows, therefore, that while generally agreeing with this report, all the members of C.C.E.M.R.I. do not necessarily subscribe to all of its recommendations. It is hoped that the monograph will be of value to those engaged in the standardization of radioactivity, especially those who may be approaching these problems for the first time.

2. General Requirements for Weighing

It is generally agreed that diluting and dispensing are best carried out gravimetrically and hence the first requirement is a balance capable of determining the mass of a liquid drop in the range 10 to 100 mg to an accuracy of better than $\pm 20\,\mu g$. Such balances are often limited in their capacity and it is thus convenient to have a second balance on which masses of the order of 50 g can be weighed and which need only have on accuracy of about $\pm 200\,\mu g$. It is important that the balances should be located in a room that is relatively drought-free and which should be large enough to carry out simple manipulations other than weighing. Mechanical balances in particular should rest on a rigid and heavy table, preferably on the bottom floor of a building , the floor being in contact with compacted or undisturbed ground. Alternatively the table should rest on brick or concrete piers with foundations in undisturbed ground. It is also important that balances should be regularly cleaned and serviced. A small thermal gradient of the order of $0.1\,\mathrm{Km^{-1}}$ within the balance enclosure (top warmer) is essential for the stability of equal-arm type of balances, but due to basic differences in design, it is not usually necessary to impose such a gradient within the enclosure of single-arm balances [1]; it is good laboratory practice to locate the balances in a part of the balance room that has a positive thermal gradient (top warmer) because the general nature of the disturbing effects of having the top cooler is applicable to some degree to all types of precise balances. The temperature in the balance room should be both spatially uniform and constant preferably to within $\pm 0.50\,°C$ over a short period, say one hour, and to within $\pm 1\,°C$ over a 24 hour period. The humidity should also be reasonably constant over the same period, say with in $\pm 5\%$ at a relative humidity preferably in the range 50 to 60%. Such stability may be achieved by careful location of the balance room (e.g. a room within a room, or a room with a very large thermal capacity) or by suitable air conditioning equipment. In the latter case it is particularly important to ensure that any vibration of the air conditioning plant is not transmitted to the balance room. It is also desirable that the air be delivered to the balance room via a perforated false ceiling or similar widely dispersed ducting ports in order to attenuate air currents as much as possible. A procedure sometimes adopted is to switch off the air conditioning plant when actually carrying out weighing. Provided the balance room is well insulated, as it should be, the temperature change over the period required for diluting and dispensing, say one hour, will be negligible and the desirable conditions of a positive thermal gradient and minimal vibration will be realized. Accurate weighings can only be started if thermal equilibrium has been reached by the balance and its environment; some experts recommend that the operator should sit in front of the balance for at least 15 minutes before weighing commences in order to attain a sufficient degree of thermal equilibrium. Smoking should be prohibited in the balance room to reduce the possibility of tar and other products condensing on the balance mechanism. The temperature and humidity fluctuations for adjacent preparatory rooms may be somewhat greater but the mean values should be the same as those of the balance room in order to avoid long delays in vessels and solutions reaching equilibrium with the balance environment.

While the stability of commercially available balance weights is normally adequate, very small amounts of dirt will introduce errors and regular cleaning and recalibration of the weights is recommended. Even when regularly cleaned, occasionally a weight has been observed to change its actual mass over a period of years due, presumably, to a surface chemical effect and small but nevertheless significant changes can take place over short periods for no obvious reason [2], [3]. It is therefore recommended that the balance weights be calibrated, independently of the manufacturer, before being put into service and annually thereafter; this requires an access to professional mass metrology services. In principle this calibration can be achieved by a single reference weight, the fractional uncertainty being the same for all the

(smaller) weights calibrated using the reference weight [4] but in view of the possible mass changes mentioned above it is advisable to have several calibrated reference weights available. It should be noted that the response of a balance on its optical scale is not necessarily linear and thus the scale should also be calibrated [3], [4], [5], [6].

Apart from the calibration of the balance weights and optical scale the following tests should be carried out by the balance user when the balance is first installed and from time to time thereafter in order to assure himself that its performance has not deteriorated :

1. the variation of sensitivity over the optical scale

2. the variation of sensitivity with time, and eventually

3. test of randomness.

These and more extensive performance tests may be found in the literature [7], [8], [9], [10], [11], [12].

Static charge may build up on glassware and plastic materials and can cause serious errors in weighing particularly when using small balance enclosures [13]. These difficulties may be avoided by means of a radioactive static charge eliminator situated within the enclosure. The source may be a β-emitter such as ^{204}Tl or ^{90}Sr-^{90}Y and in such cases, for safety reasons, a mechanical shutter is often arranged to close over the source when the balance enclosure is opened. On the other hand α-emitters are much more efficient eliminators of static charge and considerably weaker sources may be used without the necessity of a shutter [13], although with such emitters the experimenter should be aware of the possibility of recoil contamination. In this respect the use of ^{210}Po should be avoided.

A most important requirement in the manipulation of both active and inactive solutions is that all vessels used shall be scrupulously clean, and this also applies to the ampoules into which the active solutions are finally dispensed for distribution. Some typical methods for cleaning such vessels are described in Annex 1. If required, clean glassware may be given a water-repellent silicone coating. This treatment is necessary for glass pycnometers, but is not recommended for ampoules since the coating is destroyed by flame sealing. Some laboratories coat other glassware such as dilution flasks, scintillation vials, etc., whereas others recommend against this. Procedures for silicone-coating glass together with some advantages and disadvantages of doing so are given in Annex 2. Polyethylene is naturally hydrophobic, but adsorption or absorption has been observed to occur with polyethylene surfaces. Polyethylene is also porous to some solvents [14], [15], [16], [17], [18].

3.   Outline of Procedures

The procedures normally involved in distributing a standard of radioactivity and in making an accurate activity measurement are schematically illustrated in the chart of Figure 1. Naturally the details may vary in an individual laboratory or for particular radionuclides but in general Figure 1 represents the brood outline of the manipulations required.

In brief, the master solution is dispensed into as many ampoules as may be necessary for the intercomparison or distribution. A few of these ampoules are retained for the measurement of the activity per unit moss of solution and the remaining ampoules are distributed to laboratories participating in the intercomparison. Because the radioactive concentration of the master solution and the aliquot size are selected so that the filled ampoules provide a suitable ionization chamber response to give a convenient measuring time (or contain sufficient radioactivity for a particular purpose) it is usually necessary to dilute the distributed solution to a level which is suitable for making sources for counting. As will be seen below, the dilution stage should not introduce a significant error into the measurement of the radioactive concentration.

Having diluted the solution to a suitable level the next step is to prepare the counting sources. These will usually be dispensed either on to thin metal-coated VYNS[1] or other films for gas proportional counting or into suitable vials for liquid scintillation counting. The solution is dispensed from a vessel (a pycnometer) and the mass deposited may be determined in two ways. In the first method the mass of the solution deposited is obtained by weighing the pycnometer before and after dispensing the drop of solution and this is usually referred to as the pycnometer method. The second method involves the weighing of the source mount (or scintillation vial) before and after dispensing the drop of solution. To correct for the evaporation of the solution from an open source mount the mass of source mount plus solution is observed as a function of time and an extrapolation made to obtain the combined mass at the instant the drop was dispensed. This is called the extrapolation method. Only by careful attention to detail can these two methods be made to agree; in general the pycnometer method is to be preferred and is recommended in this monograph. This is not to say that the extrapolation method cannot be used successfully but only that there is an inherent systematic error in the technique due to a non constant rate of evaporation near time zero [13], [22], [23]. In order to minimise the uncertainty due to this effect the use of on electrobalance is essential.

[1] VYNS is a copolymer of vinyl chloride and vinyl acetate. Details af the production and metallising af such films may be found in the literature [19], [20], [21].

PROCEDURE

Master solution
dispensed into
ampoules

Ampoules selected
for measurement

Dilution

Preparation of (a) Ampoules for ion (b) Sources for counting
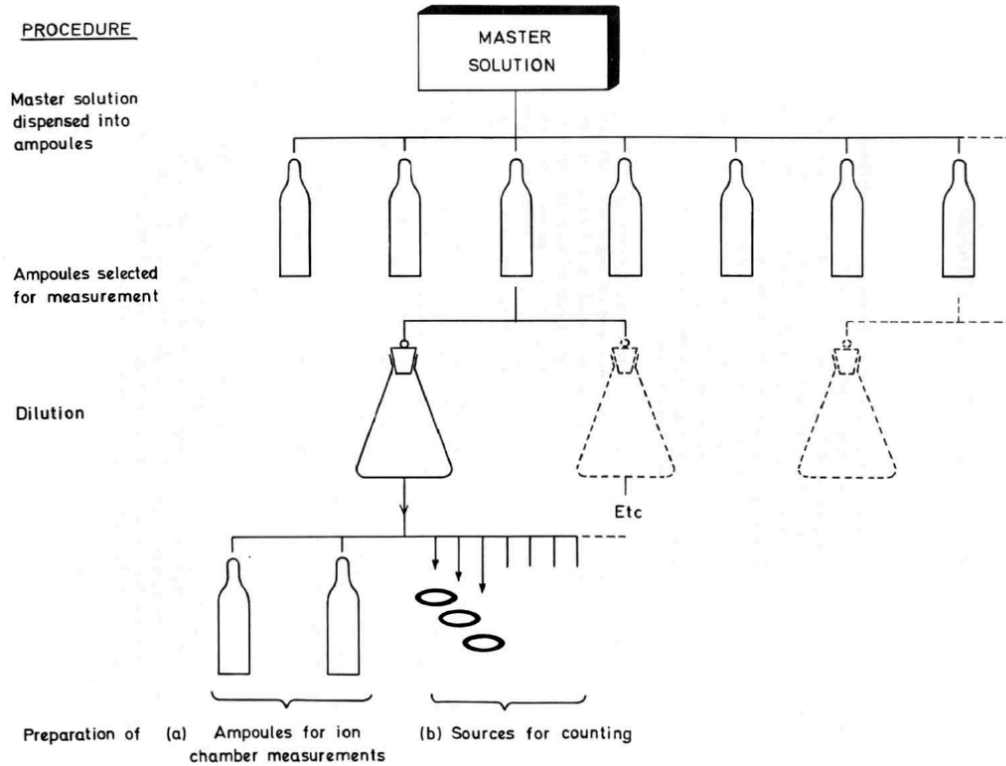chamber measurements

Figure 1 — Procedures for the distribution and preparation for measurement of radioactivity standards

4. Details of Procedures: Issuing Laboratory

The master solution

While a detailed discussion of the physical and chemical composition of master solutions is beyond the scope of this monograph it is relevant to mention some of the more important factors which should be considered when specifying such solutions. The purpose for which a standard of radioactivity is required is one such factor which may influence the choice of chemical composition, approximate radioactive concentration, and perhaps, container. This monograph is mainly concerned with the use of solutions in international comparisons where considerations of accuracy are paramount, but for distributions from standardizing laboratories other factors such as the specific application of the standard and even the cost may, in part, determine the choice of characteristics.

In general, the objective is to achieve a stable solution having negligible adsorption on container walls but at the same time having a low dissolved solids content in order that thin sources with as small a self-absorption as practicable may be prepared for 4π counting. A related consideration is that both acid and alkaline solutions tend to leach out glass so increasing the concentration of dissolved solids [24], [25], [26]. This increase depends on the strength of acid or base in the solution, the type of glass forming the container and the length of time of contact; values of the order· of $100\ \mu gg^{-1}$ of solids have been reported after several months of storage in Pyrex glass [27]. Quartz is relatively insoluble and has been used far the storage of standard solutions [14], [25] and although polyethylene vessels are also good in this respect [26] they are slightly porous. Thus, if it is necessary to achieve the absolute minimum of dissolved solids, both reagents and water should be freshly distilled using quartz utensils[1]. However, the widespread use of the coincidence technique and its extension to the tracer method for pure β-emitters reduce the need for such extreme measures and analytical grade reagents and water distilled in borosilicate stills are usually adequate.

Adsorption is another phenomenon that must be considered and the carrier concentration and the pH of the master solution should be chosen to minimise this; as a general guide a concentration of about $100\ \mu g$ of carrier per gram of on acid (usually HCl or HNO_3) solution of 0.1 mol in $1\ dm^3$ of water is acceptable but concentrations both above and below these guide line values may be required for particular radionuclides. Some radionuclide solutions are particularly susceptible to bacterial growth which can absorb activity from the solution. In such cases the solutions should contain a bacteriostat such as 0.1% formalin or be heat sterilized after having been sealed in the ampoules. The latter is in any case considered to be a desirable practice if the ampoules are to be stored for a considerable length of time. A useful guide to the chemistry of various radionuclides in dilute solutions has been published [29].

It should be noted that radiolysis can produce an increase in pressure in closed vessels containing radioactive solutions. For radioactive concentrations of the order of $100\ \mu Ci$ per gram of solution the effect is usually negligible and sealed glass ampoules can be safely used for the long term storage of solutions. For large radioactive concentrations there is the danger of mechanical rupture (for example, a gram of solution containing an activity of 10 mCi of an α-emitting nuclide will produce in six weeks about $1\ cm^3$ of gas at NTP due to radiolytic decomposition but even more important from the point of view of radionuclide metrology is the question of the chemical stability of such solutions.

The remarks made in the Introduction with regard to acceptable uncertainty limits apply with equal emphasis to the radionuclide purity of the activity; this should be checked using a

[1] Typically, once-distilled water contains solids to the extent of about $1\ \mu gg^{-1}$ while triple distillation in quartz stills will reduce this by about an order of magnitude. Triply-distilled and deionized water contains solids to the extent of about $0.01\ \mu gg^{-1}$ [26]; however deionized water is rarely free from organic matter. A recent review of the production of ultrapure water has been given in reference [28].

method whose sensitivity is compatible with the overall uncertainty limits and, if necessary, chemical separations performed before preparing the master solution.

Dispensing the master solution

A number of glass or, if necessary, quartz ampoules which can subsequently be flame sealed must be selected and prepared. Although the quantity of master solution dispensed into each ampoule is determined gravimetrically it is usually checked by means of measurements in a re-entrant , or well-type, ionization chamber; in some metrological laboratories use is made of NaI(Tl) or Ge(Li) detectors for the comparison of activities. In order that the γ-ray absorption properties of ampoules should be the same, the dimensional tolerances of the ampoules should be such that any differences in absorption are negligible. A convenient method for ascertaining this is described in Annex 5. After selection, the ampoules should be cleaned (see Annex 1, see p. 26) and left in the balance room for several hours in order to attain thermal and hydrometric equilibrium. It is convenient to identify each ampoule at this stage; this may be done by a temporary wax pencil marking, labelling, engraving the glass, or by labelling clean containers each holding an ampoule. In order to fill the ampoules a large capacity dispensing vessel having a long bent spout suitable for entering the necks of the ampoules or a pipette with a long tip can be used. Alternatively, an automatic burette can provide a convenient method for filling ampoules. The pipette or burette should be carefully cleaned as described in Annex 1. Both the master solution, in a stoppered bottle, and the dispensing vessel should be in thermal equilibrium with the balance room environment.

One particular design of pipette and associated equipment suitable for dispensing solutions is shown in Figure 2; it has a capacity of some $35\,cm^3$. The whole instrument consists of a reservoir tank connected to a manifold which, by means of stopcocks, con be connected to (a) the atmosphere (b) a vacuum pump or (c) a constant pressure supply of filtered nitrogen gas. The stopcocks can be operated manually or electro-mechanically. In the latter case it is a simple matter to arrange for stopcock (c) to be opened for a fixed time thus delivering a predetermined volume of solution ; The pipette stem is immersed in the master solution and the manifold connected to the vacuum pump; the stopcock is closed when the pipette is about two thirds full and a little solution expelled to waste by momentarily opening the stopcock (c). The stem is wiped dry with a tissue and the first ampoule is brought up to the stem and filled by opening the stopcock (c) for the appropriate time. An automatic burette, of which there are several models available commercially, may also be used provided that the tip is suitable for insertion into an ampoule. In order to keep the liquid surface well away from the hot flame when sealing,the ampoules should not be filled to capacity. For example $1\,cm^3$ of solution in $2\,cm^3$ ampoule, 3 to $4\,cm^3$ solution in $5\,cm^3$ ampoule and corresponding volumes in ampoules of other capacities are considered appropriate quantities.

The ampoules are first weighed empty, reweighed after filling and then immediately flame sealed (see Figure 3, see p. 15). It is a useful precaution to test for pinhole leaks at this stage by immersing in hot water (at about 60 °C) for 30 seconds; small bubbles of air will appear if there is a leak.

As a uniformity check on the weighing procedure the sealed ampoules should be measured in a re-entrant ionization chamber. The quotient (ionization chamber current)/ (mass of solution) should be the same for all ampoules to within the precision of the measurement. Any ampoule which shows a significant difference from the mean of this quotient should be rejected. However for those radionuclides which are not amenable to such an ionization chamber check it is advisable to duplicate all weighings on a second balance; this may be done before sealing the ampoules and preferably by a second operator in which case the second weighing can be

completed within a few minutes of the first. If however there is an appreciable time interval the ampoules may be temporarily sea led with a suitable plastic film or rubber cap. Alternatively, a second weighing is possible **after** the ampoule has been sealed; in this case the remainder of the glass stem must be included in the weighing. Tests of this method have shown that, when borosilicate glass ampoules of $2\,cm^3$ nominal capacity and containing 1 g of woter are sealed with the equipment shown in Figure 3, there is an apparent average mass loss of about 0.25 mg but that, when the ampoules are reopened, the average mass loss is reduced to less than 0.05 mg. Subsidiary experiments have shown that this phenomenon is mainly due to the expansion and partial loss of air within the ampoule on heating, most of this loss being made good on reopening. Thus, it is evident that the change in radioactive concentration due to the ampoule sealing process is negligible for all practical purposes.
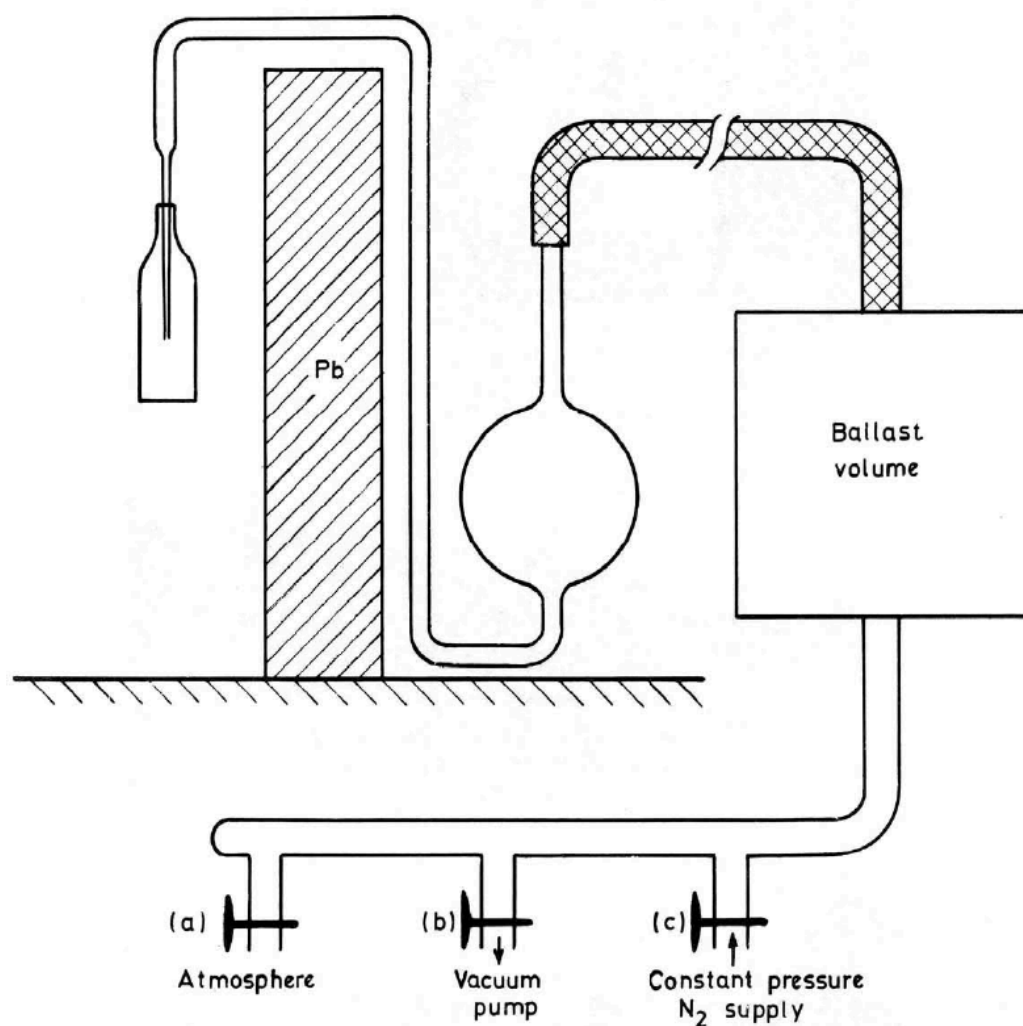

Figure 2 — Sketch of dispensing equipment as used at the National Physical Laboratory (U.K.)
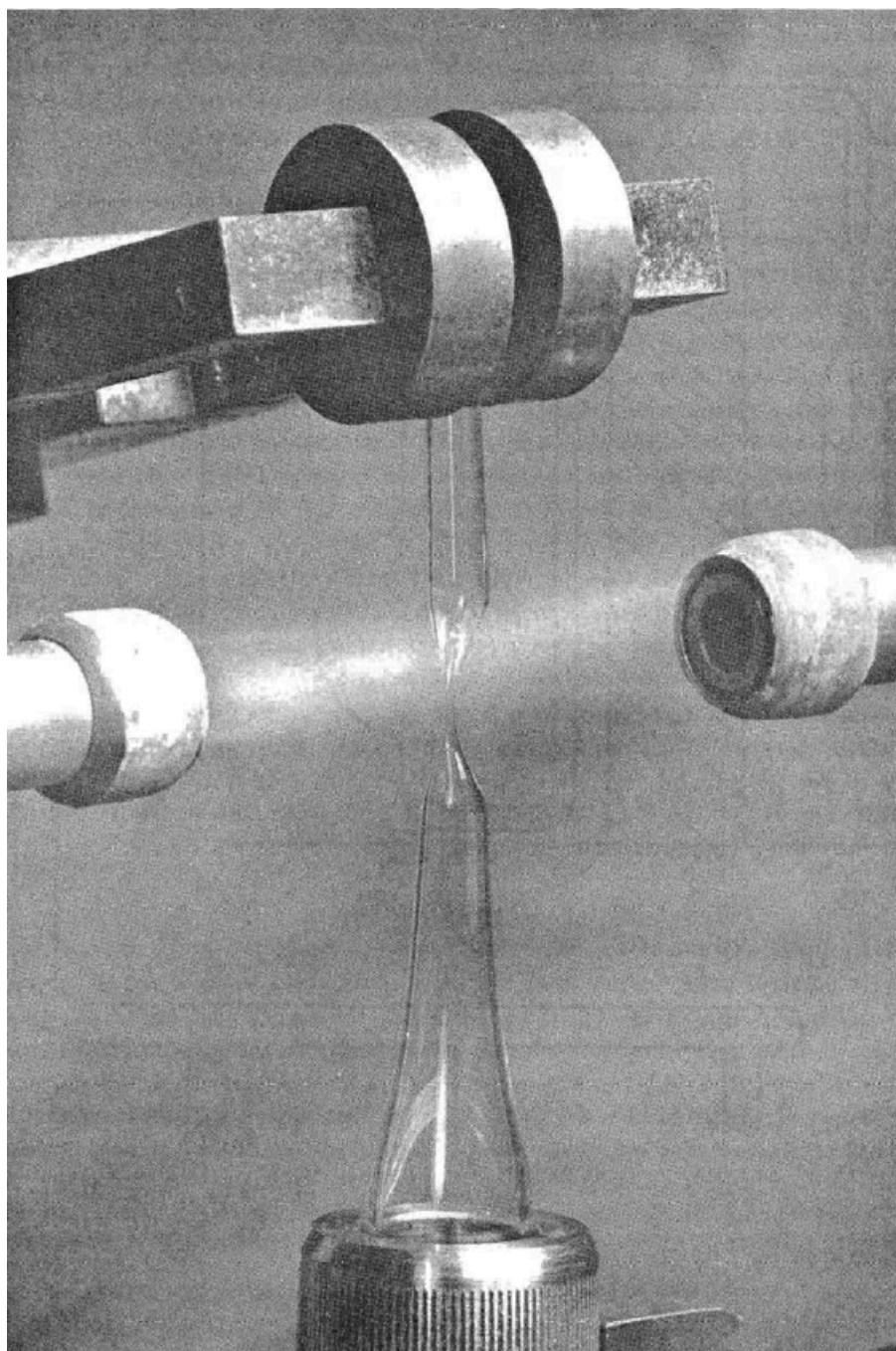
Figure 3 — Flame-sealing apparatus (National Physical Laboratory, U.K.)

As indicated above, the comparison of activities within the ampoules may also be carried out by means of NaI(Tl) or Ge(Li} detectors. Having sealed and checked the ampoules they should then be labelled. The information on the label should include at least the rodionuclide, the opproxi mote activity (with date) and a reference number. More details can be given if space permits, but in any case a separate statement (which should not be confused with the statement of the final result) should accompany each ampoule dispatched and give not only the above information but also the mass and chemical composition of the solution.

The evaporation rate from an unsealed glass ampoule has been quoted as about $0.5\,\mathrm{mgh}^{-1}$ [2] to $2\,\mathrm{mgh}^{-1}$ [18] but, even allowing 12 minutes for weighing, these rates represent possible fractional losses of only 0.01 to 0.04% for 1 g aliquots and correspondingly smaller

fractional losses for larger aliquots. Hence the change in radioactive concentration due both to evaporation from unsealed ampoules whilst weighing and to the sealing process itself, should be negligible.

Two or three ampoules for measurement should be selected at random from the batch, the remainder being available for distribution.

5.   Details of Procedures: Receiving Laboratory

On receipt by a laboratory the outside of the ampoules should be checked for activity by means of a wipe test. The contents should then be thoroughly shaken to overcome any distillation phenomena that may have occurred in transit and the solution induced to drain completely from the ampoule tip. Simple tapping of the ampoule is usually sufficient to obtain this provided a rounded flame-sealed end, rather than a pointed tip has been achieved; centrifuging would certainly ensure proper drainage. The ampoules should then be left in the balance room in order to achieve thermal equilibrium with their environment.

In order to provide an independent check on tile dilution factor as obtained by the gravimetric procedure described below, it is recommended that ionization chamber measurements be made on aliquots of both the undiluted and diluted solutions of those radionuclides which emit suitable photon radiation. If the dynamic range of the ionization chamber is adequate and the ampoules in which the solution is received are the same as those customarily used by the laboratory for ionization chamber work, then it is possible to make measurements on the ampoules before opening them. However, the second condition is rather unlikely to be fulfilled, in which case it is necessary to transfer some of the solution to "standard" ampoules. These standard ampoules should, if necessary, be topped up to a constant height in the normal way by the addition of inactive solution (see Annex 5, see p. 31). However, if the quantity of active solution is limited, no additional solution should be added so that the ampoules may be reopened after the ionization chamber measurements and the contents used in the preparation of the diluted solutions.

Dilution

The dilution procedure requires a stoppered glass dilution flask, a transfer pycnometer which may be glass or polyethylene, a suitable glass funnel and a further vessel containing the diluent. The dilution flask may be any suitable vessel and a variety of shapes have been used, but an Erlenmeyer or volumetric flask of about 10 to 20 cm^3 capacity can be recommended; volumetric flasks are available with plastic screw caps and teflon gaskets and provide a useful alternative to glass stoppers which may be lightly greased or used "dry". The advantage of lightly greasing is, of course, that the solution may be stored for a long period of time with the assurance that no loss due to evaporation can take place and that it allows the flask to be repeatedly inverted for mixing purposes; plastic screw caps are also advantageous in this respect. On the other hand the evaporation rate from a dry stoppered flask is sufficiently small that it may be used for the dilution process when sources are to be dispensed immediately. The necessity for inverting the flask to achieve complete mixing has been questioned [17], [18]. The arguments for not inverting the flask are, firstly, to avoid liquid, which is not yet mixed, being trapped in the stopper or cap crevices and, secondly, where the solution is to be assayed by liquid scintillation counting, to avoid any possible contamination of the scintillator by grease which, according to some authorities [30], may cause quenching. However, the proponents for inverting suggest it as a safeguard for complete mixing [4]. The important point is to be aware of the possible pitfalls in whichever technique is adopted. Further it is equally important that all the glassware should be clean (see Annex 1, see p. 26) and in thermal equilibrium with the balance room environment. The pycnometer may readily be made from commercially available virgin polyethylene bottles[1]. A technique for making such pycnometers is described in Annex 3. Glass pycnometers may also be used [22]; however, it is necessary to grind and flame the pycnometer tips in order to produce a smooth rounded surface and then add a water-repellent coating (Annex 2, see p. 27); they also require a detachable (via a dry cone and joint) rubber bulb or syringe to expel the solution. The

[1] Supplied by Canus Equipment Ltd., 340 Gladstone Avenue, Ottawa, Canada

polyethylene pycnometer is possibly to be preferred for diluting and dispensing sources. In general the diluent should be mode up to maintain the same inactive chemical composition and concentration as the master solution; however, if the experimenter has evidence that a lower carrier concentration is acceptable from the point of view of adsorption then the chemical composition of the diluent may be chosen so that this lower concentration is achieved in the diluted solution. The diluent can be conveniently stored in a graduated flask with a dry stopper and subsequently transferred to the dilution flask by means of the glass funnel. Both vessels and diluent should be in thermal equilibrium with their environment.

The dilution flask is first weighed. If a dry stopper is to be used then the stopper may, if desired, be weighed with the flask (but note that, when making two or more dilutions, a flask and its stopper should be clearly identified) although if a greased stopper is to be used the flask only should be weighed [4]. Opening of the ampoule containing the solution to be diluted can be accomplished by drawing a file mark near the top of the neck. The tip is then cracked by momentarily contacting the file mark with either a small bead of molten glass or a red hot wire. Immediately after the glass tip has been removed, the liquid should be withdrawn into the pycnometer. There is usually no need to withdraw all of the solution and it is much more important to remove an adequate sample (a gram or more) quickly in one operation without expelling air into the solution from the pycnometer. Because the operator's hand may disturb the thermal equilibrium of the pycnometer and contents it is essential to handle pycnometers only with long tweezers or other remote handling equipment (Figure 4, see p. 19). The time required for transfer should not toke more than a few minutes at the most. After withdrawing the solution the outside of the pycnometer stem is wiped with a tissue and, if small droplets are found to adhere to the interior, a few drops are expelled to waste. The pressure on the ampoule (in the case of a polyethylene pycnometer) or on the detachable syringe (in the case of a glass pycnometer) is then released slowly so as to leave the stem free of liquid droplets. The pycnometer should then be weighed, care being taken to ensure that the pycnometer and contents are still in thermal equilibrium with the balance enclosure.

The pycnometer is then removed from the balance and preferably not less than several hundred milligrams of the solution are dispensed into the dilution flask in such a way that droplets are not allowed to adhere to the glass walls near the neck of the flask. The pycnometer is then reweighed. Some laboratories also reweigh the (stoppered) flask ot this point. The difference in weight will be slightly less than that indicated by the pycnometer weighings {which should be used in calculating the dilution factor} owing to evaporation losses but it serves as a check on gross weighing mistakes. Next, the diluent should be added to the dilution flask via the funnel or other suitable means of transfer such as a pipette, care being again taken to prevent splashing. The dilution flask is then reweighed together with, if appropriate, its stopper[2]. Immediately after weighing, the contents of the dilution flask should be mixed. Care should be taken to ensure that any drops which may have adhered to the walls of the flask should not escape being mixed with the main volume. As indicated above, opinion is divided on whether or not the dilution flask should be inverted in order to mix the master solution and the diluent. The evidence to date suggests that complete mixing can be achieved by gently swirling the solution in the dilution flask [17] and in order to carry out this swirling effectively the flask should not be filled to more than half its nominal capacity.

[2] At the expense of making the check on the pycnometer weighings rather less sensitive, the order in which the components are added to the dilution flask may be reversed but opinion is divided on this. Adding the diluent first is done in order to occupy any adsorption sites with inactive rather than active material, while adding the active solution to the diluent is felt by some to cause more splashing. In one procedure part of the diluent is put into the flask first and the remainder after delivery of the active solution.
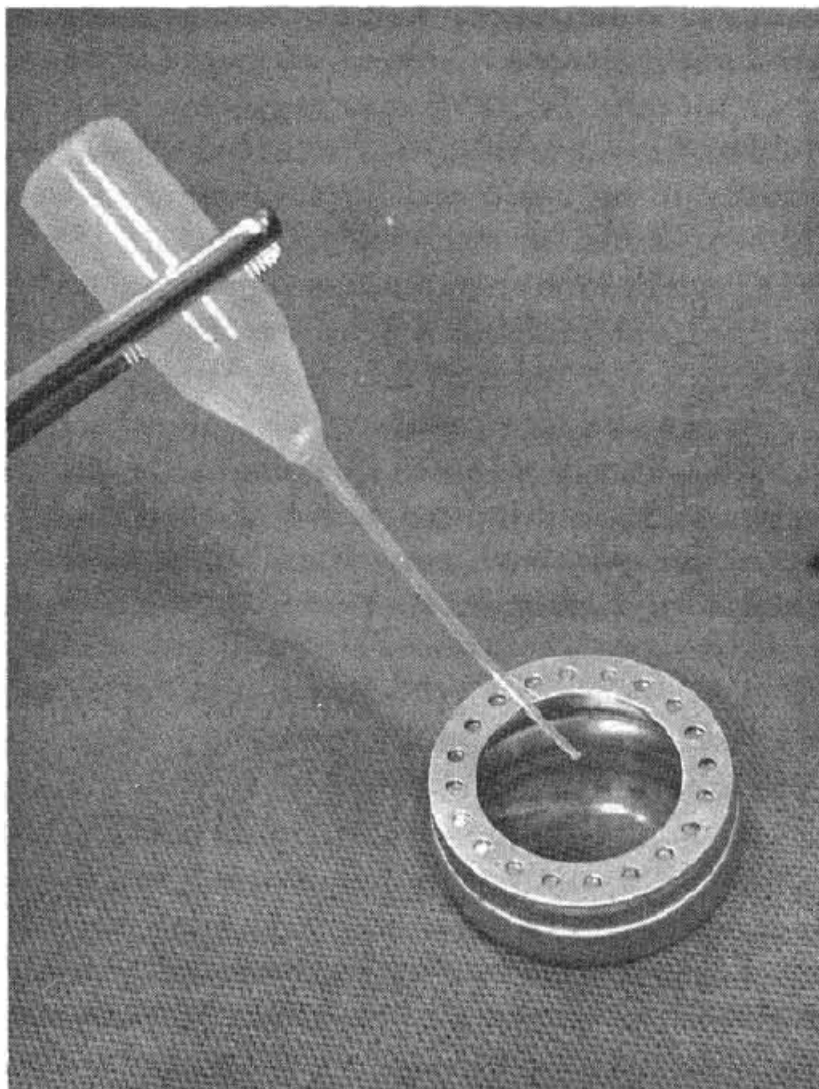
Figure 4 — Tweezers for handling pycnometers (from reference [16], see p. 32)

If A is the mass of the dilution flask empty, D the mass of flask plus total solution, and B and C the pycnometer plus solution masses before and after expelling the master solution into the flask, then the dilution factor is (D-A)/(B-C). At least one further dilution should be made from the same ampoule and the dilution factor varied by an appreciable amount, say a factor of two. In general, dilution factors should not exceed 50 in any one dilution and preferably should not be more than 30. If a larger factor is necessary it may be achieved in two or more stages. Larger factors may also be achieved provided that a balance of suitable capacity is available to accommodate a larger dilution flask; however, it should be remembered that the greater the dilution the more difficult it becomes to achieve complete mixing.

The dilution procedure itself is now complete. The remainder of the solution in the pycnometer can be stored either by delivering it to a glass ampoule which is then flame sealed or, if contained in a polyethylene pycnometer, by simply sealing the capillary in a microflame. It should be realized, however, that there is an evaporation loss through the polyethylene walls which may be of the order of 0.1 mg per day. Although this can be reduced by storing the ampoule in a closed container in which there is an open vessel containing an inactive solution of the same chemical composition as that within the ampoule [18], it is recommended that, for

storage over an appreciable period of time, a flame-sealed glass ampoule or greased stoppered flask be used.

Source preparation

The next stage is the preparation of sources suitable for counting and, if a sensitive ionization chamber is available, also of sealed ampoules in order to check the dilution factor by ionization current ratios. A series of suitable source mounts is required for 4π proportional counting or vials for liquid scintillation counting, together with a few ampoules. It is, of course, imperative that a different pycnometer be used for the transfer of the diluted solution from that used for the strong solution, and indeed pycnometers should be discarded after use. Again all glassware should be clean and in thermal equilibrium with the balance room environment.

Some solution is carefully drawn into the pycnometer without bubbling and the outside of the pycnometer stem wiped with a tissue. In one weighing technique the pycnometer is weighed using the set of balance weights and then a drop or two of the solution is dispensed on to the source mount, the pycnometer being immediately weighed again: this weighing is also the initial weighing for the second source. Thus a series of some 7 to 10 sources can be prepared and, after counting, the mean value for the activity per unit mass of the solution is calculated. In this way the uncertainties associated with the individual weights used for all but the first and lost weighings of the series are cancelled, i.e. they do not contribute any uncertainty to the mean value for the radioactive concentration. An alternative technique is substitution weighing and involves the use of the optical scale and a reference weight approximately equal to the mass of the liquid drop dispensed. The pycnometer is first counterpoised on the balance and the reading of the optical scale noted, the internal balance weigh ts being used as tares only. A drop is then expelled on to a source mount and the pycnometer together with the reference weight are placed on the balance pan. The new optical scale reading which, with care, will be close to the first, is recorded. The mass of the expelled drop is thus the algebraic difference between these two readings plus the mass of the reference weight [6]. The heavy reliance that this method puts on a single calibrated reference weight can be avoided by using a series of such weights [31]. With care both techniques can give adequate precision and accuracy; however it is not the intention of this monograph to discuss the relative merits of these two methods at this point in time particularly since the recent commercial development of electrobalances will to some extent influence such an evaluation.

In using polyethylene pycnometers particularly, it sometimes happens that, due to capillary forces, some of the solution remains in the stem after dispensing a source. Thus the air inside the pycnometer cannot come into contact with the ambient air and is at a slightly lower pressure. Hence, on reweighing the pycnometer, the volume of the dispensed drop is not replaced by ambient air as is required for the normal buoyancy correction (see Annex 4, see p. 29). This effect can be avoided by first holding the pycnometer with the stem in an upwards direction and gently squeezing. With the pressure still applied the pycnometer is turned downwards and a drop dispensed on to the mount by additional squeezing. After releasing, the pressure inside the pycnometer will reduce and allow the withdrawal of all the solution from the capillary. For solid sources prepared for 4π proportional counting, source masses in the range 20 to 50 mg have been found to be acceptable and the dilution fac tor should be so arranged that sources in this mass range give a suitable counting rate. If seeding or spreading agents are to be used to improve the uniformity of sources for 4π proportional counting these may be dispensed on to the source mount before the deposition of the active solution since any splashing resulting from the first operation is then immaterial. Different radionuclides may, of course, require different source preparation techniques: a survey of

source preparation procedures, which includes on extensive list of references to recent work in this area, may be found in reference [32].

For liquid scintillation counting the scintillator and radioactive solutions may be dispensed into the counting vials separately. In many cases this is the preferred method since the alternative, that of pre-mixing the sinctillator and radioactive solutions, involves weighing solutions having high vapour pressures, although an elegant method to overcome the problem of rapid evaporation has been described [33]. The pre-mixing method does however have the advantage of weighing a considerably larger mass of radioactive solution with the consequent reduction in the fractional uncertainty associated with this step but, because a known aliquot must be extracted from the bulk solution for each counting vial, it is essential that the components be thoroughly mixed by, for example, mechanical shaking [34]. While mixing is also desirable in the first method it is equally important that drops of the solution do not become lodged in the crevices of the vial cap or stopper and hence for this method gentle swirling is recommended; alternatively, the contents may be mixed by means of a (clean) glass stirring rod. Most laboratories which use liquid scintillation counting for the establishment of radioactivity standards use to luene (or xylene) for the main solvent with about 10 to 20% ethanol as an intermediate solvent together with PPO and POPOP as primary and secondary solutes respectively. In preparing and mixing these solutions with the radioactive solution it is convenient to add the ethanol to the mixing flask or counting vial first, then add a known quantity of the radioactive solution from a pycnometer and then, finally, add the scintillator solution itself. It is necessary to establish the maximum quantity of aqueous solution that can be incorporated into the scintillator solution and yet still maintain complete miscibility. Further, the conditions required to prevent adsorption from the final mixture on to the vial walls should also be established. For toluene based scintillators it is found that a relatively high acid concentration is required and some workers add a drop of concentrated acid to the ethanol before the addition of the radioactive aliquot and the scintillator solution. Dioxane based scintillators can accommodate considerably weaker solutions without adsorption but suffer from the fact that dioxane exhibits chemi-luminescence on contact with water. Because of the possible sensitivity of both vials and solutions to phosphore scence induced by light [34], [35] the entire source preparation should be carried out in subdued red light or, alternatively, the filled vials should be stored for several days in the dark prior to counting.

For radionuclides emitting suitable photon radiation, some ampoules should be filled with the diluted solution, sealed and measured in an ionization chamber. Two or three such ampoules can be prepared either immediately before or immediately after (or preferably both) the preparation of the counting sources. These measurements together with similar measurements on ampoules prepared from the undiluted master solution enable an independent check on the dilution factor to be obtained. Subsequently, these ampoules can be used, if necessary, for impurity checks by, for example, half life measurements and γ-ray spectroscopy. It is recommended that at least two ampoules of the master solution should be opened and at least two dilutions made from each, with the dilution factors differing by on appreciable amount.

Efficiency tracer measurements

The efficiency tracer technique for the measurement of pure β-emitters requires a known amount of tracer activity to be added to the unknown pure β-activity. It is a simple matter to prepare and calibrate a solution of the β−γ tracer activity using the diluting and dispensing procedures described above. The mixing of the two solutions is best carried out ot the diluted level (i.e. at about a concentration level of 10 μCi/ g). That is to say, both unknown and tracer activities are separately diluted and then combined together by dispensing quantities of the order of 1 gram of each into a suitable flask and mixing. Counting sources may then be

prepared; if, in 4π proportional counting, seeding or spreading agents are to be used there may be, as mentioned above, some advantage in depositing these and any inactive carrier before dispensing the active solution.

6. Uncertainties

The random and systematic errors associated with the manipulations described above have been discussed by several authors. It has been reported [16], [18] that the random uncertainties for repeated measurements are of the order of 0.02% and that any systematic uncertainties should be considerably less than this, provided that "good laboratory practice" is followed. An experimental measurement of 233 sources prepared from 33 dilutions [17] gave standard deviations ranging from 0.010 to 0.099%. Due to the widely differing measurement conditions, the 33 values cannot be combined rigorously. However, the arithmetic mean of 0.055% is perhaps representative of the standard deviation to be expected. Of this value about 0.05% is accounted for by counting statistics leaving about 0.02% due to the random uncertainty associated with diluting and source preparation,—in rather good agreement with the estimates found in references [16] and [18]. The former authors derived by experiment the random uncertainty associated with the weighing of a single drop, using their balance and dispensing technique, as about 12 µg (standard deviation) which can be compared with an earlier estimate of 10 µg for a different type of balance [22]. Another report [6] estimates an uncertainty of 12 µg for a single drop measurement; however this value includes some systematic as well as random components. In this analysis of the problem, the author emphasizes the need for careful calibration of the balance weights and optical scale by means of reference weights calibrated by a mass metrology laboratory.

A recent comparison of metal masses in the range 20 to 100 mg has suggested that professional mass metrology laboratories agree to about ± 1 µg, while the agreement obtained in a number 0.(radionuclide laboratories using Mettler M5 balances was about ± 6 µg when using either calibrated dial weights and optical scales or calibrated reference weights [3]. However deviations of ± 10 µg or more were observed using uncalibrated balances, that is to say, balances which had no calibration other than the manufacturer's specification. Since these uncertainties refer to the mass determination of solid samples, as opposed to liquid samples, and were obtained under ideal conditions they must be regarded as the ultimate limit that may be achieved by current technique. In any practical situation in radionuclide metrology the uncertainties may be considerably greater. Effects which may contribute to the systematic uncertainty include the following:

1. Evaporation from open ampoules, pycnometers and dilution flasks. In a typical situation in which the manipulative procedures were assumed to take about four hours, this effect has been assessed to be about 0.004% [18] and shown experimentally to be less than 0.03% [36].

2. Adherence of droplets on the tip of pycnometers. For carefully prepared glass pycnometers this has been shown to be less than 1 µg, i.e. 0.005% on a 20 mg drop [22]. Since polyethylene is a hydrophobic material the adherence of droplets on pycnometers made of this material is likely to be small although no experiments establishing limits have been published.

3. Buoyancy correction (see Annex 4,). The correction for commonly used solutions and balance weights is about 0.1% and this value would seldom vary by more than a few per cent.

4. Uncertainties in the balance weights and, if fitted, the optical scale of the balance. Typically, individual weights are quoted by commercial suppliers as better than ± 10 µg, or when taken in groups, better than ± 20 µg of their nominal value. However, weights may be individually calibrated to higher accuracies and in any case it is essential to check

the manufacturer's specification. There may also be some non linearity in the response of the optical scale. A useful discussion of these points is given in the recent report on mass comparisons mentioned above [3] and also in a report on the performance of various microbalances [5].

5. Uniformity of mixing. Any error due to this has been shown to be very small [17].

Systematic uncertainties are thus seen to be small but it must be emphasized that much larger uncertainties may occur if the relatively simple precautions described in this monograph are not taken.

7. Conclusion

The extensive experimental work aimed at quantifying the possible uncertainty estimates described above has shown that, with reasonable precautions, the diluting and dispensing procedures should not introduce total systematic and random uncertainties of more than 0.1% in the final result of a radioactive concentration measurement and with care accuracies better than this may be achieved. It is possible, and indeed almost mandatory, to check the efficacy of the procedures at any laboratory by carrying out the following internal check. A solution of, for example, ^{60}Co is prepared and the manipulations described in this monograph carried out. In this case several ampoules (> 5) of the master solution should be prepared, opened, diluted and sources dispensed, making two dilutions from each ampoule. The sources should be counted with sufficient statistical precision in a $4\pi\beta-\gamma$ coincidence system. If the total spread of the results from these ten or more dilutions is less than 0.2% the procedures are of sufficient precision to be acceptable. Such an internal check should be carried out by every laboratory before participating in an international comparison.

Annex 1. Cleaning Treatment for Glass and Polyethylene Vessels

While glass of one type or another is the most frequently used material for vessels and containers in chemical work, it is not possible to obtain a universally clean glass surface. What may be acceptable for one purpose may not be for another. A discussion of this together with a description of the various types of glasses, their surface properties under different conditions and detailed cleaning treatments may be found in the literature [37]. However, the following three methods for cleaning new glass or polyethylene vessels have been found satisfactory for most work in radioactivity metrology.

Method I   The vessels are soaked for 24 hours in Q solution of sodium dichromate in concentrated sulphuric acid ("chromic acid"). They are then rinsed three times in distilled water and once in ethanol and finally dried in an oven at 35 °C. Rinsing should be thorough since the presence of sulphate ions can cause precipitation or colloidal effects in solutions containing cations which form insoluble sulphates. Chromate ion is also strongly sorbed on glass [26]. It may be removed with a complexing agent, e.g. by rinsing with dilute oxalic acid followed by a distilled water rinse.

[1] The solution should be stored in a polyethylene container.

Method II (for glassware only)   The vessels or ampoules are filled with hot carrier solution of the same concentration as used later for the radioactive solution. They are then dipped for two to three hours in a boiling water-bath. Thereafter they are emptied, rinsed with deionized water and dried in an oven at about 50 °C.

Method III   The vessels are immersed in a solution comprising approximately 60% (by volume) deionized water, 35% concentrated nitric acid, 3% concentrated hydrofluoric acid and 2% liquid detergent (e.g. Teepol), for 5 to 10 minutes depending on the age of the solution[1]. The vessels are then rinsed with deionized water three times. In the case of narrow necked ampoules it may be necessary to expel the water by blowing filtered nitrogen gas into the ampoule through a thin tube inserted down the neck. The glassware is then dried in an oven at about 100 °C for a time depending on the size and shape of the article. For a glass pycnometer, for example, with a narrow orifice the time required is about three hours but is considerably less for dilution flasks. In the case of polyethylene pycnometers a lower oven temperature for a somewhat longer time is required since polyethylene becomes soft at 100 °C.

The solution should be stored in a polyethylene container.

Annex 2. Water-repellent Silicone Coatings

If it is considered necessary glassware con be made extremely water repellent by the following techniques. Glassware must first be cleaned and dried (at $< 200\,°C$ to avoid irreversible dehydroxylation of the surface). A number of commercial preparations are available [28], [37], usually as solutions of mixed chlorosilanes (chiefly dimethyldichlorosilane) in a suitable solvent such as benzene or carbon tetrachloride. On contacting the glass surface the chlorosilanes are hydrolysed by the reactive hydroxy groups and any absorbed atmospheric water on the glass surface to form a water-repellent polysiloxane film. The coating is applied by momentarily immersing the glassware in the silicone solution and rinsing with benzene or carbon tetrachloride to remove the HCl formed. The vessels are then left to drain. It should be noted that same silicone fluids (e.g. methylhydrogensiloxane, which forms 0 very durable surface, but, unlike dimethyldichlorosilone, requires baking for 2 to 3 hours at 140 °C) contain Si-H bonds which can act as a reducing agent.

Water-repellent silicone coatings are necessary for glass pycnometers for which a hydrophobic surface is essential to prevent errors caused by the adherence of small droplets to the pycnometer tip [22]. In addition, silicone-treated glassware readily retains its state of cleanliness because the adhesion of many substances to glass is reduced. Further, solutions stored in silicone-treated glass remain relatively uncontaminated as leaching from the glass surface and dissolution of the glass it self are inhibited. However, the major advantage of silanization is that it prevents loss of activity from the solution to the vessel walls for most (but not all) radionuclides. Silicone coated glassware may be useful if it is necessary to store high specific activity (e.g. "carrier free") solutions, although many laboratories prefer polyethylene containers for this application. For radioactivity solution standards, however, the carrier concentration and chemical form of the solution are chosen to ensure that activity losses to clean untreated glass surfaces are negligible.

Some disadvantages of silanization are that the film may be removed to some extent by alkaline solutions and partially filled containers may suffer an impairment of the film at the line of the air-liquid interface after standing for some time. In addition, the procedure is time consuming and found to be unnecessary by many laboratories.

Of the cleaning procedures described in Annex 1, it should be noted that only Method III employing hydrofluoric acid will remove silicone surface films completely.

Annex 3. Preparation of Polyethylene Pycnometers

Equipment required

1. Small glass blowing torch or Bunsen burner—a hot flame is not desirable as polyethylene is quite soft at 100 °C. Neither is a wide flame desirable.

2. Forceps or tweezers.

Procedure

The plastic ampoules as received from the manufacturer have a capacity of 5 cm^3 and a wall thickness of about 0.75 mm. The neck of the ampoule is drawn out in much the same way as glass tubing. The base of the ampoule is held between the thumb and first two fingers and the opening at the neck is supported with forceps. The ampoule is held approximately horizontally over the flame and rotated slowly, heating the thick portion of the neck. Gradually most of the top 2 cm of the ampoule becomes transparent. Then the ampoule is removed from the flame and drawn out slowly to the desired length. (If it is drawn out quickly it will be pulled into two pieces). It is held taut until it regains its translucent appearance.

The capillary is allowed to harden and is then cut with the flame, sealing the end at the same time. It is good practice to apply at this stage a simple manual compression test for possible pinhole leaks. When required for use, the capillary is cut to length with a sharp blade. Typically the capillary dimensions might be 80 mm long, 0.5 mm internal diameter and 1.0 mm external diameter.

Annex 4. The Buoyancy Correction

It is well known that a correction for buoyancy is necessary whenever the mass of an object whose density differs from that of the balance weights is to be determined. The true mass, m, is related to the apparent mass, μ, by

$$m = \mu\left[1 + \rho_a\left(\frac{1}{\rho} - \frac{1}{\rho_w}\right)\right],$$

where ρ_a is the air density, ρ_w is the density of the weights and ρ that of the object weighed. In the case of the pycnometer technique the use of this equation is well justified since the evaporation rate from a well designed pycnometer is very small. Thus ρ_a is sensibly constant and equal to the ambient air density. It follows that, although two apparent masses of pycnometer plus solution are recorded ond the difference taken, the ρ in the above equation refers only to the solution which for most purposes can be assumed to be water. Thus the correction can be made with some certainty. However this is not necessarily the case for the extrapolation technique where the density of the air surrounding the source mount may vary as the drop evaporates.

The calibration of a set of weights is often given in terms of mosses of hypothetical weight pieces of density $8.0\ \mathrm{gcm^{-3}}$ which would balance the members of the set in air of density $0.0012\ \mathrm{gcm^{-3}}$. The calibrated set can then be regarded as a set of masses each member of which has a density of $8.0\ \mathrm{gcm^{-3}}$. An alternative convention, common in some countries, is the 8.4/0.0012 basis, i.e. masses of assumed density $8.4\ \mathrm{gcm^{-3}}$ weighed in air of density $0.0012\ \mathrm{gcm^{-3}}$. Since it is unlikely that the weights have a density of exactly $8.0\ \mathrm{gcm^{-3}}$ (or $8.4\ \mathrm{gcm^{-3}}$ as the case may be) it follows that a further correction is necessary when weighing in air of density other than $0.0012\ \mathrm{gcm^{-3}}$. Thus the above equation becomes [38]

$$m = \mu\left[1 + \rho_a\left(\frac{1}{\rho} - \frac{1}{\rho_{w_t}}\right) + \left(\frac{1}{\rho_{w_t}} - \frac{1}{\rho_{w_a}}\right)0.0012\ \mathrm{gcm^{-3}}\right],$$

where ρ_{w_a} is the density of the weights assumed by the laboratory calibrating the set of weights and ρ_{w_t} is the true density of the weights. The last term in the square brackets is small, being about 1.2×10^{-5} for $\rho_{w_a} = 8.4\ \mathrm{gcm^{-3}}$ and $\rho_{w_t} = 7.76\ \mathrm{gcm^{-3}}$, as compared with the second term which is about 10^{-3} for aqueous samples. For measurements in air of density $\rho_a = 0.0012\ \mathrm{gcm^{-3}}$ the equation becomes

$$m = \mu\left[1 + \left(\frac{1}{\rho_{w_t}} - \frac{1}{\rho_{w_a}}\right)0.0012\ \mathrm{gcm^{-3}}\right].$$

The density of air in $\mathrm{mg/cm^3}$ as a function of pressure, temperature and humidity is given by

$$\rho_a = \frac{273.15\ \mathrm{K}}{T}\left[\frac{B - 0.3783\ p}{760\ \mathrm{mm}}\right]1.2929\ \mathrm{mg/cm^3},$$

where B is the barometric pressure in mm Hg, T is the absolute temperature in kelvin and p is the vapour pressure of water in air in mm Hg. A convenient chart for the buoyancy correction as a function of air pressure and temperature has been published; the authors point out that,

for aqueous samples, the error introduced by neglecting humidity is small [39]. The chart is based on an assumed density for the balance weights of 8.4 gcm^{-3}, but, as indicated above, the error introduced by using the charts in conjunction with weights of density 8.0 gcm^{-3} is small and may be neglected for most purposes.

Annex 5. Ionization Chamber Measurements

A review of ionization chamber techniques is beyond the scope of this monograph but because of the usefulness of ionization chamber measurements in checking weighings it is worth recording a few salient points. A recent survey of ionization chamber techniques ma y be found in reference [40].

The most useful type of instrument for this purpose is a well-type chamber often coiled a " $4\pi\gamma$" ionization chamber and which is frequently operated at several atmospheres pressure in order to increase the sensitivity. Typically this sensitivity may be several picoamperes per microcurie of ^{60}Co. Strictly, for the present purpose the chamber need not be calibrated in terms of ionization current per unit activity but such a calibration is a very desirable feature in that a rapid assay of the activity of a sample of a given radionuclide may be made. Further, the advantages of a calibrated ionization chamber in maintain in standards of activity ha ve been stressed on many occasions [41], [42]. An ionization chamber can compare ratios of activity (for the same γ-ray emitting nuclide) with a standard error of the mean of better than $\pm 0.1\%$; with care a precision of $\pm 0.02\%$ can be achieved in favourable cases.

The ampoule wall thickness and glass composition must be sufficiently reproducible from ampoule to ampoule so that any variation in γ-ray attenuation does not add significantly to the variance of the measurements. For the same reason the ampoules should be filled, if necessary, by the addition of inactive solution to a constant height. Although the use of the so-called 4π geometry makes source positioning less critical it is nevertheless necessary to examine the chamber for maximum response and to ensure that ampoules are positioned at this optimum point in a reproducible way. Care must be taken to ensure that the activity be kept below such levels that the response, as a function of activity, does not depart significantly from linearity.

The constancy of the ampoule wall thickness and glass composition can be tested by means of a point source of low energy γ-rays mounted on the end of a thin dip stick. The latter should be mounted in such a way that the source is at the centre of the ampoule to be tested; the ampoule is then positioned in a re-entrant ionization chamber and the ionization current noted. About 2 mCi of ^{241}Am, encapsulated at the end of a thin nickel tube, makes a convenient dip stick source. The principal electromagnetic radiation is a γ-ray of 60 keV for which the attenuation of the glass wall of the ampoule is appreciable and hence the method is rather sensitive. For a series of ampoules whose wall thickness is specified as being within ± 0.1 mm such ionization current measurements should be constant to within $\pm 0.12\%$ (standard deviation). This implies that, for ^{60}C radiation, the uncertainty due to wall attenuation is not greater than $\pm 0.03\%$. However for some radionuclides, for example ^{125}I, it may be desirable to select ampoules in order to obtain even better uniformity.

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