



## Chapter 10

### ASSESSMENT OF GAMMA, BETA AND ALPHA-PARTICLE-EMITTING NUCLIDES IN MARINE SAMPLES

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#### Abstract

Depending on the physical properties of radionuclides different systems must be used for their measurement. Most convenient is if gamma spectrometry can be used by germanium, Silicon or Scintillation detectors (eg. NaI). If, however, the main emission consists of beta or alpha particles or low-energy photons as is the case for radionuclides decaying by electron capture, radiochemical separation and specific source preparations must be undertaken. In such cases also the radiochemical yield must be determined. The radiochemical part mainly follows the lines presented by prof. T. Jaakkola, Department of Radiochemistry, Helsinki, Finland, at a course in radioecology in Lund, 1991. For very long-lived radionuclides other methods such as mass spectrometry are superior although often associated with sophisticated expensive instrumentation.

#### 10.1 Gammaemitters

##### 10.1.1 Detectors

Different types of detectors for gamma spectrometry can be used. Today mainly Germanium or high-pure germanium detectors are used but also sodium iodide (NaI) detectors are still in use at many laboratories. Also the silicon detector is an important instrument for gamma spectrometry. The germanium detectors are available in different configurations depending on radionuclides and concentrations. The most common types are cylindrical, planar and well-type detectors. The advantage with Ge detectors compared to NaI is the high energy resolution of the former improving the possibility to measure several radionuclides at the same time without interference (see Fig. 1). The drawback is that they are more expensive and need liquid nitrogen (77° K) or electric cooling under operation.

Well type detectors have higher efficiencies (about a factor of 6 for <sup>137</sup>Cs compared to a cylindrical detector) but sample volumes are limited to a few ml and for certain radionuclides there are problems with coincidence effects i.e photons emitted in cascades interact simultaneously and a peak corresponding to the sum is obtained making calibration more difficult.

The Si detector has a better resolution than the Ge detector but has lower efficiency for medium and high energy gamma rays and is mainly used for low energy gamma spectrometry, X-ray fluorescence and proton induced x ray fluorescence.

There are other types of detectors for gamma spectrometry but these are not important for a normal laboratory working in the field of environmental radioecology. For a more complete description of gamma spectrometry and the function of the detectors, is advised to read the books by Knoll (1) and Debertin(2) on this topic.

If the detector is cooled by liquid nitrogen it is mounted onto a cooling finger which goes into an insulated dewar filled with liquid nitrogen. The cooling finger can have different configurations depending on the purpose of the measurement and the type of the detector such as a the special low-level detector used for field gamma spectrometry (see Fig.2).

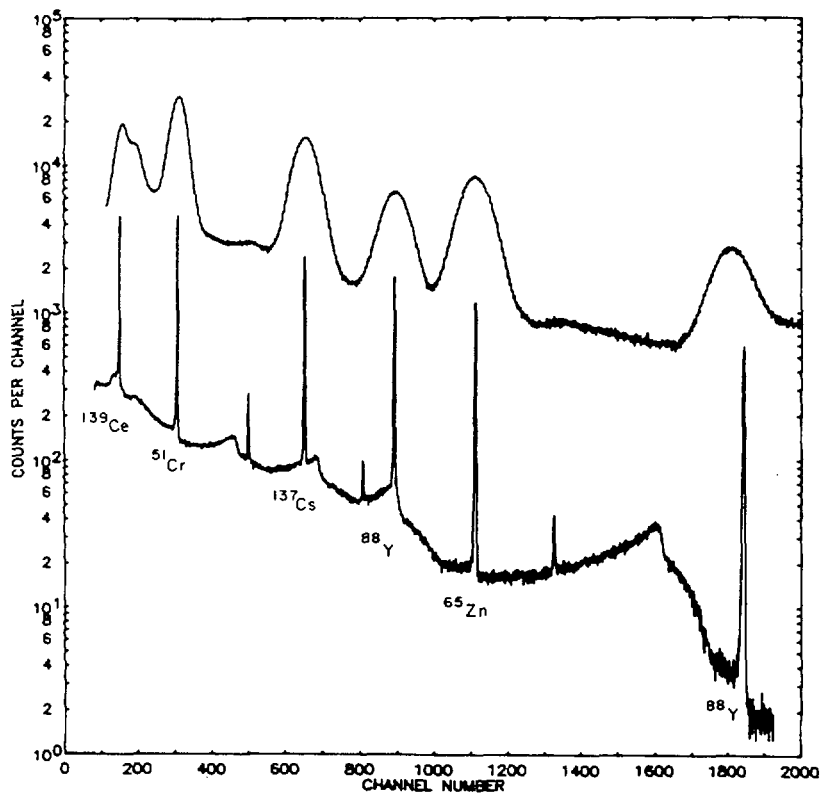


Fig. 1. Comparative pulse height spectra recorded using a NaI crystal and a Ge(Li) detector.

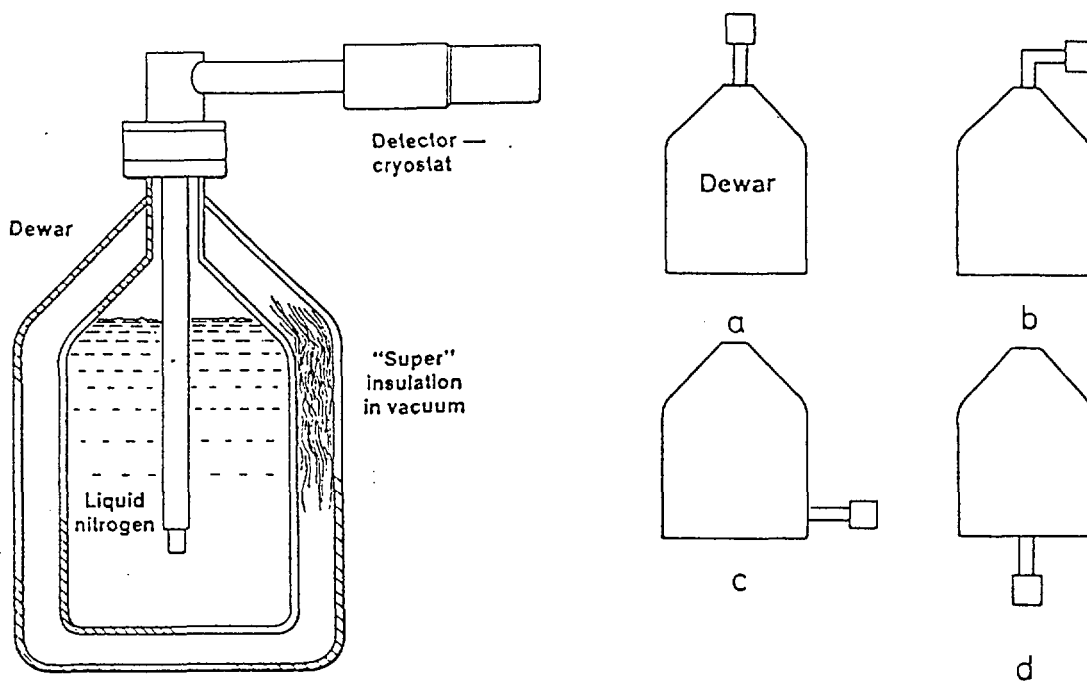


Fig. 2. Possible mounting configurations for semiconductor detectors, a) vertical, b) horizontal, c) side view d) top and transect view of a dewar.

The detector is normally under laboratory use shielded with about 10 cm lead and a lining of copper to reduce background (cosmic ray, radioactivity from building material, radon) and x-ray emissions from the lead shielding material.

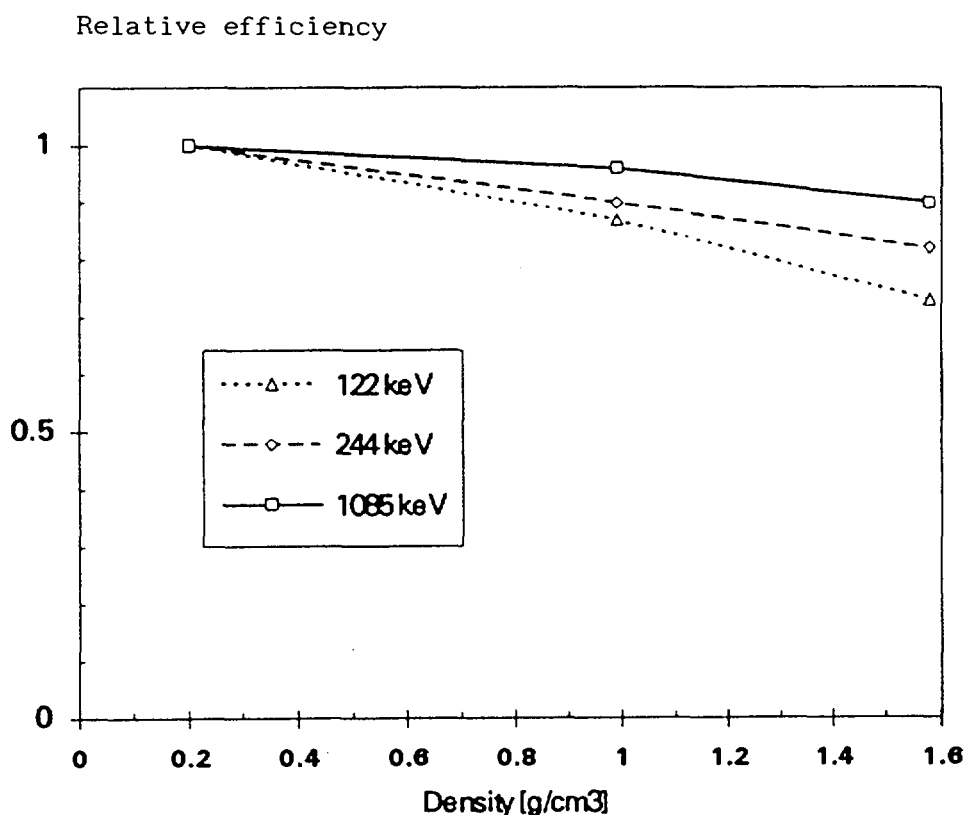


Fig.3. Relative efficiency for different sample densities measured by a Ge detector with 15% relative efficiency.

### 10.1.2 Calibration

For quantitative gamma spectrometric measurements it is necessary to know the full energy peak efficiency of the detector in the measuring geometry. Two fundamentally different ways to determine the efficiency are available, theoretically by the means of Monte-Carlo calculations or numerical integration, or by the means of preparing a calibration sample.

For *in situ* gamma-ray spectrometry and for samples with great physical extent a combination of the two methods is often used. For this case we refer to the description by Bjurman (3).

Radioecological studies mostly concern samples with low radionuclide concentrations where high full energy peak efficiencies and thereby close sample to detector geometry are employed. For uptake studies higher concentrations are normally used and the detector size can be smaller. Both cases will introduce special problems such as nuclide specific coincidence effects and high sensibility to uneven distribution.

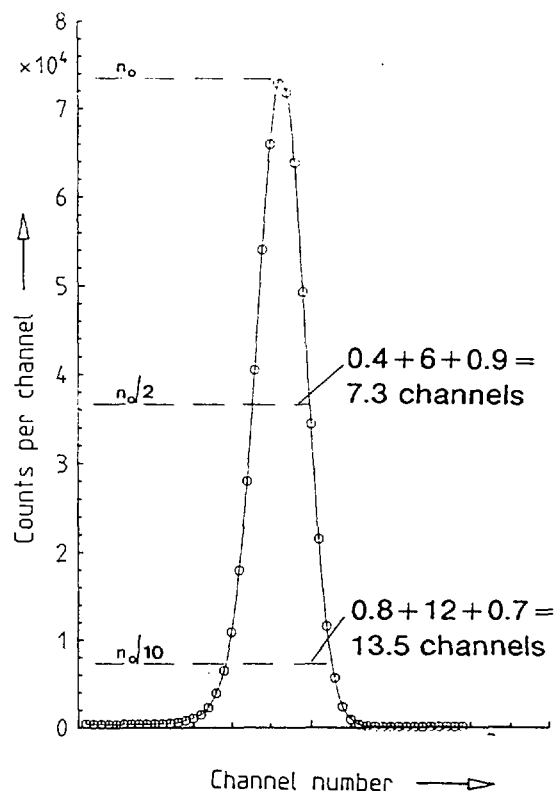


Fig. 4 Pulse-height distribution demonstrating the determination of FWHM and FWIM.

In most laboratories plastic tubes with volumes between 50 and 300 ml volumes are used. For lower energies, the attenuation in the sample itself is also considerable, and a change in the density of  $0.5 \text{ g cm}^{-3}$  will change the efficiency by up to 10% (Fig.3). If a geometry is calibrated for three densities between 0.2 and  $1.0 \text{ g cm}^{-3}$ , the uncertainty in measured radionuclide concentration can be kept to less than 3% for most environmental samples.

Radionuclide specific coincidence effects due to cascade gamma-rays can, in close geometries, cause systematic errors of up to 40%, and this effect can therefore be the dominating uncertainty in low-level radionuclide concentration measurements. The coincidence effect is highly geometry dependent. The radionuclide coincidence must not be misinterpreted with the coincidence effect due to a high count rate. Even if no sum-peaks are found in the spectra the coincidence effect can be substantial, since full energy peak pulses are lost with a higher probability due to summing with Compton pulses from other cascade gamma-rays than the summing of two full energy pulses.

For the efficiency calibration of high resolution gamma-ray detectors it is recommendable to use radionuclides with as little cascade gamma-rays as possible. Some years ago it was common to use  $^{152}\text{Eu}$  for calibration purposes.  $^{152}\text{Eu}$  will however give rise to coincidence effects.

Most methods today are based on commercially available well-calibrated standard solutions with overall uncertainties between 1.5 and 5%. This standard solution is then diluted in an acid with suitable carriers to minimize losses on the wall of the flask. In Table 1 is given examples of radionuclides suitable for the efficiency calibration of Ge-detectors.

The diluted solution can be used directly in a measuring beaker, or dripped onto and mixed with a matrix material. The overall uncertainty of the activity in a calibration sample produced is not likely to be better than  $\pm 4\%$ .

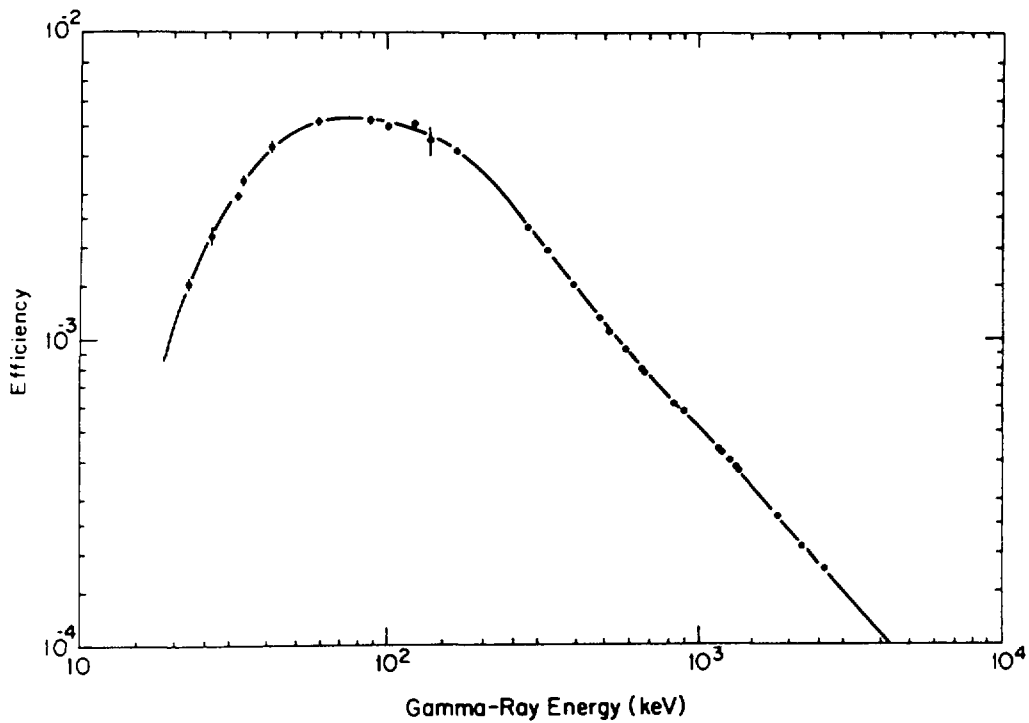


Fig. 5. Example of full-energy-peak efficiency as a function of the photon energy for a Ge(Li) detector.

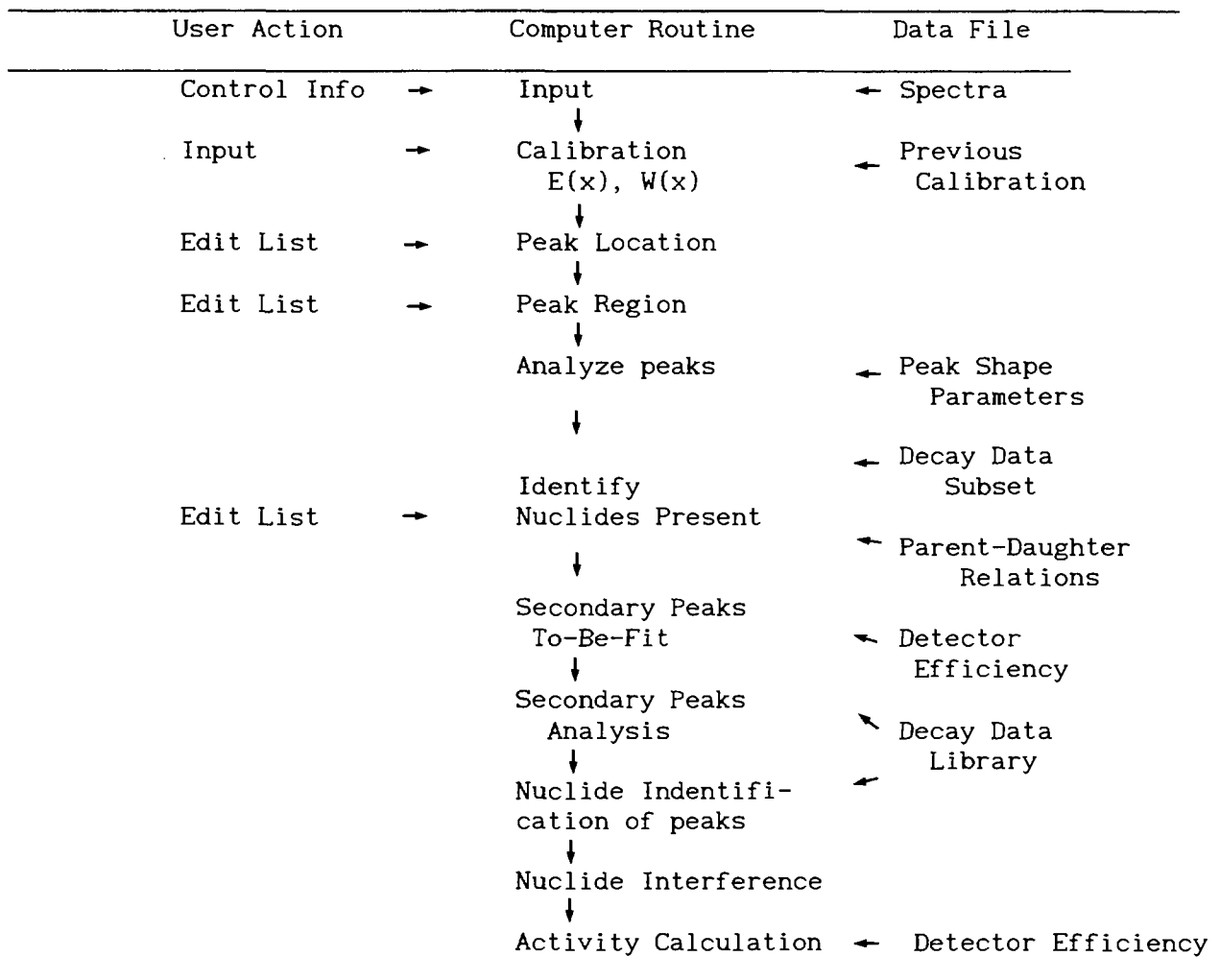


Fig. 6. Flowchart of program for evaluation of gamma spectra

Another calibration procedure is based on sorbtion of a multi radionuclide solution onto mixed cation and anion exchange resin which is and homogenized. There is then no strict demand on knowing the activity of the mixed solution. A fraction of the mixed exchange resin is the calibrated against a reference source at a relatively great distance from the detector (3).

### 10.1.3 Evaluation of data

The principal task in gamma and x-ray spectrometry is the analysis of the peaks in pulse-height spectra that correspond to full-energy absorbtion of events. This can simply be done by hand when only one or a couple of energies/radionuclides are of interest. A reference material/standard source is used and background is taken as a mean of a selected number of channels below and above the peak of interest. Important parameters for the performance of a gamma spectrometer are FWHM(Full Width at Half Maximum) and FWTM (Full Width at one Tenth Maximum) (see Fig. 4)

Often spectra are complex with many full energy peaks and peaks overlapping each other. Although it is possible to make evaluation by hand, it is too time consuming and several computer-based programmes are now available for the evaluations/calculations. Such programmes take into account the full energy-peak efficiency as a function of the photon energy (see Fig. 5). The programme contains a library with possible radionuclides, their energy emissions and emission probability and the geometry in which the sample was measured. It can also directly take into account density corrections and coincidence effects. The result can be given as Bq kg<sup>-1</sup> at any desired time, mostly the time of collection taking decay into account. In the early phase of the Chernobyl accident the situation was very complex and no commercial available programmes could completely master hundreds of full energy peaks, build-up of daughter products and decay of short-lived radionuclides during counting. In Figure. 6 a flow chart of a programme for the evaluation of gamma pulse height distribution is shown.

## 10.2. General radiochemistry

For the assessment of alpha and beta emitters in environmental materials, radiochemical separation and specific source preparation is generally necessary. Also if the concentration of gamma emitting radionuclides is very low, radiochemical procedures are required to concentrate these radionuclides from large volume water samples. Gamma emitters are also generally beta emitters at the same time. The counting techniques for beta emitters is, in principle, much more sensitive than gamma spectrometry techniques. For example a radiochemical separation permits the determination lower levels of <sup>137</sup>Cs and <sup>60</sup>Co at much lower levels. A general description of radiochemical separations is given by Jaakkola (4).

The special features of radiochemical analysis compared to conventional analytical chemistry are a) the amounts of radionuclides to be handled are small, 10<sup>-12</sup>-10<sup>-18</sup> g, b) the decay of radionuclides, c) the effect of radiation, d) high decontamination factor required, e) source preparation for assay, f) the possibility for radiochemical yield determination and g) the use of carriers. Concentrations are often in the order of 10<sup>-11</sup>-10<sup>-16</sup> M and it is obvious that the chemical behaviour may be different than at higher concentrations

### 10.2.2 Adsorption

Solutes in contact with surfaces have a tendency to be sorbed to them. In order to cover the glass surface of a one liter vessel, only 10<sup>-8</sup> moles are required and in principle all the radioactive atoms present in a

sample could be adsorbed on the walls of the vessel. In general adsorption increases with ionic charge in the order  $M^+ < M^{2+} < M^{3+} < M^{4+}$ . For adsorption the importance of the nature of the surface is such that platinum < silver < stainless steel < polyvinylchloride. Addition of isotopic carrier dilutes the radiotracer and a smaller fraction of tracer is adsorbed. Radioactive species also frequently adsorb on precipitates. The nature of the precipitate as well as precipitation procedure are major factors in the amount of adsorption that occurs.

Losses due to adsorption can be decreased by a) maintaining a high acid concentration, b) using complex forming agents, c) avoiding fine-divided precipitations with large surface, d) avoiding storage of dilute solutions, e) adding carriers.

### 10.2.3 Carriers

Chemical operations with small amounts of radioactive materials are often greatly facilitated by diluting the radionuclides with isotopic or chemically similar material. The added material is called carrier. As an example stable sodium acts as carrier for radiosodium and barium for radium increasing the weight of material to  $10^{-2}$  g instead of  $10^{-15}$  g. The carrier reduces the specific activity and the amounts should not be unnecessary large.

The carrier provides sufficient weight of material to form a precipitate from aqueous solution or collect the radioactive material as a precipitate in the distillation processes. The carrier also prevents losses of radioactive material by adsorption. In addition the carrier can make it possible to determine the chemical yield. The known amount of carrier added from the beginning will end up as a known compound and the chemical yield can be determined gravimetrically or by other methods such as AAS.

### 10.2.4 Hold-back carrier

By precipitation or solvent extraction carriers may be added to unwanted species. For example separating  $^{140}\text{La}$  from  $^{140}\text{Ba}$  can be done by lanthanum fluoride precipitation. Both lanthanum and barium carriers are added and the former makes it possible to form the precipitate. The barium is a competitive carrier which reduces the adsorption of  $^{140}\text{Ba}$  on the precipitate.

### 10.2.5. Scavengers

Another feature of many radiochemical purification procedures is the formation of precipitates such as ferric hydroxide which adsorb and occlude other substances from solutions. They are called scavengers. The precipitate leaves behind radioactive elements for which hold-back carriers

have been added. Electropositive cations such as caesium also remain behind.

### 10.2.6 Holding oxidants and reductants

Holding oxidants and reductants are used when a radiotracer exists in several valency states, and it is desired to hold it in one particular oxidation state during separation. For example plutonium can be held in the reduced +3 oxidation state and neptunium in the +IV oxidation state with iodine. Uranium is held in the easily oxidised IV-state with small quantities of iron(II) and technetium in the reduced +IV state with sodium disulfite. Neptunium can be held in the VI-state with bromate or persulphate as oxidant.

### 10.2.6 Isotopic exchange

One must obtain an exchange equilibrium between the added isotopic carrier and the radioactive isotope. The carrier is added to the solution in

the form of some compound and the radioactive isotope may be present in a form of different valency, but for obtaining a correct result complete isotopic exchange must have taken place.

The rate of isotopic exchange may be expressed as

$$t_{1/2} = \frac{a b}{(a+b)} \ln 2$$

where a and b are the numbers of molecules in unit volume and R is the exchange velocity constant, which depends on the reaction, the concentration of the components and the presence of other substances. The half exchange time can vary from seconds to days. A cycle of reducing and oxidation reactions is normally an effective way to achieve isotopic equilibrium.

#### 10.2.7 Separation methods

Co-precipitation is a process in which a tracer ion is carried by another precipitate when the concentration is too low for it to be precipitated on its own. Co-precipitation occurs if the compound of the tracer and the oppositely charged ion of the precipitate are isomorphous with the precipitate tracer in solution. In these cases the active ion may be included

As examples can be given ferric hydroxide for separating trace yttrium from strontium. Precipitation of Sr and Ba from strong (70%) nitric acid solution. Precipitation of the lanthanide (III) fraction from dilute  $\text{HNO}_3$  solution as  $\text{LaF}_3$  which can also be used for separating oxidation states of plutonium from aqueous samples. Plutonium in oxidation states (III) and (IV) is coprecipitated with  $\text{LaF}_3$  while plutonium in higher oxidation states (V) and (VI) stay in and decay of short-lived radionuclides during counting.

#### 2.8 Liquid-liquid extraction

Liquid-liquid or solvent extraction plays a very important role in radiochemistry. The method is simple and fast, the risk for contamination is low and it has a wide applicability. It also has a high selectivity and the method is easy to automate.

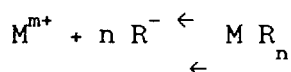
Solvent extraction selectively transfers species from a mixture in an aqueous solution to an organic phase by equilibrating the organic phase with an organic solvent. The distribution ratio is described as:

$D = \text{Total concentration in organic phase} / \text{Total concentration in aqueous phase.}$

The percentage extraction is

$$\% E = \frac{100 D}{D + (V_w / V_o)}$$

The formation of an uncharged species for extraction into organic solvents is written as:



Two different types of extraction, chelate and ion association extraction are employed.



### 10.2.9 Ion exchange

Solid organic resin ion-exchangers consist of organic polymeric networks containing basic or acidic groups attached to the organic lattice. For the acidic cation exchangers the overall exchange process takes place according to the equation:

$$K_{\text{dex}} = \frac{(\text{MR})_{\text{resin}} (\text{H}^+)_{\text{aq}}^n}{(\text{M}^{n+})_{\text{aq}} (\text{RH})_{\text{resin}}^n}$$

The equilibrium constant depends on the specific properties of the ion exchange material, such as the amount of cross linking of the polymeric network as well as the nature of the metallic ion, ion strength of the solution, temperature etc. The sorption on the resin increases with the valency of the cation.

In practice the radioactivity is sorbed on the top layer of the column containing the ion exchange resin in cationic or anionic form. Following sorption, it is eluted by passing a solution (eluant) through the column.

### 10.2.10 Distillation

Elements can also be separated depending on their volatility. The halogens can be distilled in the elemental state; fluorine as hydrofluoric acid, ruthenium, osmium, manganese and technetium as the higher oxides, and chromium as chromyl chloride. The following elements can be distilled as halides: As, Sb, Sn, Re, Hg and Ge.

### 10.2.11 Electrodeposition

Electrodeposition techniques have mainly been used for preparing thin sources for counting alpha emitters rather than separation by controlled potential deposition. Electrodeposition can for example be performed in oxalate solution, sulphate solution at pH 2-3, or in mineral acid-alcohol solutions.

Spontaneous electrodeposition is used as a final step in the separation of polonium. Electrodeposition of metals may be sensitive to the presence of other substances.

## 10.3. Assessment of beta emitters

### 10.3.1 Preparation of suitable sources for various measurement procedures

Samples of water, air and biota require different sampling, concentration and homogenization procedures for further treatment. Some elements or compounds are volatile, so that evaporation, drying and ashing may be difficult.

The  $\beta$ -particles emitted are not mono-energetic as is the case for conversion electrons. Most counting devices are also constructed with little or no energy resolution. A radio-chemical procedure involving precipitation, ion exchange, and/or liquid-liquid extraction for separating the elements is generally required before source preparation. In this case a radio-chemical yield determinant is necessary. This can be accomplished with, for example,  $^{99}\text{Tc}^m$  for  $^{99}\text{Tc}$  ( $E(\beta^{\text{max}})=292$  keV), stable cesium for  $^{137}\text{Cs}$  ( $E(\beta^{\text{max}})=514$  keV)

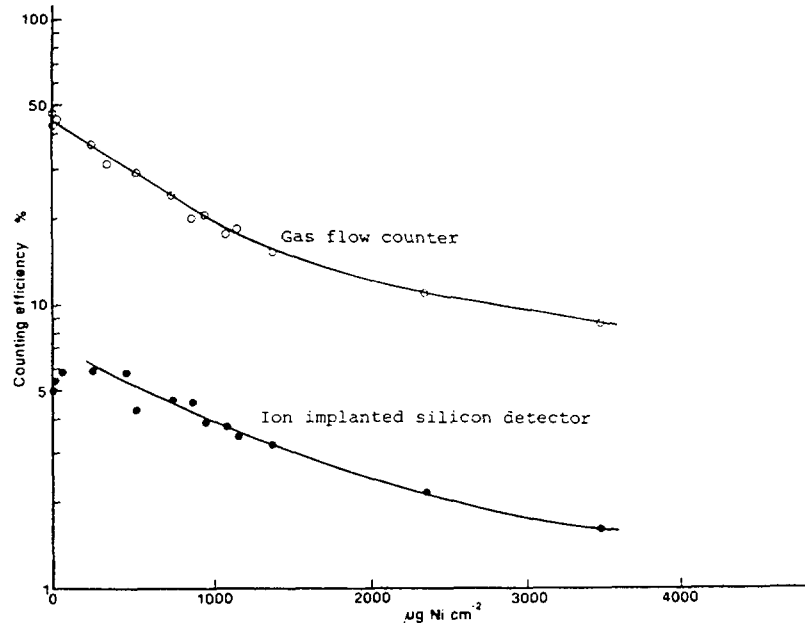


Fig. 7 Efficiency calibration for  $^{63}\text{Ni}$  in an open gas flow counter and ion implanted silicon detector for different amounts of stable nickel in the source ( From Holm et al., 1990).

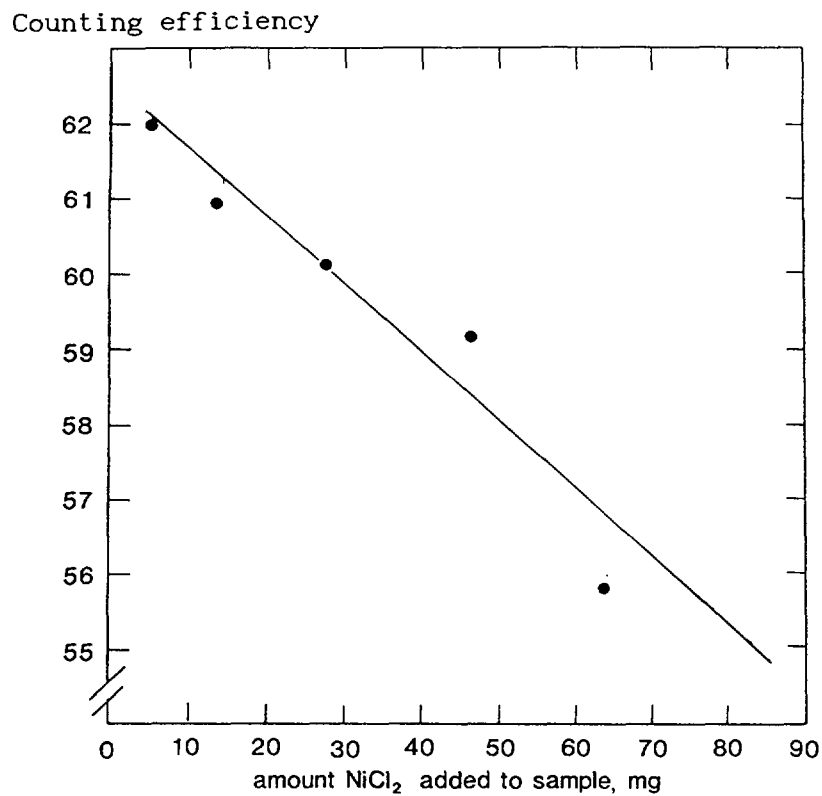


Fig. 8 Counting efficiency as a function of  $\text{NiCl}_2$  concentration in liquid scintillation counting.

and stable nickel for  $^{63}\text{Ni}$  ( $E(\beta^{\text{max}})=67$  keV). Cesium-137 can be measured with  $\gamma$  spectrometry, but the sensitivity of the radio-chemical separation followed by  $\beta$  counting is better and is still sometimes applied at very low concentrations.

### 10.3.2 Sources for liquid scintillation counting

Radionuclides which emit low-energy particles can best be measured by liquid scintillation. A good example is  $^{14}\text{C}$  which very often is measured as the  $\text{CO}_2$  gas in a solution thus giving a carbonate which can be dissolved in toluene. A good trap for  $\text{CO}_2$  is fenylethylamine. Carbon dioxide can be directly trapped into the scintillation liquid where fenylethylamine has been added. Apart from fenylethylamine a scintillation solution may consist of methanol, toluene, PPO (2, 5-difenyloxasol), and POPOP (1,4-di-(2-(5-fenyloxasylol))-benzene).

For water solutions the source preparation is usually made as an emulsion of water in toluene. For example Triton X-100 (iso-octylfenoxypolyethoxy-ethanol) can be used. As little water as possible should be used in order to obtain small water drops to minimize self-absorption.

Biological samples are either dissolved in a secondary solvent (salt of ammonium) or ashed, in which case  $\text{H}_2\text{O}$  and  $\text{CO}_2$  can be trapped ( $^3\text{H}$  and  $^{14}\text{C}$  measurement). For heterogeneous samples which cannot be dissolved, a solution can be simulated by a gel which is liquid when agitated and otherwise solid (Carb-O-Sil, or Instagel).

Also filter papers and electroplated samples can be placed on the bottom of the scintillation vial and the scintillation solution added. Different vials are used for liquid scintillation counting. There are certain requirements for these: (a) they should not be affected by the samples or the scintillation solution, (b) transmission of the scintillation light should be good, (c) natural and induced background should be low, and (d) vials should be temperature independent and e) cost should be low. The vials are mostly made of glass or polyethylene. Polyethylene vials give a lower background but they are more easily affected by scintillation liquid.

### 10.3.3 Sources for gas multiplication detectors

Measurement with GM or proportional counters are common at higher  $\beta$ -particle energies. The main advantages are that the background is lower and counting efficiency is less variable from sample to sample than with liquid scintillation counters. The source preparation is often electrodeposition or evaporation, both of which give rather homogeneous and thin sources. Some kind of specific precipitation is also common, e.g., copper sulfide for  $^{99}\text{Tc}$ , strontium carbonate for  $^{90}\text{Sr}$ , yttrium oxalate for  $^{90}\text{Y}$ , cesium chloroplatinate for  $^{137}\text{Cs}$ , and nickel dimethylglyoxime complex for  $^{63}\text{Ni}$ . These sources can be rather thick and calibration and correction for self-absorption in the sample must be performed. If significant quantities of a stable element are added, the counting efficiency by gas counters will decrease with increased radio-chemical yield due to increased attenuation of the  $\beta$ -particles (eg Fig. 7) The same is true if liquid scintillation counting is applied, due to increased quenching as shown in Fig. 8. The sources are often covered, for example, with a Mylar foil. Beta-particle absorption in this foil will reduce the counting efficiency for low- $\beta$ -energy radionuclides.

#### 10.3.4 Liquid Scintillation counting of beta emitters

Good performance of liquid scintillation counting results because the counter is windowless and the geometric counting efficiency is almost  $4\pi$ . This means that there is a high probability of counting the low-energy  $\beta$ -particles emitted. The amplification system of a liquid scintillation counter can be either linear or logarithmic. With logarithmic amplification a large energy range can be covered. The linearly amplified spectra of three different  $\beta$  emitters are shown in Fig. 9.

##### 10.3.4.1 Solvent

Solvents should (a) effectively transfer their excitation energy to the scintillator, (b) be transparent for the scintillation light, (c) be chemically stable and unaffected by the presence of the scintillator, (d) be temperature independent, and (e) be able to dissolve the radioactive sample.

Several solvents such as toluene, benzene, and 1,2,4,-tri-methylbenzene fulfill most of these requirements, however, their ability to dissolve the sample is limited. A secondary solvent can be used. However, this can reduce the light exchange and the pulse height.

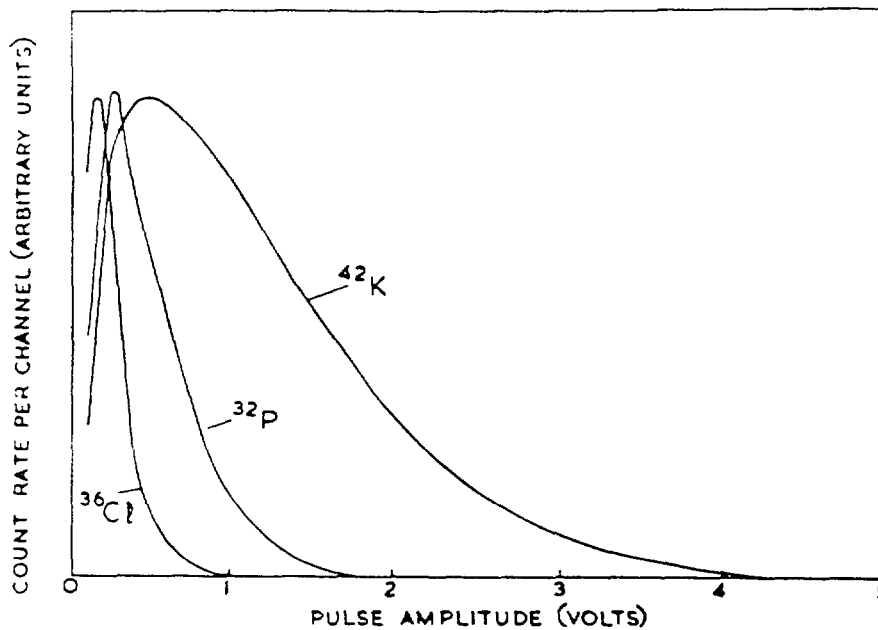


Fig. 9 Pulse-height spectra obtained from liquid scintillation counting with alkali PM tubes for  $^{36}\text{Cl}$ ,  $^{32}\text{P}$ , and  $^{42}\text{K}$  ( $E(\beta)^{\text{max}} = 0.71, 1.71, \text{ and } 3.6 \text{ MeV}$ , respectively).

##### 10.3.4.2 Scintillator

For the scintillator the following requirements must be met: (a) the probability to emit a light photon at excitation should be large, (b) the emitted photon should have a wavelength matching the maximal sensitivity of the photo cathode, (c) it must be chemically stable and not change the characteristics of the solvent, and (d) it must display minimal self-sorption of the scintillator light.

There are a number of such scintillators and they are all aromatic hydrocarbons. Examples such as PPO and POPOP were mentioned earlier; POPOP is a secondary scintillator, which is used to obtain a wavelength of emitted light for which the photo cathode is more sensitive, as well as to decrease the effect of colored samples. The absorption spectrum of the secondary scintillator must closely match the emission spectrum of the primary scintillator.

#### 10.3.4.3 Quenching

There are processes which result in a decrease of the maximal counting efficiency. If the sample is not in solution but consists of small particles, part of the  $\beta$ -particle energy will be absorbed in the sample. This is most important for low-energy  $\beta$  particles such as those from  $^3\text{H}$ .

When a secondary solvent is used, excitation energy can be lost if the secondary solvent cannot transfer energy. This chemical quenching causes energy to be transferred to molecules other than the scintillator. Examples of strongly quenching substances are nitrates and iodides. Optical quenching occurs if the sample is colored or contains light-absorbing particles. The pulse height decreases because of quenching, resulting in an increase of the minimum detectable energy. This means that the counting efficiency decreases for  $\beta$ -particle emitters. Correction for quenching is often necessary since the counting efficiency may vary among samples, cf. Fig. 2. This can be done by (1) use of an internal standard, (2) sample-channels ratio, (3) external-standard gross count, or (4) external-standard channels ratio.

The method using an internal standard means that a known activity of the same radionuclide is added and the measurement repeated. The counting efficiency of each individual sample can then be calculated. With quenching, a shift of the pulse-height distribution is obtained. The channel-ratio correction method implies that the sample is measured in two pulse-height channels. From this ratio and a calibration of the pulse-height shift, the counting efficiency can be calculated. A  $\gamma$ -emitting radionuclide is used in the external-standard correction method. Interaction will produce electrons which give excitation light. The counting efficiency for the external standard changes with volume of scintillation solution and geometrical changes. These problems can be solved by use of the external-channels ratio. For further details the reader is referred to the work of Horrocs (5).

#### 10.3.4.4 Background

Thermal noise from the photo multipliers is a source of background. This is, to a great extent, eliminated by coincidence connection of the photo multipliers. Radioactivity in scintillator vials and other construction material, as well as natural radioactivity and other radiation sources close to the apparatus, may also contribute to the background. To reduce the contribution from external sources the photomultipliers and scintillator are shielded with lead. The chemoluminescence decreases with time after initiation of the reaction, thus the background will not be constant. Hydrogen peroxide and strongly alkaline substances often give chemoluminescence. The sample has to be stored in darkness for more than 24 h to eliminate chemiluminescence and light induced phosphorescence.

#### 10.3.5. Counting beta emitters with plastic scintillators

Plastic scintillators coupled to one or several PM tubes can be used for  $\alpha$ ,  $\beta$ , and  $\gamma$  counting. A coarse spectrometric resolution is obtained; the conversion electrons of some radionuclides may be displayed this way. A disadvantage of plastic scintillators is their relatively high background.

### 3.6 Assessment of beta emitters by gas multiplication detectors

Gas multiplication detectors operate in either the proportional or the GM region, often with a continuous flow of counting gas. The advantage with a continuous gas flow is that the consumption of quenching gas does not limit the lifetime of the detector. A guard detector which operates in anti coincidence with the main detector may be used, as well as shielding around the detectors, to reduce background counts. The source is placed close to the window which consists of Mylar film ( $0.1 - 1 \text{ mg cm}^{-2}$ ).

At very low  $\beta$  energies the window will reduce the counting efficiency. The source (depending on detector construction) can also be placed inside the detector, and it is then possible to reduce the low-energy limit to 250 eV. This is lower than that which is possible with semiconductors or scintillation detectors. Frequently used gases are 90% argon + 10% methane or 96% helium + 4% isobutane for proportional counters, and 99% helium or argon + 1% isobutane for continuous gas-flow GM counters. Bromide can be added as quenching gas for noncontinuous gas-flow counters. The background is on the order of  $0.005 \text{ s}^{-1}$  for a 2.5-cm-diameter window and a counting efficiency  $\geq 40\%$ . Variable backscattering from the source mount caused by use of different materials must be corrected for. Due to backscatter from the source supporting material, a higher counting efficiency than that given by the geometrical conditions may be obtained. The background will be due to surrounding materials and sources, but also to radionuclides in the construction materials of the detector device. If a radio chemical procedure is involved, the reagents can also contribute to the background. Variation in counting efficiency can occur for thick sources. Thus the experimental conditions must be maintained as constant and reproducible as possible.

As stated previously, great care must be taken to ensure that only the desired radionuclide is counted. Elimination of different nuclides likely to be present must be tested in the radiochemical procedure. Sources can be recounted after some time to see if any short-lived radionuclides were present at the initially performed counting. Pure  $\beta$ - emitters such as  $^{99}\text{Tc}$ ,  $^{90}\text{Sr}$  and  $^{63}\text{Ni}$  are measured advantageously with the detectors described. Proportional counters offer an advantage over GM counters in that one can test by spectrometry if the maximal  $\beta$  energy corresponds to that of the radionuclide measured.

Gas multiplication detectors may be employed in the assay of gaseous sources such as  $^3\text{H}$ ,  $^{14}\text{C}$ , or  $^{133}\text{Xe}$  by introducing the radioactive gas directly into the detector together with a suitable counting gas. Such counters are generally constructed with a cylindrical cathode and an axial wire as an anode. Internal-gas counting is a  $4\pi$  method which avoids problems of source self-sorption.

#### 10.3.7 Assessment of beta emitters by semiconductor detectors

Semiconductor detectors can be used for measurement of  $\beta$ -particle emitters in environmental samples. The good energy resolution makes counting of conversion electrons an attractive approach. Si(Li) detectors can be used but must be cooled with liquid nitrogen. In addition detector sizes are small, geometrical conditions are unfavorable, and the counting efficiency is low. It is more convenient to use a silicon surface-barrier detector, junction silicon detector, or an ion-impacted silicon detector, such as are normally used for  $\alpha$ -particle spectrometry or spectrometry of other heavy charged particles. Different detector sizes and depletion depths are available.

Such a counting system will be inexpensive and easy to use. The background is approximately the order of  $0.05 \text{ s}^{-1}$  (30-300 keV) and the counting efficiency is about 25%. The background is, to a large extent, due to the construction material and thermal noise of the detectors. Special low-noise and low-background detectors of a given material are available. In

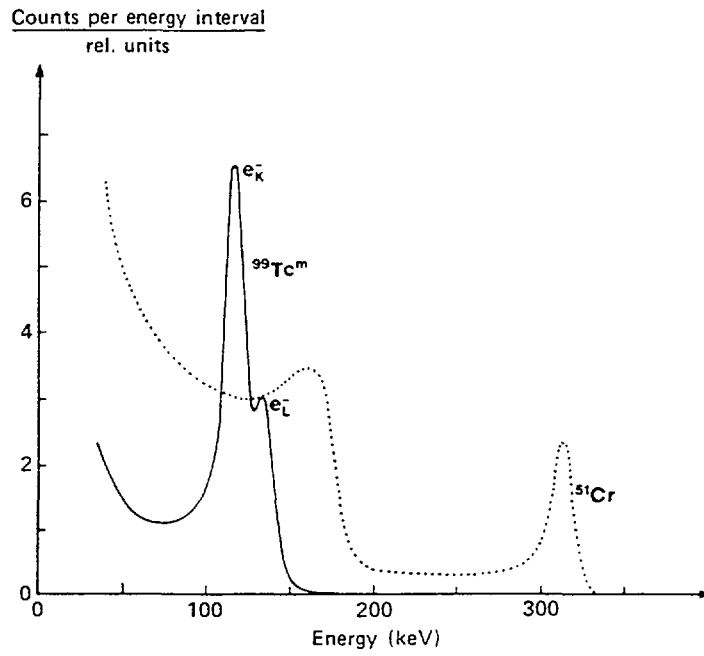


Fig. 10 Pulse-height distribution of conversion electrons from  $^{99}\text{Tc}^m$  ( $e_K = 119$  keV,  $e_L = 137$  keV) and  $^{51}\text{Cr}$  ( $e_K = 315$  keV,  $e_L = 324$  keV).  $e_K$  and  $e_L$  from  $^{51}\text{Cr}$  are not resolved.

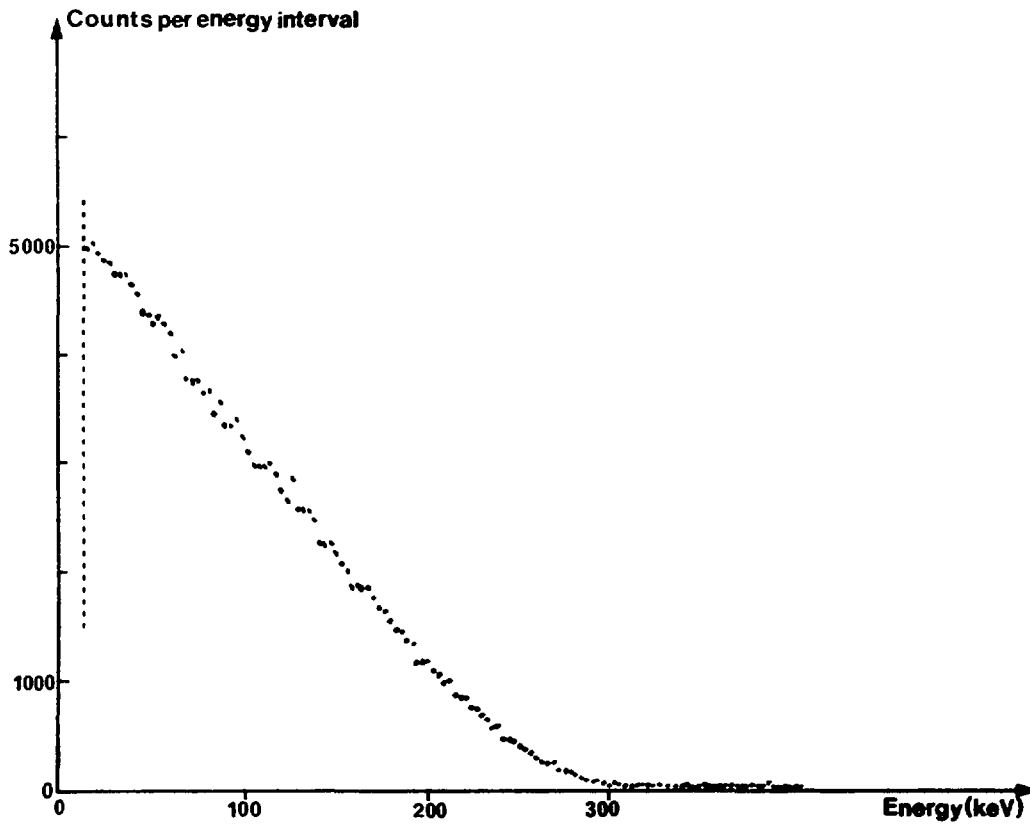


Fig. 11 Pulse-height distribution from  $\beta$  particles of  $^{99}\text{Tc}$ .

Fig. 10 are shown the pulse-height distribution of conversion electrons from  $^{99}\text{Tc}$  and  $^{51}\text{Cr}$ , and in Fig. 11 the pulse height distribution of the pure  $\beta$ -emitter  $^{99}\text{Tc}$ . The shape of the pulse-height distribution in the low-energy region is markedly influenced by the backing material.

Cooling of a silicon surface barrier detector improves resolution since the thermal noise is reduced as shown in Fig.12. An ion-implanted detector has already a low leakage current and cooling has little effect. The background as well as the noise level can be reduced by applying a GM-coincidence screen between the sample and the detector. This is especially useful for studies of conversion electrons since the electrons from Compton interaction in the detector material will no longer be counted.

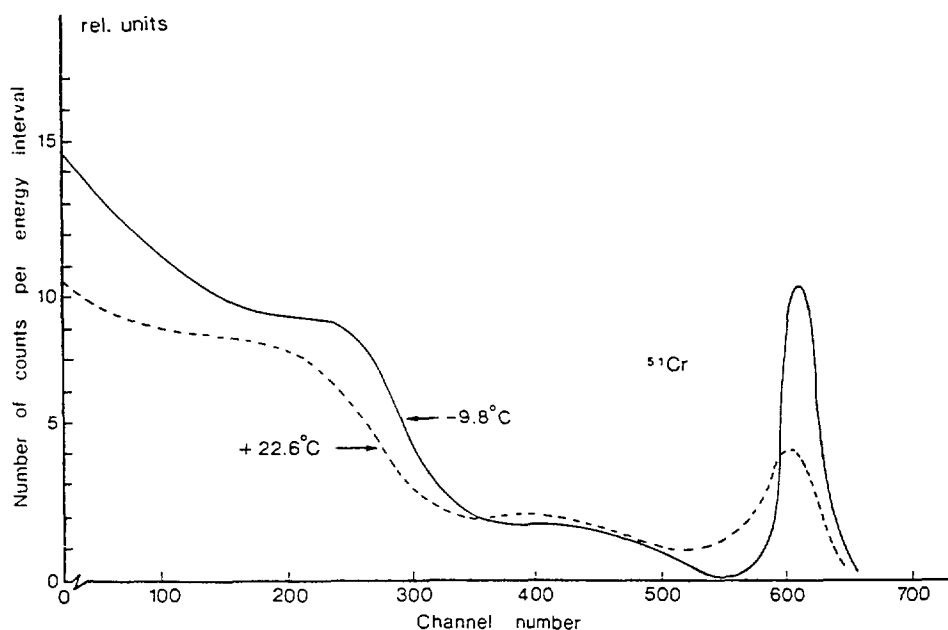


Fig. 12 Effect on pulse height distribution from  $^{51}\text{Cr}$  by cooling of a surface barrier detector ( From Holm et al, 1988).

In the previous Figure. 7 the measurement of  $^{63}\text{Ni}$  in an environmental sample after chemical separation is compared for an open anti-coincidence shielded gas-flow counter and an ion-implanted silicon detector. The activity was electroplated onto a copper disc with different amounts of stable nickel as the radiochemical yield determinant. The gas flow counter has a higher counting efficiency but will detect all events from ionizing radiation while energy discrimination can be obtained from the ion implanted detector. For the GM counter low energy beta particles will contribute to the counting and have to be discriminated due to the noise level of the silicon detector system. For the GM counter the counting efficiency decreases more rapidly for the GM counter with the amount of stable nickel in the source since the effective mean beta particle energy detected is higher.

10.3.8 Special methods such as use of Cerenkov effect, coincidence technique and beta particle spectrometry

10.3.8.1 Cerenkov effect

A charged particle can have a higher velocity,  $v$ , than light in a transparent medium. Electromagnetic radiation called Cerenkov radiation is emitted if  $v \geq c/n$ , where  $c$  is the velocity of light in vacuum and  $n$  is the



relative index of the medium. The method of Cerenkov counting in aqueous solutions can only be used for  $\beta$  particles having energies greater than than 0.26 MeV. The sample is placed in a liquid scintillation vial and counted in a similar manner to that employed in liquid scintillation counting. Much of the Cerenkov radiation emitted is in the UV region and is absorbed by the glass window of the photo tube and the glass vials. Cerenkov radiation is also emitted anisotropically, which reduces the counting efficiency. The detection efficiency can be improved by use of wavelength shifters. The counting efficiency can be improved with increasing  $\beta$ -particle energy, but is lower than that for normal liquid scintillation counting. The advantage of the method is the easy source preparation and absence of chemical quenching.

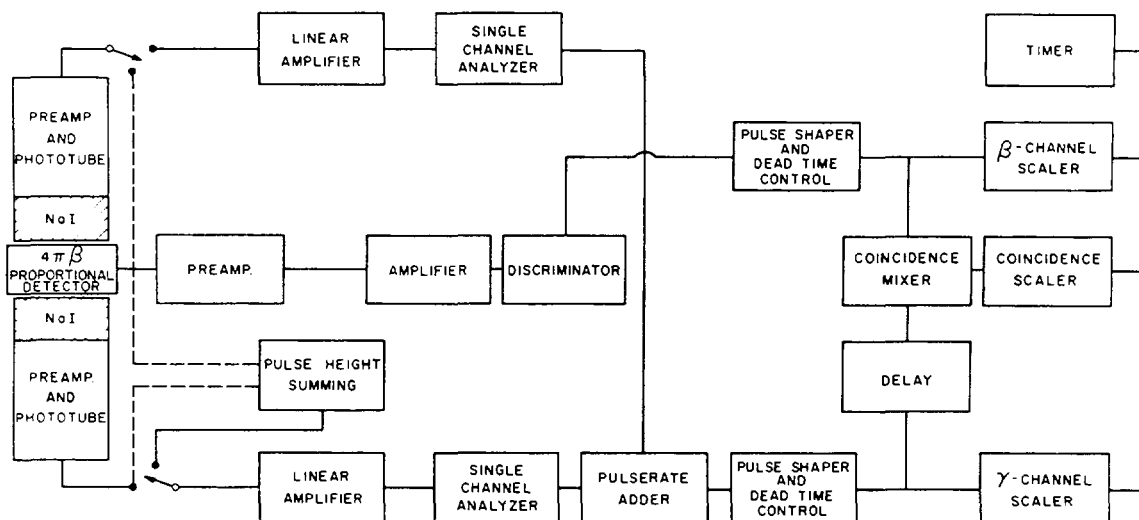


Fig. 13 Block diagram of the basic components of a typical  $4\pi$   $\beta$ - $\gamma$  coincidence system ( From NCRP, 1978).

Nevertheless optical quenching does occur Since the pulse height is lower in Cerenkov counting than with the use of scintillation solution, the energy window in which counting is performed should be adjusted accordingly.

#### 10.3.8.2 Coincidence counting

Coincidence counting is applied to nuclear decays involving two ( or several) transitions in prompt succession. Two detectors are then required. A third counting channel records those events from the two detectors that occur in coincidence. Background counts may be strongly reduced and radionuclide identification improved; however a smaller MDA is achieved in spite of a sometimes reduced counting efficiency. One of the most usual applications of coincidence counting is the determination of activity by coincidence of  $\beta$ - $\gamma$  decay. The pulse length must be large enough to avoid loss of coincidence. The rate of accidental coincidences increases with pulse width. This requires an optimization of the electronic system, illustrated in Fig. 13. The method can be applied for radionuclides such as  $^{134}\text{Cs}$  (  $E_{\gamma} = 605, 796$  keV,  $E(\beta)^{\text{max}} = 662$  keV) and  $^{60}\text{Co}$  (  $E_{\gamma} = 1.17, 1.33$  MeV,  $E(\beta)^{\text{max}} = 314$  keV). The coincidence counting method can also be used for other modes of decay, such as  $\gamma$ - $\gamma$  coincidence, EC- $\gamma$  coincidence, and  $\alpha$ - $\gamma$  coincidence.

### 10.3.8.3 Beta particle spectrometry

Apart from what was described in the paragraph on beta particle measurement with semiconductor detectors, beta-particle spectrometry has been performed with proportional counters operating at different pressures. Spectra

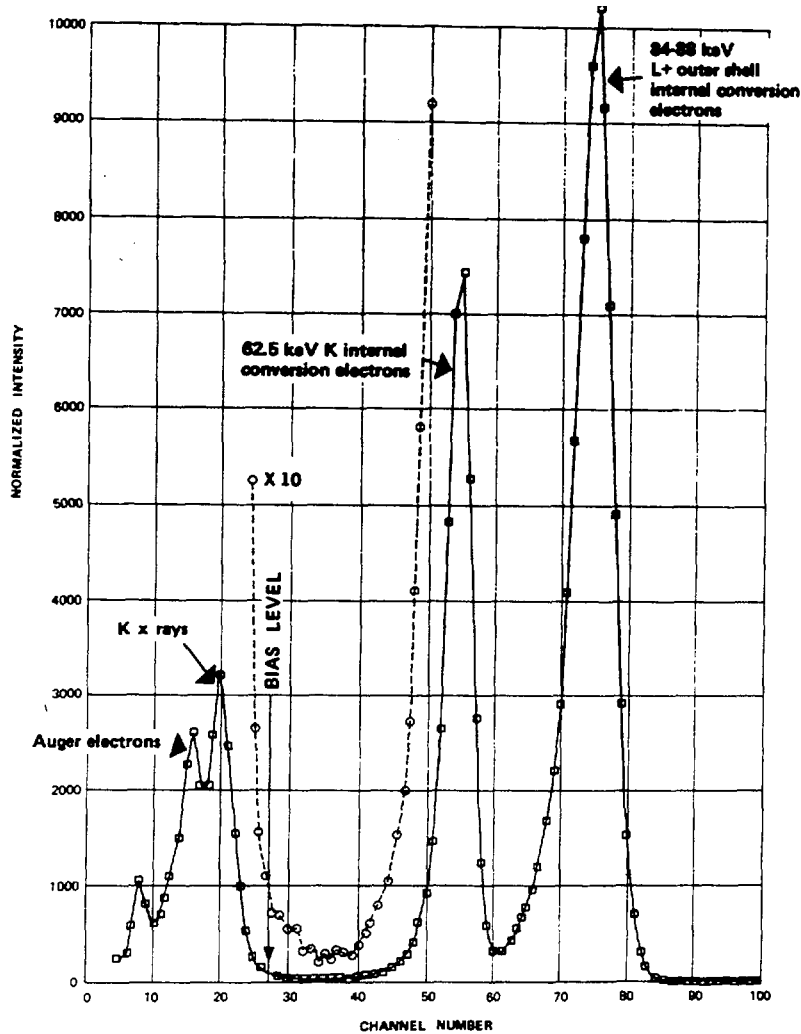


Fig.14  $^{109}\text{Cd}-^{109}\text{Ag}^m$  conversion-electron spectrum taken in a 30cm-diameter, cylindrical,  $4\pi$  gas-flow proportional counter. ( From NCRP, 1978)

of conversion electrons and Auger electrons can be obtained as shown in Fig. 14. The activity can be calculated from known internal conversion probabilities. As discussed previously, liquid or plastic scintillation counting offers the possibility of  $\beta$  spectrometry, but with poor resolution.

### 10.3.9 Standardized sources for calibration and intercomparison reference sources

It is of course, also important to determine the absolute activity of  $\beta$ -particle emitters in environmental samples. Beta emitters are measured as sources prepared on disc or as liquids for liquid scintillation counting after chemical separation. Standard disc sources of different pure  $\beta$ -particle emitters ( such as  $^{63}\text{Ni}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{90}\text{Sr}$  and  $^{99}\text{Tc}$ ) but also  $\beta$ - $\gamma$  emitters ( such as  $^{137}\text{Cs}$  and  $^{60}\text{Co}$ ) are commercially available. Such sources are useful for energy calibration purposes but less suitable for determination of counting efficiencies if the geometric design is different from what otherwise

is used. Standard solutions of the isotopes mentioned are also available allowing any laboratory to prepare sources of desired design or to use the solution for liquid scintillation counting.

International intercalibration exercises have taken place for samples of water, soil, vegetation, and animal tissue for the determination of such nuclides as example,  $^{14}\text{C}$ ,  $^{90}\text{Sr}$ , and  $^{99}\text{Tc}$ . Reference samples of these kinds are available from IAEA (Vienna) or NBS (Washington).

#### 10.4. Alpha particle emitting nuclides

##### 10.4.1 Preparation of sources by radiochemical and/or physical procedures

Alpha-sources for spectrometry must be very thin, preferably less than  $0.5\ \mu\text{m}$ . Thick sources can be used with very specific precipitation methods, such as barium sulfate for radium and lanthanum fluoride for certain actinides. The gases  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$ , as well as some of their short-lived decay products, are also alpha emitters. They are usually measured in a bottle, coated on the inside with ZnS, in contact with a photomultiplier.

During the final source preparation, after radiochemical separation, electrolysis is often used since it generally produces thinner deposits than evaporation. The only advantage with evaporation is that no losses occur. In electrodeposition the cathode material consists of a disc of stainless steel, platinum, or other metals such as copper or nickel. Since the anode must not be dissolved by the electrolytic process, platinum or carbon are most suitable. A widely used method has been described by Talvitie (9) where the

Table 1  
Yield determinants in radiochemical analysis of  $\alpha$ -emitting radionuclides.

Radionuclide	$E_{\alpha}$ (MeV)	$T_{1/2}$	Yield determinant	$E_{\alpha}$ (MeV)	$T_{1/2}$
$^{210}\text{Po}$	5.30	138 d	$^{288}\text{Po}$ $^{209}\text{Po}$	5.11 4.88	$2.9 \cdot 10^5$ a 103 a
$^{239}\text{Pu}$	5.16	$2.41 \cdot 10^5$ a	$^{236}\text{Pu}$	5.77	2.85 a
$^{240}\text{Pu}$	5.16	6570 a	$^{242}\text{Pu}$	4.90	$3.8 \cdot 10^5$ a
$^{238}\text{Pu}$	5.50	87.7 a			
$^{241}\text{Am}$	5.48	433 a	$^{243}\text{Am}$ $^{244}\text{Cm}$	5.27 5.80	7370 a 18.1 a
$^{242}\text{Cm}$	6.11	163 d	$^{243}\text{Am}$	5.27	7370 a
$^{244}\text{Cm}$	5.80	18.1 a	$^{241}\text{Am}$	5.48	433 a
$^{234}\text{U}$	4.76	$2.5 \cdot 10^5$ a	$^{232}\text{U}$	5.32	72 a
$^{235}\text{U}$	4.40	$7.0 \cdot 10^8$ a			
$^{238}\text{U}$	4.20	$4.5 \cdot 10^9$ a			
$^{228}\text{Th}$	5.42	1.91 a	$^{229}\text{Th}$	4.8-5.05	7300 a
$^{230}\text{Th}$	4.69	$8.0 \cdot 10^4$ a			
$^{232}\text{Th}$	4.0	$1.4 \cdot 10^{10}$ a			
$^{231}\text{Pa}$	5.0	$3.3 \cdot 10^4$ a	$^{233}\text{Pa}(\beta, \gamma)$		27 d
$^{237}\text{Np}$	4.78	$2.1 \cdot 10^6$ a	$^{239}\text{Np}(\beta, \gamma)$		2.35 d
$^{226}\text{Ra}$	4.78	1600 a	$^{224}\text{Ra}$ $^{225}\text{Ra}(\beta, \gamma)$ $^{223}\text{Ra}$	5.69 5.72	3.7 d 14.8 d 11.4 d

deposition takes place from an ammonium sulfate medium. Deposition from anoxalate medium is also useful (10).

Many other methods have been described but a modification of that described by Talvitie, mainly by the addition of sodium sulfate solution is a method to recommend (11). Assessment of  $^{210}\text{Po}$  and source preparation is relatively easier since polonium spontaneously deposits on nickel or silver from acid solution (12, 13,). A yield determinant should be used in the radiochemical procedure. Preferably it should be another isotope with different  $\alpha$ -particle energy. The physical half-life and radiochemical purity should be suitable, and the  $\alpha$  peaks must be resolvable. Unfortunately, such isotopes do not always exist or are difficult to produce. In Table I are listed the radiochemical yield determinants for analysis of a number of different  $\alpha$ -particle emitters.

#### 10.4.2 Assessment of alpha emitters by liquid scintillation counting

Due to the short range of  $\alpha$  particles, many scintillation detectors with entrance windows, such as  $\text{NaI(Tl)}$ , cannot be used. By using thin  $\text{ZnS}$  discs in contact with a photomultiplier it is possible to perform total  $\alpha$  counting. It was also pointed out above that measurement of  $\text{Rn}$  is performed in a bottle coated with  $\text{ZnS}$  and placed on a PM tube. Both  $\text{Rn}$  and its short lived daughter products are  $\alpha$ -emitters which increase measurement sensitivity. Such a scintillation device has no energy resolution but can be useful in some chemical separations..

Liquid scintillation is sometimes a useful method when isotopes of both  $\beta$ - and  $\alpha$ -particle emitters of an element are measured. In spite of the poor energy resolution one can discriminate between  $\alpha$  and  $\beta$  particles. An illustrative example is the counting of  $^{241}\text{Pu}$  and  $^{239+240}\text{Pu}$  together ( see Fig. 15 (14)).  $^{241}\text{Pu}$  can also be counted by an open GM gas-flow counter, together and after assessment of the alpha emitting isotopes,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{238}\text{Pu}$ , since the activity of  $^{241}\text{Pu}$  in environmental samples generally is 10 to 100 fold higher than the activity of the  $\alpha$ -emitting plutonium isotopes.

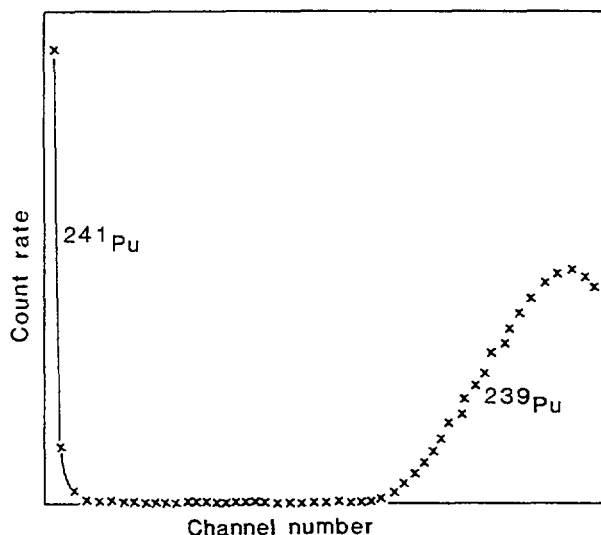


Fig. 15 Liquid scintillation spectrum, at a single logarithmic gain setting, of a mixture of the  $\beta$  emitter  $^{241}\text{Pu}$  and the  $\alpha$  emitter  $^{239}\text{Pu}$ . Activity ratio is 40 to 1(From Darall et al.)

### 10.4.3 Assessment of alpha emitters by gas-filled detectors

Gas-filled detectors can be used with  $\alpha$ -particle emitters. Windowless proportional counters are preferred because energy resolution is required. The gas is usually argon with the addition of methane. Large sources can be used with high counting efficiency. In this sense the gridded ionization chamber, in which the induction from the positive ion track is effectively shielded, is an important instrument especially when large sources are measured. Under special conditions (i.e. the pre-amplifier is cooled and the source collimated), an energy resolution down to 11-12 keV can be obtained.

Geiger-Muller counters can also be used, either windowless or with small windows. Their use is, however, limited to total  $\alpha$  counting and specific separations and precipitations. Gas scintillation counters have also been successfully applied by using the light emitted from noble gases at the passage by an  $\alpha$  particle.

### 10.5. Alpha particle spectrometry

It is generally not possible to perform spectrometry of all  $\alpha$ -particle emitters in a source at the same time because many  $\alpha$ -particle emitters interfere with each other. It is very difficult to obtain adequate elimination of stable elements existing in high amounts, however, a group separation of actinides can be done (15). Since the lanthanides are also co separated, this process limits the amount of sample to be processed to obtain a good source for  $\alpha$  spectrometry.

Currently silicon surface-barrier detectors are most often used, but gridded ionization chamber also give adequate resolution for spectrometry and can be used with relatively large area sources. Most element of interest emit  $\alpha$ -particle in the energy region 3.95 (  $^{232}\text{Th}$ ) to 8.8 MeV (  $^{212}\text{Po}$ ). Alpha-particle emitters with lower energies, such as  $^{146}\text{Sm}$  ( $E(\alpha) = 2.46$  MeV) and  $^{148}\text{Gd}$  ( $E(\alpha) = 3.18$  MeV) have been used for energy calibration and stabilization of  $\alpha$  spectrometers.

Quantitative evaluation of  $\alpha$ -particle spectra is simpler than for  $\gamma$ -ray spectra, since the detector efficiency does not vary with energy. Correction for peak tailing into a lower energy region of interest must be made. The energy resolution improves with increasing source-to-detector distance and with decreasing detector diameter but then the counting efficiency is also lower. Since most  $\alpha$ -particle emitters are not monoenergetic, often two or more  $\alpha$  energies from the radionuclide are present which cannot be resolved. The most important conditions is to obtain clean sources without a thick deposit of foreign matter. Poorly prepared sources can never be compensated for by better electronics or computer analysis. The detector system is calibrated with sources of known energies. A source of  $^{233}\text{U}$  ( $E(\alpha) = 4.82$  MeV) and  $^{244}\text{Cm}$  ( $E(\alpha) = 5.80$  MeV) are suitable. Americium-241 is often used as reference.

The background of the detectors can be kept as low as  $0.3 \times 10^{-5} - 2 \times 10^{-5} \text{ s}^{-1}$  for an energy interval of 100 keV in the  $\alpha$ -energy region of 4 to 6 MeV. Contamination of the detector may occur, for instance, by evaporated polonium isotopes if spectrometry is performed under vacuum. Contamination by recoil nuclei can also occur for instance, by the production of  $^{224}\text{Ra}$  from  $^{228}\text{Th}$ .

To keep background low, high-activity sources should not be used and detectors should be carefully handled. Contamination by recoil nuclei can be avoided by applying a positive potential of a few volts on the source disk. Several detectors are normally connected via routing systems to one multi channel analyzer. Counting times are often long, 1 to several days. In Fig. 16 a typical  $\alpha$  spectrum of thorium isotopes in a source prepared from a large volume of sea water is shown. Thorium-229 was used as the yield determinant.

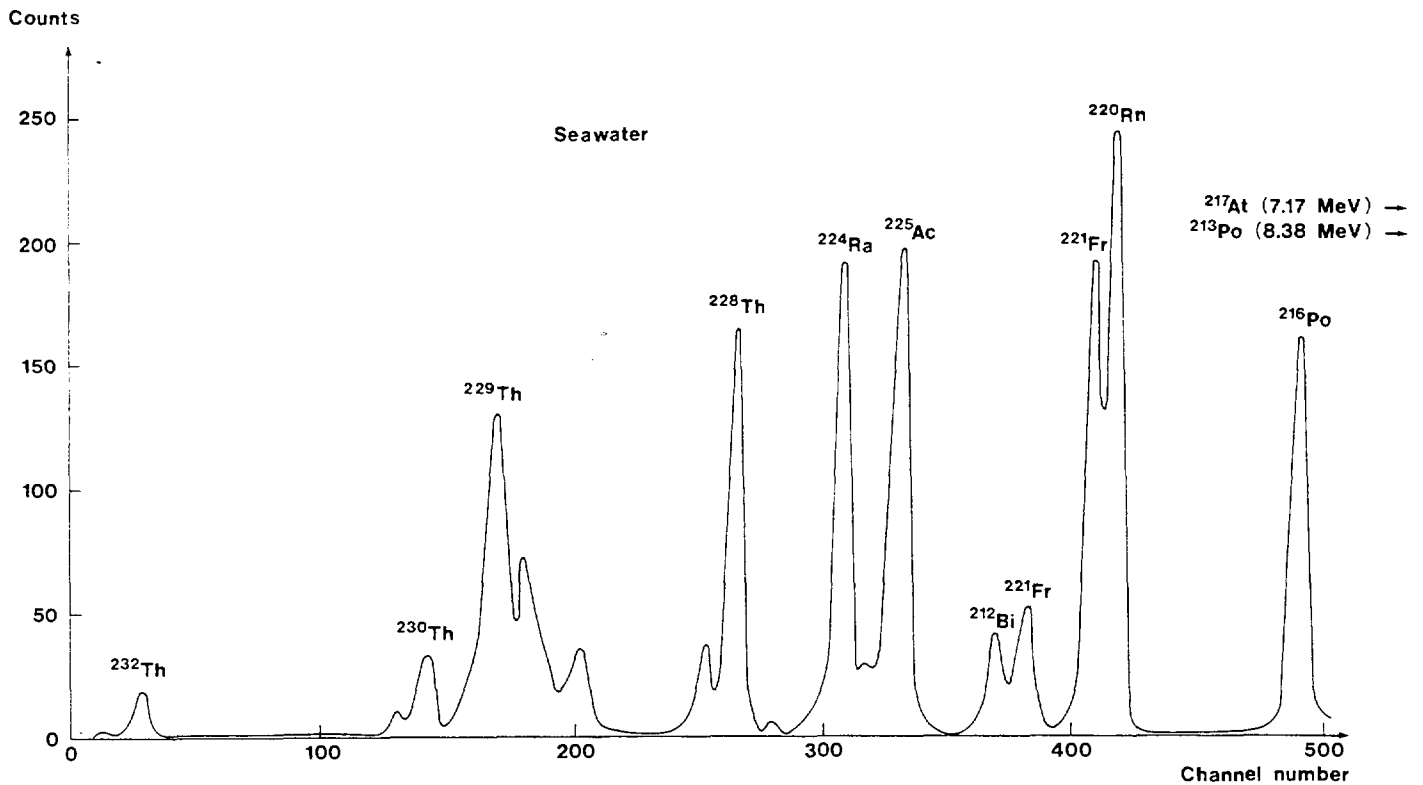


Fig. 16 Alpha spectrum of a natural thorium sample, with  $^{229}\text{Th}$  added as yield determinant, separated from sea water,  $300\text{-mm}^2$ , surface-barrier silicon detector,  $100\ \mu\text{m}$  depletion depth, and  $5.7\ \text{keV}$  per channel. (From Holm 1984).

#### 10.6. Special methods

Some special photographic emulsions can detect tracks of  $\alpha$ -particles and fission fragments, but require long exposures at low activities. The tracks in the developed emulsion are counted. Alpha-particles also leave etchable tracks in plastics and glasses. The latter technique has been widely applied for measurements of radon and radon decay products in air. In such measurements plastic films coated with cellulose nitrate are frequently used. The evaluation of such measurements is subject to significant uncertainties partly caused by the rather complicated calibration procedure. Further details are given by Becker (17).

#### 10.7. Standardized sources for calibration and intercomparison reference sources

Electroplated sources of,  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ , and  $^{244}\text{Cm}$  for example, are commercially available and which are calibrated with an overall uncertainty of 1% to 10%. Calibrated solutions of  $^{241}\text{Am}$ ,  $^{242}\text{Pu}$ ,  $^{229}\text{Th}$ ,  $^{210}\text{Pb}$  (in radioactive equilibrium with  $^{210}\text{Po}$ ), and many other  $\alpha$ -particle emitters can also be obtained. Calibrated sources from these solutions can be prepared by evaporation of known amounts. Calibration can then be checked with detectors having previously known counting efficiencies, or with  $2\pi$  proportional or GM counters. Usually it is difficult to obtain a detector calibration giving an overall uncertainty better than 5%.

Specifically prepared sources and solutions for inter calibration exercises have been used much less for  $\alpha$ -particle emitters than for  $\gamma$ -emitting radionuclides. Intercomparison based on samples of different matrices such as sediments, water, soil, etc., have been performed. Many of these samples are now available from NBS or IAEA as reference materials.

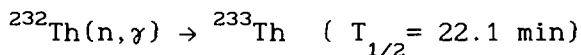
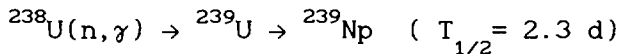
## 10.5. Non-conventional methods for assessment of radionuclides

### 10.5.1 Neutron activation

An activation technique for measurement of radioactive isotopes is sometimes used when the physical half-life is long and thus the specific activity is low, or the decay characteristics are unfavourable for conventional counting. The possibility of performing this type of measurement depends on cross sections, flux, and energy spectral distribution of the neutrons.

The radionuclide produced, which will be subject to counting, must have a much shorter half-life than the target nuclide. For environmental samples a radiochemical separation sometimes has to be performed before neutron activation. The material of the sample holder must be carefully selected to avoid creating undesired activity. The thermal neutron fluence rate required is of the order of  $10^{14}/\text{cm}^2\text{s}$ . the irradiation time depends upon what is practical by the physical half-life of the product. A few examples of usable reactions are:

(i) Measurement of  $^{238}\text{U}$  ( $T_{1/2} = 4.5 \times 10^9$  a) and  $^{232}\text{Th}$  ( $T_{1/2} = 1.4 \times 10^{10}$  a) by the reactions



$^{239}\text{Np}$  and  $^{233}\text{Th}$  can be measured by  $\beta$  or  $\gamma$  counting. The other more short-lived uranium and thorium isotopes present in the sample will not be measured, which is one disadvantage compared to  $\alpha$  spectrometry.

(ii) Technetium-99 ( $T_{1/2} = 2.1 \times 10^5$  a) has been successfully measured after chemical separation and activation by the counting of  $^{100}\text{Tc}$  ( $T_{1/2} = 15.2$  s) (18).

(iii) The measurement of  $^{237}\text{Np}$  ( $T_{1/2} = 2.1 \times 10^6$  a) is a good example where neutron activation gives better minimum detectable activity (MDA) than  $\alpha$  spectrometry. The reaction  $^{237}\text{Np}(n,\gamma) \rightarrow ^{238}\text{Np} \rightarrow ^{238}\text{Pu}$  ( $T_{1/2} = 86$  a) is used. The maximal ingrowth of  $^{238}\text{Pu}$  takes about 14 d and the  $^{238}\text{Pu}$  is then measured with  $\alpha$  spectrometry. The troublesome peak interference between  $^{237}\text{Np}$  and  $^{238}\text{U}$  is also avoided.

(iv) Iodine-129 measurements are currently being made in a number of laboratories. The procedure involves isolation of iodine from the sample, followed by irradiation with thermal neutrons to yield the product  $^{130}\text{I}$  ( $T_{1/2} = 12.4$  h) (19).

### 10.5.2 Mass spectrometry

In special cases mass spectrometry can be applied with advantage for measurement of certain radioactive isotopes, if the specific activity is low

and the conventional and activation techniques are unfavorable, such as with  $^{10}\text{Be}$ ,  $^{36}\text{Cl}$ , uranium isotopes and several transuranium elements. A radiochemical separation must be done before the application of mass spectrometry. A mass spectrometrically suitable yield determinant should be present or added to the ion source, as the spectrometer and its detector system are adapted to isotope-ratio measurements. A long-lived yield determinant such as  $^{97}\text{Tc}$  for  $^{99}\text{Tc}$  measurements, and  $^{236}\text{Np}$  for  $^{237}\text{Np}$  detection are required. There are several types of mass spectrometers such as Magnetic Spectrometer, Accelerator Tandem Van de Graaff Mass Spectrometer, and Inductively Coupled Plasma Mass Spectrometer (ICPMS). Today ICPMS is applied in many laboratories. Both  $^{99}\text{Tc}$  and  $^{237}\text{Np}$  have been measured in environmental samples with high sensitivity (20, 21) Table 2 gives a comparison of detection limits for  $^{99}\text{Tc}$  using various methods.

Table 2  
Detection limits in various methods for the determination of  $^{99}\text{Tc}^m$ .

Analytical method	Detection limit
Low background gas flow counting	1.5 - 5.0 mBq
Neutron activation analysis (n, $\gamma$ )	3 - 5 mBq
(n, n')	0.3 - 0.6 Bq
Liquid scintillation counting	25 - 30 mBq
ICP-mass spectrometry	0.002 - 15 mBq

An example of the usefulness of mass spectrometry is measurement of samples contaminated with artificial and natural uranium isotopes. The long-lived  $^{236}\text{U}$  ( $T_{1/2} = 2.4 \times 10^7$  a),  $^{235}\text{U}$  ( $T_{1/2} = 7.1 \times 10^8$  a) and  $^{238}\text{U}$  ( $T_{1/2} = 4.5 \times 10^7$  a) isotopes may be determined this way. Uranium-236 is especially difficult to measure by  $\alpha$  spectrometry due to peak interferences. Another example is measurement of  $^{242}\text{Pu}$  and  $^{240}\text{Pu}$  in samples contaminated with other plutonium isotopes. Plutonium-242 ( $T_{1/2} = 3.8 \times 10^5$  a) has low specific activity and  $^{240}\text{Pu}$  is impossible to resolve from  $^{239}\text{Pu}$  by  $\alpha$  spectrometry. In addition,  $^{241}\text{Pu}$ , a low-energy  $\beta$  emitter, may also be determined (Krey et al., 1976).

Carbon-14 is now frequently determined with mass spectrometry which is often advantageous compared to conventional counting technique.

### 10.5.3 Other techniques

Activation techniques using high-energy photons or protons can also be used in special cases. Reactions of the ( $\gamma$ , n) and (p, n) type are the most likely ones to be applied. The techniques using x-ray fluorescence and generally applied to long-lived radionuclides. Counting is performed with Si(Li) detectors or planar Ge(Li) or Ge(Hp) detectors. The advantage of these techniques is that they are non-destructive and the x-ray fluorescence method can be applied *in vivo*.

Auto radiography may be used to determine the distribution of activity in organs and plants. Exposure time of films can be long. nevertheless it is not a quantitative method, and it is seldom used for environmental analysis.



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