Seminar on Detectors and Measurements Techniques
3-4 May 2001, Lund, Sweden

Edited by E. Holm
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Abstract

A Nordic Seminar on detectors and radionuclide measurement techniques was held in Lund, Sweden, May 3-4, 2001. The objective was to highlight recent progress and problems for techniques to study environmental radioactivity. It covered the aspect of detector sample geometry's and methods for evaluation of gamma gamma pulse height distributions. Within the field of alpha-spectrometric techniques gridded ionisation chambers, semiconductor detectors and a general description for analysis of alpha-particle-spectra were presented. Recent development in mass spectrometric techniques, AMS (Accelerator Mass Spectrometry) and ICPMS (Inductively Coupled Plasma mass Spectrometry) for long-lived radionuclides was described. Principles for analysis of beta particle emitters, especially by liquid scintillation were presented. The seminar also covered radiochemistry such advantages and disadvantages between ion exchange, solvent extraction and extraction chromatography. The use of controlled laboratory conditions for discerning the dynamics of accumulation in organisms was demonstrated. Other techniques such as neutron activation were also shown to be useful analytical tool for certain long-lived radionuclides. The results of the intercalbration exercises within the Nordic countries showed the importance of such analytical quality control.

Keywords

Seminar on Detectors and Measurements Techniques

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Project NKS/BOK-1.1

Foreword

Nuclear measurement and laboratory techniques are vital tools for understanding the behaviour and fate of radioactive elements in our environment. By studying present levels from controlled and accidental releases, the processes and pathways to man under emergency conditions can be predicted. Radionuclides play also an important role for the study of bio-geochemical processes. For improved mathematical modelling of radionuclides in the environment, values of for example C_fs and K_ds must be updated. With the exception of certain environments levels are decreasing on a world-wide basis. This requires new more sophisticated techniques combined with laboratory experiments.

It is important that new as well as and experienced analysts are informed about current development in this field. This can be implemented in various ways. A time- and cost-effective way is through seminars with invited experts as lecturers together with the people active in the field. Such a seminar was held in Lund, Sweden, May 3-4, 2001 under the financial support of NKS.

Risø, Denmark 2001-06-06. (The Swedish National Day)

Elis Holm

Contents:

AGENDA

NKS. Seminar on detectors and radionuclide measurement techniques.

Time: May 3-4, 2001

Place: Lund, Sweden, Grand Hotell, Bromansalen

Language: English

Thursday, May 4.

09.00 – 09.45.	Registration and coffee
09.45 – 10. 00.	Welcome addresses and general information (*Elis Holm*, *Risoe/Lund*)
10.00 – 12.00.	**Detectors and measurement geometry.** *Mika Nikkinen, STUK, Seppo Klemola, STUK*)
12.00 – 13. 00	Lunch
13.00 – 15. 00	**Principles for analysis of alpha particle emitters.** *Eduardo Garcia-Torano, CIEMAT, Per Roos, Risø, Christer Samuelsson, Lund*
15.00 - 15.30	Coffee
15.30 – 17. 30	**Mass spectrometric techniques including** AMS, ICPMS. *Grant Raisbeck, CNRS, France, Miranda Keith-Roach, Risø*
19.30	**Dinner at SPOT**

Friday, May 5.

09.00 – 10.30	**Principles for analysis of beta emitters, EC elements**. *Franz Schönhofer, Vienna*
10.30 – 11.00	Coffee
11.00 – 12.00	**Principles for ion exchange, and liquid-liquid extraction.** *Timo Jaakkola, Rad. Kem. Inst, Helsinki*
12.00 – 13.00	Lunch
13.00 –14.30	**Laboratory techniques for dynamic studies, K_d and C_f determination.** *Scott Fowler, EML, Monaco*
14.30 –15.00	Coffee
15.00 –15.40	**Other techniques such as neutron activation.** *Xiaolin. Hou, Risö*
15.40 – 16.20	**The Nordic experience in intercalibration exercises.** *Christian Fogh, Risø.*
16.20 – 16.45	Conclusion remarks, discussion and suggestions for future seminars. *Elis Holm, Risoe/Lund.*

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1 On detectors and samples for gamma-ray spectrometry

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Continuous progress in development of radiation detection instruments have improved their capability in different applications. While there has been progress also in alpha- and beta-devices, the most dramatic improvement concerns measurements of X- and gamma-rays. In 1950s and '60s simultaneous development of both detectors and electronics led to the era of modern gamma-ray spectroscopy. This interdependence is still important. The development of high purity germanium crystals has been characterised by improvement in properties like increase in crystal diameter, lower impurity concentrations and greater axial uniformity of the impurity concentration.

There is continuing increase of typical detector size: mass of germanium can be few kilograms, diameter up to 95 mm and volumes up to almost 800 cm^3. Relative detection efficiency is nowadays up to 200%. Increased solid angle for a source means more gamma-rays are hit to the detector. Increased mass means higher interaction probability. The sensitivity of a HPGe spectrometer system depends not only on detector efficiency but also on detector resolution, background radiation, sample constituency and geometry and naturally on counting time.

Efficiency

Effectiveness of counting can be increased by using larger and optimally shaped detectors, more sample and closer geometry.

The sensitivity of a spectrometer improves also as the resolution improves. Better energy resolution makes full-energy peak widths smaller. Fewer background counts are therefore included in peak areas. But since the sensitivity is inversely related to the square root of the background, improvements in resolution will not improve sensitivity as dramatically as increased efficiency.

The nominal characterisation of detector sensitivity is done by the concept of relative efficiency. The efficiency of an HPGe detector is quoted relative to that of a 3"×3" NaI detector. A 100% detector has a counting efficiency of 1.2×10^{-3} for 1.33 MeV photons of ^{60}Co at a source-detector distance of 25 cm. However, this way of specifying the detector's efficiency is poor measure of performance. It is not adequate to predict the performance for all experimental situations.

The active volume (effective interaction volume) of the detector determines its efficiency. Relative efficiency ε_{rel} is depending on the volume V (cm^3) of the detector approximately[1]

$$\varepsilon_{rel} = \frac{V}{4.3}$$

and on the diameter d (dm) and length l (dm)

$$\varepsilon_{rel} = k \, d^\alpha l^\beta \, ,$$

where k=243.21, α = 2.8155, β = 0.7785. E.g. a 100% detector has a volume of about 400 cm^3.

The most effective way to increase the detector volume is often specific for application. A large detector is a good solution for high-energy photons (> 1 MeV) but it is not necessarily the optimum solution if the main interest is at medium energies (0.1 MeV - 1 MeV). More

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[1] Product Catalogue of EG&G ORTEC, Inc, Oak Ridge (1997

than 90% of the medium energy photons interact in a germanium crystal with thickness of 60 mm. Increasing the thickness further would not affect much the full-energy peak count rate. However, the thick detector increases the background continuum in the spectrum because the sample and the surrounding materials contain natural radionuclides (^{208}Tl and ^{40}K) emitting high-energy photons. A detector with optimum volume gives better performance with lower costs as compared with straightforward investment to a large detector.

The overall counting geometry, including the shape of the sample and the dimensions of the detector, should be optimised. E.g. a 40 % detector can have very different dimensions: diameter can vary 50 – 80 mm and length 20 – 100 mm. The optimisation of the detector should be based on the dimensions of the sample and the energy interval of interest.

When counting weak samples with low and medium gamma energies (< 1 MeV), the following considerations to the detector design are important:

- the detector should have an adequate diameter. This assures that the efficiency at medium and low energies will be high relative to the efficiency at 1.33 MeV, according to which it is prized.
- the detector-to-end-cap distance should be minimal - five millimetres or less.

For many environmental applications, a planar detector provides optimum efficiency with minimum background and additionally has the best energy resolution. The front contact can be manufactured with thin dead layer providing high counting efficiency at low energies.

Well-type detectors absolute efficiency can be in more than 90% for energies of 50 to 200 keV. The sensitivity in a well is five times of 80% standard coaxial detector. Counting efficiency will depend on the location of the sample in the well. With very small sources at the bottom of the well the efficiency is almost independent of location: a movement of 0 to 10 mm changes efficiency < 2%. Due to the almost 4π geometry the detector measures radiation from all sides of the sample. This increases the efficiency of low energy photons emitted from a high Z material, because self-absorption losses in the sample are decreased. Due to the slightly worse resolution compared to equivalent coaxial detectors, MDA is increased about 7%. Because of high probability of true coincidence summing well type detectors are not recommended for measurement of nuclides having complicated decay scheme with cascades of gamma-rays.

Sample geometry

How large sample volume is to be used depends
- how much sample is available
- how much sample can be processed taking into account laboratory resources for collection, transport, pre-treatment, archivement etc.
- self-attenuation in large sample
- larger the sample, smaller the coincidence summing because of the increase of average distance between the decaying atom and the detector.

As it is often impossible to have enough sample material or to concentrate it to a proper volume, one has to be able to measure activities of the order of 0.1 Bq per sample. Low detection limit requires long counting times even with the most efficient detectors. The only way to improve analysing capacity is measure the available sample material in the most efficient geometry.

When considering various sample volumes and shapes it is the full energy peak count rate that demonstrates the effect rather than the counting efficiency.

For a given sample size, the sample should be distributed to minimise the distance between the sample volume and the detector.

A narrow beaker diameter can be recommended only for rather small volumes. Depending on energy and density samples larger than 25-35 ml should be measured in wider beakers.

Due to the self-absorption in tightly packed samples (soil, sediment, ashed organic material etc.) wider beakers are preferred already for 15-20 ml volumes.

A container with a radius about the same as that of the detector crystal is useful for wide range of volumes, the largest being almost 300 ml (low energy, low density, large detector). A low sample density favours a narrow beaker to wide one at low energies due to the attenuation of gamma-rays in absorbing layers of the detector. When the sample is wider than the detector, part of the photons enter into the crystal from the side with small angles of incidence.
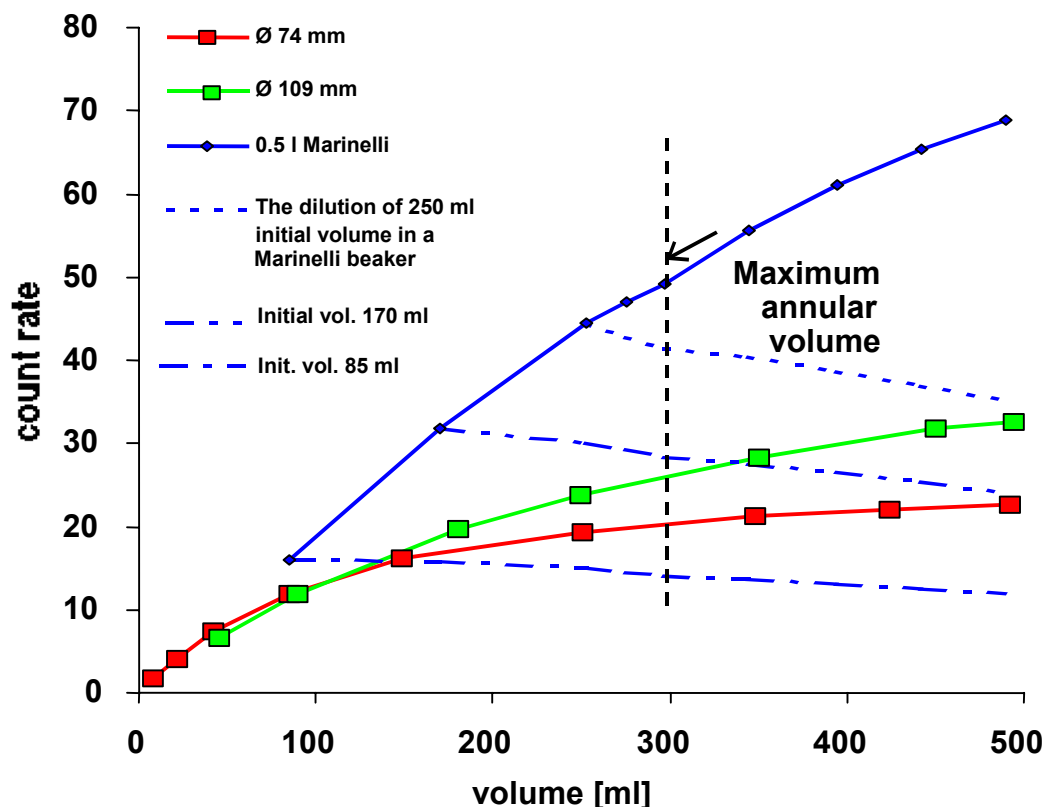

Fig. 1. The comparison of count rates of simple cylindrical beakers and a 0.5 l Marinelli beaker for 700 keV gamma rays. Dashed lines show the decrease of the count rate due to the dilution of the initial sample volume up to the full Marinelli volume.

A Marinelli beaker is efficient also for small sample volumes and superior for volumes more than 300 ml. Although the beaker should have no efficiency calibration for different filling heights, it can be utilised with smaller liquid samples by dilution to a calibrated volume. The count rate of the diluted sample in a Marinelli is still equal or better than count rate of the corresponding activity in a simple cylindrical beaker. For a small initial volume the change of the count rate depends on the ratio of a detector crystal length and the height of the annular part of the beaker. If the crystal is short, increasing the volume from 100 ml to 200 ml might even enhance the count rate by reducing the overall average distance from sample to crystal.

Potential geometry related problem is the possibility of source placement error at close distances (2-mm inaccuracy insignificant at large distances but at 0-1 cm distance 0.2-mm inaccuracy is very significant). To minimise placement error each detector should be equipped with sample holder (or several) that ensure reproducible geometries.

Samples containing particles

A particle within a sample can have a different aspect on the detector and therefore will contribute to the overall gamma ray intensity to a different degree depending on location. Ignoring the presence of particles can lead to over- or underestimation of activity. The range of the eventual results can be estimated by comparing the efficiencies in two extreme conditions: 1) activity is homogeneously distributed in the whole sample, 2) all activity is concentrated in one single particle at different locations. An example is given in Fig 2. The ratios of point source efficiency to bulk source efficiency at several particle locations in 35-ml beaker. The values represent directly the relative error made by supposing homogenous sample when there is actually a particle producing the observed count rate alone.

The results give general idea of the effect of source inhomogenieties: a wide range of results can be obtained even for rather small volume. The vertical source-to-detector distance is more important than the radial displacement, as long as the source radius is smaller than the radius of the detector. This is very good reason to prefer low and wide sample shape to high and narrow.
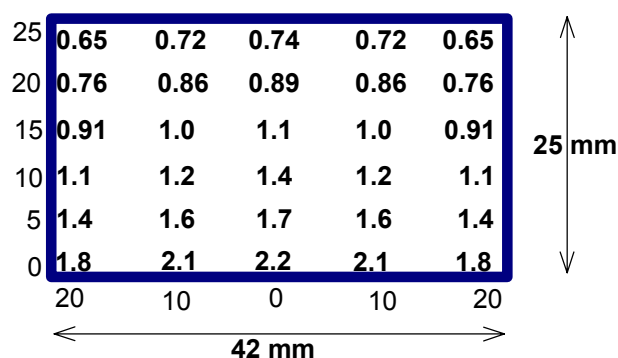
25	0.65	0.72	0.74	0.72	0.65
20	0.76	0.86	0.89	0.86	0.76
15	0.91	1.0	1.1	1.0	0.91
10	1.1	1.2	1.4	1.2	1.1
5	1.4	1.6	1.7	1.6	1.4
0	1.8	2.1	2.2	2.1	1.8
	20	10	0	10	20

25 mm

42 mm

Fig. 2. Ratio of point source efficiency to bulk sample efficiency at different point source locations.

If particles have tendency to locate in the lower part of the sample volume (e.g. liquid samples) then the results are systematically overestimated. Random location of particles gives on the average same result as homogenous source.

Shielding and background radiation

To minimise the amount of background radiation in the measurement of a low activity sample, the environmental samples should be measured in a shield. However, shield can also be a source of background and should be considered carefully when setting up. It has been established that the optimal shield thickness is 10-15 cm. Less thickness may not provide enough shielding and more thickness produces more background due to cosmic interactions with the shield.

Interfering background in gamma spectra originates either from within the sample being counted (Compton-produced) or from the environment. If the sample being analysed has a high content of high-energy gamma emitting radioisotopes, the Compton-produced background will easily outweigh the environmental background. For extremely weak samples, the environmental background becomes more significant.

The HPGe detector should be located in the centre of the shield so as to minimise scatter from the walls. Sample entry should be convenient to the operator and sample placement should be accurately repeatable and easily verified by the operator.

Spectral background consists on
- counts due to the sample, largely Compton events from higher energy gammas
  - efficient detectors have larger peak-to-Compton ratio
    - 90% detector reaches a particular MDA **four** times sooner than 30% detector i.e. four times as many samples can be counted on 90% detector compared to 30% in a given period. 90% detector is cheaper than three 30% detectors.
- counts from the environment of the detector
  - background count rate per channel is directly proportional to the detector efficiency
    - 90% detector reaches a particular MDA **three** times sooner than 30% detector i.e. three times as many samples can be counted on 90% detector compared to 30% in a given period

However, it is not perhaps good strategy to consider one large detector as an alternative to several smaller
- due to the redundancy.
- increased true coincidence summing
- for low-energy gammas, < 300 keV, large volume detector is less important as such than how it is geometrically disposed
- most laboratories find that a mix of detectors of various sizes and configurations give them flexibility and redundancy

X-ray summing in detectors of extended energy-range

In addition to summing of gamma rays, other radiation, especially X-rays, can be in true coincidence with the gamma rays. The summing effects with most of the X-rays can be ignored for the p-type Ge detectors having thick dead layer. On the contrary, the detectors with a thin entrance window, e.g. n-type detectors and new extended range p-type detectors, can experience severe summing of X-rays and gamma rays.

Unfortunately many of the common calibration nuclides decay by electron capture with subsequent emission of characteristic X-rays of the daughter nuclide. The effect of X-ray summing can be decreased using a suitable absorber, e.g. copper. The efficiency curve is always difficult to interpolate in the range 60-150 keV due to the rapid change in this region but without absorber it is almost impossible to obtain reliable curve. Using the absorber most of the cascading X-rays are strongly attenuated and a more plausible fit can be achieved. The count rate of some peaks might even increase when using the absorber.

The multiple summing of gamma and X-ray peaks and additional Ge escape peaks complicate also the peak identification. This feature of the detectors with high efficiency for low-energy photons has perhaps not fully been realised.
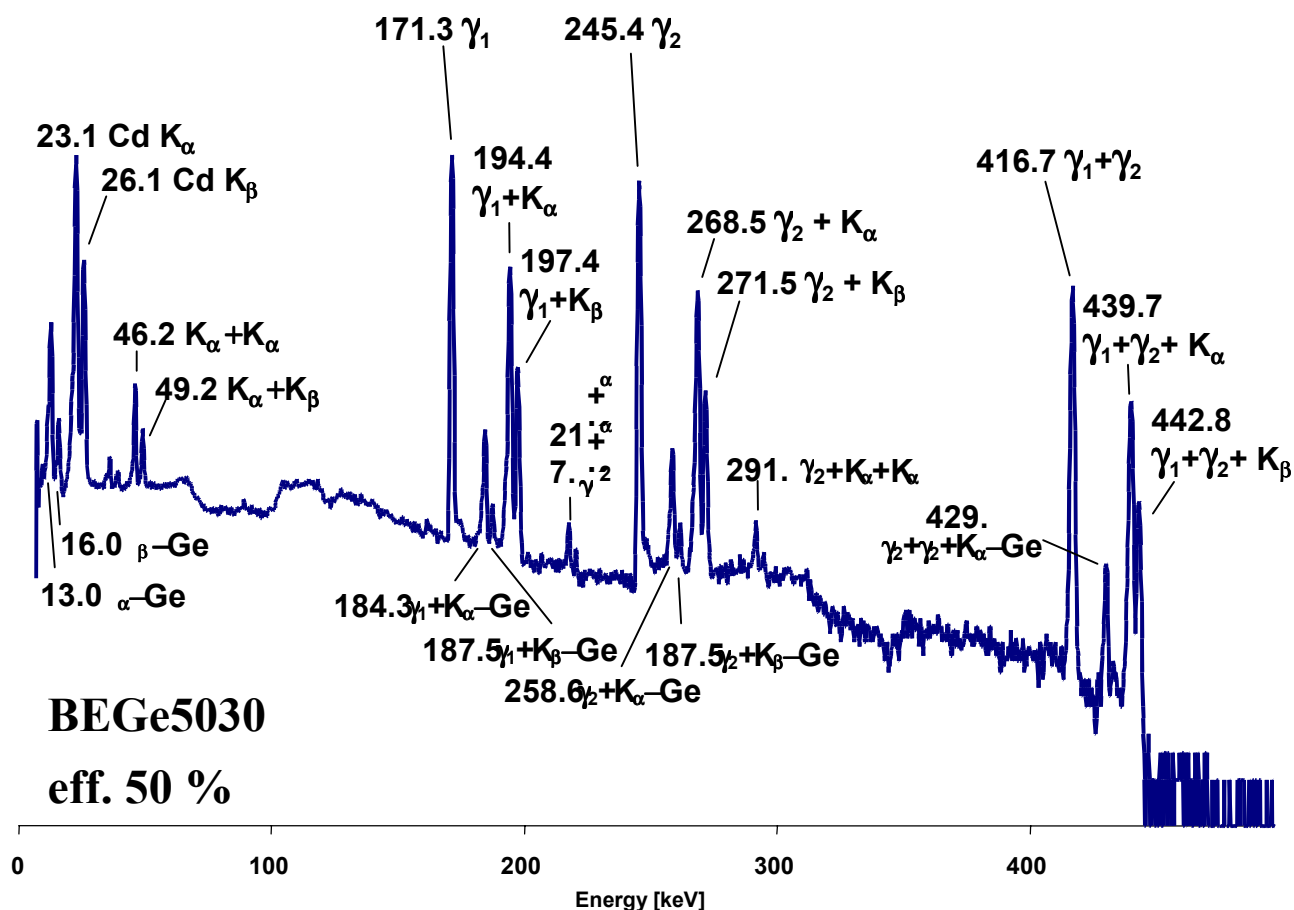
Fig 3. Spectrum of ^{111}In acquired with an extended energy range detector Canberra BE5030. ^{111}In has practically only two gamma energies, but multiple summing of gamma and X-ray peaks and additional Ge escape peaks creates very complex spectrum.

New semiconductor materials

An alternative semiconductor materials which has good energy resolution without cooling below room temperature has been sought for decades; although progress but general answer still not found. There are difficulties e.g. to grow crystals bigger than about a centimeter and to obtain sufficient crystal perfection and purity for efficient charge collection from bigger volumes. Room temperature operation requires relatively wide band gap, ≥ 1.5 eV. Among possible candidates are compounds of two or more elements, e.g. CdTe and HgI. Recently cadmium-zinc-telluride, CZT has been found to have potential of being grown in larger sizes. Amptek Inc is manufacturing CZT detector for X- and γ-ray spectrometry, which consists of a 2-mm thick $Cd_{1-x}Zn_xTe$ crystal behind a 250 μm Be window.

Although compound semiconductors have certain advantages over Ge and Si, e.g. higher attenuation coefficient and lower leakage current (in theory), they also have some disadvantages. Primary one is the far higher defect density resulting in a large number of trapping sites, leading to inferior carrier transport properties. Practical detector sizes are quite limited

and even with small size considerable spectroscopic distortion is observed. Further, leakage currents are often dominated by the defects. Other disadvantages are related to uniformity and stability of the material.
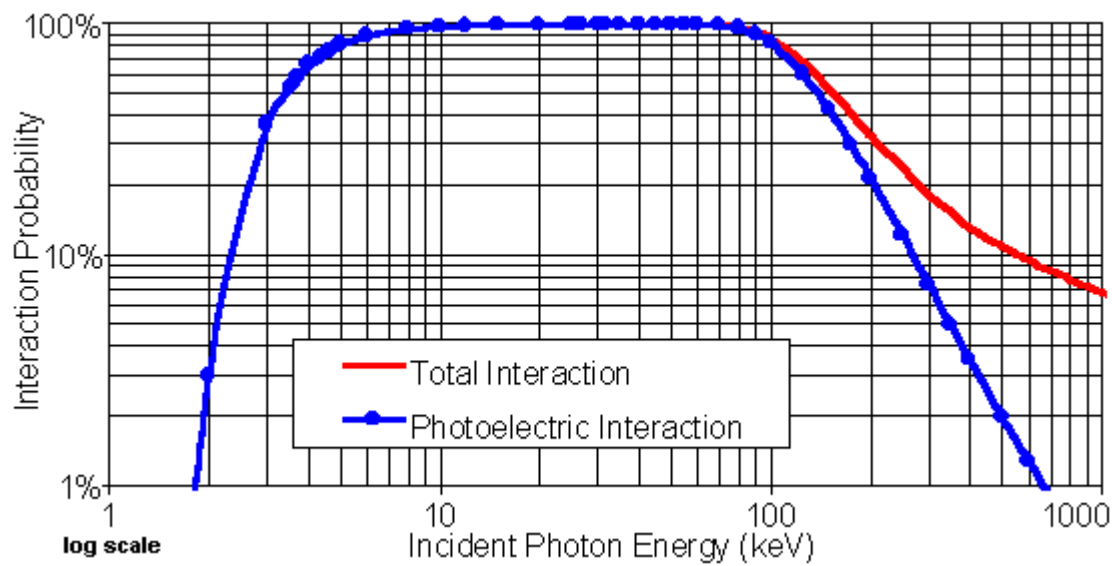
Fig. 4 Probability of an interaction occurring in the 2 mm physical thickness of CZT. It includes the effects of transmission through Be window and of stopping in the CZT, but neglect the effects of trapping and hole tailing (Trapping length of holes in CZT is much smaller than the linear dimensions of the detector. For interaction occurring near the anode, virtually the entire signal is due to electrons and so the full charge is collected. For interactions occurring near the cathode, virtually the entire signal is due to holes and so a much smaller charge is collected. The result is that the measured signal, the measured "energy", depends upon the depth of the interaction on the detector, decreasing with increasing depth. In the output spectrum, one observes a tail of counts towards lower amplitudes, an effect known as "hole tailing".) Amptek Inc.

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2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) – Progress and Problems

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Introduction

ICP-MS is a relatively new technique, it was developed in the 1970's and the first commercial instrument was used in 1984. Since then, it has been used more and more routinely, and it is now quite a common method for measuring stable and long-lived isotopes around the world. However, it also remains an area of intense research and development, and so the detection limits of ICP-MS keep falling, the instruments are increasingly more robust and user-friendly and novel ways of overcoming problems are designed. As ICP-MS becomes more common-place and the analysis cheaper, it is increasingly important to be aware of the technique and the possibilities it presents for carrying out ultra-trace analysis of long-lived radionuclides. Here, we shall look at the instrumentation and some of the benefits and problems of using ICP-MS, discuss how to overcome the problems in order to make the most of this technique, and introduce some recent developments.

Background to Mass Spectrometry

Mass spectrometry takes advantage of the fact that an ion of charge, z, travelling with velocity, v, through a magnetic field, B, will experience a force, F, so that

$$F = Bzv$$

This force is exerted perpendicular to the flight direction and magnetic field, resulting in the ion being deflected in a circle of radius, r_m, so that

$$mv^2/r_m = Bzv$$

or
$$mv/z = Br_m$$

From this, we can see that for an ion beam travelling with a constant velocity through a fixed magnetic field, the angle of deflection is dependent on the mass/charge of the ion. Therefore, ions can be separated according to m/z and, by changing B, different m/z isotopes can be deflected to a fixed detector.

ICP-MS

It is relatively simple to interpret mass spectra and so by coupling a mass spectrometer with a very efficient ion source and a sensitive detector (*e.g.* an electron multiplier), one has a very useful, sensitive technique. ICP-MS does just this, using an inductively coupled plasma (ICP) as the ion source. The plasma is created by a radio frequency (27 MHz) current in the load coil (see Figure 1) encircling the ICP torch. The magnetic field associated with this induces a current in the argon stream passing through the torch, giving a region with a high density of energetic electrons - the plasma.
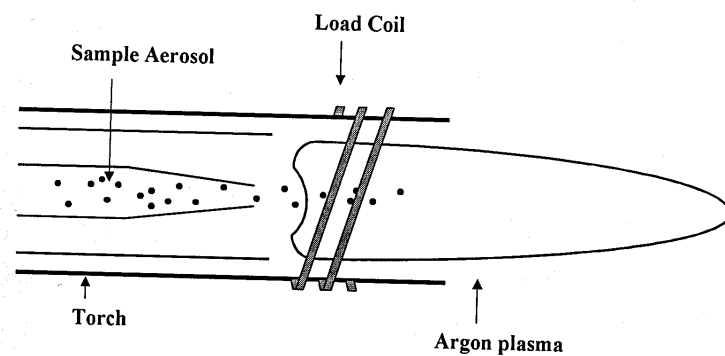
Figure 1: The Inductively Coupled Plasma

Ar has a first ionisation potential that is higher than the first ionisation potential and lower than the second ionisation potential of most other elements. This means that the vast majority of ions formed are singly charged. Since ions are deflected according to m/z, a uniform value of z is very important in obtaining a clear, simple spectrum. The ICP is therefore beneficial both because of its high ionisation efficiency and because the charge state of the ions is controlled to a much greater extent than in other ion sources.

Figure 2 shows the main hardware components of a modern quadrupole ICP-MS. Quadrupole instruments are the most common instruments today, and utilise four rod shaped electromagnets to deflect the ion beam. Samples are typically prepared in 5-10 ml of 1% HNO_3, and the sample is pumped into the sample introduction system (the nebuliser and spray chamber) by a peristaltic pump. Here, the sample is made into an aerosol by spraying the sample with Ar gas, and the aerosol is carried into the ICP torch by a stream of Ar gas. In the plasma, the sample is vaporised, atomised and ionised and the resultant ions are then accelerated away from the torch, through "cones" (labelled the sampler and skimmer in Figure 2) and an ion lens, which collimate the ion beam prior to entering the magnet. Here, the isotope of interest is selected, and directed into the detector.
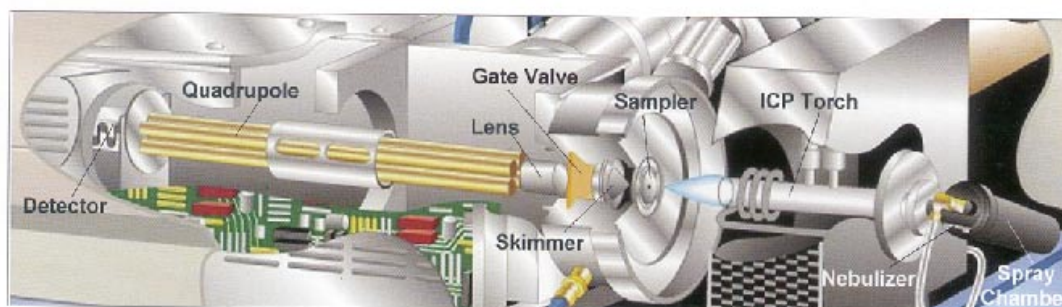
Figure 2: Major Hardware Components of the Elan 6100 ICP-MS (Perkin-Elmer)

Advantages/Disadvantages

ICP-MS offers several advantages over traditional radiometric techniques and these include:

- high sensitivity for isotopes with $t_{1/2} > 1000$ y (since $A = N\lambda$); for example, Becker and Dietze (1999) obtained detection limits for the actinides in the sub femtogram to femtogram range using state-of-the-art equipment. In Bq, the detection limit for ^{239}Pu was 1 μBq, and for ^{238}U, 4×10^{-11} Bq.
- isotope ratio measurements (*e.g.* ^{239}Pu and ^{240}Pu; see Figure 3)
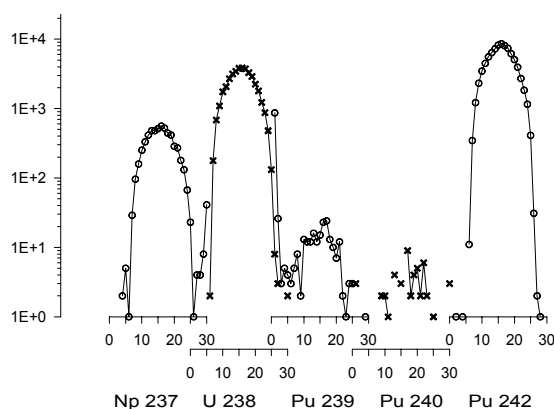
Figure 3: Mass Spectrum of Selected Actinides

- the simultaneous analysis of several elements in one sample (again, see Figure 3)
- analysis of isotopes regardless of their mode of decay
- fast analysis
- less separations chemistry required (for high level samples where digestion and dilution can be used)

Additionally, it is not subject to the uncertainties associated with beta-counting, where different beta-emitters cannot be identified separately. Measuring ^{99}Tc by ICP-MS is therefore becoming increasingly popular, with detection limits on typical instruments being equal or lower to beta-counting (~0.02 - 4 mBq). Using sophisticated instrumentation, Becker and Dietzer (1999) obtained a detection limit of ~1.5 µBq.

However, there are certain points to be aware of which may present complications if not particular disadvantages in using ICP-MS, these include:

- consumption of the sample
- non-competitive sensitivity for isotopes with $t_{1/2} < 1000$ y
- possible carry-over between samples, or a build up in the background over time
- isobaric (e.g. ^{99}Ru when measuring ^{99}Tc) and polyatomic (e.g. $^{238}U^{1}H$ when measuring ^{239}Pu) interferences
- spectral overlap (e.g. a large ^{238}U peak can tail off into a ^{237}Np peak; see Figure 4)
- matrix effects (for some sample introduction systems)
- fluctuations in the signal over time
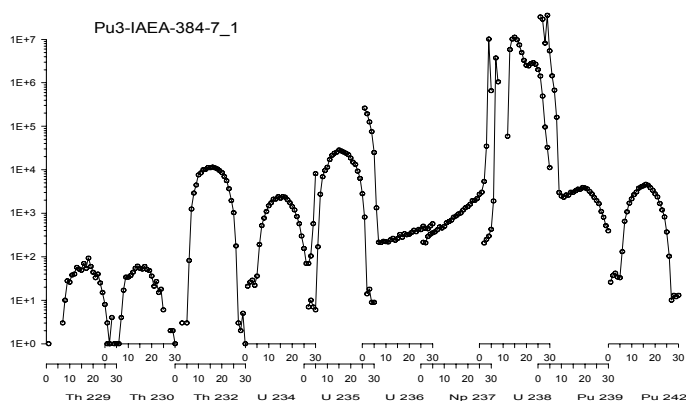- reduction in signal as the cones block

17

Figure 4: Spectral Overlap from a Large ^{238}U Peak

Obviously most of these "problems" can be overcome by using a sensible approach including careful washing between samples, not running very active samples on a machine intended for ultra-trace analysis, and using appropriate internal and external standards and blanks for monitoring both changes in ion transmission and background over time. Matrix effects have to be assessed for different sample types if one is using a sample introduction system that is prone to this problem (e.g. electrothermal vaporisation, see later), and the probability of polyatomic interferences forming should be assessed and all types of interference monitored. Moreover, when working with samples containing ultra-trace levels of radionuclides, it is always necessary to use radiochemical separations to prepare the samples for ICP-MS.

It is important to note that is not always possible to take advantage of all the benefits of ICP-MS simultaneously. The sample is aspirated into the machine over a period of less than 10 minutes, and with traditional systems there is only one detector built into the machine. Therefore, if the magnet scans over many masses to measure several isotopes in a sample, less time is spent counting each isotope than if just two or three masses were being measured. There therefore has to be a balance between the sensitivity of the measurement and the number of masses counted.

Sector Field ICP-MS

One alternative to quadrupole ICP-MS is the sector field (or high resolution) ICP-MS, which combines a magnetic mass analyser with a electrostatic mass analyser, giving much better resolution in the mass spectrum. We have discussed the problem presented by polyatomic and isobaric interferences, and by increasing the resolution from 1 amu, as obtained by quadrupole systems, to a maximum of 0.02 amu, these peaks can be resolved separately in the resultant mass spectrum (see Figure 5). However, it is only possible to run samples in a high resolution mode when there is a relatively high concentrations of the isotope of interest because, as the resolution setting is increased, the ion transmission efficiency falls (see Figure 6). The machine design means that in low resolution settings (1 amu resolution), the sensitivity is better than that of quadrupole instruments, and the excellent detection limits quoted earlier from Becker and Dietze (1999) were obtained using a sector field instrument.

Figure 5: Improvement in Mass Resolution using a Sector Field Instrument
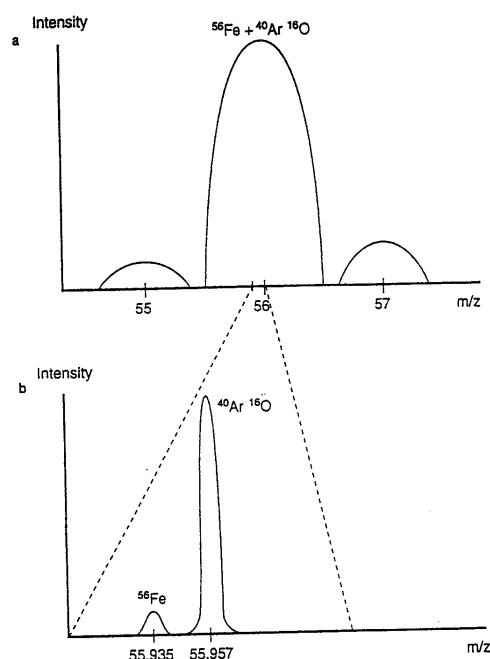
Figure 6: Relationship between Ion Transmission and Mass Resolution
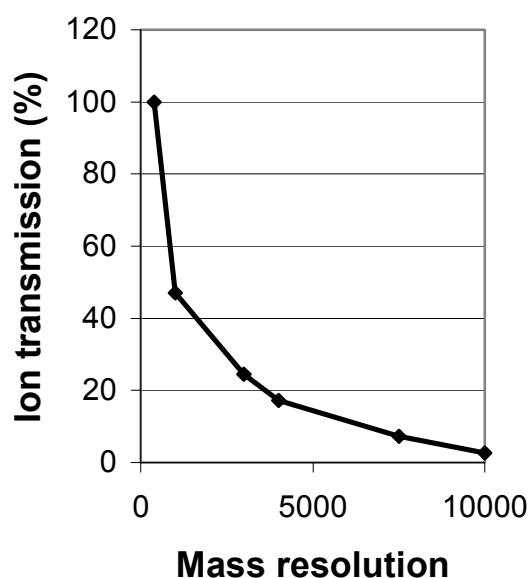
Sample Introduction Systems

In order to maximise the sensitivity of a measurement on a given instrument, the sample introduction system can be changed, improving the efficiency with which the sample is carried into the plasma. There are a variety of sample introduction systems available on the market. The most widely used system is the cross-flow nebuliser, which comes as standard on most instruments. As mentioned earlier, the sample is in 5 – 10 ml of 1% nitric acid and this is con-

verted into an aerosol in the nebuliser. Only small droplets can be allowed to reach the plasma torch or it would be extinguished, and with the cross-flow nebuliser only ~1% of the sample reaches the plasma. The ultrasonic nebuliser increases this to ~20%, by creating a much finer aerosol and then drying it, so that the sample can be taken into the plasma without putting out the torch with excess solvent. Further improvements can be obtained by using "dry" systems, such as the electrothermal vaporisation unit (ETV) which dries the sample prior vaporising it into the carrier Ar gas.

There are a number of other sample introduction systems, and these can be read up on in Montaser (1998).

New Developments

As mentioned earlier, ICP-MS is a field where new developments are constant, both in the commercial development of instruments and in new approaches within research. The most recent development in instrument design is the Dynamic Reaction Cell (DRC) technology. In this system, a reaction cell is placed in between the ICP and the mass analyser, containing a quadrupole magnet and a low volume of reaction gas. In this cell, the conditions are adjusted to remove polyatomic, or even isobaric interferences by reacting the interfering species with the reaction gas, to give a non-problematic species. The reaction depends on the interference and analyte, and this technology has only been available for a year or two, and so methods for removing interferences from radionuclides have not yet been developed. However, to illustrate the power of this tool, NH_3 can be used to remove the ^{40}Ar interference when measuring ^{40}Ca, so that Ca can be measured at less than 100 ppt. The reaction is:

$$Ar^+ + NH_3 \rightarrow Ar + NH_3^+$$
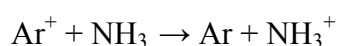
and so Ar ions are efficiently removed from the system. Ca^+ ions do not react with NH_3, and are accelerated into the quadrupole. Given that the Ar is the carrier gas in ICP-MS, this is potentially a very powerful tool and is expected to have an enormous impact on ICP-MS use.

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3 The use of ion exchange, liquid-liquid extraction and extraction chromatography for separation of radionuclides

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The progress in detection methods of radionuclides since the 1960s decreased significantly the need of radiochemical separations for radionuclide analyses. Especially the development of semiconductor detectors and computerised multichannel analysers made in most cases the determination of gamma-emitting radionuclides from different samples possible directly without radiochemical separations. However, the radiochemical separations are needed:

- For all determinations of alpha-active radionuclides from different materials

- For most determinations of beta-emitting radionuclides

- If the content of the gamma-emitting radionuclides to be determined is very low, radiochemical procedures are required to concentrate these radionuclides from samples (e.g. concentration of low ^{137}Cs and ^{7}Be contents from large volume water samples

In the studies of environmental radioactivity the need to analyse lower concentrations of radionuclides than earlier is increased. In addition, to identify the source of release of radionuclides to environment accurate values of isotope ratios are required. For this reason more specific and faster radiochemical separation methods have to be developed especially for the actinide elements.

The main separation technologies available for radiochemical analysis are:

- Precipitation
- Ion exchange
- Solvent extraction
- Extraction chromatography

The aim of this presentation is to give a short description on ion exchange and liquid-liquid extraction and consider in more detail the extraction chromatography that can be regarded as a combination of liquid-liquid extraction and chromatographic technique. After development of special resins by Horwitz and co-workers the extraction chromatography have been used for separation of radionuclides since the beginning of the 1990s (1, 2). The advantages and limitations of the extraction chromatography will be compared with those of the traditional ion exchange method.

1 Liquid-liquid extraction

The separation of radionuclides by liquid-liquid extraction is based on distribution of element between aqueous and organic phase, these two phases being practically immiscible. The liquid-liquid extraction has a very important role in radioanalytical chemistry. The advantages of this method are:

1) Method is simple and fast
2) The risk of contamination is low
3) Wide applicability
4) High selectivity (Can be increased by adjusting the pH and using masking. Masking agents are added to prevent some disturbing elements to be extracted with radionuclide studied. The method is based of formation of highly water-soluble complexes of the elements to be kept in the water phase).
5) Method is easy to be automated

Liquid-liquid (or solvent) extraction is a technique for selective transfer of a species from a mixture in an aqueous solution to an organic phase by equilibrating the aqueous phase with an organic solvent of suitable composition.

Distribution ratio:

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

The formation of an uncharged extractable complex is a prerequisite for extraction process. The formation of uncharged complex involves first reactions of the metal in the aqueous phase leading to the formation of extractable species. Complex formation is accomplished by coordination that includes chelation or by ion association.

The case of coordination may be described by

$$M^{m+} + nR^- \leftrightarrow MR_n,$$

where M^{m+} is an n-valent metal ion and R^- is an anion of a suitable chelating or coordinating agent. In ion association the metal may be incorporated by coordination in either the cation or the anion of extractable ion-pair (3).

Chelate extraction

The formation of the uncharged complex by chelation is the mechanism mostly used for liquid extraction processes in radiochemical separations. To consider the extraction process based on chelate formation let us assume that we have a system where metal will be chelated in water solution using a weakly acidic chelating agent. The metal chelated formed will be extracted into organic solvent. Using the main equilibrium equations the distribution ratio D can be expressed:

$$D = K^* \frac{[HR]_{org}^n}{[H^+]^n}$$
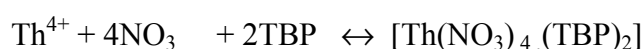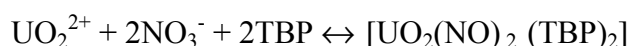
where K^* is the combined equilibrium constant, $[HR]_{org}$ is the concentration of chelating agent in organic phase and $[H^+]$ the hydrogen ion in aqueous phase. It can be concluded that in the ideal case distribution ratio is dependent on concentration of the chelating agent in the organic phase and the pH in the aqueous phase but independent on the original concentration of the metal.

Ion association extraction

In addition to coordination compounds, there are a large number of uncharged extractable compounds formed by the association of oppositely charged ions.

The use of ion association extraction has been quite a long history. The solubility of uranium nitrate in ether and the extraction of ferric chloride into ether have been known for many years (3). Many other oxygenated solvents including ethers, ketones and esters have been used in the extraction of metal ions. Ether was used in the separation of uranium in nuclear fuel processing before the introduction of tributyl phosphate (TBP).

The mechanisms of the ion association extractions are more complicated than those of the chelate extractions. The following examples of the ion association extraction by tributyl phosphate can be given (3):

$$UO_2^{2+} + 2NO_3^- + 2TBP \leftrightarrow [UO_2(NO)_{2,}(TBP)_2]$$

$$Th^{4+} + 4NO_3^- + 2TBP \leftrightarrow [Th(NO_3)_{4,}(TBP)_2]$$

2 Ion Exchange

Ion exchange methods have been widely used in radioanalytical chemistry. The reasons for the importance of radiochemical separations based on ion exchange are:

a) Radionuclides can be separated without carrier
b) High specificity
c) High decontamination degree to be received (up to 10^6)
d) Practically the only method to separate elements having very similar chemical properties (e.g. Ra-Ba, lanthanides, trivalent actinides (Figure 1) (4).
e) Simple to be automated

In ion exchangers there is a solid insoluble framework containing charged groups the counter ions of which are changeable. The material of ion exchangers consists usually of organic or inorganic polymers. To maintain the electric neutrality ion exchangers include mobile ions with opposite charges that can be replaced almost reversibly with other ions having the same charge. The ion exchangers are called anion or cation exchangers depending on the sign of the charge of the mobile ions (3,5).

Some basic requirements are essential for the ion exchange resins. Firstly, the resin must be sufficiently crosslinked to have negligible solubility. Secondly, the resin must be sufficiently hydrophilic to permit diffusion of ions through the structure at a usable rate. In addition, the resin must contain a sufficient number of accessible ionic exchange groups. The resin structure must also be chemically stable so as not to undergo degradation during use.

A breakthrough in the use of ion exchangers in the 1930s was due to observation that the number or organic substances had ion exchange properties. In 1935 Adams and Holmes found that ion exchange could take place at the phenolic group of resins prepared by reacting polyhydric phenols with formaldehyde (5).

The modern ion exchange chromatography is mainly based on the use of organic ion exchange resins which are crosslinked polymers containing functional groups where the exchangeable ions are located. Most typical polymeric framework consists of polystyrene crosslinked with divinylbenzene. To obtain a cation exchanger this polymer is sulphonated, i.e. $-SO_3H$ groups are attached to the benzene groups. Sulphonic acid is strongly acidic and dissociates in all conditions in the following way $R-SO_3H \leftrightarrow R-SO_3^- + H^+$. Thus this exchanger is capable of exchanging ions in all pH values.

Weakly acidic cation exchangers cannot be prepared from polystyrene-divinytlbenzene polymers. They are prepared by polymerising acrylic metacrylic acids and crosslinking them with divinylbenzene. The copolymer thus formed does not been to be functionalised since the acrylic acids already contain carboxylic acid groups in their structure. Carboxylic acids are weakly acidic and the dissociation $R\text{-}COOH \leftrightarrow R\text{-}COO^- + H^+$ takes place only in neutral to basic solutions. Thus these exchangers cannot be utilised as ion exchangers in acidic solutions at all.

Anion exchangers are prepared from polystyrene-divinylbenzene polymers by attaching amines into their benzene groups. To get a strongly basic anion exchangers a quaternary amine, such trimethylamine group, is used. Trimethylamine functionalised anion exchanger dissociates in all pH values in the following way: $R\text{-}N(CH_3)_3OH \leftrightarrow R\text{-}N(CH_3)_3^+ + OH^-$. These exchangers are probably most often utilised in radiochemical analyses.

The distribution coefficient D has been usually used to define the ion exchange process. The absorbability of the ion X is given by distribution coefficient D. This coefficient is given by

$$D = \frac{\text{weight of ion X per kg dry resin}}{\text{weight of ion X in solution per litre of solution}}$$

or by a volume distribution coefficient D_v.

$$D_v = \frac{\text{weight of ion X per litre of resin bed}}{\text{weight of ion X in solution per litre of solution}}$$

The D and D_v are related by

$$D_v = D\,r, \text{ where}$$
$$r = \text{is the resin bed density.}$$

When we have two ions X_1, and X_2 to be separated by ion exchange the ratio of their distribution coefficients (α) indicates the separation factor (that is the ability of the ion exchange system used to separate these two ions).

$$\alpha = \frac{D_1}{D_2}$$

Ion exchange resins are most often produced in bed form that enables their use in column operation that is the most common ion exchange method used in radiochemical separations. In this elution chromatography the ions to be separated are absorbed on the top of column and an eluent is passed through the column. If the zone in the resin column where the ions to be separated are absorbed, is only a few per cent of the column capacity and the flow rate is slow, the shape of the eluation curve (concentration of ion versus volume eluated) will resemble the Gaussian curve.

The peak elution volume v (v = the elution volume with which the maximum concentration of ions in elute is received) is related to the total volume V.

$$D_v = \frac{v - iV}{V}$$

where i is the void fraction of the column (3).

The ion exchange methods have been used especially widely for the determination of the actinide elements (U, Th, Np, Pu, Am and Cm) in environmental samples. For determination of the transuranic elements in the environmental samples optimisation of the ion exchange method is needed due to the presence of interfering natural alpha-emitting radionuclides the concentration of which can be several orders of magnitude higher than the concentrations of the radionuclides to be determined (Figure 2) (6).
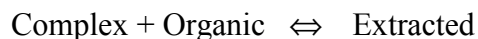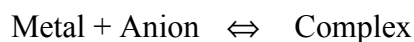
3 Extraction chromatography

The extraction chromatography combines the advantages of solvent extraction and ion exchange. The method is quite selective and specific for many radioelements like solvent extraction and its technically simple like column chromatography. The extraction chromatography produces much less acidic waste and hazardous organic solvents than solvent extraction.

In extraction chromatography the mobile phase is an aqueous solution and the stationary phase is an organic solution loaded into an inert support. A resin bead is a solid sphere, which contains many pores. The pore is filled with organic solvent. The sample passes by the organic solvent in the pore. The compound to be analysed form an extractable species at the boundary of the aqueous and organic phases (Figure 3)(7).

When a solution containing metal ions to be determined is passed through the resin column, the metal ions are moving downwards. The metal ions are moving all the time. This is one clear difference between the extraction chromatography and ion exchange chromatography. The moving of metal ions is faster or slower depending on how strongly the complex is extracted by organic phase.

In extraction chromatography two processes will happen simultaneously. The metal and the anion form a complex. The organic solvent in the pores of the resin then extracts the complex.

$$\text{Metal} + \text{Anion} \quad \Leftrightarrow \quad \text{Complex}$$

$$\text{Complex} + \text{Organic} \quad \Leftrightarrow \quad \text{Extracted}$$

In the case where a certain amount of metal is to be extracted, an increase in the concentration of the anion will drive the reaction to the right toward complex formation and extraction. Conversely, a lower concentration of the anion will drive the equilibrium to he left toward back extraction and de-complexation.

Since the 1980s several methods on extraction chromatography have been published. Philip Horwitz et al. have developed special resins for determination of radioactive elements (Sr, Pb, actinides, lanthanides, Tc) (1, 2, 7). These resins are commercially available from Eichrom Industries, USA.

In the figure 4 the separation of Sr from other alkaline-earth metals by Eichrom's resins. The Ca and Ra elute quite quickly. In this case the Ba is completely eluted after about 20 millilitres.

For separation of actinides and lanthanides from environmental samples the Eichrom's TRU resin has been widely used during the last ten years (Figure 5). In this resin the extractant is octylphenyl-N,N-di-isobutyl carbamoylphospine oxide (abbreviated CMPO). It is dissolved in TBP for coating onto the resin. In the figure 6 the separation scheme of the actinides from bone samples are described (8). In this procedure the Eichrom's TRU and U/TEVA resins have been used.

Advantages and limitations

Extraction chromatography combines the advantages of solvent extraction and ion exchange. Its selectivity is high and the method makes e.g. the separation of several actinide elements with simple resin system possible. The many papers on the use of extraction chromatography for radiochemical analysis indicate high reproducibility of the results. One practical advantage of the method compared to conventional ion exchange method the significantly lower volumes of mineral acids and reagents needed. The large amounts of mineral acids used usually to dissolve big environmental samples (wet oxidation) and in ion exchange procedures cause waste problems and also corrosion problems to the pipeline of the hood used for radiochemical separation.

One limitation of the extraction chromatography is the high price of the resins. Due to the small size of column the volume of the loading solution must be quite small. This means that dry oxidation (thermal decomposition) should be used instead the wet oxidation. For some elements e.g. Pu) the dissolution may face difficulties due to the formation of scanty soluble form of oxides.

The application of the extraction chromatographic methods published is not always suitable for some sample types. Sometimes matrix constituents that do not normally cause a problem can be troublesome because of their magnitude in the sample. In the analysis of the transuranic elements special attention should be paid to complete separation of the alpha-emitting natural radionuclides the traces of which can interfere significantly the determination of low concentration of Pu, Am, Cm and especially the determination of radioactivity ratios of their isotopes.

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4 Activation Analysis for the Determination of Long-lived Radionuclides

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Introduction

In general, determination of radionuclides is performed either by direct activity measurement, i.e. radiometric analysis, or by mass spectrometry. According to the particles emitted by target radionuclides, α-, β-, and γ-spectrometry are used in the radiometric analysis. Mass spectrometry is the typical method for isotope analysis, in which thermal ionization mass spectrometry TIMS) and accelerator mass spectrometry (AMS) have a high sensitivity for the determination of some nuclides, and recently a easily accessible ICP-MS is widely used for the determination of some radionuclides, specially long-lived radionuclides.

Activation analysis is well know as a sensitive and reliable method for the determination of trace elements, but it is actually a analytical method of nuclides, because it is based on the nuclear characteristics and nuclear reaction of the isotope of a element. It can therefore be used for the determination of radionuclides, especially long-lived radionuclides.

According to the bombarding particles, activation analysis is divided into neutron, photon and charged particle activation analysis. In which, the most used is neutron activation analysis (NAA) using nuclear reactor as neutron source because of its high sensitivity and accuracy.

The principle of activation analysis for long-lived radionuclides is that of conversion of the analyte radionuclide by activation to another nuclide having a much shorter half-life and more favorable measurement characteristics preferably for γ-spectrometry. As a result, activation analysis is favorable only for some radiionuclides, in which ^{99}Tc, ^{126}Ra, ^{129}I, ^{135}Cs, ^{226}Ra, ^{230}Th, ^{232}Th, ^{235}U, ^{238}U, ^{237}Np, ^{231}Pa and ^{242}Pu are more interesting on the view of environmental radioactivity and nuclear waste disposal (Rosenberg, 1992).

Comparing to other techniques, activation analysis has following advantages for the determination of long-lived radionuclides: (1) The detection limits for some nuclides are lower than those obtained with radiometric method and most kinds of mass spectrometry; (2) High resolution γ spectrometry allows the qualitative identification of the nuclides present and also their quantitative determination; (3) The low density of γ-lines allows their separation easily and their higher energy reduces the matrix errors; (4) Purely instrumental method can be used for some radionuclides, such as ^{232}Th and ^{238}U, which avoid the contamination in the preparation of sample. In this article, the principle of activation analysis and its application for the determination of some long-lived radionuclides are presented.

Principle of activation analysis

In activation analysis, the target nuclide is exposed to a flux of bombarding particles, such as neutron, photon and charged particles. In which, neutron from the nuclear reactor are most used, because many nuclides have high cross section for neutron capture reaction and nuclear reactor can supply a high flux of neutrons. Neutron activation analysis (NAA) is mostly based on (n, γ) reaction, i.e. the target nuclide bombed by neutron undergoes a nuclear reaction, in which the nucleus absorbs a neutron and simultaneously some excitation energy in the form of γ-radiation is emitted. The product nuclide may be either radioactive or stable, where only reaction producing suitable radionuclides can be used for activation analysis. The activity of a product radionuclide is given as follow:

$$A = N\left(\Phi_{th}\sigma_{th} + \Phi_{epi}I\right)\left(1 - e^{-\lambda ti}\right)$$

Where, N is number of the atoms of target nuclide; Φ_{th}, the thermal neutron flux; Φ_{epi}, epithermal neutron flux; σ_{th}, the average thermal neutron activation cross section; I, the effective resonance integral cross section; λ, the decay constant of the product radionuclide ($\lambda = \ln2/T_{1/2}$, $T_{1/2}$ is the half life of the product radionuclide), Ti, the irradiation time.

Because it has to take some time to get the irradiated sample out of the reactor and some times the irradiated sample need to be "cooled" for some period of time to reduce the radiation of impurity nuclides with a short half-life. Thus, the measured activity of the product radionuclide should be:

$$A = N\left(\Phi_{th}\sigma_{th} + \Phi_{epi}I\right)\left(1 - e^{-\lambda ti}\right)e^{-\lambda td}$$

Where, t_d is the decay time (the interval between the end of irradiation and start of measurement).

The amount of the target nuclide (N) can be calculated from the above equation when the radioactivity was measured and all physical parameters are known. However, in most case, it is obtained by relative comparative method because of the poor accuracy of some parameters and the instability of the neutron flux in the reactor. In this case, a standard with a know content of the same nuclide is irradiated together with the sample and measured under the same condition as the samples, by comparing the activity of the sample with that of the standard, the amount of the target nuclide can be calculated by using the following equation:

$$N_s = \frac{N_{st}A_s}{A_{st}}$$

Where, N_s and N_{st} are the amounts of the target nuclide in the sample and standard, respectively; A_s and A_{st} are the activities of product radionuclide in the sample and standard, respectively.

Activation Analysis of Long-lived Radionuclides

The benefit of activation analysis compared with direct radiometric method is based on the improved analytical sensitivity and accuracy. For some long-lived radionuclides, activation can produce a radionuclide with a shorter half-life than the target nuclide. If the reaction cross

section and other nuclear characteristics are favorable, a considerable improvement can be obtained. When a γ-emitting nuclide is produced from a nuclide which only emits β-particle or low energy γ and X rays, a especially significant improvement of analytical accuracy can be obtained because the measurement of γ-radiation is more specific than that of β-radiation which does not have a discrete energy. Meanwhile, the interference from other impurity radionuclides can be omitted without a tedious purification procedure.

The advantage of activation analysis with respect to radiometric method of the long-lived radionuclides can be quantified in the term of an advantage factor(Byrne & Benedik, 1999). The original activity of the target radionuclide is given by:

$$A_1 = N\lambda_1$$

Activation produces a new radionuclide 2, its activity A_2 is given by:

$$A_2 = N\left(\Phi_{th}\sigma_{th} + \Phi_{epi}I\right)\left(1 - e^{-\lambda ti}\right)$$

Hence, the advantage factor(AF) can be calculated by the ratio of A_2/A_1:

$$AF = \frac{A_2}{A_1} = \frac{\left(\Phi_{th}\sigma_{th} + \Phi_{epi}I\right)\left(1 - e^{-\lambda_2 ti}\right)}{\lambda_1}$$

Some long-lived radionuclides, their neutron activation product nuclides, the relevant parameters and the calculated AF are listed in Table 1. It shows that a much significant improvement can be obtained for these long-lived radionuclides by NAA, especially for those with very long-lived nuclides such as ^{239}U, ^{232}Th and ^{129}I. There is of course a large literature on NAA of U, Th and I-129. A 10^{-11} g (10^{-6} Bq) level of ^{238}U and ^{232}Th and 10^{-13} g (10^{-6} Bq) level of ^{129}I can be determined by radiochemical NAA, whereas, radiometric method at this level is impossible. Since the detection limit of NAA is proportional to the counting efficiency, counting time and the radiation emission probability of the product radionuclide, the actual improvement of NAA may be slightly lower that the level shown in Table 1. However, it is not doubt that NAA is a more sensitive method for the determination of ^{129}I, ^{237}Np, ^{232}Th and ^{238}U and had already been widely applied in the analysis of environmental samples. The detailed discussion of NAA of some long-lived radionuclides is highlighted below.

Table 1. Advantage factors of NAA and relative nuclear parameters of NAA for some long-lived radionuclides ($\Phi_{th}=10^{13}$ n cm^{-2} s^{-1}, $\Phi_{epi}=5\times10^{11}$ n cm^{-2} s^{-1}, Ti=15 h.)

Target nuclide	T$_{1/2}$ of target nuclide (years)	Product nuclide	T$_{1/2}$ of product nuclide	Eγ (keV)	σth (b)	I (b)	AF
^{99}Tc	2.1×10^5	^{100}Tc	15.8 s	539.5	20	30	2.1×10^4
^{129}I	1.57×10^7	^{130}I	12.3 h	536	30.4	27.6	1.3×10^6
^{135}Cs	2.06×10^6	^{136}Cs	13.2 d	818.5	8.7	90	3.86×10^3
^{230}Th	7.54×10^4	^{231}Th	25.5 h	84	23	1010	8.6×10^3
^{232}Th	1.4×10^{10}	^{233}Pa	27 d	312	7.4	72.4	2.5×10^6
^{238}U	4.46×10^9	^{239}U(^{239}Np)	23.5 min (2.36 d)	75 (228)	2.7	277	3.4×10^8
^{237}Np	2.14×10^6	^{238}Np	2.12 d	984	169	660	3.6×10^5
^{231}Pa	8.27×10^4	^{232}Pa	1.31 d	969	210	1500	1.2×10^4
^{242}Pu	3.75×10^5	^{243}Pu	4.96 h	84	19.1	100	3.6×10^4

Application of Activation Analysis in the Determination of Some Long-lived Radionuclides

Iodine-129

Iodine-129 (1.57×10^7 years) is a naturally occurring as well as manmade long-lived radioisotope of iodine. The ratio of $^{129}I/^{127}I$ in the environment was estimated to be 10^{-12} in the prenuclear era (Fehn et al. 1986), but the present ratio has exceeded 10^{-10} because of the release from the nuclear weapon tests and the peaceful utilization of nuclear energy, especially the reprocessing of spent fuel elements (Raisbeck & Yiou 1999; Hou et al., 2000a).

^{129}I decay emits a beta particle, a γ ray of 39.6 keV and X-rays with a low intensities. The activity of ^{129}I can therefore be measured by β- and γ-spectrometry. In this case, a very pure ^{129}I have to be separated from the sample. However, even this, the sensitivity of radiometric method is too low to be used for the analysis of really environmental samples.

In order to determine environmental levels of ^{129}I, radiochemical neutron activation analysis (RNAA) and mass spectrometry in different forms were developed. Table 2 lists the methods used for ^{129}I and their detection limits, in which RNAA is the first and very often used method for the determination of ^{129}I in the environmental samples.

Table 2 Detection limits for the determination of ^{129}I with different method (Rosenberg, 1993)

Method	Detection limits	
	atoms	$^{129}I/^{127}I$ ratio
Liquid scintillation	3.5×10^{13}	$> 10^{-6}$
Ge-γ-spectrometry	10^{13}	$> 10^{-6}$
ICP-MS	3×10^{11}	$> 10^{-8}$
TEMS	10^7	
AMS	2×10^6	10^{-13}
NAA	10^8	$10^{-11} \sim 10^{-10}$

NAA of ^{129}I is based on the following nuclear reaction:

$$^{129}I \xrightarrow{(n,\gamma),\sigma=30b,I=27.6b} \,^{130}I \xrightarrow{\beta-,12.3h} \,^{130}Xe$$
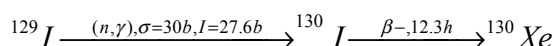
There are some interfering nuclear reactions from some nuclides exist in the samples other than iodine isotopes through with the production of ^{130}I in the samples can be simulated, these nuclides include ^{235}U, ^{238}U, ^{128}Te, and ^{133}Cs. Table 3 lists these reactions and the magnitude of various interferences calculated under the experiment condition used in Risø (Hou et al. 1999). Because of the extremely low concentration of ^{129}I in the environmental samples ($10^{-14} \sim 10^{-11}$ /g), these interfering elements have to be separated before irradiation against their nuclear interference which will generate spurious results. The radioactivity produced from the activation products of matrix elements of the sample, such as ^{24}Na, ^{47}Ca, and ^{82}Br, is much higher than that of ^{130}I, it makes the direct measurement of ^{130}I impossible after irradiation. In addition, because of the low concentration of ^{129}I in the samples, a large quantity of sample have to be treated, if no separation and preconcentration of iodine, a very high radioactivity

from the matrix elements will make the post-separation of iodine very difficult. Thus, a pre-irradiation chemical separation of iodine from the samples is necessary.

Table 3 Nuclear interferences calculation in the determination of ^{129}I (Hou et al. 1999)
($\Phi_{th} = 4\times10^{13}$ n cm^{-2} s, $\Phi_{epi} = 2\times10^{11}$ n cm^{-2} s, $\Phi_f = 1\times10^{11}$ n cm^{-2} s, Irradiation time:10h,
activities at the end of the irradiation are given)

Nuclear reaction	Induced activities of iodine isotopes	Amount of element required to produced ^{130}I equivalent to 10^{-12} g ^{129}I
$^{235}U(n, f)^{129}I (n, \gamma)^{130}I$ and $^{235}U(n, f)^{130}I$	4.6×10^5 Bq^{130}I/g U	2.6 µg
$^{128}Te(n, \gamma)^{129}Te (\beta^-)^{129}I(n, \gamma)^{130}I$	5.2×10^5 Bq^{130}I/g Te	2.3 µg
$^{133}Cs (n, \alpha)^{130}I$	6.4×10^2 Bq^{130}I/g Cs	1.9 mg
$^{127}I(n, \gamma)^{128}I(n, \gamma)^{129}I(n, \gamma)^{130}I$	7.2 Bq^{130}I/g ^{127}I	170 mg

Since bromine is chemical similar to iodine and γ-rays of ^{82}Br produced by the reaction of ^{81}Br$(n,\gamma)^{82}$Br interfer the measurement of ^{130}I, pre-irradiation separation usually can not completely separate it, a post-irradiation chemical purification has to be directed to provide a necessary decontamination with respect to this nuclide.

Therefore, the analytical procedure for the determination of ^{129}I by RNAA involves four steps to minimize the effects of the above mentioned nuclear and chemical interference, they are pre-irradiation separation of iodine, neutron activation in a nuclear reactor, post-irradiation purification of iodine, and measurement of ^{130}I by γ-spectrometry.

A typical procedures used for the pre-separation of iodine from solid samples (vegetation, soil, sediment, and tissues) is show in Fig.1 (Hou et al. 1999, 2000a,b). In addition, a combustion method is also widely used for the separation of iodine from solid samples (Aumann et al. 1981, 1985; Handl et al. 1990, 1993), it is based on that iodine can be released from the samples as gaseous forms in a higher temperature (>1000°C) and trapped by alkali solution or active charcoal. For water sample including milk and urine, iodine can be separated by anion exchange method. In which, iodine as iodide is absorbed by anion exchange resin (AG1) and separated from other element, the iodine absorbed is eluted by nitrate solution, and concentrated by extraction with CCl$_4$ from the eluate (Hou et al. 2001). A simple post-irradiation separation method (Fig.2) is usually used for the further purification of ^{130}I, which is based on that I$_2$ can be easily extracted by CCl$_4$, and iodide back-extracted by sulfite is precipitated as PdI$_2$ (Hou et al. 1999).

In addition to the nuclides mentioned above, stable iodine, ^{127}I, can also cause interference to the determination of ^{129}I by three continuous neutron capture reactions, ^{127}I$(3n, \gamma)^{130}$I. This interference varies as the square of the neutron flux and increases with the length of the irradiation time. By simultaneous determination of ^{127}I concentration via a fast reaction of ^{127}I$(n, 2n)^{126}$I, this interference can be corrected. But, this interference limits the activation under contain neutron flux and for contain irradiation time for the analysis of sample with very low ^{129}I /^{127}I ratio. However, for normal environmental sample, this interference is very small.

Solid samples

| KOH and ^{125}I tracer
↓ Ashing

ashed sample

| leaching with hot water,
| filter

filtrate   residue

Extracting with CCl₄, ↓ discard

aqueous phase   organic phase

solution ↓   Back-extracting with H₂SO₃

discard

aqueous phase   organic

phase ↓

| extracting again with CCl₄   dis-

card

aqueous phase   organic phase

↓ | Back-extracting with H₂SO₃ solu-

tion

discard

aqueous phase   organic phase

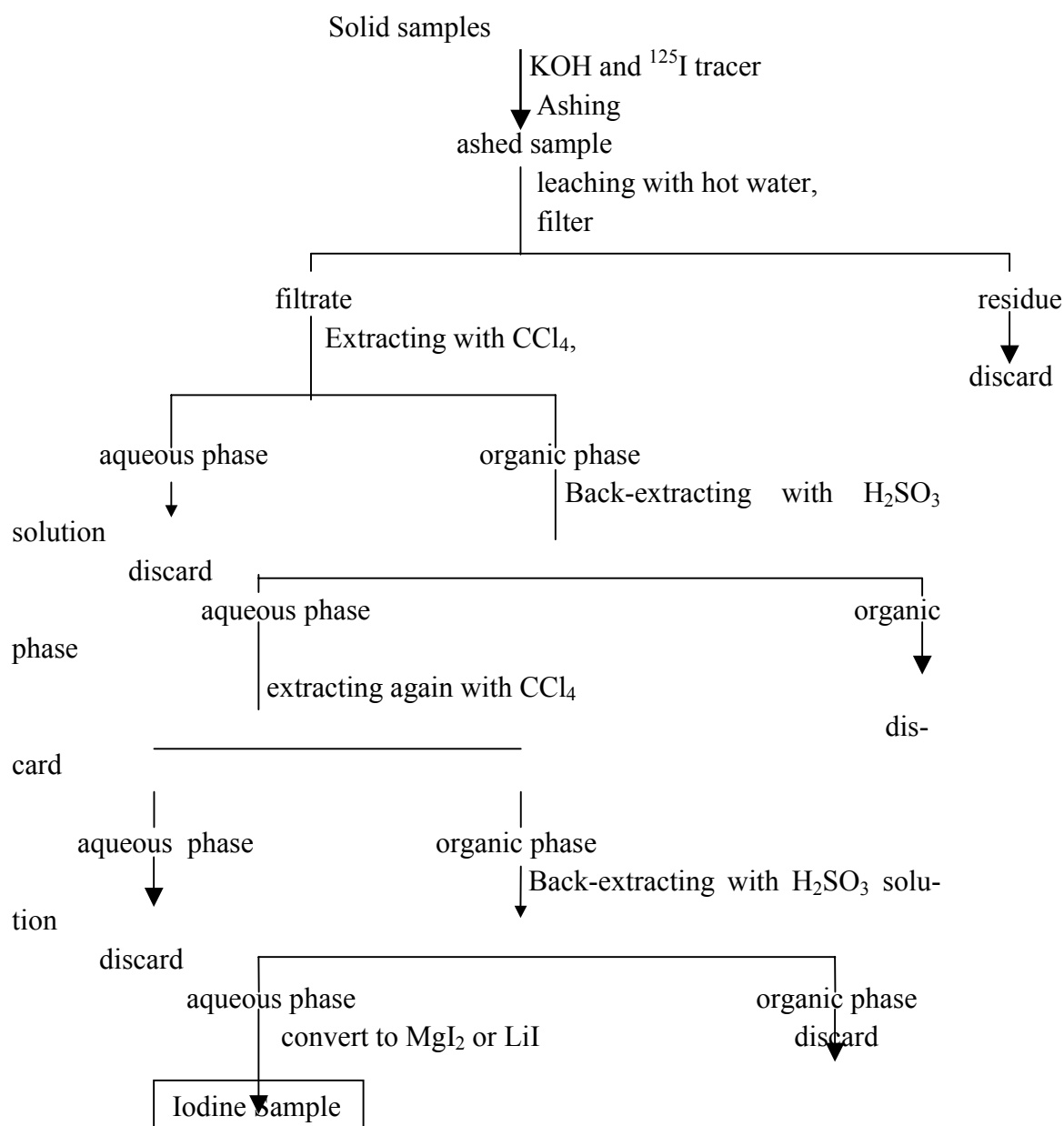convert to MgI₂ or LiI   discard ↓

Iodine Sample

Fig. 1. Pre-irradiation separation procedure of iodine from environmental samples

For the measurement of chemical yield, some radioisotopes of iodine are used as a tracer. Because [129]I can be simultaneously produced during the production of ^{131}I, the ^{131}I tracer contains some amount of [129]I, the addition of ^{131}I as a tracer will interfere the determination of [129]I. It was reported that the isotope ratio of [129]I/^{131}I ranges from 2.6×10^{-13} g/kBq[131]I to 1.8×10^{-12} g [129]I/kBq ^{131}I in the ^{131}I tracer solution (Chao et al. 1998; Hou et al. 1999). Therefore, ^{125}I is usually used for this purpose because no [129]I is produced in the production of [125]I.

A large number of literatures on the NAA of ^{129}I in various environmental samples are available (Edwards, 1962; Handl, et al.1990, 1993; Aumann, et al. 1981, 1985; Hou et al. 1999, 2000a, 2000b, 2001; Raisbeck & Yiou, 1999; Chao et al. 1998). NAA is also a main method used for the determination of ^{129}I in environmental samples.
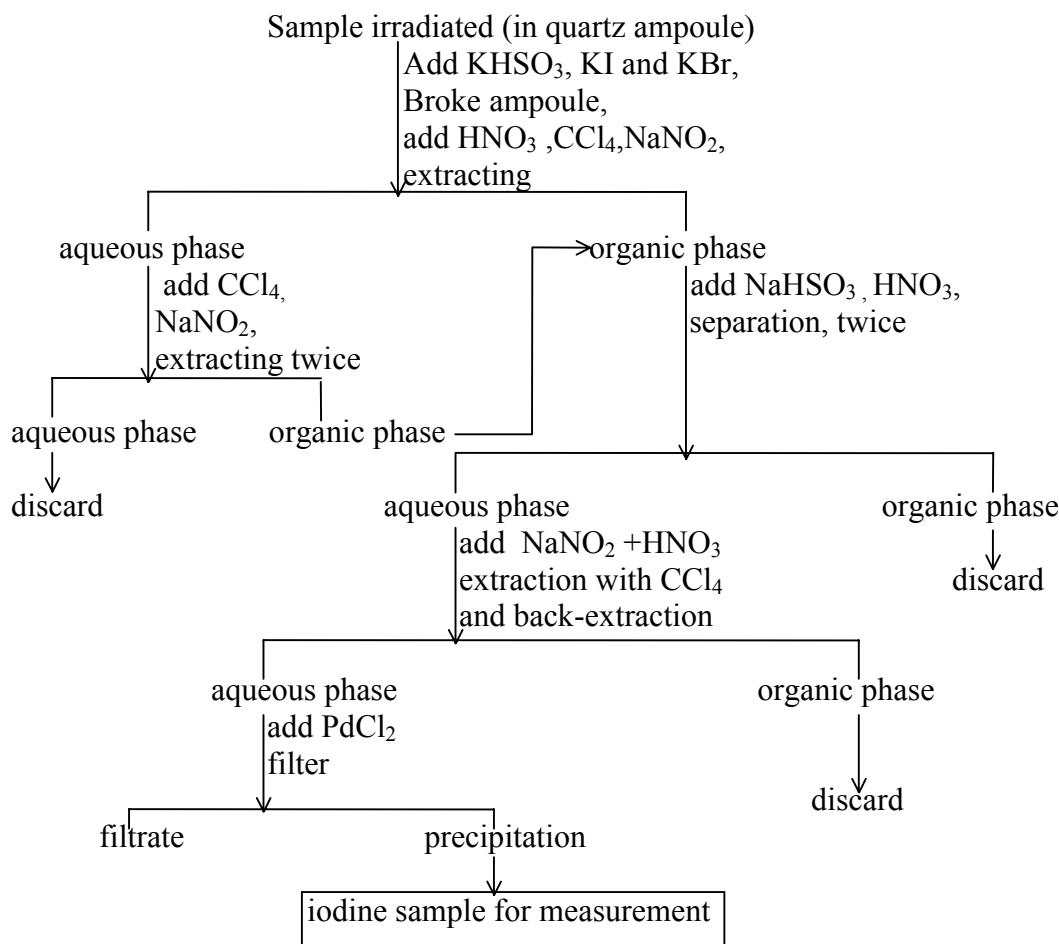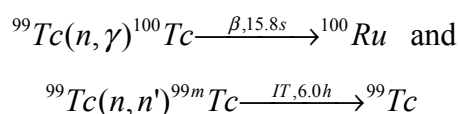
Sample irradiated (in quartz ampoule)
Add KHSO₃, KI and KBr,
Broke ampoule,
add HNO₃ ,CCl₄,NaNO₂,
extracting

aqueous phase
add CCl₄,
NaNO₂,
extracting twice

organic phase
add NaHSO₃ , HNO₃,
separation, twice

aqueous phase   organic phase

discard

aqueous phase
add NaNO₂ +HNO₃
extraction with CCl₄
and back-extraction

organic phase

discard

aqueous phase
add PdCl₂
filter

organic phase

discard

filtrate   precipitation

iodine sample for measurement

Fig. 2 Post-irradiation purification procedure for the measurement of ^{130}I

Technetium-99

Technetium-99 decays by low energy beta emission with a specific activity of 0.625 mBq/pg. The concentration of ^{99}Tc in uncontaminated environmental samples is of the order of a few mBq/g or less. In addition to radiometric method, many other method, such as atomic absorption spectrometry, NAA, ICP-Ms and AMS can be used for the determination of ^{99}Tc.

The NAA of ^{99}Tc is based on two reactions:

$$^{99}Tc(n,\gamma)^{100}Tc\xrightarrow{\beta,15.8s}{}^{100}Ru \quad \text{and}$$

$$^{99}Tc(n,n')^{99m}Tc\xrightarrow{IT,6.0h}{}^{99}Tc$$

When counting ^{100}Tc, which has a very short half-life, ^{99}Tc has to be separated from the sample prior to irradiation, in addition, a fast sample transfer system has to be used to shorten the

decay time. Although NAA is theoretically a more sensitive method for ^{99}Tc (Table 1), a poor detection limit (>10^{-8} g, or >10 Bq) was obtained because of the quickly decay of the product nuclide ^{100}Tc and some interference from the activation products, such as ^{19}O, ^{28}Al, ^{38}Cl and ^{41}Ar (Goerner et al. 1988). If a cyclic activation model is used, the detection limit can be improved, but it is still not enough for the analysis of real environmental samples.

^{99m}Tc has a relative longer half-life, but the low neutron activation cross section of (n, n') reaction limits its analytical sensitivity (Ikeda et al. 1989). In addition to NAA, photon activation analysis can also be used for the determination of ^{99}Tc by the nuclear reaction of ^{99}Tc(γ,γ')^{99m}Tc. By using this reaction, the detection limit for ^{99}Tc was improved to 10^{-9} (Sekine et al. 1989), it is still not low enough for the analysis of environmental samples. Up to date, activation analysis was just used for the analysis of samples with a high ^{99}Tc concentration, such as radioactivity waste. No paper on the analysis of real environmental samples using this method is available.

Caesium-135

^{135}Cs is also a β-emitter with a specific activity of 43 mBq/ng, its determination by radiometric method is therefore very difficult. A few method can be used for its determination, but only NAA and thermal ionization mass spectrometry was applied for the analysis of real samples (Lee et al. 1993; Chao &Tseng 1996; Stamm, 1973). The NAA of ^{135}Cs based on the reaction:

$$^{135}Cs \xrightarrow{(n,\gamma)} {}^{136}Cs \xrightarrow{\beta,13.16d} {}^{131}Ba$$
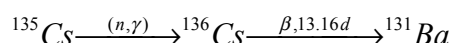
Because of the very low concentration of ^{135}Cs in the environmental samples, a pre-irradiation separation has to be used to separate Cs from a large amount of sample. The most used method for the separation and concentration of Cs is based on its specific absorption on ammonium phosphomolydate (AMP) and copper ferrocyanide.

The detection limit of NAA for ^{135}Cs depends on the concentration of other Cs isotopes, especially ^{134}Cs from the stable caesium isotope ^{133}Cs and ^{137}Cs, the main radionuclide in the environmental samples. A detection limit as low as 10^{-4} Bq (10^{-12} g) ^{135}Cs was reported for a sample with a ratio of ^{133}Cs:^{135}Cs:^{137}Cs=1:1:1 (Chao & Tseng, 1996) . In addition, the interference from ^{86}Rb with a half-life of 18.6 days, which produced by reaction ^{85}Rb(n, γ)^{86}Rb and emits a γ-ray of 1077 keV, is also very important for the analysis of environmental samples. Because Rb can be also absorbed by AMP and copper ferrocyanide, and concentrated together with Cs and have a higher concentration than Cs in most environmental samples, the Compton background produced by ^{86}Rb will overlap the γ-lines peak of ^{135}Cs (818.5 keV and 1048 keV). Up to date, only two papers on NAA of ^{135}Cs are available for the analysis of radioactive waste and sodium coolant (Chao &Tseng 1996; Stamm, 1973), but it will be a potential useful method for the determination of Ca-135 in environmental samples by developing a suitable pre-separation and concentration procedure.

Neptunium-237

[237]Np is an α-emitting long-lived radionuclide with a specific activity of 26mBq/ng. In the environmental samples, it originates from the nuclear weapon tests and reprocessing of nuclear fuel. In addition to α-spectrometry, [237]Np has been determined by NAA, AMS and recently ICP-MS. Hursthouse et al.(1992) evaluated three analytical methods for the determination of [237]Np, the detection limits of them are shown in Table 4.
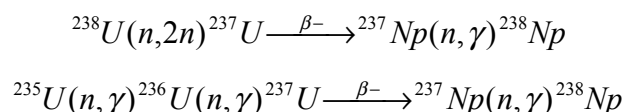
Table 4 Detection limits and time consumption of three method for the determination of [237]Np (Hursthouse et al.(1992))

Method	Detection limit (mBq)	Counting time
α-spectrometry	0.1	>7 days
ICP-MS	0.3	5 days.
NAA	0.4	7 days

The following nuclear reaction is used for the NAA of [237]Np:

$$^{237}Np \xrightarrow{(n,\gamma),\sigma=169b} {}^{238}Np \xrightarrow{\beta-,2.1d} {}^{238}Pu$$
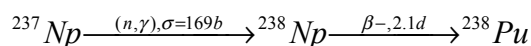
Uranium may interferes with the analysis by the following reactions:

$$^{238}U(n,2n)^{237}U \xrightarrow{\beta-} {}^{237}Np(n,\gamma)^{238}Np$$

$$^{235}U(n,\gamma)^{236}U(n,\gamma)^{237}U \xrightarrow{\beta-} {}^{237}Np(n,\gamma)^{238}Np$$

Although these interferences are said to be small, uranium has to be separated from the sample prior to the neutron irradiation. In addition, the pre-irradiation separation can also be used to concentrate Np from a large sample, and avoid working with high activity. A post-irradiation chemical separation is also necessary in order to remove interfering nuclides produced from remaining impurities, such as [82]Br and [24]Na. Fig. 3 shows a typical procedure of RNAA for [237]Np. [239]Np is usually used as a tracer for the measurement of chemical yield which can be prepared by irradiation of uranium (Germain et al. 1987).

NAA has been used for the determination of [237]Np in various environmental samples, such as soil, sediment, seawater, seaweed and fish by many authors (May et al.,1987; Germain et al. 1987, 1990; Hursthous et al.,1992; Jha &Bhat, 1994; Ruf & Friedrich, 1978; Kim et al.,1988; Byrne, 1986) and a good agreement was obtained by NAA with that by α-spectrometry and ICP-MS.

Uranium-235/238 and Thorium-232

Uranoum-235/238 and thorium-232 are important natural radionuclides with a very long half-life ($>10^8$ years). Radiometric methods based on α-spectrometry are very time consuming, needs a large sample, and is limited by reagent blank. Although the recent ICP-MS has a high sensitivity for the determination of these radionuclides, and can significantly reduce the amount of sample used, the sample has to be decomposed before measurement, the reagent, laboratory and instrumental blanks limit its detection limit.

NAA is an excellent method for the determination of low level ^{238}U, ^{235}U and ^{232}Th due to its high sensitivity and virtual freedom from blank problems when instrumental neutron activation analysis (INAA) or RNAA are used.
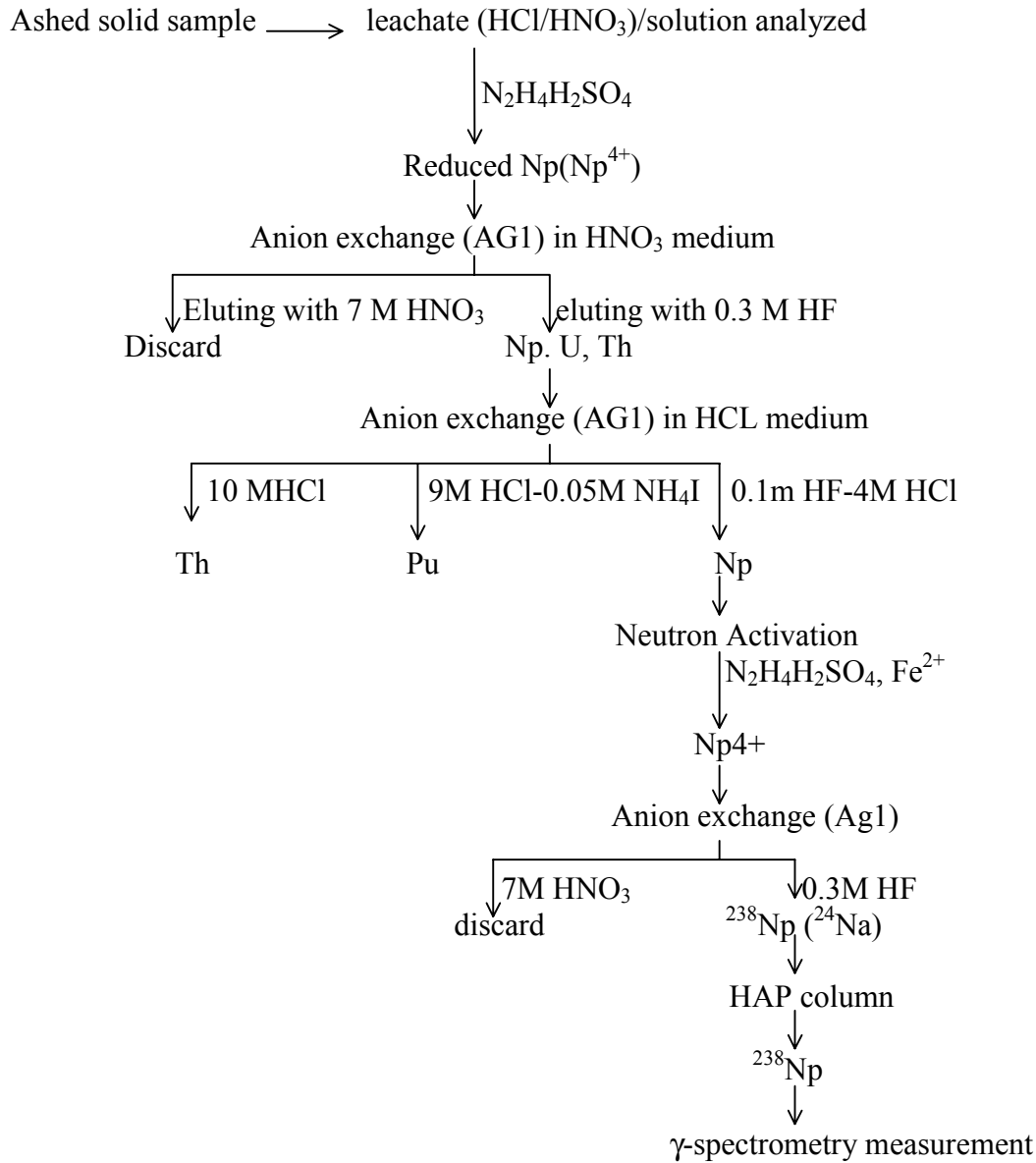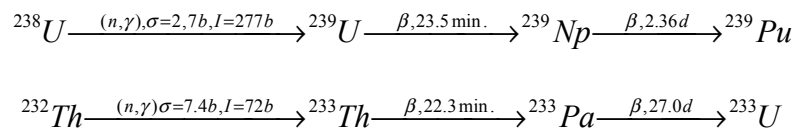
Ashed solid sample $\longrightarrow$ leachate (HCl/HNO$_3$)/solution analyzed

$\downarrow$ N$_2$H$_4$H$_2$SO$_4$

Reduced Np(Np^{4+})

$\downarrow$

Anion exchange (AG1) in HNO$_3$ medium

$\downarrow$ Eluting with 7 M HNO$_3$ $\downarrow$ eluting with 0.3 M HF

Discard   Np. U, Th

$\downarrow$

Anion exchange (AG1) in HCL medium

$\downarrow$ 10 MHCl $\downarrow$ 9M HCl-0.05M NH$_4$I $\downarrow$ 0.1m HF-4M HCl

Th   Pu   Np

$\downarrow$

Neutron Activation

$|$ N$_2$H$_4$H$_2$SO$_4$, Fe^{2+}

$\downarrow$

Np4+

$\downarrow$

Anion exchange (Ag1)

$\downarrow$ 7M HNO$_3$ $\downarrow$ 0.3M HF

discard ^{238}Np (^{24}Na)

$\downarrow$

HAP column

$\downarrow$

^{238}Np

$\downarrow$

γ-spectrometry measurement

Fig. 3 Analytical procedure of NAA for ^{237}Np

The NAA of ^{238}U and ^{232}Th are based on the following nuclear reactions:

$$^{238}U \xrightarrow{(n,\gamma),\sigma=2,7b,I=277b} {}^{239}U \xrightarrow{\beta,23.5\,min.} {}^{239}Np \xrightarrow{\beta,2.36d} {}^{239}Pu$$

$$^{232}Th \xrightarrow{(n,\gamma)\sigma=7.4b,I=72b} {}^{233}Th \xrightarrow{\beta,22.3\,min.} {}^{233}Pa \xrightarrow{\beta,27.0d} {}^{233}U$$

^{239}Np and ^{233}Pa are usually used for the determination of ^{238}U and ^{232}Th, respectively, because the interferences of ^{24}Na (15h) and other short lived nuclides produced from the matrix elements make the measurement of ^{239}U and ^{233}Th more difficult in INAA. However, epithermal

NAA can largely reduce these interferences because of the high resonance integral cross section of these two reactions. The reported detection limit of INAA for ^{238}U and ^{233}Th are 10^{-8} g, it can therefore be used for the determination of ^{238}U and ^{232}Th in the most of environmental and biological samples.

For the analysis of samples with a very low concentration of ^{238}U and ^{232}Th, RNAA has to be used. In this case, a detection limit of 10^{-11} g of ^{238}U and ^{232}Th can be obtained. Because the separation is carried out after irradiation, the contamination and reagent blank can be avoid. For some samples, such as blood, urine and tissue, RNAA can supply a very accurate result. When ^{239}Np is used for the RNAA of ^{238}U, the radiochemical separation procedure is the same as that for ^{237}Np. For the separation of ^{239}U and ^{233}Pa, solvent extraction is usually used using extractants of HDEHP, TBP or TOPO (Benedik & Byrne, 1995; Becker & Lafeur, 1972).

NAA of ^{235}U can be carried out by measuring some fission products, such as ^{140}La, ^{141}Ce, ^{133}I and ^{134}I (Dermelj & Byrne, 1997; Augustson et al. 1980). In addition, delay neutron counting and fission tracts are also used for the determination of ^{235}U (Vasconcellos et al. 1987; Armellin & Vasconcellos, 1986). The detection limit of NAA for ^{235}U can reach to 10^{-11} g.

Conclusion

1) Neutron activation analysis as an alternative method other than radiometric method and mass spectrometry can be used for the determination of some long-lived radionuclides.
2) NAA has be proved to be a very sensitive method for the determination of ^{129}I, ^{238}U, ^{235}U, and ^{232}Th, a useful method for ^{237}Np, and a potential useful method for ^{135}Cs in the environmental samples.
3) Comparing to radiometric method and ICP-MS, the disadvantage of NAA is the requirement of nuclear research reactor.

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5 The Nordic Experience in Intercomparison Exercises and Magnitude of Common Corrections for Gamma Measurements.

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Introduction

During the numerous NKS BOK 1.1 meetings I have participated over the last three years the importance of various corrections have been discussed thoroughly. I have found it useful to use the first part of my talk to summarise the magnitude of the typical corrections applied for different detectors at Risø. In the second part I will give some examples of the results of the first intercomparison and a few preliminary results of the second intercomparison. In this paper I have omitted most of the figures presenting the results of the intercomparisons as separate reports exists (or will in the near future) on this topic.

Part A: corrections for gamma counting

Some of the most common corrections are:

Density corrections
Filling corrections
Pile-up corrections
Coincidence corrections

I will give some examples for these four types.

Density corrections used by Risø for Ge-detector γ-spectrometric analyses of environmental samples (from Sven P. Nielsen)

The corrections are based on work done by Lippert (1983) on a mathematical model of various sample densities and configurations of Ge-detector and sample geometries. From this work a simple expression has been derived involving three parameters: density, geometry and gamma-ray energy. The correction factor (CF) is calculated according to the following expression

$$CF = \exp((\rho - 1) \cdot xabs \cdot \exp(m_0 - m_1 \cdot \ln(E\gamma))),$$

where ρ is the sample density (g cm^{-3}), xabs a characteristic length (cm) for the sample geometry, m_0 and m_1 constants (0.4628 and 0.4767, respectively) and E_γ the gamma energy (keV).
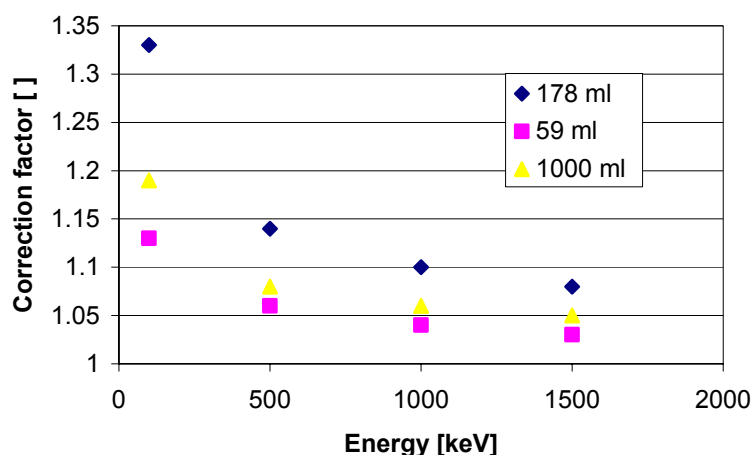
The following table gives values of xabs for various geometries used by Risø:

Geometry	xabs (cm)
1-L Marinelli, full	1.2
200-mL Cylinder, 178 mL	2.05
200-mL Cylinder, 103 mL	1.30
200-mL Cylinder, 59 mL	0.85
200-mL Cylinder, 36 mL	0.65
200-mL Cylinder, 20 mL	0.50

Example correction factors of a sample of density 1.8 g cm^{-3} in three geometries are given in the following table (two fillings (178 and 59 mL) of a 200-mL cylinder geometry and a full 1-L Marinelli container):

| Gamma energy (keV)	Correction factor 200-mL Cylinder 178 mL	Correction factor 200-mL Cylinder 59 mL	Correction Factor 1-L Marinelli Full
100	1.33	1.13	1.19
500	1.14	1.06	1.08
1000	1.10	1.04	1.06
1500	1.08	1.03	1.05

Examples of density corrections

Density corrections for a 1.8 g/cm3 sample as a function of energy for three different geometries.

Filling corrections

Fillings corrections is often used when the amount of sample material is limited and variable. The example is from a yearring study where the obtained samples varied some in both amount and density. Wood chips were filled into a plastic container with a diameter of 50 mm and a height of 56 mm. The sample was pressed in a hydraulic press according to weight, until the height of the sample corresponded to a uniform density of 0.22 g cm^{-3}. The detectors used for the analysis were efficiency calibrated with 4 standards consisting of standard containers 10, 33, 66 and 100 % filled with an isotope mix absorbed on a material of a suitable density. The figure below shows the efficiency calibration for the three detectors used in the study.

Three parameter fit
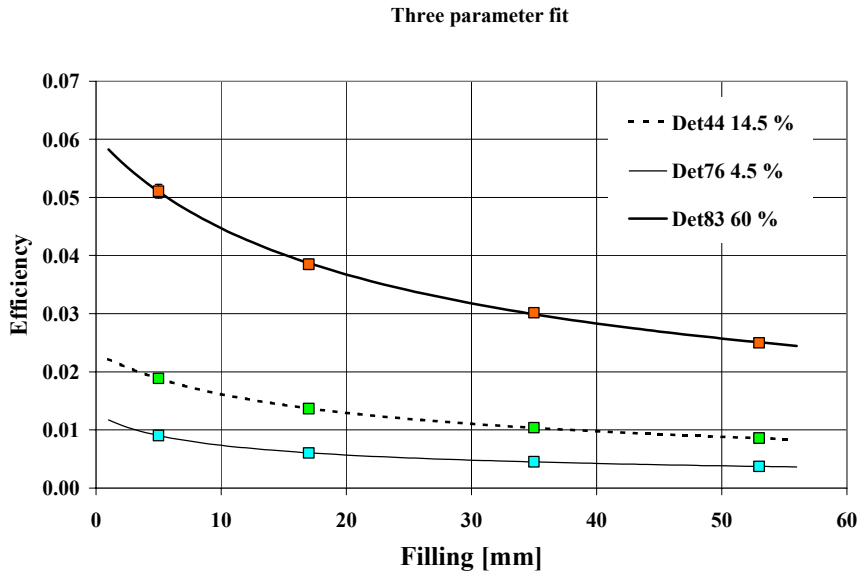
Efficiencies of the three detectors (DET44, DET76 and DET83) used for the analysis of the wood samples as a function of the filling of the sample container.

The efficiency factors obtained from the four standards were fitted with an analytical expression for the efficiency (*Eff*) as follows:

$$Eff = A(f + B)^C ,$$

where A, B and C are empirical constants and f is the filling height in the container. A depends on the crystal size, B is dependent on the distance to the crystal and C was almost constant.

Example of corrected data
Cs-137 in wood in Zaborie, Russia


Yearring
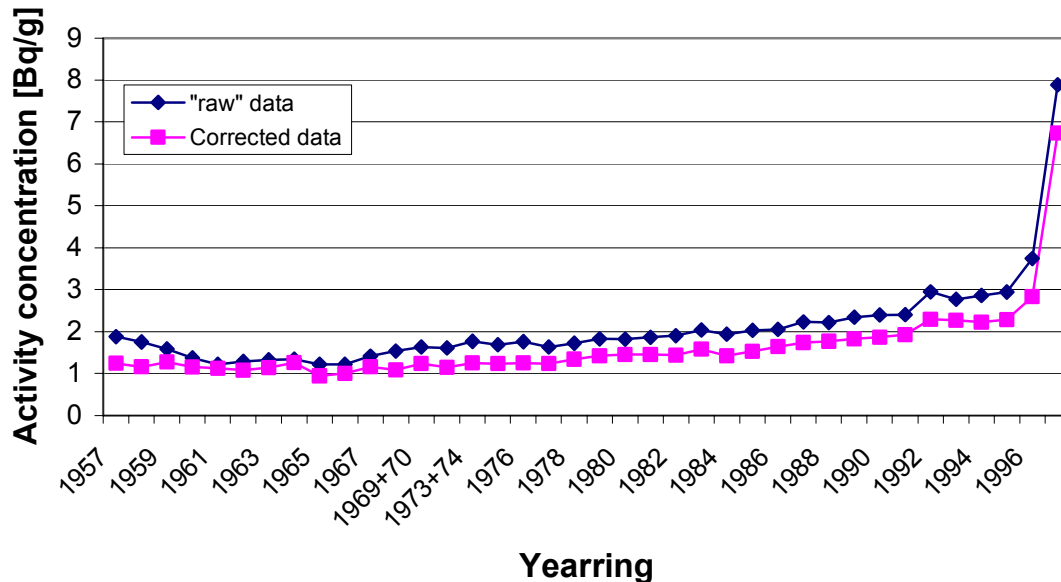
This figure shows the result with and without correction applied. The main effect of the correction is a lower activity level and the 'strange' increase of activity near the center disappears. However, the main conclusion is the same. Cs-137 is very mobile in the tree stem.

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Pile-up corrections

The following example have been used to empirically correct the activity calculation of In-115 and Dy-165 after neutron activation of tracer particles deposited on various materials. The optimal solution would have been to use pulsers, but none were available at the time. The samples were usually counted on the two small detectors, but the large detector was included for completion. The experiment was carried out by counting three In standards for ten hours after pile out in a fixed position. At 20 % dead time the correction is up to 10 %.

### Pil-up losses as a function of live time
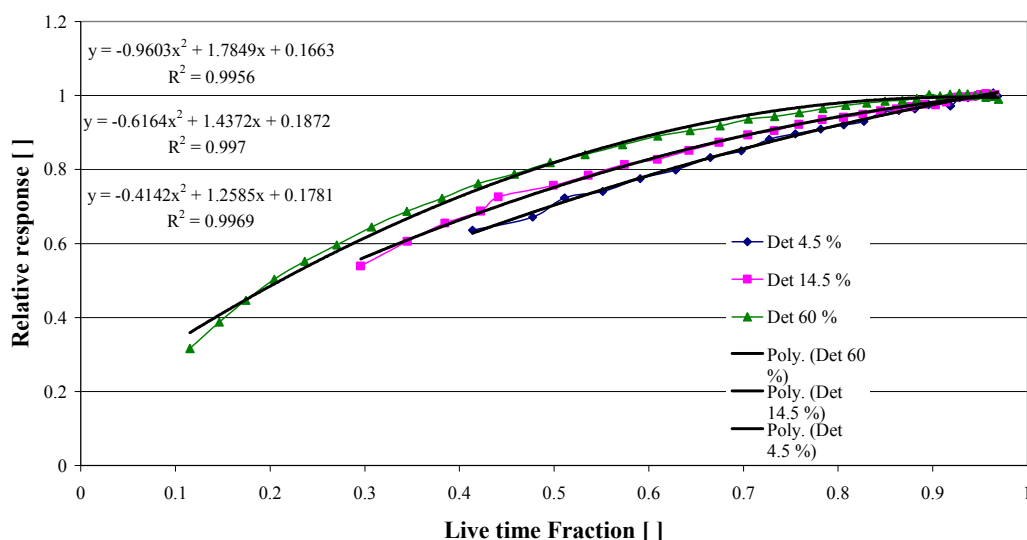
Coincidence corrections

In order to examine coincidence losses a solution of Cs-137 and Cs-134 in a 1:1 activity ratio was produced. Seven sources from 10 Bq to 100 kBq was produced from this master solution. further a 1 kBq source was produced in a 200 ml standard geometry.

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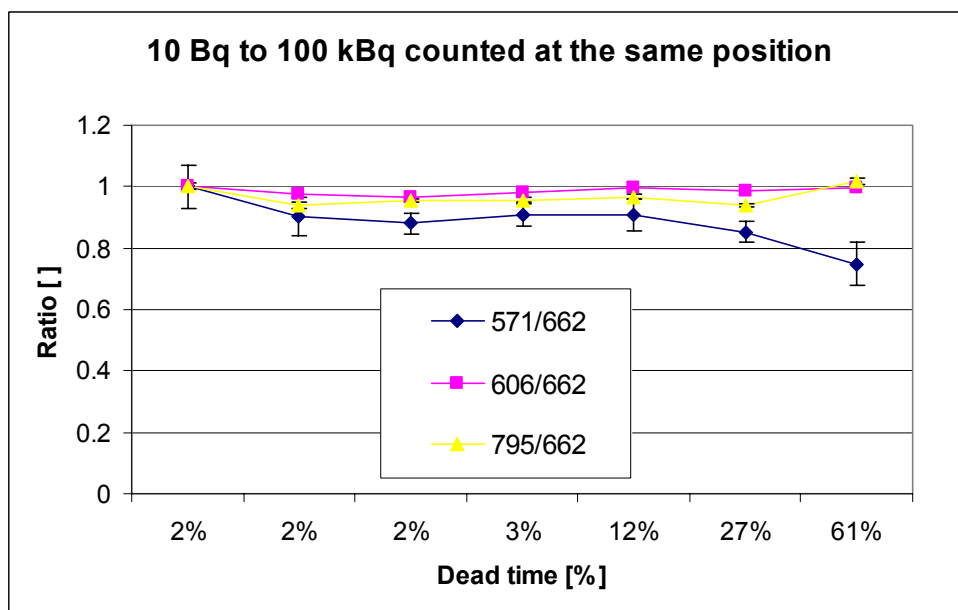
The seven different activity soulutions where counted at a position closest to the detector to demonstrate that the the peak ratio was indepent of the count rate, figure above. After that the 10 kBq sample and the 100 kBq sample was counted at 7 different distances from the detector to find the coincidence free ratio between the Cs-137 peak and the Cs-134 peaks, see figure below.

605 keV line compared to 662 keV line
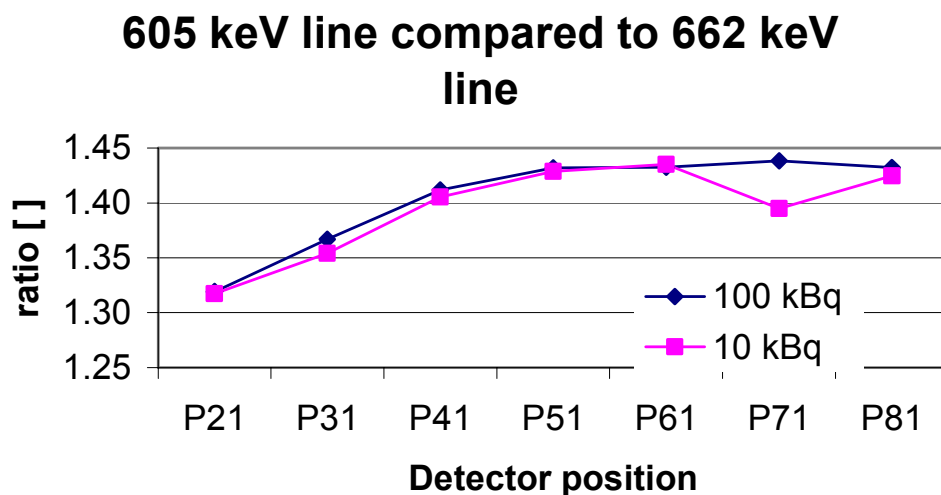
Finally the 1 kBq sample in the 200 ml geometry was counted on a number of Risø's detectors. The next figure shows the result for the ratios found sorted after detector size. A dramatic effect can be seen for the well detector. Otherwize there is a weak dependence on detector size in the range 15 to 40 % relative crystal size with a typical correction of 10 - 15 %.
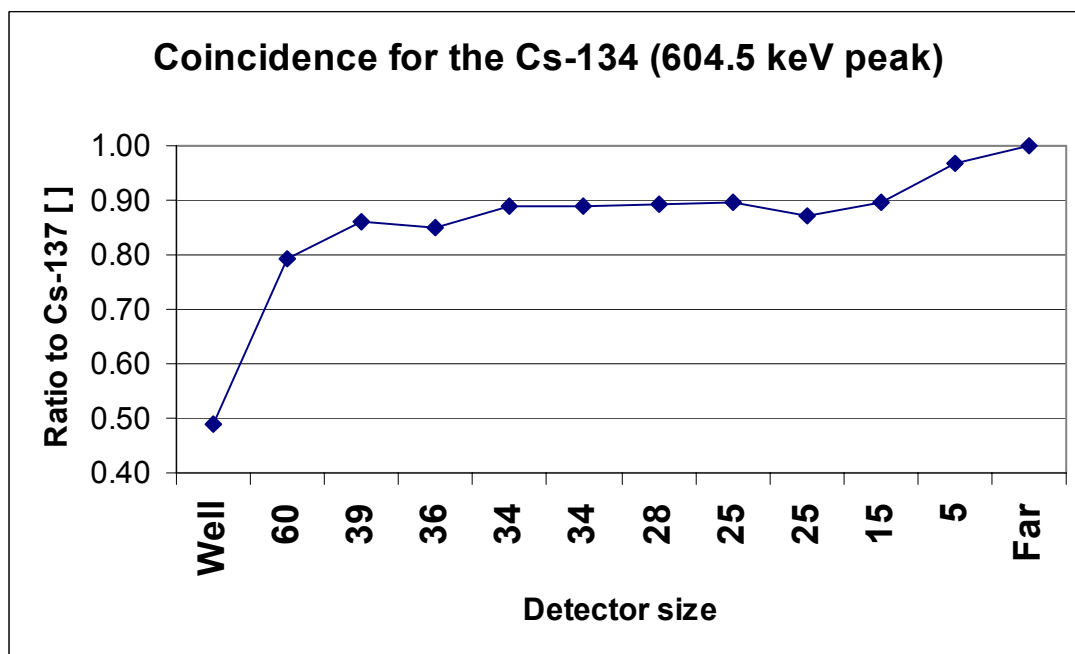
Part B: Intercomparisons

Two intercomparisons have now been held during the NKS BOK 1.1 programme. In the first intercomparison 34 laboratories returned radioactivity measurements on six different environmental samples. The samples were analysed for their content of gamma emitters, Sr-90, transuranics and Tc-99. The samples materials are described and the results presented. Some scatter was observed in measurements of Cs-137 in low-level samples such as dry milk, meat and hay. The scatter was less pronounced for sediments and seaweed material that had higher levels of radioactivity. In general, the most of the results were consistent with a few laboratories reporting outlying values. An exception was seawater where no clear agreement could be found for the activity of Cs-137. These results have been reported by Fogh (2000).

In the second intercomparison samples have been distributed to 30 laboratories. Today 23 laboratories have returned results. The deadline have been prolonged to 31/5 as the remaining participants all have expressed interest in delivering results before the results are published.

Data treatment: A weighted mean was calculated for each activity reported. A reduced mean (RM) was calculated for all radionuclides where 6 or more results were reported. The RM was achieved by excluding all results that was more 1.7 standard deviations from the weighted mean.

Gamma:

For the gamma analysis the results have been mixed. For activity levels above 10 Bq kg^{-1} between 70 and 90 % of the results could be included in the RM. For lower activity levels only 50 to 70 % of the results was included in the RM. The worst result was for seawater where only 4 out of 14 results were included the RM. An effort has been made to identify the main sources of variance. Ashing of samples (to improve counting efficiency) was examined, but could not be shown to improve results. Also it could not be shown that using single nuclide calibrations gives better results than using efficiency curves based on mixed calibration sources. There seemed to be a tendency that laboratories that handled many samples scored better than those handling fewer samples. The assumption is that good laboratory practise above any special corrections is the key to good results.

Sr-90

For Sr-90 analysis the results showed larger scatter than for the gamma analysis. Only between 33 and 75 % of the results could be included in the RM. However some of those results that is not included in the RM was reported as 'below detection limit'. Sr-90 is a complicated analysis and this is clearly reflected in the large scatter.

In the second round the results received so far implies a considerable improvement as they all agree well.

Transuranics

Analysis of transuranics was done by relatively few laboratories. The results for sediments (done by most laboratories) were useless as it was realised that the sediment material was not homogeneous with respect to transuranics. Three results were reported for seaweed, but they were all in good agreement.

In the second round special care was taken to ensure that the soil sample was suitable for transuranics analysis. Five results have been received for Pu-239/40 so far and they all agree (very!) well. In contrast to gamma analysis only few specialists do Pu analysis. It seems that these specialists then manage better even though the analysis is more difficult?

Tc-99

Tc-99 was analysed by 4 laboratories during the first round. Good agreement was found between the reported values.

Additional laboratories have expressed interest in analysing for Tc-99 in the second round, but few results have been received so far.

Overview of scores
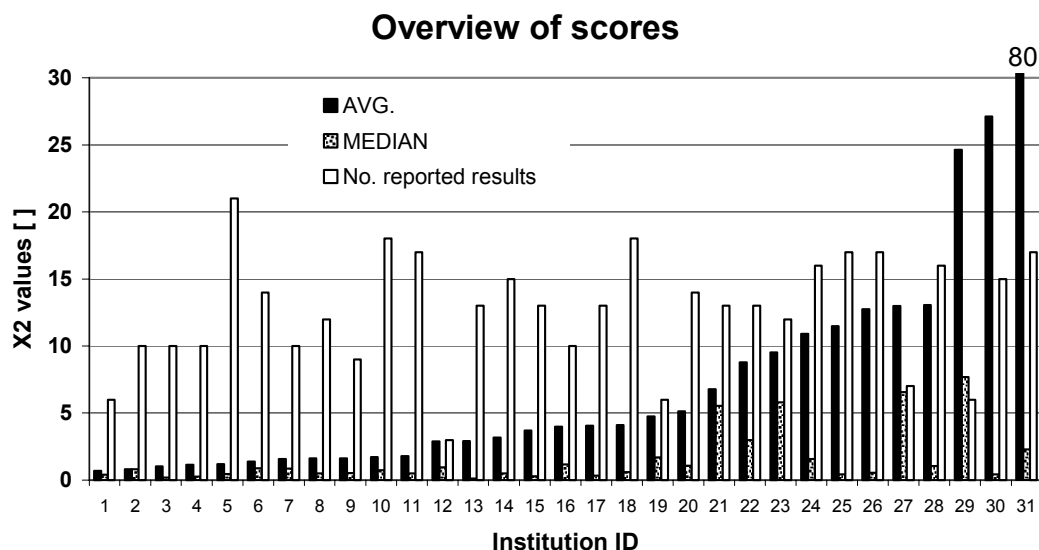
Average and median score for each participant printed together with the number of reported results - for the gamma analysis. The numbers have been sorted according to increased average score. Four participants had meadian scores worse than five => more than 50 % of their results deviated by more than two standard deviations from the RM.

Median score as a function of number of isotopes identified
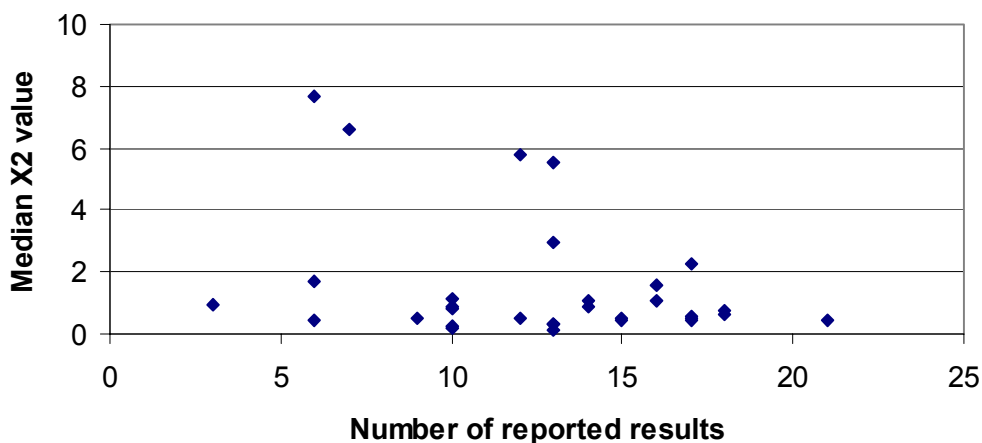
Median score shown as function of the number of results. This figure can be taken as an indication that the laboratories that handle many types of samples also manage better.
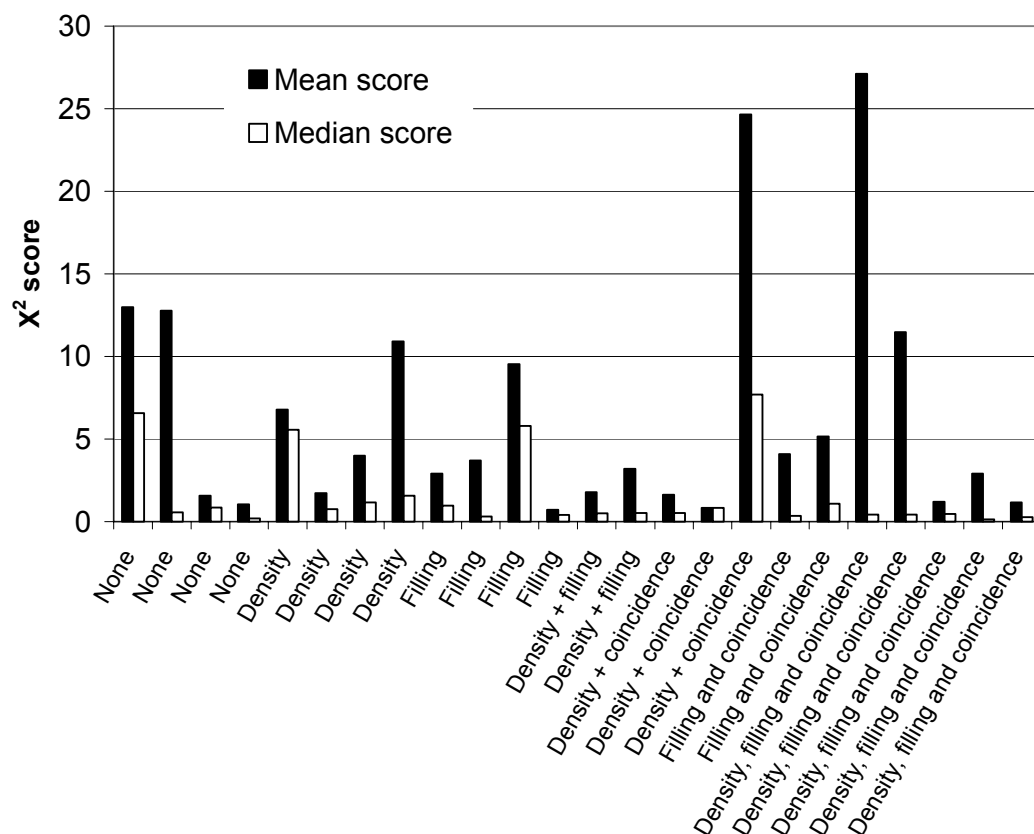
Correction methods applied

Laboratory scores showed as a function of the corrections that are used on a routine basis by the individual participants. All laboratories doing all corrections nice median scores. An indication that higher level of expertise leads to better results - mostly.

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6 Liquid scintillation spectrometry in environmental measurements

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Abstract

The power of liquid scintillation spectrometry for low-level measurements of radionuclides in the environment is demonstrated by some successful applications for the determination of tritium, α-emitters, Kr-85, 5r-90 and excretion analysis. The advantages of this technique are discussed as well as some limitations and difficulties which have to be considered.

Keywords: Liquid scintillation spectrometry Environmental measuremcnt; α -emitters; Tritium; Krypton-85; Strontium-90

1. Introduction

Liquid scintillation spectrometry (LSC) has become of widespread interest during approximately the last 15 years. This is due to the fact that more attention is paid to α - and β-emitters than before and because the performance and the features of liquid scintillation spectrometers have improved considerably. Parallel new measurement methods have been developed and introduced, which take advantage of the new instrumentation and result in simplified, yet accurate and precise procedure,.

This paper is dedicated to the memory of WJ. `Jack' McDowell, who died on Nov. 30. 1994, 1994. Jack was not only a pioneer in alpha-particle liquid scintillation spectrometry, but also a man of warmth, humour and personality. We'll miss him.

In this paper only a short overview on some applications used by the author are given; further information can be found in the literature [1]

2. Development of LSC in environmental applications.

Peng [2] has given an interesting overview on the development of liquid scintillation spectrometry. From the point of view of low-level LSC one may briefly outline the development as follows:

In the early days of I.SC the determination of soft β-emitters like tritium (for instance in hydrology following enrichment) and C-14 (age determination) were the most important applications. From the standpoint of environmental surveillance there was no need for low-level liquid scintillation spectrometry in the 1960's. Envi-

3. Instrumentation

The author uses four commercially available ultra low-level liquid scintillation spectrometers ('Quantulus', Wallac OY, Turku, Finland). They are equipped with passive; heavy lead shielding and an active guard, which consists of a stainless steel tank surrounding the measurement chamber, filled with a mineral oil based scintillation cocktail and viewed by photomultipliers (Fig. 1). Any event detected simultaneously in the guard and the sample will be rejected, thus reducing the background to extremely low values. Further reduction can be achieved in
α-measurements by α- β-discrimination and for certain applications suppression of some types of background events can be achieved by pulse amplitude comparison. The x-axis of all spectra shown in this paper represents a logarithmic pulse height scale.

4. Tritium in water

Tritium is a very weak β-emitter (Em_{max} 18 keV). Due to the absence of self absorption in liquid scintillation spectrometry this radionuclide can be measured with relatively high efficiency even in the form of water. Modern commercially available gel-forming scintillation cocktails can accept up to 50°lo water or more. A large volume

ronmental contamination from atmospheric nuclear tests was very high and methods for gross α-and β-measurements as well as for Sr-90 and Cs-137 using for instance gas flow counters were well established. Towards the end of the 1970's interest grew in the determination of other β-Sand also α-emitters.

Onc important advantage of LSC is the high counting efficiency; which for hard β-emitters is between 80 and 90°%, and for a-emitters is 100%. Another important advantage is homogeneous distribution of the sample in the scintillation cocktail, therefore no self-absorption occurs. Sample preparation is often very simple and extraction methods may yield solutions of the desired radionuclide which can be mixed directly with a scintillation cock-tail and counted without further sample preparation. Use of an internal standard is a very convenient and simple method for accurate efficiency determination especially in low-level counting.

There were disadvantages associated with lowlevel applications of LSC. One is the high background of commercially available counters. Another, the energy resolution for alphas which was poor compared with surface barrier detectors. Sample volume was limited in commercially available systems to - 20 ml and quenching could pose a serious problem.

The scientific community wanted to expand the measurement capabilities to lower activities - either to be able to measure the now low environmental contamination or to extend the time scale for age determination or to achieve more accurate measurements, for example in hydrology. This led to the development of commercially available instruments like a high volume LS counter which has been used successfully in the determination of tritium in water and to two types of low-level counters with standard 20 ml vials. One type achieves low background mainly by the use of active shielding, the other one with electronic analysis of pulses. Multi-channel analyser technique is nowadays a standard feature of counters and α-β-discrimination is offered by several manufacturers. A special system for α-measurements ('PERAIS') -using α-β-discrimination has been developed [3].
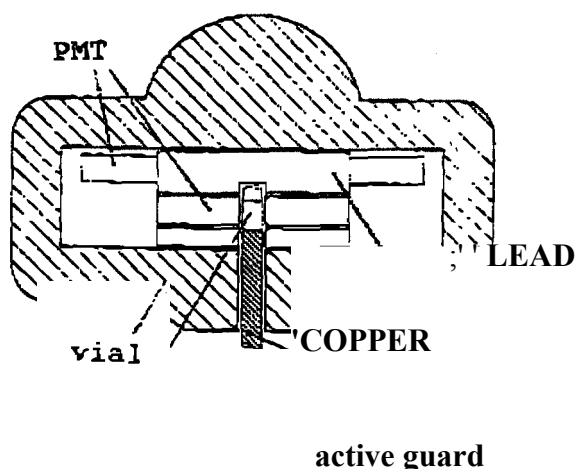

active guard

Fig. 1. Passive and active shield of the Quantulus liquid scintillation spectrometer.

of water lowers the lower limit of detection (LLD), but since water acts as a quencher, the efficiency is lowered as well, which counteracts the positive effect of the larger water volume. Careful studies concerning different cocktails and the water to cocktail ratio are necessary to optimize the method. The type of vial also plays an important role. Glass vials have always higher background than polyethylene vials in the tritium energy range due to the Cerenkov radiation of K-40. Normal polyethylene vials have low backgrounds, but sol vents may diffuse into the wall - causing the `wall effect' - or even diffuse out of the vial, so that measurement has to be carried out rather rapidly. Vials made from solid polytetrafiuoreThy lene (PTFE) and with solid copper caps are best with respect to both background, diffusion and efficiency, but their price is prohibitive for rou tine work in enviromaental applications. A good compromise arc polyethylene (PE) vials coated inside with PTEE (Zinsser, Frankfurt). They are resistant against diffusion, but have fairly good background and efficiency [4].

Tritium is monitored in Austria in precipitation, in surface water and in drinking water. The water is usually distilled, but if it is not highly colored it can be measured directly. The standard condition in the authors laboratory is measurement in PTE coated PE vials, 8 ml of water and

12 ml of Quicksziat 400 (Zinsser). **Fig.** 2 shown the pulse height spectra of a tritium standard [1], .surface water of the river Thaya at Bernhardsthal [2] and tritium free water as the background [3]. The figure of merit obtained is 1576, The tritium concentration thus determined is 18.6 Bq/1 dearly enhanced over the usually found 2 Bq/1 in precipitation. A few kilometers before the Austrian border a small Czech river ('Jihlava') discharges into the Thaya and situated on the Tihlava river is the Dukovany nuclear power plant. Calculation shows that the dose to the population would be – 400 nSv/year, if alt water consumed would contain 18.6 Bq/1_ This is absolutely insignificant compared with doses of natural origin in this area, but it is a clear demonstration of the sensitivity of ultra low-level liquid scintillation spectrometry.

5. Measurement of α-mitters

Since ~1964 it is known that α-emitters can be easily measured by LSC [S]. Compared with spectra of β-emitters, relatively sharp peaks are obtained, bur the resolution in α-spectrometry with surface barrier detectors is far better. The full width half maximum (FWHM) depends very much on the type of cocktail. If the radionuclide is present as an
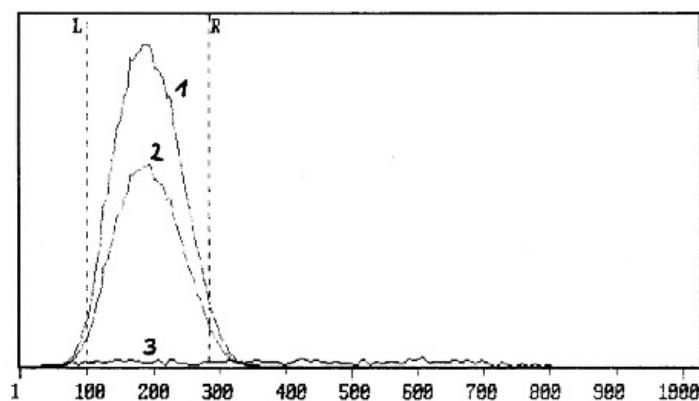

Fig. 2. Spectra of (1) tritium standard, (2) surface water sample and (3) background.

organic scintillation cocktail the FEHM is 200-300 keV. The counting efficiency is 100%.

The pulse height of α-emitters corresponds approximately to the pulse height of β-emitters with 10% of the α-energy. The position of the α peak is relatively insensitive to quenching and the efficiency is not affected.

'Ihc poor energy resolution in many applications is of little concern, especially when it is possible to isolate the radionuclide radiochemically. In the case of Rn-222 and Ra-226, the enhanced efficiency provided by the daughter produce of the radionuclides is question is an advantage [6]. Another alternative is to use mathematical means to resolve overlapping a-peaks. Pock [7] was able to resolve the peaks of Rn-222 and Po-218 in equilibrium using commercially available software for gamma spectroscopy.

Fig. 3 shows the spectrum obtained by mixing 500 mBq of Pu-239 in 8 ml water with 12 ml of Instagel and measuring for 20 min with a Quantulus. This concentration is approximately the maximum permissible concentration in drinking water according to Austrian legislation. In spite of the

short measurement time, a clear signal can be seen. The background is the α- window is ~ 0.2 counts/min, which is < 1% the couatrate of 30 counts/min and therefore negligible. This is the basis of the use a£ LSC for surveillance of drinking water or waste water of nuclear installations. Water can be mixed directly with the cocktail and measured without any further sample preparation or chemical separation for compliance with regulations. This method has bees successfully used by the Federal Institute for Food Control and Research for some years for drinking water surveillance and for the control of discharges from nuclear research installations [8]. In some cases of waste water, the presence of α's could be easily detected by the shape of the α-peak on top of the α- background (Fig. 4). Ra-226, the α-emitter with the strictest limit could be excluded because of the obvious absence of its daughter products. Comparison with a spike of Pu-239 showed also that this α-peak was not due to Pu-239. The activity concentration could be easily estimated to be well below the limits of all other possible α-emitters, so no further investigation
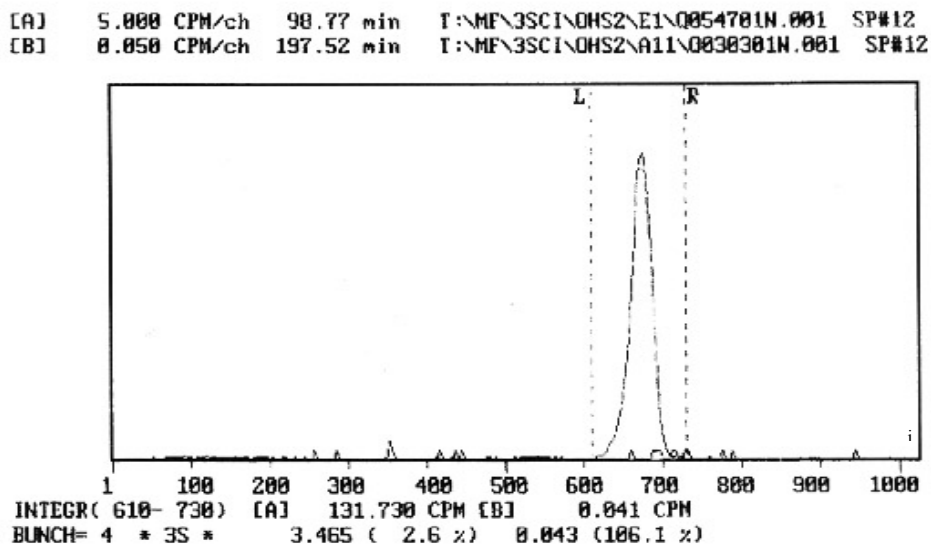

| [A] | 5.000 CPM/ch | 98.77 min | T:\MF\3SCI\OHS2\E1\0054701N.001 | SP#12 |
| [B] | 0.050 CPM/ch | 197.52 min | T:\MF\3SCI\OHS2\A11\0030301N.001 | SP#12 |

INTEGR(610- 730) [A]   131.730 CPM [B]   0.041 CPM
BUNCH= 4   * 3S *   3.465 (2.6 %)   0.043 (106.1 %)

Fig. 3. Pulse height spectrum equivalent to the maximum permissible concentration of Pu-239 in water.

```
[C]    0.384 CPM/ch   120.96 min   A:\AI\1\8203\Q013801N.000   SP#12
```
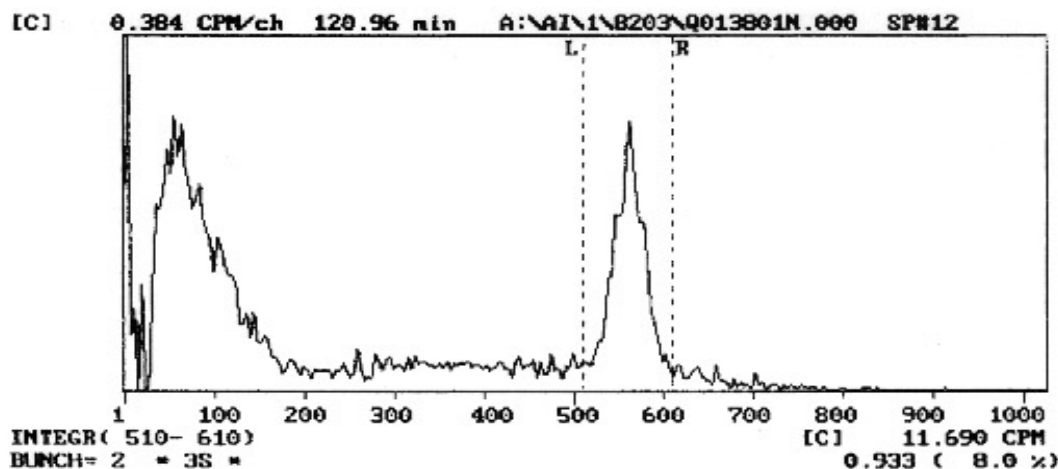

Fig. 4. Pulse height spectrum of a waste water sample containing an α-emitter.

was necessary and compliance with the regulations was verified.

5. Krypton-85

Kr-85 is a fission product with a half life of 10.76 years. Small amounts escape under normal operation of nuclear reactors. Large quantities are liberated during the reprocessing of spent nuclear fuel but methods are known to isolate it from the offgas and to keep it safe until it has decayed. Some year ago the concentration in the atmosphere was rising steadily by ~ 5%/year, being ~1 Bq/m~ at that time. It is not yet known whether the political changes during the last 2 years had any influence on the reprocessed quantities of nuclear fuel for military purposes. On the other hand, it may be assumed that in the near future enhanced quantities of civil fuel will be reprocessed, (the new T14OP-P facility in Sellafield is ready to start operation) with no retention of Kr-85.

Kr-85 is a weak β-emitter (E_{max} ~ 0.7 MeV). Being a noble gas, Kr-15 is not incorporated into the human body and has no dangerous daughters, which, for example, Rn-222 bass. However, if only for political reasons the monitoring of the concentration of radioactive substances in the environment and any changes should be known. A scientific reason for Kr-85 monitoring relates to

long range transport. Since reprocessing is carried out discontinuously, plumes of Kr-35 are emitted which can then act as tracers. By observing the plumes at different sampling stations models for long range transport of pollutants can be tested.

A feature common to all measurement methods is that krypton has to be isolated due to its small abundance in air. Usually it is preconeentrated on a charcoal column cooled with liquid nitrogen by pumping air slowly through it. Simple refining and concentration steps follow, the final step comprising a gas chromatographic separation. In a common liquid scintillation method the krypton is dissolved in a LSC-cocktail – krypton is soluble in aromatic hydrocarbons. Salvamoser and Schönhofcr [91 chose another approach: a special vial wa% constructed, which consists in principle of a bottom and a top made of aluminium glued to a quartz tube in which there is a hollow cylinder of a plastic scintillator. The thickness of the hollow cylinder is such that all β-particles of Kr-85 are absorbed within it. The krypton is introduced into the vial by a syringe through a septum in the top of the vial. The dimensions are such that the vial fits into the liquid scintillation spectrometer. Fig. 5 shows the spectrum obtained from an air sample. The efficiency is ~90 %. These values are expected to be improved by using copper instead of aluminium (which may sometimes contain remarkable activi-

```
[A]    0.150 CPM/ch 1979.51 min   A:\KRVIAL\TEST1\Q013701M.000  SPI12
[B]    0.150 CPM/ch  990.05 min   A:\KRVIAL\TEST1\Q023001M.000  SPI12
```



```
   1   100  200  300    400  500  600  700  800  900  1000
INTEGR( 370- 825) [A]      0.871 CPM [B]     34.092 CPM
BUNCH= 5  * 3S *      0.063 ( 7.2 %)  0.557 ( 1.6 %)
```
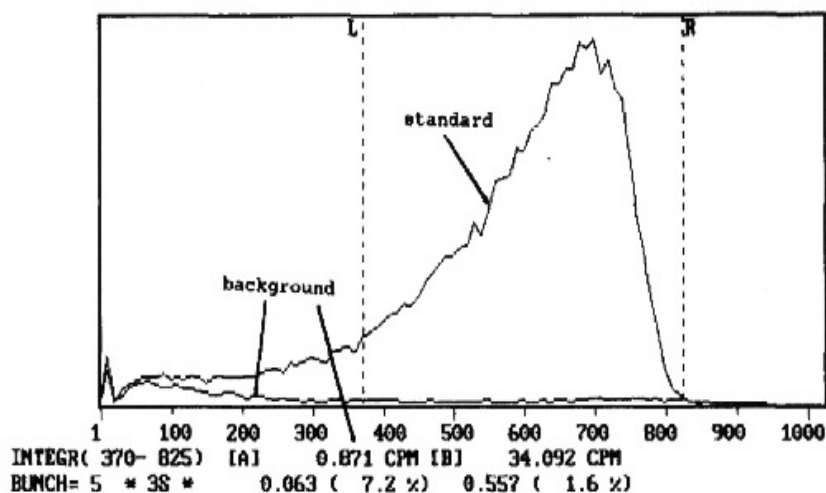
Fig. 5. Pulse height spectrum of Kr-85 obtained within a plastic scintillator vial.

ties of thorium!) and additional disks of plastic scintillator at the top and the bottom of the vial.

The low background and high efficiency of the method using the `Quantulus' will make it possible to use smaller air samples in the future, this will speed up the sampling, the

7. Strontium-90

Sr-90 is a fission product and a pure β-emitter *with* E_{max} *0.5 MEV.* Its daughter Y-90 is also a pure β-emitter with E_{max} 23 MeV. As result of its short half life of 64.1 h, it is quickly in equilibrium with Sr-90. Since Sr-90 is a bone seeker and has a long half life of 28.5 years, high uptake of it may result is damage of bone marrow. Monitoring of Sr-90 is therefore necessary. Historically, the levels of Sr-90 and Cs-137 in the environment were approximately the same during the time of the atmospheric bomb tests because of similar fission yield.

According to the authors knowledge it was only in 1977 that Laina Salonen [10] published the first paper describing the use of LSC for the determination of Sr-90 [10]. She dearly described the advantage of this method, but obviously her work was so revolutionary that the editor put a note

after the paper, doubting her findings and stating that other methods were still better.

The stated approach at the Federal Institute for Food Control and Research was the following: the superior specifications of the `Quantulus' should be used to develop methods which require little material, are as simple as possible, fairly quick and need little manpower.

In principle Sr-98 can be determined by LSC in the absence of Sr-89 by (a) measuring Sr-90 immediatly after isolation, (b) wait until it is in equilibrium with Y-90 and measure the sum of both (or set the window to Y-90 alone) or (c) to use the Cerenkov radiation of Y-90 for determination.

An LSC-spectrum of an Sr-90 standard in equilibrium with Y-90 and a corresponding background spectrum obtained with. a `Quantulus' is shown in Fig. 6_ The contributions of the two radionuclides can be easy distinguished. To measure Y 90 alone a window from approximately channel 665 to 875 would be chosen, thus cutting off Sr-90 entirely. Fig. 7 shows a Cerenkov spectrum of Y-90 being in equilibrium with Sr-90 and the background spectrum. The specification for the three alternatives are given in Table 1. The figure of merit (Flue is given as E^2/B, the basis of the LLD is 3 sigma of the background,

```
[A]    10.000 CPM/ch    29.63 min    I:\MF\3SCI\OHS2\E1\Q034501N.001    SP#12
[B]     0.100 CPM/ch   197.52 min    I:\MF\3SCI\OHS2\A1I\Q030301N.005    SP#11
```



```
INTEGR( 340- 900) [A]  2762.578 CPM [B]      2.248 CPM
BUNCH= 4  * 3S *         28.968 (  1.0 %)    0.320 ( 14.2 %)
```
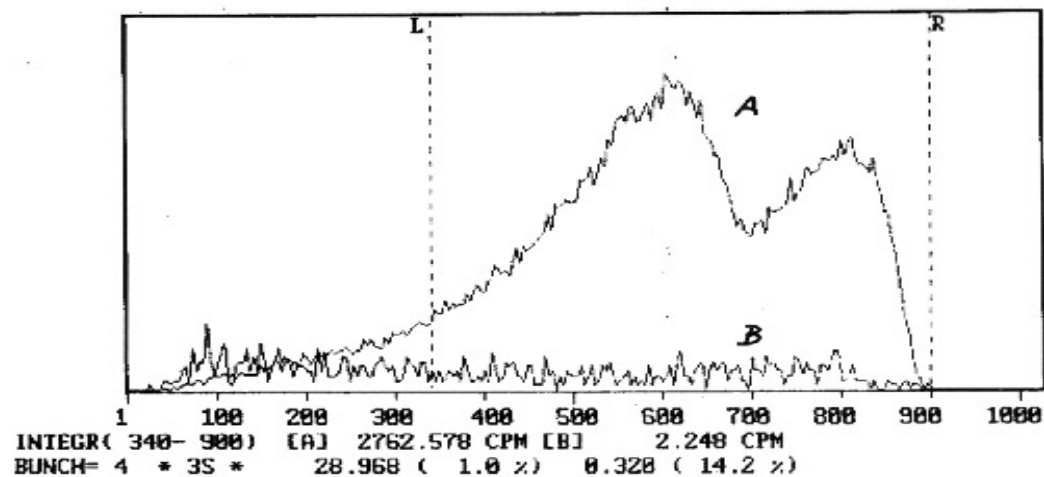
Fig. 6. Pulse height spectra of (A) an Sr-90/Y-90 standard and (B) the background.

500 min counting time and is per sample (the yield of the chemical isolation procedure which is ~90% is not included).

The LLD is excellent, which means that analysis with very sma11 samples is possi'ble. The technique developed at the Federal Institute for Food

```
[A]     5.000 CPM/ch   987.52 min    I:\MF\3CER\DIV1\Q023701N.000    SP#12
[B]     0.050 CPM/ch   298.41 min    I:\MF\3CEREN\LH1\Q010301N.000    SP#12
```



```
INTEGR(  50- 390) [A]   799.890 CPM [B]      1.267 CPM
BUNCH= 4  * 3S *          2.700 (  0.3 %)    0.195 ( 15.4 %)
```
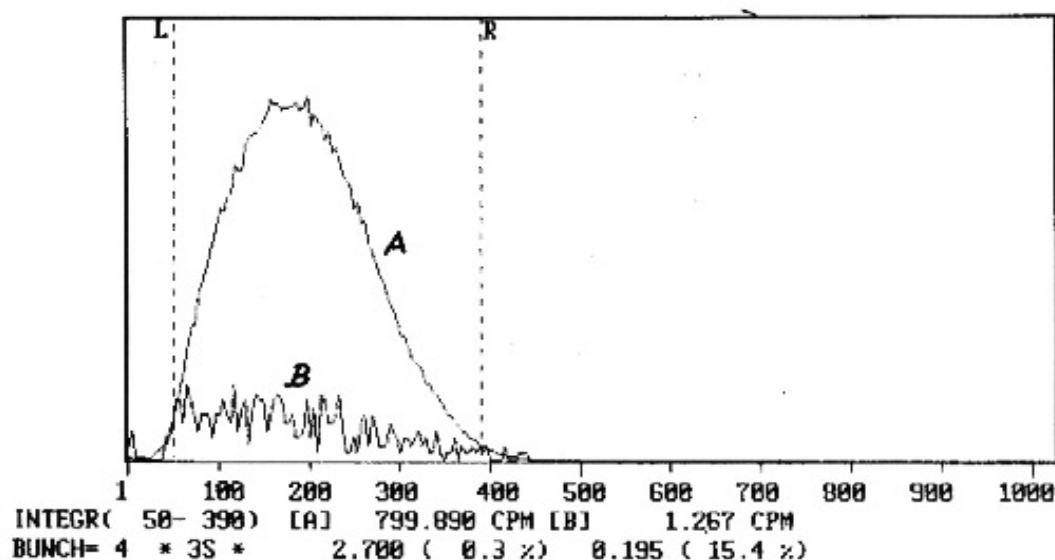
Fig. 7. Cerenkov spectra of (A) an Sr-90/Y-90 standard and (B) the background.

Control and Research involves carrying out all the separation procedures in centrifuge tubes, which speeds up the process enormously. Using this technique, an overview on Sr-90 in food in the years 1986-1990 was easily achieved (11). It was shown that the Sr-90 concentration in food was very small and mostly due to the Sr-90 which had been deposited in the late 1950's and beginning of the 1960's. Sr-90 concentrations in milk and milk-products showed only a show and small rise in 1986. For 1987 the dose due to ingestion of Sr-90 from milk and dairy products was estimated to be - 4 μSv, compared with - 27 μSv due to Cs-137 and Cs-134. These investigations ware the basis and the justification for the decision to reduce the number of these costly

8. Incorporation of tritium from wrist watches

In the course of routine surveillance of persons working in a factory where tritium is used in large quantities it was found that the urine of some persons of a control group contained surprisingly high concentrations of tritium. In the case of a routine tritium surveillance, it was found that persons why were wearing a. popular Swiss brand of wrist watch [12] (the watch had a luminuous dial and plastic case) had high levels of tritium in their urine.

Since watches are consumer producrs, the Austrian legislation on food and consumer products has to be applied and the case had to be checked by the Federal Institute for Food Control and Research.

A simple method had earlier been developed for measuring tritium in urine. Urine is not only colored, but the intensity of the color varies greatly. In a mixture of 8 ml urine with 12 ml Quichszint 400 quench is so severe, that in some casts efficiencies of < 1% result. In principle the urine may be distilled which gives only the concentration of tritium in water whereas the organically bound tritium remains in the residue. Using the `QuantuIus' it is possible, because of the low background, to use only 1 ml of urine, to dilute it with 7 ml of water and measure after mixture with 12 ml Quickzint 400. Quenching is reduced, but is still variable, so that a parallel sample with an internal standard is always measured to determine the efficiency. The background varies very little with different quench levels and regarding the relatively high levels of tritium rneasured this small uncertainty can be neglected.

Urine samples from volunteers who wore watches of the broad in question all showed elevated levels of tritium, same as high as 1300 Bq/l. In the urine of a control person (the author), whose watch has no luminous dials, no elevated tritium concentration could be found

In a second step the emission of tritium from watches was measured by simply piecing the watch into a glass container with 1 l of water and taking samples at intervals (the watches were all waterproofl. Within 24 h up to 34 600 Bq were emitted The emission was in all cases constant over the duration of the experiment - up to 12 days (Fig. 8).

A volunteer without detectable tritium in their urine (the author) started then to wear the watch with the highest emission. The concentration is

Table 1
Specification for the measurement of Sr-90 with Quanrulus

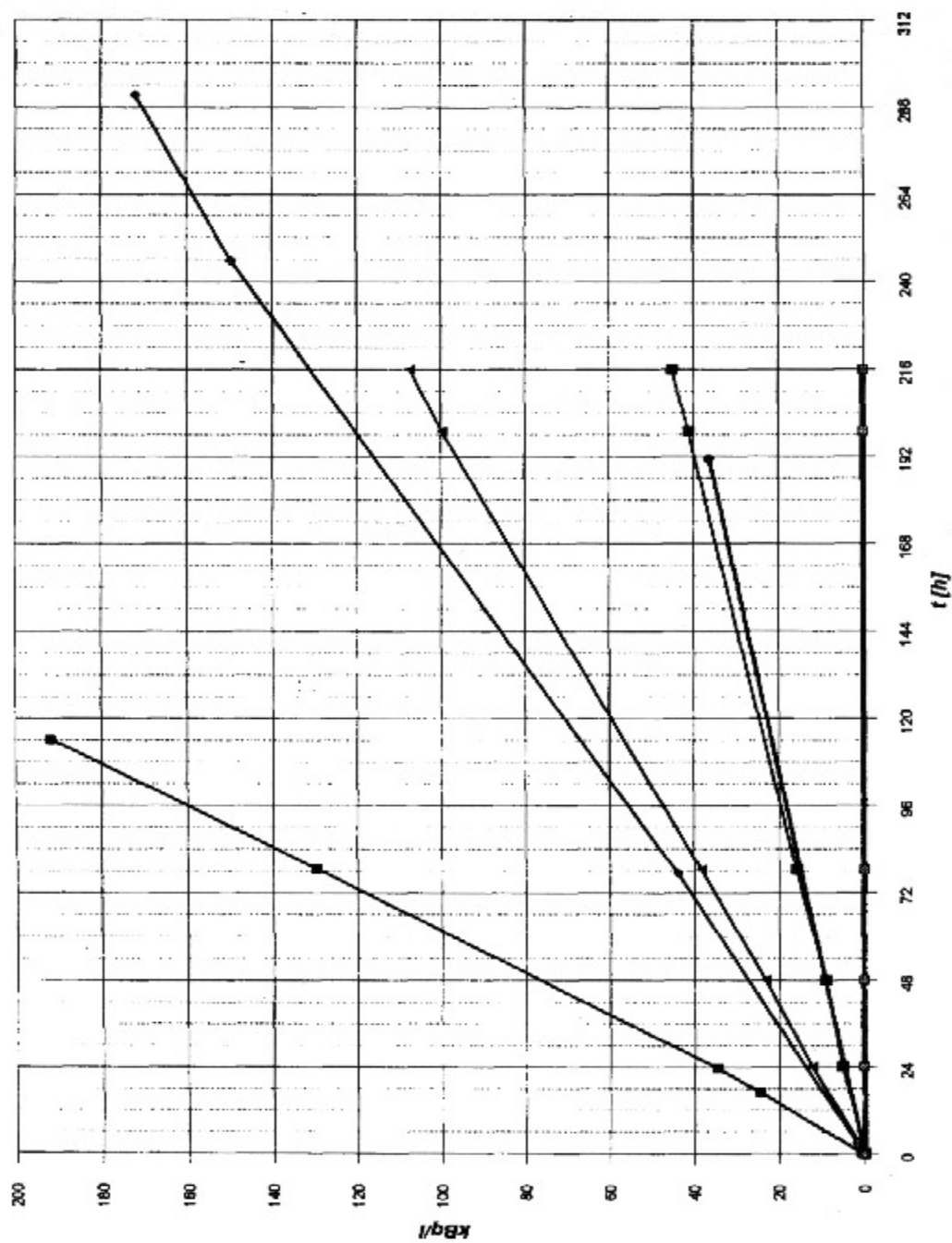| Measurement condition	Background (counts/min)	Efficiency (%)	FM	LLD (mBq)
Cerenkov counting	0.75	69	6367	2.8
LS counting, open window	1.99	185	17136	1.7
LS counting, narrow window for Y-90	0.60	58	5604	3.0

Figure 8. Emission of tritium from different wrist watches with plastic cases.
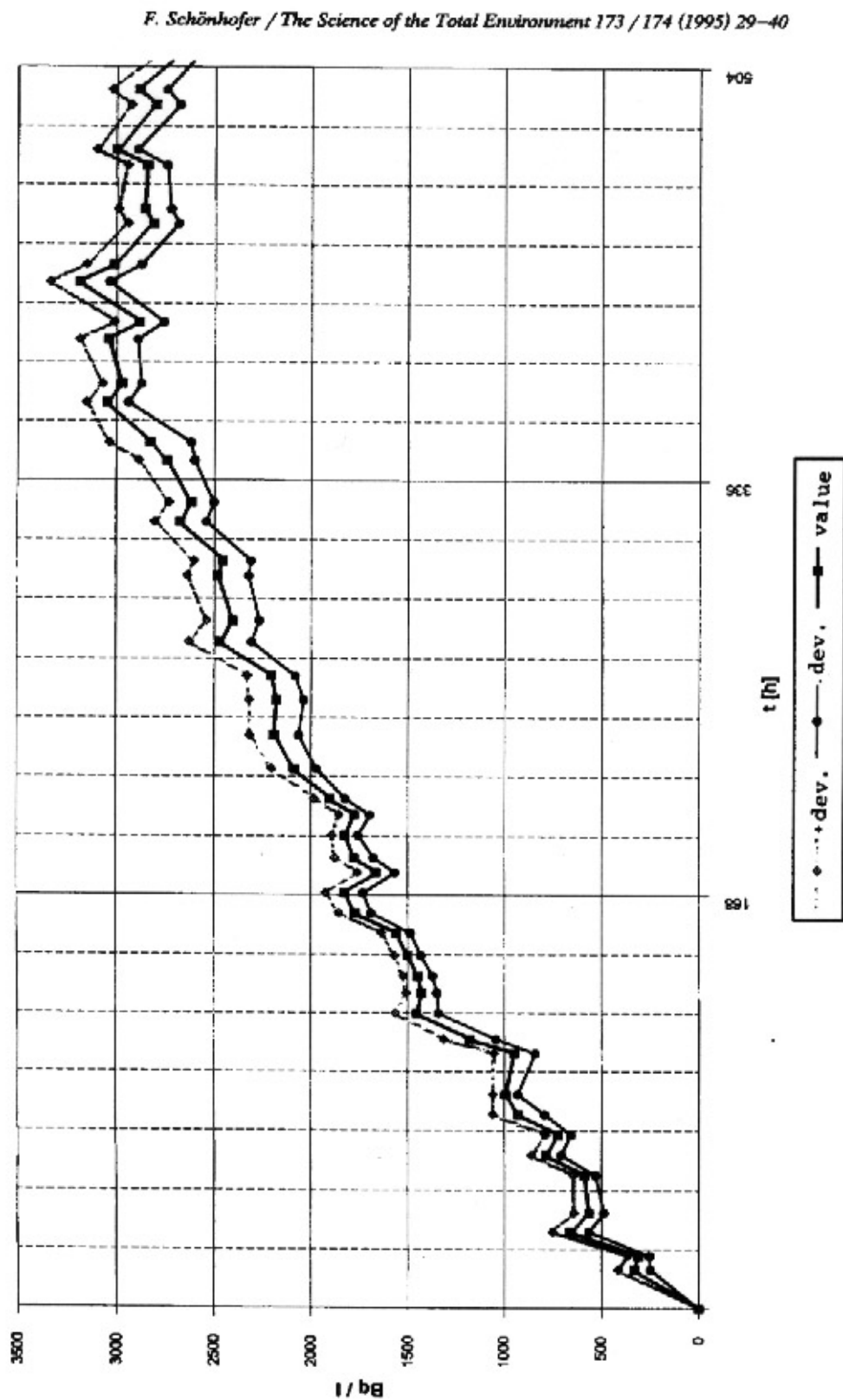
Figure 9. Tritium in urine.

57

his urine started to rise sharply and after ~ 15 days an equilibrium concentration of ~3000 Bq/1 was established (Fig. 9)_ This corresponds to - 130 000 Bq tritium body burden.

This phenomenon is not limited to plastic cases alone. It was found that a watch, ended in titanium emitted also considerable amounts of tritium (12500 BV24 h), but the concentration in urine was relatively low (113 Bq/1).

It is well known that the luminous paint emits tritium, but in traditional watches with steel or brass cases the tritium obviously hardly diffuses through these metals. For all renown estimations of the radiological hazards of tritium from luminous dials only *the* pathway of liberation to the sir, slow transformation of HT into HT0 and inhalation has been considered. *In* the case of plastic cases, tritium obviously diffuses easily through the plastic and is absorbed quantitatively through the skin (the latter affect is also well known). For titanium it is well known that hydrogen gas is dissolved easily and diffuses through the metal. It is known as well, that hydrogen is easily converted eataiytieally to water in acidic media. Hence, the most probable pathway for incorporation seems to be liberation as HT, fast diffusion through the plastic as HT, catalytic conversion at the skin to HTO and absorption. Once absorbed, tritium is rapidly distributed in the organism and also partly bound to organic molecules

In spite of these relatively high count rates, one should be aware that the dose calmed by the tritium is very low. If the volunteer *with 3000* Bq/1 urine carried the watch for a whole year an effective dose equivalent of 0.075 mSv/year would result. During air travel from Vienna to Phoenix, Arizona and back the same person received 0.08 mSv. During the 1960'x, up to 800 Bq/1 was measured in precipitation in Vienna. Compared with other exposure from natural radionuclides (K-40, Rn-2?2) these figures seem to be negligible. On the other. hand, the main principle of radiation, protection is ALARA - `as low as reasonable achievable, which can be easily achieved by carrying different watch. The con

sumer should therefore decide for himself whether being fashionable (wearing a modern style plastic watch) and being able to read the rime in the dark justifies the additional radiation dose.

9. Conclusion

The applications of low-level liquid scintillation spectrometry in environmental measurements mentioned *in* this paper are not exhaustive. Many more applications have been reported [i]_ But *it* has been shown that this technique can be used to solve a very wide variety of problems. Questions of radiation protection (measurement of environmental contamination, incorporation, etc.), radioecoiogical questions such as the transfer of radionuclides in the environment and surveillance of nuclear installations are only a few. Not all measurement problems can be solved *with* this technique, but *with* proper, simple, time and cost-saving

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7 Alpha -Particles Spectrometry of Large-Aera Samples using an Open-Flow Pulse Ionisation Chamber

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8 Alpha Spectrometry with Pulse Ionisation Chambers

by
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Introduction

The modern renaissance of the alpha spectrometer from the 1950's is due to the domestic radon issue. Today the very few remaining pulse chambers for gaseous alpha samples at reference laboratories have been complemented by widespread commercial equipments for on-line radon gas measurements and special open-flow constructions for large-area spectrometry of long-lived ^{222}Rn decay products. Analysing airborne alpha emitters spectrometrically with pulse-ionisation techniques is not straightforward due to the low mobility of negative ions in the air-sample filling the chamber. Two approaches have been taken to utilise slow responding negative ion chambers for radon-in-air measurements. One relies on a small distance between the electrodes. The pulse length out from an array of anode and cathode wires 1 cm apart is manageable by special electronic amplifiers. The Atmos detector manufactured by Gammadata, Uppsala, Sweden, is bases on this principle (cf page 12). The second approach is to connect a sophisticated pulse shape analysing system to the overlapping pulse train out from a cylindrical pulse ionisation chamber of conventional dimensions. Singlet, doublet etc alpha pulses and noise can be distinguished from each other and by accepting certain pulse height distributions only, an efficient and stable alpha in air detector is obtained (cf page 13).

In radon dwellings roughly 50% of the short-lived radon decay product inventory is surface deposited. In all surfaces alpha recoil implanted long-lived radon daughters build up and this activity constitutes a weak by ideally thin ^{210}Po alpha source. In order to take advantage of this naturally created alpha source, special open-flow pulse ionisation chambers accommodating semi-infinite samples have been developed (cf. page 7). The construction is described by Johansson et al. in Appl. Rad. Isot., **43** 119-125, 1992 (the interested reader may ask the seminar secretary for a copy). The apparent advantage is that plane samples from dwellings, e.g. mirrors, can be analysed without destroying the object. Today these large-area alpha spectrometers are utilised as reference detectors in the field of retrospective radon monitoring with surface track-etch devices measuring implanted ^{210}Po.

The principle behind gridded parallel plate pulse ionisation chambers is since long well established. (Our internal report APlane-parallel pulse ionisation chambers@ give the details and you are welcome to ask the secretary of this seminar for a copy). By keeping all negative ion constituencies out, a pure electron pulse device is obtained, and the problem of amplifying the alpha pulse is very much relaxed.
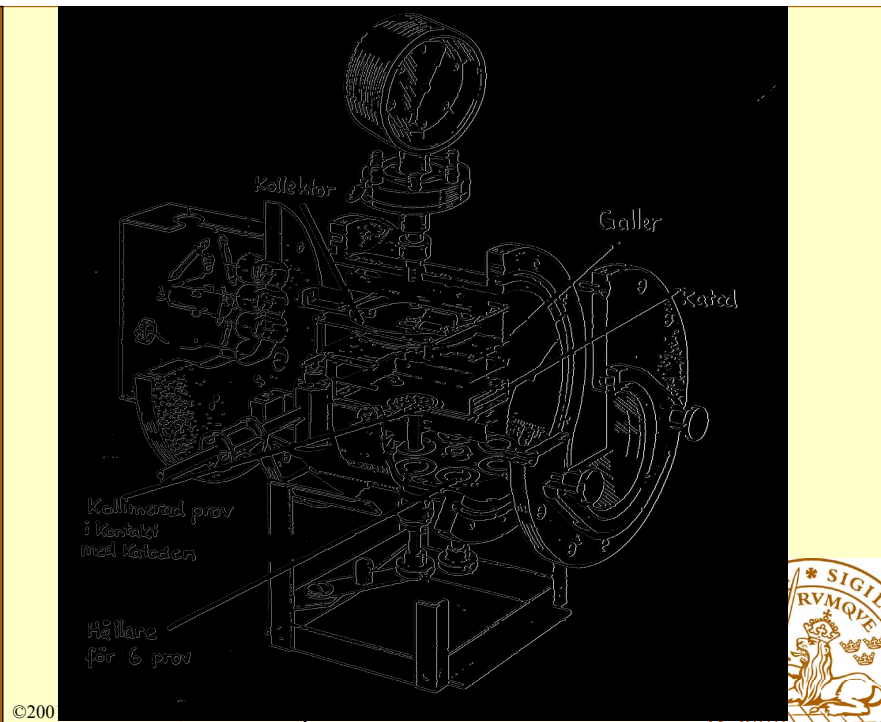
Before the silicon era closed pulse ionisation chambers (PIC) were common at most physical departments as alpha spectrometers. The pulse formation theory for gas-filled detectors was developed during the late 1940´s and the early 1950´s. The introductions of a third electrode (the Frisch grid) to shield the anode from influencies from the electric field of the positive ions improved the energy resolution.

The drift velocity for electrons
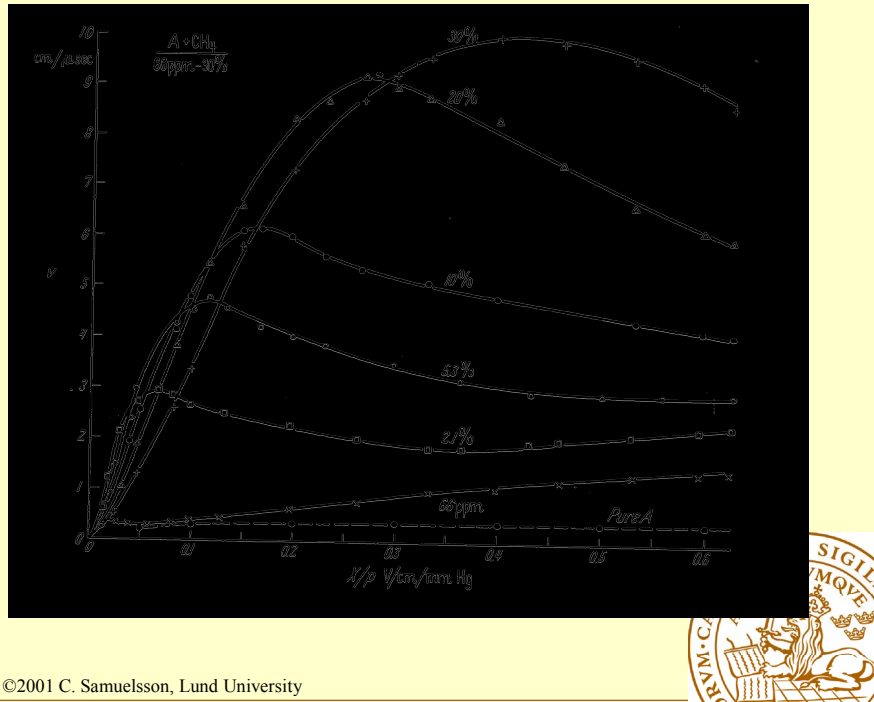
Drift velocity in cm per microsecond for electrons in different mixtures of Argon an methane. The x-axis quantity is the electric field strength divieded by atmospheric pressure in units of V cm^{-1} per mm mercury. (Ref: Fulbright: Handbuch der Physik, Band XLV Nuclear Instr. II, Springer Verlag, Berlin, 1958).
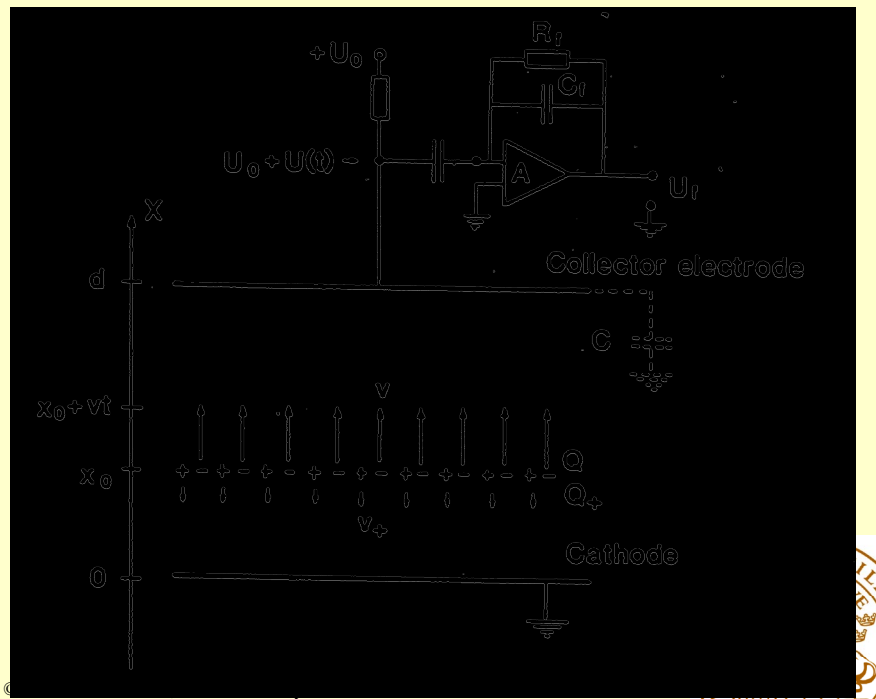
A schematic view of a plane-parallel ionisation chamber coupled to a change sensitive amplifier. The total capacity of the anode collector is denoted by C. The ionisation track is parallel to the electrodes. The electrons drift velocity v is roughly 1000 times larger than the velocity for positive ions.
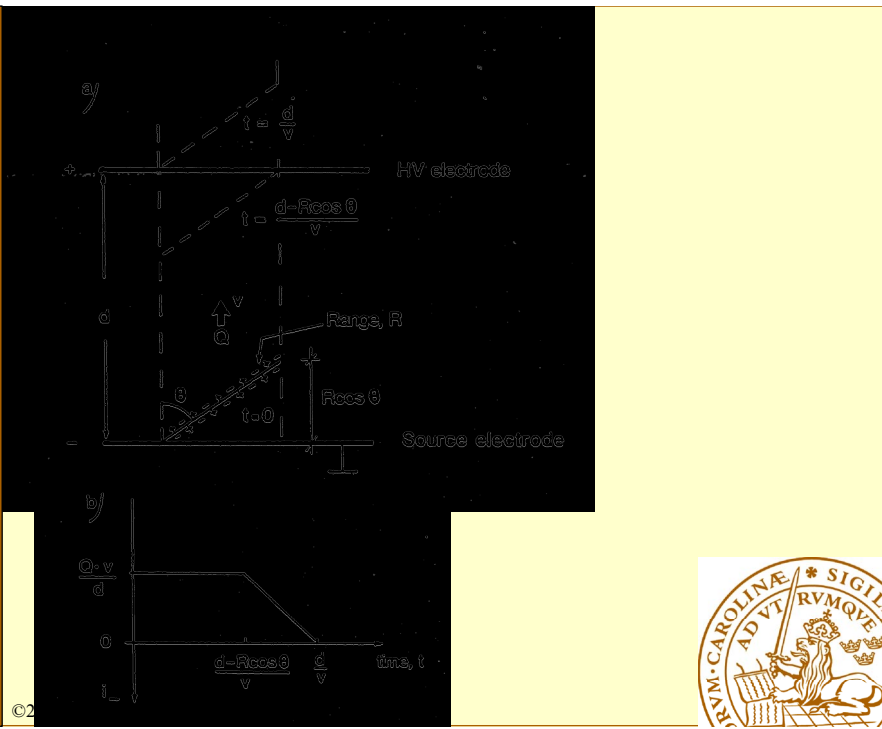
a) An alpha track emmited from the cathode ionises the gas.
b) The current in the ionisation chamber caused by the movement of the electrons.

Sample

Gas out

Grid

Anode

Gas inlet
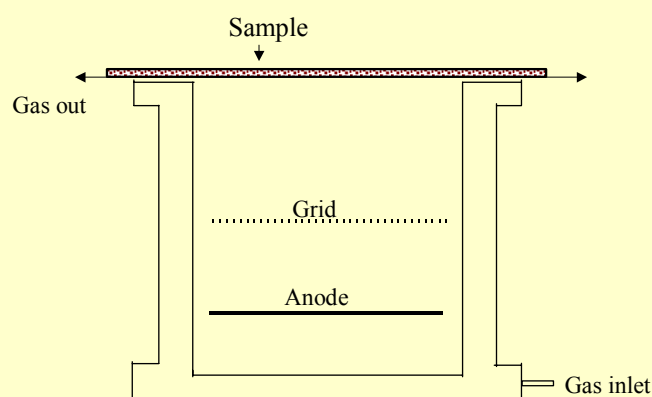
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The sample on top constitutes the cathode. The Frisch grid and anode are made of stainless steel and the chamber walls of plastic, electrically shielded on the outside with aluminium. The counting gas is a mixture of 10% methane and 90%Argon.

Count rate dependence on sample diameter

P/cph vs Sample diameter/ cm
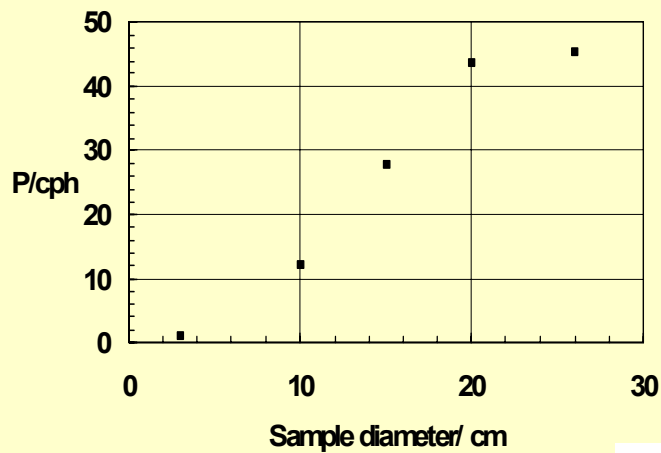
©2001 C. Samuelsson, Lund University

The alpha-peak counts rate normalised to a surface alpha activity of 1 Bq per cm^2 as a function of sample diameter. The inner diameter of the pulse ionisation chamber is 26 cm and the diameter of the Frisch grid is 22 cm. The source is a glass sheet from a radon dwelling with a fairly homogeneous surface distribute distribution of implanted ^{210}Po.

ALFASÖNDERFALL AV ^{218}Po

^{214}Pb ^4He

$v = 0,3 \cdot 10^6 \ m\ s^{-1}$ $v = 17 \cdot 10^6 \ ms^{-1}$

$T = 0,1 \ MeV \ (0,02 \ pJ)$ $T = 6 \ MeV \ (1 \ pJ)$

$R_{luft} = 0,1 \ mm$ $R_{luft} = 52 \ mm$
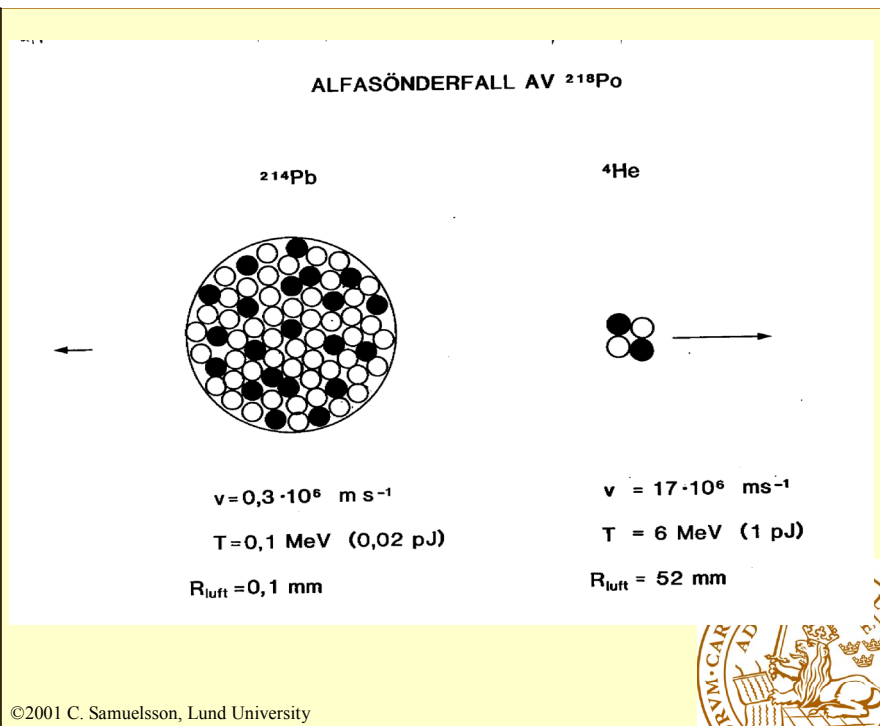
The energy gained by the alpha recoiling atom is large enough to
Embed the atom into solid materials such as vitrious glass.
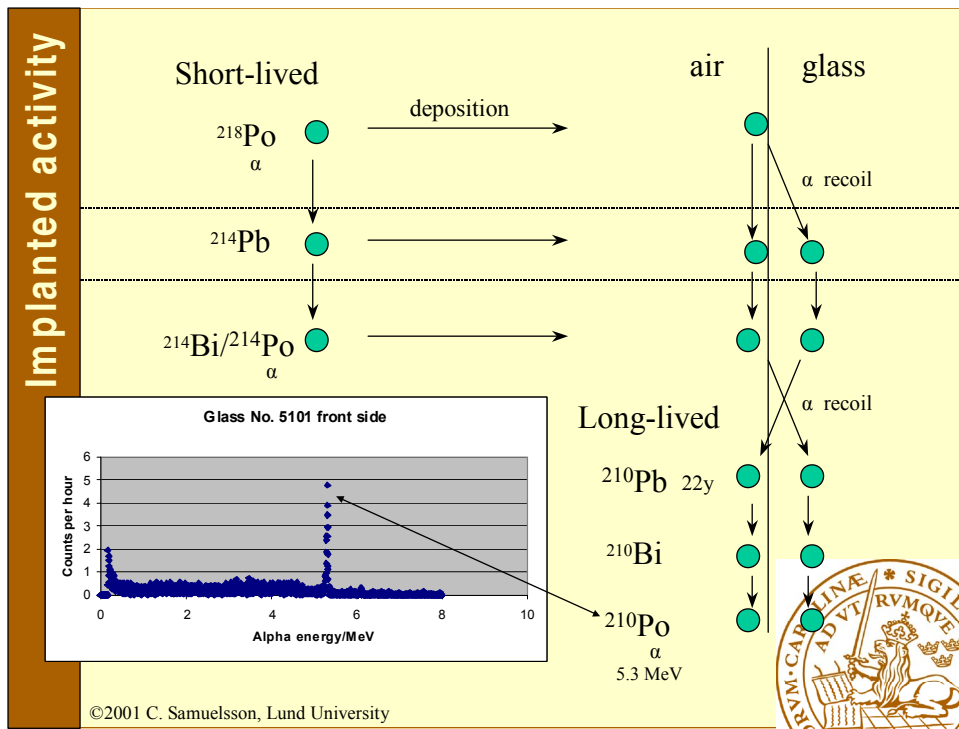
The alpha recoil process embeds the daughter atom into the underlying surface. This implantation makes the atom unreachable for normal household procedures, e.g. cleaning. In a radon house the implanted activity of Pb-210 (Half-life=22 years) and its decay product are used as long-term integraters of airborne radon gas exposure.

In these retrospective radon exposure assessments, the common Substrate is a glass sheet of known age.
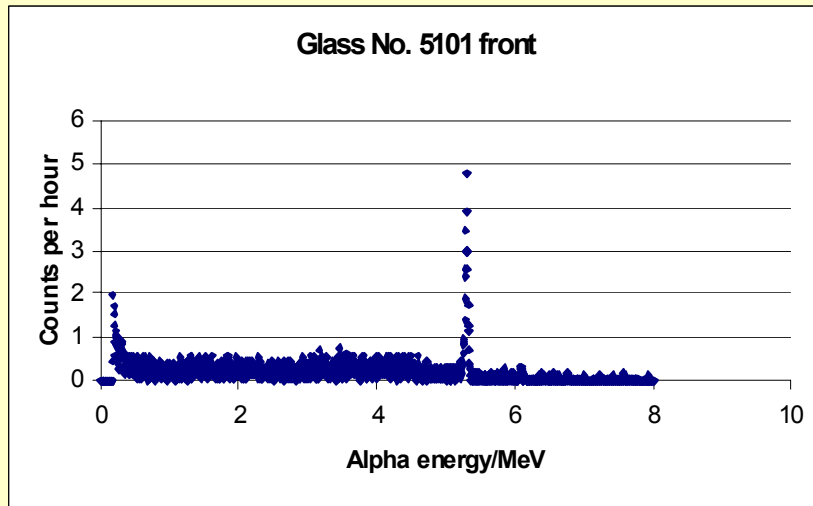
Alpha spectrum, normalized to a counting time of 1 hour, obtained with a PIC collimated down to a diameter of 10 cm. The ^{210}Po implanted activity of the glass sample is 3 Bq/m^2. The Polonium peak, with a full with at half maximum (FWHM) of 42 keV, is at 5.3 MeV, and the measuring time is 15 hours and 52 minutes. The peak in the lower part of the spectrum is due to eletronic noise.

The electrode assembly of Atmos
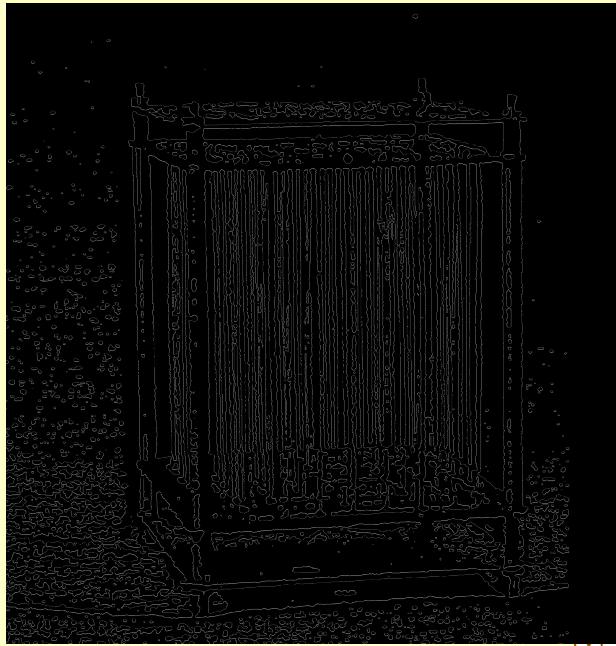
The electrode configuration of radon-in-air detector Atmos, Manufactured by Gammadata, Uppsala, Sweden. The anode and cathode wires are separated by a distance of 1 cm. In this geometry the time to collect the negative and positive ions is short enough to be handled by pulse discriminating devices.

The Alpha-Guard pulse processing
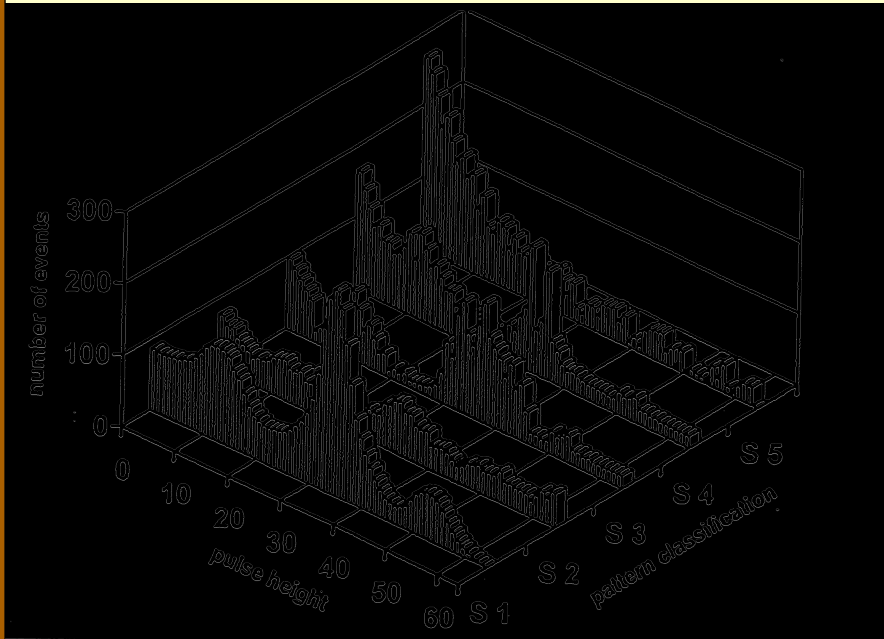
The commercial Alpha-Guard radon monitor relies on a sophisticated on-line pulse form analyzing technique on order to reveal the proper alpha signal. At low count rates the detector is essentially a pulse ionization chamber and at high count rates the behavior is more like a mean current ionization chamber.

9 Analysing alpha particle emitters using semiconductor detectors.

Detector operation and source preparation.

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Semiconductor alpha detectors

Advantages in using semiconductor detectors in front of many other type of radiation detectors include an excellent energy resolution, fast charge collection and the possibility to grow fairly large crystals. The later meaning a possibility to use detectors large enough to absorb most of the radiation impinging on them, thus leading to detectors with high efficiency. The perhaps most dominant advantage of semiconductor detectors lies in the smallness of the ionisation energy. The average energy needed to create an electron-hole pair is only about 3 eV; about ten times less the 30 eV needed to create an ion-pair in gas-detectors. This relatively large amount of charge carriers is the reason for the good energy resolution associated with semiconductor detectors.

When considering parameters such as atomic number (z), crystal growth possibilities, energy gap, electron/hole mobility and the possibility to withstand high electric fields only two suitable semiconductor materials exist, germanium and silicon. Depending on the specific application there are at present three different ways of producing radiation detectors of high resistivity from germanium and silicon.

° Reversed pn-junction
° Li-drifting
° Growing high-purity crystals

While only the two later methods are applicable when producing large detector sizes they have been used to produce detectors for gamma and x-rays. For charged particles only the first method has been used. There are at least two reasons why charged particle detectors are manufactured almost exclusively from silicon. Due to the larger energy gap in silicon (1.12 eV at room temperature as compared to 0.66 eV for germanium) low reverse currents (minority carriers) may be maintained at room temperature while this is impossible for Ge-detectors. Silicon charge-particle detectors may thus be operated at room temperature while germanium detectors need to be cooled. The larger energy gap in silicon also means that the impurities plays a larger role at room temperature than in germanium, this makes it possible to grow silicon crystals having either p-type or n-type characteristics depending on the added impurities. Another advantage in using silicon instead of germanium is the lower atomic number which reduces the back scattering (Rutherford scattering) in silicon. This effect is proportional to z^2.

In order to produce detectors for charged particles via a reversed pn-junction three methods have been used.

° Diffused junction (DJ-detectors)
° Surface Barrier (SSB-detectors)
° Ion implantation (Passivated Implanted Planar Silicon, PIPS-detectors)

Today only ion-implanted detectors are manufactured but in many laboratories a large part of detectors are still of the surface barrier type. In order to understand the different characteristics of the three detector types a short description of each type is given below.

Diffused Junction detectors

The basic reason in producing the pn-junction is to be able to eliminate free charge carriers (majority carriers) in the transition zone between the p and n-layers when a reversed bias is applied. In the case of the DJ-detectors the pn-zone was manufactured by evaporating a strongly n-doped material onto a p-type crystal. The diffusion length of the n-type material into the p-type silicon defined the depletion layer and thus the active detector zone. In order to enhance the diffusion of the n-type material the silicon was normally heated to 800-900 ˚C for half an hour. The high conductivity of the applied n-type layer meant that it also could be used as an ohmic contact (+HV) while the backside of the silicon chip was connected to a metallic (gold) contact.

The obvious disadvantage with these early charge particle detectors was the large dead-layer (0.1-2 μm equivalent of silicon) associated with the entrance window (the n-region). For silicon the energy loss for 5.5 MeV alpha particles are in the order of 100 keV per μm so the energy resolution obtained for close detector – sample distances was much poorer than later detector types. The thick entrance window however had one advantage, it facilitated the cleaning of loosely deposited material. A further disadvantage with these detectors was the relatively high concentration of crystal defects caused by the heating. These worked as charge traps thus shortening the lifetime for the charge carriers in the detector.

Surface Barrier Detectors

Normally an n-type silicon wafer was used, and the surface was allowed to oxidise (forming SiO_2) in air before evaporating a thin (40 μg cm^{-2}) goldcontact. After a few days the SiO_2 layer close to the gold contact had formed a high concentration of electron traps, thus effectively working as a p-layer. In contrast to the DJ-detectors the concentration in the p-layer was not high enough to make it work as an ohmic contact thus making the gold contact necessary. The deadlayer (gold + p-layer) in these detectors is in the order of 0.1 μm equivalent of Si, a great improvement in contrast to the older DJ-detectors. The main disadvantage with these detectors is the sensitive gold contact which cannot be touched without damaging the detector. The thin contact is also transparent to some chemicals and light and so could not easily be used in all environments. In order to also produce more ruggedized detectors a version of SB-detectors were manufactured from p-type silicon having aluminium instead of gold as the entrance ohmic contact. The Al-contact was thicker (around 0.2-0.5 μm) and allowed the detector surface to be cleaned.

Ion-implanted detectors

Instead of creating doped material by evaporation (like with the DJ-detectors) or by oxidation (Surface barrier types) the doped material may be introduced into the silicon by accelerating them to a suitable energy depending on the chosen depth. Typically boron ions are used at an intensity of some 10^{15} cm^{-2}. They are accelerated at low voltages (some 10kV) reaching some 0.1 μm into the silicon wafer. During the intense ion bombardment the crystal structure is damaged why annealing (heating the detector to about 300 ˚C for half an hour) is used to reduce the effects. Note that the damage is only affecting the upper implanted region whereas for DJ-detectors the whole detector volume is affected. Compared to both the DJ and SB-detectors there are several advantages with ion-implanted detectors. Firstly, the entrance win-

dow may be done very thin (0.05 μm) due to the controlled ion-implantation process. Secondly the contacts (ion-implanted) are buried in the silicon which significantly reduce the leakage currents to about 1/10 of those seen in SB-detectors. Thirdly, in the SB-detectors the silicon wafer is placed in an epoxy encapsulation to reduce surface leakage currents. This encapsulation is sensitive to temperature changes and chemicals which makes the detector much less rigid as compared to ion-implanted detectors where isolating layers may be implanted. The thin deadlayer and the low leakage current means that for given sizes of detectors the energy resolution in general is better than for corresponding SB-detectors. Due to the absence of sensitive metal contacts at the surface (contrary to the SB-detector) ion-implanted detectors are cleanable. Commonly ion-implanted detectors are abbreviated 'PIPS'-detectors which stands for Passivated Implanted Planar Silicon.

Detector characteristics relevant to alpha spectrometry

For the typical alpha spectrometry user there are some parameters which are of more relevance than others. These parameters are mainly detector *efficiency, resolution* and *stability*. Factors influencing these parameters are shortly described below.

Detector efficiency

In figure 1 the counting efficiency (recorded counts relative to emitted alpha particles) is shown for different distances detector-source. The efficiency depends both on this distance and on the size of the source itself. Since all alpha particles reaching the active surface of the detector will be counted the efficiency is more or less the same as the geometrical efficiency, in theory there might be discrepancies for alpha particles impinging close to the edges of a SB-detector where the charge collection may be less good. It's interesting to see in figure 1 how little the change is in efficiency when at close detector-source distances the detector size is increased. Normal detector-source distances in low-level alpha counting is some 2-4 mm and at this distance the increase in efficiency is only about 15% when going from the 400 to the 1000 mm^2 detector. For smaller discs the change would be even less. Considering the increase in detector capacitance by a factor 1000/400 (resulting in worse resolution) and a significantly higher price there is little talking for using large detectors at close detector-source geometries. Furthermore, the extra alphas 'seen' by using a larger detector at close detector-source geometry are collected at large angels, thus further contributing to the reduced resolution. For typical alpha PIPS detectors the resolution for a 450 mm^2 detector is about 17-19 keV while for a 1200 mm^2 it is 30-37 keV (not taking the contribution from the source itself into consideration).
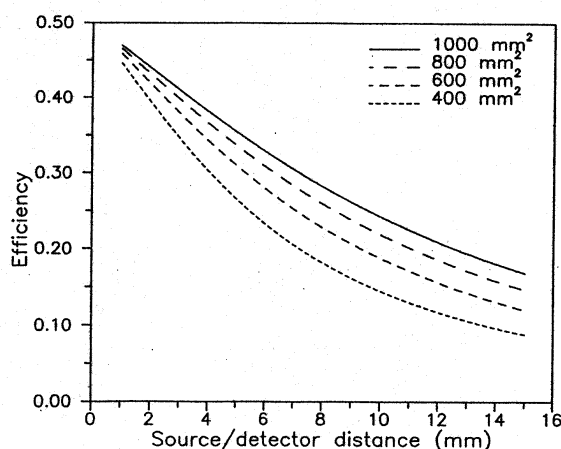

Figure 1:

Counting efficiency as a function of source-detector distance for a circular 17 mm source for 4 common detector sizes.

Counting efficiency as a function of source-detector distance for a circular 17 mm source for 4 common detector sizes.

The geometrical efficiency may be calculated for extended sources by for instance Monte Carlo methods or by analytical methods when the source and detector have aligned centres. The overall detector efficiency may of course also be measured using different techniques such as:

° Electrodeposition of 'known' activity (re-plating the remaining liquid to ensure no losses).
° Spontaneous plating of 'known' amount of polonium on Ag or Ni discs.
° Evaporation of known activity on electrosprayed (Si) discs.
° Using small point sources and scanning as a function of source radius followed by integration.

Of these methods electrodeposition gives the nicest sources and therefore produces the most distinguished peaks, this is of importance when reading the counts from the alpha spectrum. With thick sources the tailing of the peaks may be severe and even disappear below discriminator levels. The disadvantage with the electroplating method is however that there is an uncertainty in how much activity that is actually deposited. Performing the deposition carefully (pH adjustment) and allowing for an extra long deposition time will normally plate 95-100% of the activity. Only rarely will 'by unknown reasons' low recoveries occur. To partly overcome this inherent uncertainty the remaining solution after plating may be evaporated and again taken to electrodeposition to see if any activity remains. Performing some replicates may also give hints as to large variation to expect. A difficult disadvantage to overcome with this technique is to determine how homogenous the deposit is. Depending on the variations in electrical field strength at the cathode variations in the deposit is to be expected. Using imaging techniques or collimating various parts of the disc is the only way of finding out if a specific disc is homogenous or not.

Using known activities of polonium (^{208}Po, ^{209}Po or ^{210}Po) and allowing them to spontaneously plate onto silver or nickel (Cu, Pt, Pa, Au or Bi will also do) discs is an alternative to the electrodeposition method. The advantage is that the deposition of polonium on these metals is rather insensitive over a large pH interval (from 0.1M HCl to 8M HCl). The possibility of adjusting the pH wrong is thus much less likely as compared to the much more pH sensitive electrodeposition. The disadvantage is that polonium sublimes under vacuum and therefore may introduce an extra background on the detector. For that reason it may be worth choosing a suitable polonium isotope. Po-208 has an energy of 5.114 MeV and will thus position itself in the $^{239+240}$Pu region. Po-209 has almost exactly the same alpha energy (4.90 MeV) as the tracer ^{242}Pu. Po-210 has an alpha energy of 5.3 MeV, the same as the uranium tracer ^{232}U. Since the amount of polonium that will sublime during an efficiency measurement is rather low and since ^{232}U normally is used in higher activities than 242Pu the most suitable isotope to use is probably ^{210}Po. It also has the fastest decay of the three (138 days). The least suitable isotope is probably ^{208}Po since the activities measured of $^{239+240}$Pu usually are very low.

Evaporation of a known amount of alpha standard on the disc may be done to produce a calibration disc. The deposit must however be homogenous and there will always be a risk that the loosely held salt deposit is removed in the vacuum chamber. If the deposit may be done homogenous (small drops or using a spreading agent) it may be covered by a thin organic film to prevent it from being lost. VYNS is a vinyl chloride copolymer commercially available in liquid form. It may be dropped on the disc to produce coatings as thin as 0.01 μm or even less (thus not affecting the energy resolution).

Alternatively, colloidal silica which has been electrosprayed on the disc may be used as substrate for holding the known activity which is dropped on. The hydrated silica oxide colloids on the disc constitute a very large surface area and has over a large pH interval a negative surface charge. It will thus adsorb the positively charged ions dropped onto it. In order not to increase the energy resolution it's important not to use silica particles of to large size, otherwise the selfabsorption in the source will be significant. Also this type of deposit may be covered by VYNS even though the deposited material is much more tightly attached to the disc as compared to plain evaporites.

Finally, if a well defined point source (mm sized) is available it is possible to perform the efficiency determinations as a function of radius (r) from the normally positioned disc centre. The overall efficiency for a disc is then obtained by integrating over the radius, weighting for the relative area each radius dr is occupying. This method is not advisable for small/normal detectors (300-450 mm^2) used in routine alpha spectrometry simply because of the difficulties in placing the source in an accurate manner. The work connected to this type of calibration makes it worth while first when the detector size is so large so that the other methods described above becomes more difficult to perform.

In most applications for alpha spectrometry an internal standard is used, this has the function of correcting for losses during the radiochemical separation and to correct for detector efficiency. With the internal alpha standard the detector efficiency need not to be known. Since alpha emitting tracers are available for most of the radioisotopes analysed by alpha spectrometry (Pu, Am, Th, U, Po) the only reason for knowing the detector efficiency is when the absolute value of the chemical recovery is to be determined. For many laboratories the detector efficiency therefore is not so important.

There are however occasions where there are no alpha emitting tracer available (or alternative non alpha-emitting tracers are chosen instead) and the only way of quantifying the alpha emitting radioisotope is by having a well known detector efficiency (and a well defined counting geometry). Such occasions appear for instance when analysing isotopes of radium, neptunium, protactinium and actinium where gamma/beta emitting tracers may be chosen ([133]Ba for Ra and [239]Np for Np) or is the only one available ([233]Pa for Pa).

There is also a need to know the detector efficiency when the beta emitting [234]Th is analysed because the alpha emitting [229]Th (or [230]Th) is normally used as a tracer. The major problem in analysing these isotopes is that the discs (normally electrodeposited) may have inhomogeneous deposits, meaning that the tabulated efficiency for the detector may be more or less useless. The only way in overcoming this problem is either by counting at a large detector-source distance (provided the source is strong enough) or by choosing deposition methods which produce homogenous deposits. This is discussed further at a later stage in this chapter.

Resolution

The term 'resolution' we would like to define as the overall capacity of the counting system to distinguish between two nearby alpha peaks. The factors influencing the observed resolution is not only the detector inherent resolution but also the contribution from the source (+ chamber pressure), preamplifier and remaining electronics. During long counting times also the long-term stability of the electronics will influence the resolution (drifting).

In the early days of alpha spectrometry the bottle-neck in obtaining good resolution was often in the (DJ) detectors since the entrance windows and leakage currents were much higher than in present days SB- and PIPS-detectors. Problems in obtaining good sources was also somewhat more common than today but the increase in detector quality has not been parallelled by a corresponding development within source preparations.

A limitation when discussing resolutions is that it is often only the full width at half maximum (FWHM) that is considered. Since peak tailing is an extremely important feature in alpha spectrometry the FWHM may not be accurate in describing whether or not it will be possible to analyse low-level alpha activity in the presence of high alpha activity having a higher energy (for instance being able to distinguish the ^{242}Pu tracer from high levels of $^{239+240}$Pu). To do this peak fitting algorithms have to be used instead, fitting the alpha peaks to a sum of a gaussian and an exponential describing the tailing. The tailing may be an effect of both high angle incident alphas (straggling in the deadlayer) and the alphas collected close to the detector edges. At close detector-source distances the FWHM increases as seen from figure 2b but at the same time the low energy tailing decreases, contrary to what is expected from intuition. However, when *increasing* the detector-source distance a successive larger proportion of the alphas will hit the edges of the detector and due to inefficient charge collection become registered as lower energies, contributing to the tail. This effect may be reduced by collimating the edges of the detector.
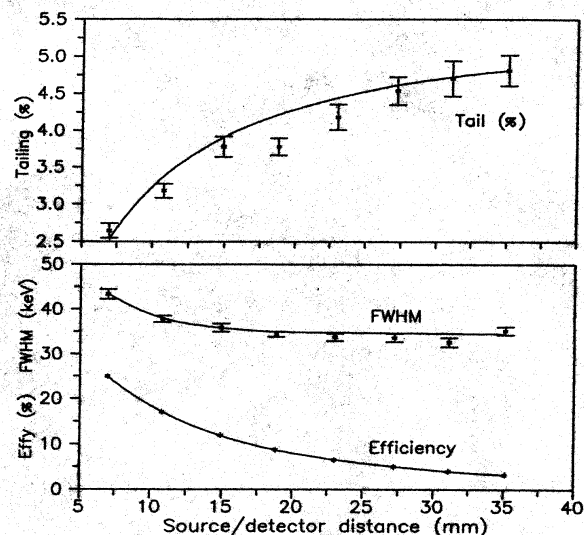
Figure 2

FWHM and peak tailing as a function of source-detector distance for a 600 mm^2 detector.

The overall resolution may be written as:

$$(FWHM_{TOT})^2 = (FWHM_D)^2 + (FWHM_X)^2 + (FWHM_E)^2 . \quad \text{Where:}$$

$(FWHM_D)^2$ is the varians in the amount of electron-hole pairs formed at a given energy.

$(FWHM_X)^2$ is depending on the efficiency with which the charge is collected, especially in regions where the electric field is weak relative to other positions in the detector. This term is often of less importance for planar alpha particle detectors.

$(FWHM_E)^2$ is the contribution from the electronics which partly is determined by the detector capacitance. The leakage currents are determined both from thermal action (proportional to detector volume) and from surface leak currents due to voltage gradients caused by improper encapsulation, contacts etc. Especially the preamplifier and the detector-preamplifier combination is of importance for the noise level

The noise level for the preamplifier is probably one of its most important specifications. This figure is normally given as the equivalent energy spread in the type of the detector for which the preamplifier is designed. The noise figure is a strong function of the capacitance with which the preamplifier input is loaded. A good preamplifier may have a noise equivalent to 2 keV when the input capacitance is near zero but may double if the input is loaded with 100 pF. The detector capacitance arises from the fixed charges which are built up on either side of the pn-junction and which therefore gives the pn-zone a capacitance characteristics. The capacitance is proportional to detector area and inversely proportional to depletion depth. Since the depletion depth increase with the square root of applied voltage over the pn-junction the noise will also decrease as voltage is applied to the detector. This is clearly visible when viewing the detector output on a oscilloscope or on the MCA.

The leakage current from the detector also means that the applied voltage will not entirely be over the depleted detector region but also over the preamplifier resistance. Since the leakage currents from present days PIPS detectors are very low (30-60 nA) the voltage drop over the preamp resistor (typically 110 Mohm) may be neglected. For the earlier SB-detectors (still in use) the leakage currents were an order of magnitude higher and so the voltage drop over the preamp resistor could be equally large as over the detector. This had to be compensated for when applying the detector voltage.

In most PIPS detectors used today the contribution to resolution from detector noise and capacitance is negligible. Exceptions occur for large detectors (large surface area) where the detector capacitance seriously may reduce the resolution. In most cases however it is the varians in the amount of electron-hole pairs formed which determines the resolution.

Stability

In many applications the amount of alpha activity measured is extremely small, sometimes down to some tens of microBq, meaning counting times sometimes up to 50 days or more. Needless to say, perhaps the biggest problems when counting such low activities is not the detector problems but rather the blanks. In any way it's also important to have a detector system stable over such time periods. Earlier SB-detectors were often claimed to have higher sensitivity to changes in temperature and long-time storage under vacuum, it is usually said to depend upon the epoxy edge encapsulation that is required for this type of detector. For PIPS detectors no such encapsulation is necessary due to the junctions being buried in the silicon bulk. It is also commonly said that the leakage currents from SB-detectors doubles every 6-8 °C and would thus cause a significant voltage change over the detector. From personal experience it has however been evident that most SB-detectors have excellent performance characteristics, in Lund many SB-detectors (300-450 mm^2) have been in use for more than ten years with sometimes heavy temperature changes of almost ten degrees without significant changes in detector resolution. In fact, all of them still have excellent resolution of around 18-25 keV, even for long-term measurements of up to two months. This perhaps illustrates what was concluded about resolution above, that it is the variance in the number of electron-hole pairs that determines the resolution.

Apart from long-term stability it's also important during long counting times to have a low background. As mentioned above this is most likely a more difficult problem than keeping the detector stable. Radiochemical laboratories have a very wide range in 'available contaminants' which merely reflects the near history and the discipline of the lab. Another factor influencing long-term measurements is the degree of recoil contamination from routine counting of samples. This is very severe for elements like radium and polonium but is very limited for plutonium and americium. In order to reduce the recoil contamination the air pressure in

the vacuum chamber may be kept such that an air layer of about 10 mg cm^{-2} is present between the sample and detector. This reduces the recoil contamination by up to a factor of 1000 while only increasing the FWHM by some keV. Also the source may be biased negatively by a few volts, this creates a necessary field strength between detector and source so as to prevent recoil fragments to hit the detector.

Source preparation

This is an important field in that in a single operation both the energy resolution and the efficiency is heavily affected. It is fascinating to imagine that this single procedure may mean so much for a sample that may have taken weeks or even months to prepare when considering all preparations around sample collection, tracers, radiochemistry etc. It is equally fascinating, considering its importance, to realise how little that has been done in order to improve source preparation techniques. For some elements like the actinides U, Th, Pu, Am and Np the source preparation usually is very satisfactory using electrodeposition but there are exceptions. For radium and actinium source preparation techniques are more complicated and usually result in both low radiochemical recovery and low resolution.

In general, source preparation techniques may be the same as those described above during detector efficiency calibration. Other techniques may however also be used since not in all cases a 100% recovery is needed (like with efficiency calibration sources).

I will try to give an overview of source preparation techniques available for the different elements of interest below. They will be divided into what may consider the simple elements (U, Th, Pu, Am and Np) and the more difficult elements (Ra and Ac).

Source preparation for U, Th, Pu, Am and Np

For the first group (U, Th, Pu, Am and Np) electrodeposition is the dominant technique in source preparation. In this technique the elements of interest are deposited as oxides on a cathode. Obviously elements which easily form insoluble oxides are favoured by this principle. Since there are many elements (like the Fe and Al) forming insoluble oxides it is of importance to 'completely' clean the sample from these elements before going to electrodeposition. The radiochemical separation technique as a whole is thus critically linked to the source preparation technique and the following alpha spectrometry. Two methods has been predominantly used for electrodeposition: the sulphate method (Talvitie, 1972; Hallstadius, 1984) and the oxalate method (Puphal and Olsen, 1972). In neither method does problems normally occur. Occasionally there are however samples which may turn out to be more problematic than others. Usually this shows up as low recoveries. The difficulty in finding the reason for the low recoveries is that normally only one tracer is used for the whole procedure, that is it is not possible to tell where the losses occurred. In a recent paper by Rodrigues *et.al.* (2001) the reasons for observed low recoveries (<15% and 1% respectively) for U and Th when analysing soil and sediment samples were investigated. They found that the aluminium content in the electroplating solution seriously affected the deposition (figure 3) even for sample sizes as small as 0.5g.
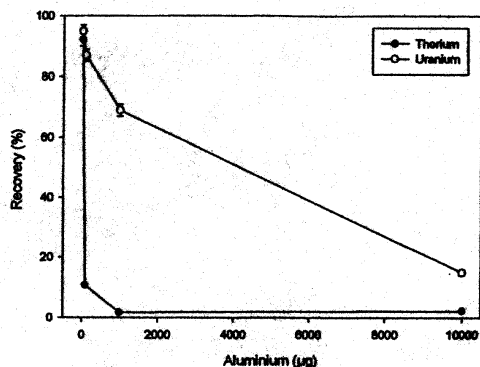
Figure 3:

Variation of U and Th electrodeposition recoveries with different aluminium present in solution.

This is not surprisingly since aluminium also forms oxides and thus may deposit on the cathode thus preventing deposition by other elements, perhaps due to charge polarization. In their method they used an ion-exchange method which had a rather poor separation of most macro elements. For U and Th one of the best and most reliable separation methods is based on extraction with Tri-n-Butyl-Phosphate (TBP). When using this method instead the authors found no problem during electrodeposition simply because the aluminium removal in the TBP method is nearly complete. Actually, it is not uncommon to add $Al(NO_3)_3$ in quite high amounts when extracting from nitric acid. The nitrate concentration is then raised without increasing the pH which increases the extraction coefficient (salting out effect).

If, for some reasons, the major elements turn out to be difficult in removing Zarki et.al (2001) proposed a method for electroplating from solutions of 70% ethanol and 0.45M HCl. With this technique Fe, La Bi was allowed to be present in sub mg concentrations but again aluminium turned out to be a problem (figure 4). In general, a suitable electrolyte for electroplating should both act to ensure sufficient conductivity and to complex the ions present in the solution, this is especially important for elements known to hydrolyse even at low pH.
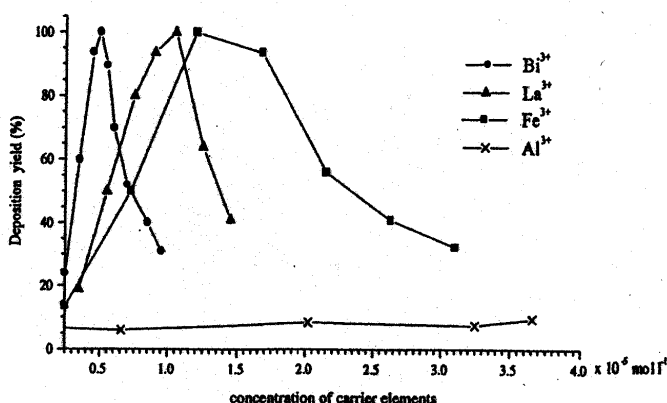
Figur 4

Variation of U deposition versus the amount of added metal in a 70% ethanol-0.45M HCl solution.

The deposition mechanism is generally understood as an oxide formation at the cathode. During electrolysis a very dense hydroxyl layer is formed close to the cathode, positive ions have to diffuse through this layer before reaching the cathode. Increasing the current means increasing the hydroxyl boundary layer and therefore hamper the diffusion through the layer. A decrease in current density should in other words result in an increase in deposition. This was shown by Tsoupko-Sitnikova et.al (2000) for currents in the 1-10 mA region. It was also

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shown that for very low currents corrosion of the deposit started to occur . The same workers also elaborated on the effect on resolution when heating the disc, something which sometimes has been suggested in order to fix the deposit and to burn away potential organic films. They concluded that heating had nearly no positive effect on the resolution, apart from a very limited improvement when heating to 100 ˚C (removing easily bound water?) a serious reduction of the resolution was noted when heating to 700 ˚C, attributed to diffusion of activity into the disc.

Further investigations regarding the 'common' electrodeposition techniques for actinides was performed by Vera Tome and Sanchez (1991) who compared uranium yield and energy resolution for the sulphate salt method by elaborating with deposition time, salt content, current intensity and electrode distance. The main conclusion of their work is that electroplating times should not be too long. Most actinides deposit fairly quickly and elements less prone to form oxides will then deposit at a slower rate. This means that resolution will only decrease when extending deposition times. In their work the optimum deposition time was about 20 minutes, the time needed to deposit roughly 90% of the uranium.

For elements with a long half life (U and Th) there is an upper limit as to how much activity that may be plated on to the disc. For ^{238}U the specific activity is about 12.3 mBq per µg and for ^{232}Th about 4 mBq per µg. This means that activities of around 500 mBq and 150 mBq of U and Th respectively will result in deposits of around 50 µg which is where the resolution starts to become affected. Although thick deposits also may follow with americium electrodeposition the situation is different in that the deposit consist of rare earth elements (REE) which is difficult to remove completely from A, especially when analysing soils and sediment.

Alternative techniques to electrodeposition for the (U, Th, Pu, Am and Np) elements include REE fluoride precipitates (100 ug on membrane filter) and evaporation of eg. TTA (theonyl tri-fluoroaceton) on disc. A typical spectrum showing three different sources done using 100 µg lanthanum as LaF_3 and collected on a 0.1 µm membrane filter is shown in figure 5. The energy resolution achievable is worse (FWHM 50-100 keV) than what may obtained by electrodeposition. Only +III and +IV actinides can be used in this technique.
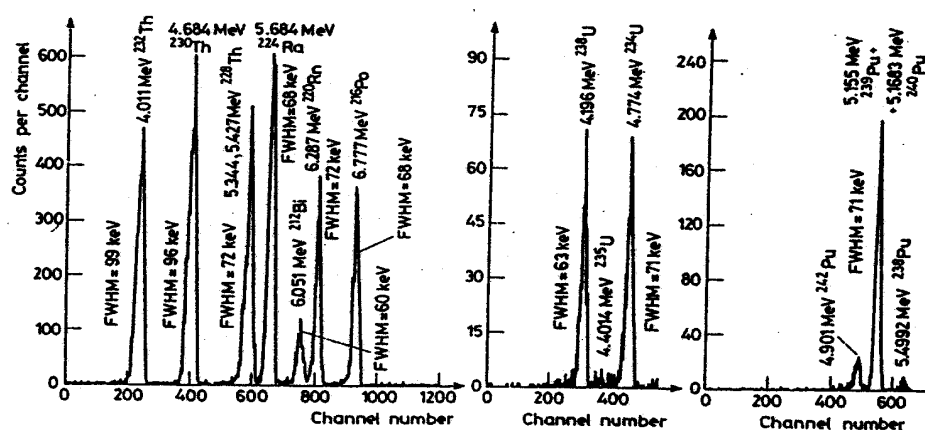

Figure 5:

LaF3 precipitate sources for Th, U and Pu. Uranium was reduced using $TiCl_3$ before precipitating. Source preparation for radium and actinium

Source preparation for Ra and Ac.

Since radium and actinium oxides/hydroxides are much more water soluble than the first group of elements aqueous solutions have proven less good when plating these elements. Instead combinations of alcohols and weak acids have proven more suitable. Electroplating (molecular plating) in these solutions is however not straightforward since the dissolution power of any salts in the sample is very low. Remaining salts also affect the efficiency, especially barium (chemical analogue element to radium) has proven important to remove before plating (figure 6). It has been shown that added platinum to the electroplating solutions significantly has improved the recovery, this is seen in figure 7.
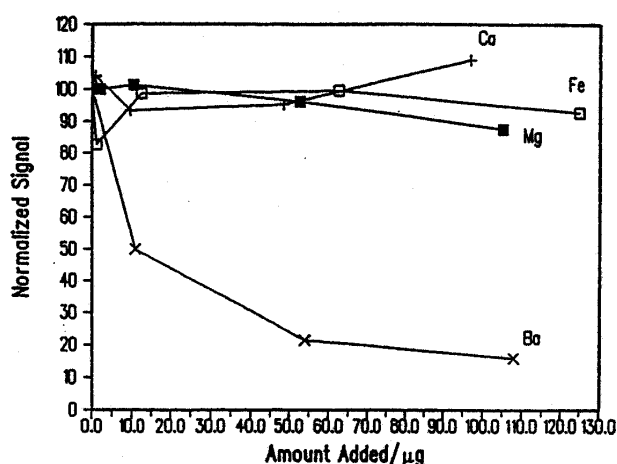
Figure 6:

Matrix effects on ^{224}Ra electrodeposition with Ca, Mg, Fe and Ba.
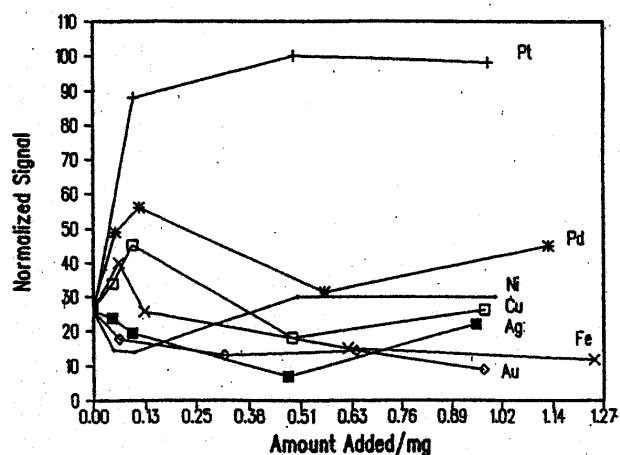
Figure 7:

Effect on radium electrodeposition recovery when adding different elements to the plating solution.

Due to the generally large problems in plating especially radium isotopes there has been other techniques developed. One easy-to-use method is the adsorption of the radium isotopes to a thin polyamide film impregnated with MnO_2. By stirring the solution containing radium for about 6h in a cell containing the impregnated film more than 80% of the radium may be adsorbed and then directly alpha counted after drying.

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10 MEASUREMENT OF LONG LIVED RADIONUCLIDES BY ACCELERATORMASS SPECTROMETRY

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Motivating Principle
- for long lived radionuclides, it is more sensitive to count atoms, even with modest efficiency, than radioactive decays. For example : for a nuclide with half-life of 106 y, fraction decaying during one week is 1.3x10-8 !

Why not classical mass spectrometry ? -interference by isobaric molecules and nuclides of stable elements, usually many orders of magnitude more abundant.

Consequences of using ion energies *of* Megavolts (ie velocities comparable to orbital electron velocities), rather than Kilovolts as for classical mass spectrometry

1) Can destroy all molecules 2) Can take advantage of phenomena related to nuclear charge of species being investigated to obtain partial or complete isotopic identification

-Rate of energy loss differences; absorption (1°Be), dE/dX identification (loBe'36Chs9M,99Tc), qas filled magnet (3Mn,6°Fe)
-Complete stripping; Be, 26A1, 36C1, 41Ca, 81Kr
-Projectile X-ray detection (PXD) ; 59Ni, 36C1, 41Ca, 79S e, 99Tc,126Sn

Other methods *of* eliminating or reducing interference from isobaric nuclides

1) Use of negative ions - 14C-, 26 Al-, 1291-, 41CaH3-, 32SiH3
2) Natural absence - actinides

Sample preparation (can't escape chemistry !).
1) Isotope dilution vs direct isotope ratio measurement
2) Dissolution (for solids), isotopic homogenization with carrier, if used
3) Extraction, purification
4) Appropriate form for cathodes (good electrical and thermal conductivity)

Typical elements of a tandem based AMS system
1) Ion source (Cs sputtering, negative ions, mutiple sample changer)
2) Injection -slow

       -rapid

       -simultaneous
3) Accelerator
4) Stripper (negative ions to positive ions, destruction of molecules)
5) Analyzing section   -magnetic (my/z)

                  -electrostatic (E/z)
6) Detector (gas ionization or solid state)

      -Energy, rate of energy loss, position, X-ray energy

Advantages of AMS compared to analysis by radioactivity measurements
1) Sensitivity (105 atoms)
2) Selectivity more specific than beta counting, no interference from other isotopes, eg 7Be
 ioBe, 59N1 6 Ni)
3) (rapidity)

Disadvantages
1) equipment size
2) equipment cost
3) equipment complexity

Future directions
  - Big vs small accelerators
  - Centralized vs dispersed facilities
  - Expanded range of isotopes

Entry into literature
Proceedings of triannual AMS conferences, published in Nuclear Instruments and Methods;
B172 (2000), B123 (1997), B92 (1994), B52(3-4) (1990), B29 (1-2)(1987), 233,135 (2)(1984)

Research program at Gif-sur-Yvette AMS facility
-^{10}Be in ice cores - proxy for past variations in solar activity, help establish ice chronologies
-^{10}Be in marine sediments - proxy for past variations in magnetic field, primary cosmic ray
intensity, dating
-^{129}I, in seawater - oceanographic tracer
-^{129}I, in soils and thyroids as retrospective proxy for ^{131}I dispersion from Chernobyl
- ^{lo}Be and ^{26}Al in « cosmic spherules » (cometary origin)
-^{26}A1 as tracer for aluminum toxicology studies (dialysis, neurological and bone dieases,
anemia, possible implication in Alzheimers, vaccines)
- ^{lo}Be and ^{26}A1 in rocks exposure age dating, geomorphology, climate studies
-^{lo}Be, ^{36}C1, ^{41}Ca ^{59}Ni, ^{79}Se, ^{126}Sn,^{129}, - for monitoring nuclear waste materials

Tandetron

Gif-sur-Yvette

Analyzing magnet
15° Electrostatic deflector
Terminal 2,5MV
Injection magnet
Quadrupole doublet
Accelerator tube
Tank lens
Insulated vaccum chamber
Stripping canal (argon)
Oscillator 40kHz
Heavy ion line
Transformer
Rotating electrostatic deflector
Ionisation chamber
Generator Cockroft-Walton
Carbon source
High intensity source
Cesium

Slits
Einzel lens
Steerers
Faraday cup
Gate valve
Retractable carbon foil
Thin window

Target foil
45° Electrostatic deflector
Quadrupole triplet
HPGe detector
Ionisation chamber

TANDETRON
GIF SUR YVETTE

11 Laboratory Radiotracer Techniques in Radioecological Studies: Comments on Basic Procedures

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Measurements of radionuclide bioaccumulation potential in marine organisms can be made either in the field or in the laboratory. Many factors can complicate obtaining unambiguous concentration factor (CF) data from one-time field measurements of existing radionuclide levels, and radiotracer studies are often used to estimate CFs under controlled laboratory conditions. This has the added advantage of discerning the dynamics of accumulation, something that can not be determined by single field measurements. The following comments and examples pertain specifically to pelagic marine zooplankton, but are general in nature and can serve for many benthic organisms as well.

Collection and handling of animals

Zooplankton, by virtue of their delicate nature, are in most cases extremely difficult to maintain for long periods of time in the laboratory. Most examples of techniques cited here pertain to crustaceans, partly because they form the largest portion of the zooplankton biomass in most regions and partly because they can withstand the rigous of collection and handling better than many of the soft-bodied forms. Therefore, we will concern ourselves principally with examples of pelagic crustaceans.

1. Collection

All types and sizes of plankton nets can be used to collect zooplankton. In most cases the mesh size of the netting will dictate the size of the organisms trapped. The net aperture will also dictate to some extent the size of the organisms caught because many larger forms and presumably stronger swimmers are able to avoid the net as it moves through the water. Several workers have collected euphausiids for laboratory experiments by vertically or horizontally towing a half-metre or metre plankton net for several minutes through the deep scattering layer. We have had consistently good results in the Mediterranean by making oblique hauls with an Isaacs-Kidd midwater trawl from a depth of 400 metres to the surface. This net has proved particularly successful for collecting the large euphausiid, *Meganyctiphanes norvegica*, as well as certain pelagic shrimps. Towing speeds generally range between 0.5-2 knots, but can be slightly faster for some of the larger pelagic crustaceans. The time for towing will depend on the biomass but is usually not longer than 30 minutes. Longer tows generally cause compaction and subsequent damage to the plankton in the cod end. It is of utmost importance to use a closed cod-end bucket, glass jar, or canvas bag of the appropriate size to keep water flow at a minimum and lessen damage to the organisms by physical means. Collections can be made either at night or during the day. Night collections usually have the advantage of finding the vertical migrators in the surface waters.

2. Shipboard handling

When the net is brought abroad ship the cod end should be dipped into a large basin of sea water near the temperature in the animals' normal environment. Upon opening the cod end most of the plankton will be released to the water. As soon as all plankton are in the basin, separation by species should begin. Sorting by means of wide-bore pipettes and a kitchen basting syringe is ideal for smaller forms. Larger specimens can be trapped in small beakers and then transferred through a series of washes to eliminate all foreign matter. Once the organisms have been cleaned of all adhering material, they should be sorted according to species in carboys of large volume containing clean sea water at a temperature normally encountered by the plankton.

Frequent checks will allow detection and removal of dead organisms. If the length of the cruise is relatively short, feeding the plankton will not be necessary. For this reason plankton should always be collected towards the end of the voyage during extended cruises.

3. *Transfer to shore laboratory*

The critical condition for relatively short transfer times is the temperature. During the hot months containers can be cooled by surrounding them with ice. Small species can be placed in plastic bottles which are then packed in polystyrene ice chests with enough ice to last the journey. If insulation is sufficient, the plankton can be freighted in this manner to almost anywhere in the world.

4. *Laboratory maintenance*

Most plankton should be removed from transfer carboys and placed individually in appropriate laboratory containers as soon as possible upon arrival at the laboratory. Polystyrene bottles or glass specimen jars of varying sizes serve adequately for holding pelagic animals. Frequent changes of sea water of the same temperature are imperative, and all debris such as moults and faecal pellets should be removed by pipette as often as possible to avoid decomposition. Oxygenation is not needed in most cases if the water is kept at near-saturation levels by changing frequently.

For increased longevity in the laboratory, proper diet is a prime factor. The maintenance of herbivorous zooplankton on phytoplankton, particularly mixed-species cultures of phytoplankton, has proved successful. Larger omnivorous forms have been maintained for long periods of time on a diet of *Artemia salina* nauplii. We have had good results in our laboratory by feeding euphausiids frozen *Artemia* carcasses; however, dead *Artemia* tend to promote rapid bacterial growth, thus, frequent water changes are necessary. Knowledge of the feeding habits of the experimental zooplankter is mandatory if long-term laboratory radiotracer studies are to be successful.

Pre-experimental procedures

1. *Animal selection*

Acclimation time depends on the individual species; however, it is recommended that a period of at least 48 hours be given to the animals before use in the experiments. Nevertheless, only those organisms displaying 'signs' of good health should be selected for the experiments.

The fact that many planktonic crustaceans moult regularly at frequent intervals complicates interpretation of radionuclide flux experiments. For this reason prior knowledge of the moulting cycle and frequency of moults will aid in designing the experiments.

The sex and reproductive status have been shown to affect various physiological functions. Thus, the possibility exists that radionuclide and trace metal metabolism might also be a function of the animals' reproductive physiology. To determine the reproductive status of the animal in question, manuals of invertebrate physiology and taxonomy should be consulted.

2. *Physico-chemical parameters*

The general approach to laboratory experimentation has been one of trying to approximate conditions found in nature. In radioecological accumulation experiments the concentration of the radionuclide in question should be held constant because in nature (except in small-scale acute contaminations) the accumulation of the isotope by the organism will probably not affect the radioisotope concentration in the surrounding waters. The ideal situation in the laboratory would be a flowing system with a constant radioisotope concentration. Such an experimental array is usually beyond the reach of most researchers; thus, a closed system in which the radioactive solution is periodically renewed, is frequently employed. Radionuclide losses due to accumulation by the organisms themselves can be kept to a minimum by maintaining a relatively high solution-volume to zooplankton-biomass ratio. This ratio is relatively easy to accomplish with zooplankton because their biomass is so small; thus, small-volume containers can be used.

Careful attention should be paid to the specific activity of the isotope employed. Whenever possible, high specific activity or carrier-free isotopes should be used. Isotopes of low specific activity have the disadvantage of adding large amounts of stable carrier isotope to the sea water, and consequently the concentration of the stable element can be increased several orders of magnitude over the normal levels. As a result, relative uptake rates and concentration factors of the radionuclide can be considerably reduced by isotopic dilution.

If the forms of the radioisotope and its stable counterpart can be characterized, great aid is rendered to the interpretation of the uptake data. It is imperative that the radioactive and stable counterpart are in the same form.

Many radionuclides form particulates which can precipitate to the bottom of the vessel. If particulate forms are accumulated differently than soluble forms by marine biota, differences in uptake rate can result. Isotope solutions should be prepared in advance and aerated 24-48 hours before use to avoid any large-scale changes in forms that might take place during the experiment. To measure the amount of the radionuclide in particulate form, the double-layer membrane filter technique is adequate. This technique involves filtering an aliquot of solution through a double layer of $0.45 \mu m$ filters and subtracting the amount of radionuclide 'adsorbed' on the bottom filter from the total amount trapped on the upper filter.

The formation of particulate forms of a given radionuclide is in some cases strongly pH dependent. To simulate the natural environment, the normal pH of sea water should be held relatively constant throughout the experiment so that changes in the physico-chemical forms of the radionuclide will not alter the accumulation pattern.

Salinity, temperature and oxygen content are variables that are known to affect invertebrate metabolism and thus might also affect the incorporation of radionuclides. These parameters should be monitored during the experiments for use in the final interpretation of data. Temperature changes can significantly alter physiological mechanism which in turn affect metabolism and subsequent cycling of radionuclides.

Experimental procedures

1. General

The prime reason for performing radioecological experiments in the laboratory is to gain information on the rates of radionuclide and/or stable element flux in nature. The ideal method for simultaneously measuring influx and outflux of an element is the double-tracer technique; however, very few elements have two suitable radioisotopes, and the investigator usually must study uptake and loss processes by other means.

With large plankton experiments can be designed in which individuals are monitored live and then replaced in sea water for further uptake or loss. This design eliminates the large number of animals needed when specimens are sacrificed and radioanalysed at each specified time. It also has the advantage of allowing the investigator to follow the kinetics in individuals, while at the same time allowing the calculation of a group mean (if a sufficient number of individuals live through the entire experiment). Measurement of individual kinetics allows the investigator to assess the health of each animal and discard those animals from the group that are obviously not performing as the others. Monitoring radioisotope kinetics in individuals usually cannot be done with very small zooplankters such as copepods.

If one assumes the mechanism in any given organism involves a simple one-to-one isotope exchange, either an accumulation or loss experiment should lead to the same rate constants. In some cases this situation holds especially over the long term. Long-term experiments are difficult to perform with zooplankton, however, so that in many experiments radioisotope uptake times are short.

In these cases, equilibrium levels of radioisotope in the organisms are not attained and complete labelling of all possible sites in the organism is not realized. Rates of isotope loss under these conditions need not mirror uptake rates and mechanisms involve something more than simple isotope exchange (Fig. 1). The uptake and loss processes must be studied independently.

2. *Uptake from water*

One general concept is that zooplankton, by virtue of their small size and short mean generation time, turn over radionuclides and trace metals very rapidly and therefore reach isotopic steady-state in a relatively short time. Uptake experiments in which non-fed euphausiids were allowed to accumulate ^{65}Zn from water only showed that steady-state was not completely reached even after two weeks (Fig. 2). True steady-state might never be completely achieved if different forms of an isotope create sinks that do not readily exchange with the added form in the water. Many invertebrates have the ability to regulate the ion content of certain tissues. If the ability of zooplankton to absorb certain elements is a regulated process, radionuclide uptake would also be regulated if the radioisotope is in the same physico-chemical form as the stable element. The ability to regulate the absorption of trace elements can be tested by allowing zooplankton to accumulate radiotracer from solutions containing varying amounts of the stable element. In the case of zinc (Fig. 3), whole-body absorption was strongly dependent upon zinc concentration in sea water, a finding that would not be the case if the animals were strictly regulating their zinc intake.

Uptake of radionuclides by some crustaceans is strongly controlled by moulting. Moulting accounts for a great loss of incorporated trace elements and radionuclides; hence, these organisms never maintain an isotopic steady-state with respect to their water or food. Instead, an oscillating 'plateau' may be reached in their uptake kinetics, the amplitude of the oscillations being a function of the amount of isotope lost through moulting (see Fig. 2).

Another factor that affects the rate of uptake of certain radionuclides is the size of the zooplankton. Small organisms such as euphausiids have a large surface area to volume ratio. Consequently, there is often greater uptake per unit weight in smaller individuals than in larger ones (Fig. 4). Because adsorption has been cited as the principal mechanism for the accumulation of many radionuclides from water by organisms, care should be taken to choose animals of similar size for experimental use.

During any uptake experiments the concentration of radioisotope in the water should be carefully followed. Rapid depletion of the isotope will lead to both anomalously reduced uptake rates and anomalous CFs. If uptake from water is to be followed in healthy individuals for long periods of time, the plankton must be fed. This can be accomplished, for example, by resuspending the animals in non-radioactive sea water and feeding algae or other food for short periods of time. As long as the time spent out of the radioactive medium is short relative to the time in uptake, the kinetics of accumulation will not be significantly altered.

3. *Uptake from food*

Marine animals certainly obtain a good fraction of their radionuclide body burdens by ingesting food. Any attempt to measure the fraction accumulated by allowing the animal to feed on labelled food is extremely dubious, however, mainly because of the lack of sound information on zooplankton ingestion rates in nature. Short-term experiments utilizing arbitrarily labelled prey are of little use because radioisotope uptake curves of almost any shape can be generated by regulating such parameters as food organism concentration, prey size, container volume, and radioisotope concentration in the food. Whereas radioisotope uptake from water is a more or less continuous process, zooplankton feeding (hence radioisotope uptake from food) is not.

Finally, because ingestion of prey by zooplankton is not an instantaneous process, the specific activity of the food organism will continue to decrease because of loss of radioisotope to the water. This, in turn, often leads to recycling of the radioisotope between the food organism and predator by way of the water. This effect should be minimized as much as possible.

4. *Uptake from food and water*

One way to attack the problem is a comparison between uptake from water and simultaneous, uptake from food and water. In the studies involving uptake from food and water simultaneously zooplankton are allowed to accumulate the radioisotope from water in the presence of a copious supply of food labelled to steady-state in the same medium. If the animal is fed *ad libitum*, it will be able to ingest food at will and possibly will reflect more closely the situation in the natural environment. When the radioactivity in the zooplankton in both systems approaches a steady-state with that in the medium, a comparison of the generated uptake curve from food and water with that from water only will give, by difference, the relative importance.

Most of the studies on foodchain dynamics of radionuclides in zooplankton have led to the general conclusion that a greater portion of the radioisotope or stable element content is derived from the foodchain rather than by direct accumulation from water. The experimental methods that have been utilized to measure these differences are open to criticism, however. Often uptake experiments are not carried out long enough to see if animals accumulating activity from water will, indeed, reach a steady-state level lower than that of organisms obtaining radioactivity from food. Ideally, long-term accumulation experiments of the type outlined above should be performed to explore whether there are certain isotopic 'compartments' in organisms that do not exchange with the isotope in water.

5. *Assimilation efficiency*

Assimilation efficiencies for biologically essential radionuclides will vary with the zooplankton species as well as the element. Figure 5 shows the results of one such study in which a euphausiid was fed *Artemia* labelled with four isotopes for 5 days. After the last feeding the euphausiid was measured and found to have accumulated the four isotopes in about the same relative proportion as they were originally present in the food. The animal was then fed non-radioactive *Artemia* and resulting faecal pellets were collected and measured for radioactivity 10 hours later. No ^{54}Mn was present in the faecal pellets, indicating complete absorption from the food across the gut and/or lack of excretion from tissues to non-radioactive *Artemia* debris in the gut during the 10-hour feeding period. Faeces collected after 5 days feeding on non-radioactive brine shrimp indicated that only small amounts of ^{65}Zn were being excreted at this time, although the animals' spectra still indicated the presence of all 4 radionuclides.

Non-biologically essential radionuclides, originally ingested, will be excreted very rapidly by zooplankton with little or no incorporation into internal tissues. Rapid egestion of non-assimilable fission products accentuates the problem of measuring and interpreting uptake rates and subsequent concentration equilibria for these isotopes in zooplankton. Radioactivity in animals picked from contaminated areas at sea might be only a measure of radioactive food contained in their digestive tracts. Were these animals allowed to clear their tracts before analysis, little or no activity may, in fact, be associated with tissues. Clearly, the dynamics of the radionuclides in the organisms in question must be known before interpreting field measurements.

6. *Loss of isotope*

Measuring the rate of radioisotope loss from zooplankton offers the best means for calculating flux rates of the element. If the radioisotope is thoroughly mixed with its stable counterpart in all tissues of an organism, the loss of the radioisotope will give a measure of the flux of the stable element as well. For the assumption of thorough isotope mixing to be valid, the organism must have attained a specific activity similar to its food and/or surrounding medium. This concept of 'isotopic equilibrium' is often overlooked or disregarded by researchers; hence, errors are incurred when one extrapolates radioisotope exchange kinetics to arrive at stable element flux rates.

To ensure reasonably good radioisotope mixing within the organisms as well as an 'isotopic equilibrium' with the surrounding environment in the shortest time possible, one should 'tag' with radiotracer all possible pathways of stable isotope to the animal. This necessitates labelling both food and water as discussed earlier. The animals should be periodically counted, along with a sample of the radioactive sea water, until there is no noticeable increase in the animals' radioactive content. The time to attain a steady-state in zooplankton depends on the isotope, the species of animal and its size and metabolism, and water temperature, to name some important factors. At steady-state it is assumed that the specific activity of the animal is the same as that of the medium and/or the food; however, this will only hold if both stable and radioactive isotope are in the same physico-chemical form and thus equally available for exchange with the organism. When isotopic mixing has been ensured, the animals are radioanalysed and placed in non-radioactive medium to follow loss of the radioisotope. The ideal medium is a flowing sea water system that rapidly renews itself in order to avoid recycling of the radioisotope lost by the plankton. However, most loss experiments are performed in closed systems of large enough volume that recycling of radioisotope will not pose a problem. Frequent water changes will sufficiently simulate flowing sea water and avoid a build-up of metabolic wastes as well as excreted radioisotope. One possible method for assessing the degree of isotope bioavailability lost to the water in a closed system is to place a non-labelled animal in the same jar that contains the radioactive animal. This non-labelled animal can be periodically monitored to see if any of the excreted isotope is being accumulated.

Ideally, one wants to measure excretion from tissue components and not that due to defecation. Therefore, zooplankton removed from radioactive sea water containing labelled food should be fed non-radioactive food until their digestive tract is cleared of radioactive debris. This is usually a matter of 6-8 hours for actively feeding euphausiids. In order to know if the radioactive material has been egested, faecal pellets can be periodically collected and monitored during the period of gut flushing. When the gut has been cleared the amount of radioisotope remaining in the animal can be assumed to be associated with tissues. If too much time is allowed before the start of the excretion experiments, some of the isotope may already have been excreted from compartments with rapid turnover rates. This situation leads to an artificial enhancement of the importance of pools with very slow radionuclide turnover rates. This 'pinpointing' of time zero for tissue excretion becomes increasingly more important with isotopes that display poor absorption characteristics and rapid turnover rates.

Most radioisotope loss curves for zooplankton are not exponential but are curvilinear on semi-log paper which indicates a type of power function. Often these curves are reduced by curve-stripping techniques into a series of logarithmic segments, the slope of each representing loss from a given 'compartment' within the animal. This practice is an oversimplification of the processses involved, but does nevertheless afford a means of approximating the turnover rates of both stable element and radioisotope within the animal if certain experimental conditions are met. To ensure that turnover rates of most or all of the stable isotope are measured, for example, excretion experiments should be of a long-term nature. On the other hand, turnover rates of radioisotopes recently absorbed by animals, and therefore not mixed with the stable element, can be estimated by short-term experiments. An example of ^{65}Zn excretion in animals labelled for several days is given in Fig. 6. Clearly, total loss is not exponential and rates comparable with those from short-term labelling experiments are only evident over the first 3 days of the experiment. These relatively rapid rates are associated with a pool containing only a small fraction of the animals' ^{65}Zn content. If stable element turnover times are based on excretion rates of only a small portion of the animals' total element pool, large underestimates of stable element turnover time will result. It is obvious that radioisotope loss experiments can be designed for different purposes, and interpretation of results is strongly coupled to the length of the loss period as well as the uptake period.

7. Radionuclide excretion via particulate products

Certain zooplankton species that form part of the deep-scattering layer vertically migrate several hundred metres twice daily. This large translocation of biomass affords a means for enhancing the dispersion of radionuclides that would otherwise be limited if the population were to remain at one level. The rapid metabolism and relatively short generation time of zooplankton and their ability to

ingest and process microorganisms and detritus leads to a large production of particulate products in the form of faecal pellets, moults and carcasses. In the case of radioactive contamination of the population, the 'rain' of particulate products from surface waters would accelerate the downward transport of radioisotopes to bottom sediments, as well as act as a vector of redistribution of the contaminants in the water column. Estimating the production of particulate products by *in situ* measurements would be a formidable problem; therefore, estimates depend on measurements made in the laboratory. Euphausiids, for example, moult regularly approximately every 5 to 10 days depending upon animal size and species. Moulting is strongly dependent upon temperature; therefore, this parameter should be carefully considered when measuring the moulting rate. Moults from euphausiids well-labelled with radioisotope can give additional information on radionuclide and trace element recycling. Radiotracer flux rates measured from exuvia in fresh sea water, coupled with estimates of sinking and disintegration rates, can be used to assess moulting as a means for vertical transport of radionuclides in the sea. Information on the production and impact of faecal pellets is more difficult to obtain. Faecal pellets, although small, can be collected with eye droppers and are easily differentiated from other particles. After a period of several days enough pellets are obtained to facilitate weighing. As with moults, faecal pellets collected from well-labelled animals grazing on labelled food can be used to measure radioisotope flux rates in faeces. This information together with data on stable element content, sinking rates, and disintegration rates of faecal pellets will allow assessing the ability of this material to transport and recycle radionuclides and trace metals.

Suggested reading

1. Fowler, S.W. 1982. Biological Transfer and Transport Processes. In: Pollutant Transfer and Transport in the Sea. Vol. II, G. Kullenberg, ed., pp. 1-65, CRC Press, Boca Raton, FL, USA.

2. IAEA. 1975. Design of Radiotracer Experiments in Marine Biological Systems. Tech. Rep. Ser. No. 167, IAEA, Vienna.

3. IAEA. 1997. Strategies and Methodologies for Applied Marine Radioactivity Studies. Training Course Series No. 7, 377p, IAEA, Vienna.
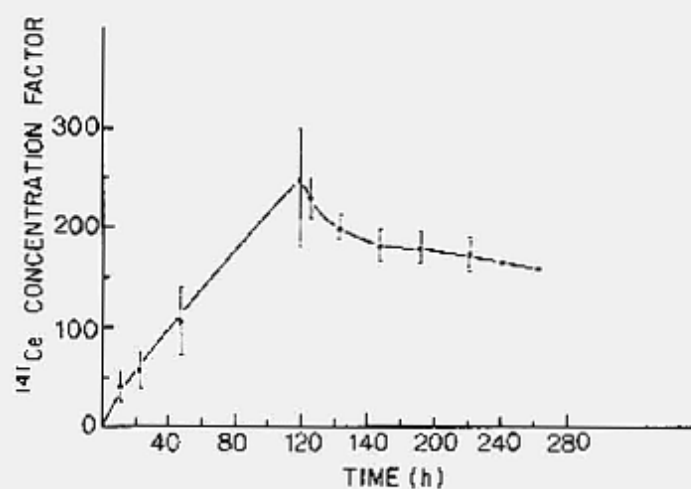
FIG.1. Meganyctiphanes norvegica: uptake and subsequent loss of ^{141}Ce by non-moulting euphausiids. Bars indicate range around mean values. Last two points represent values from a single individual.
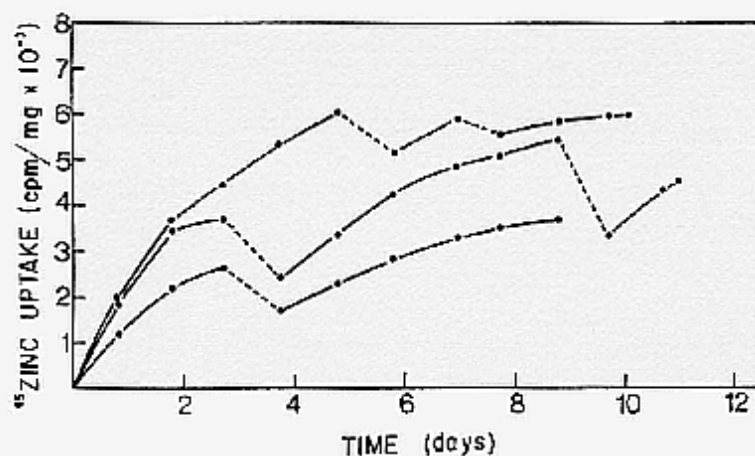

FIG.2. Euphausia pacifica: uptake of ^{65}Zn from solution by euphausiids. Initial ^{65}Zn concentration was 25 µCi/litre, temperature 10°C. The dashed line indicates moulting. Animal dry weights ranged from 7.7 to 12.7 mg.
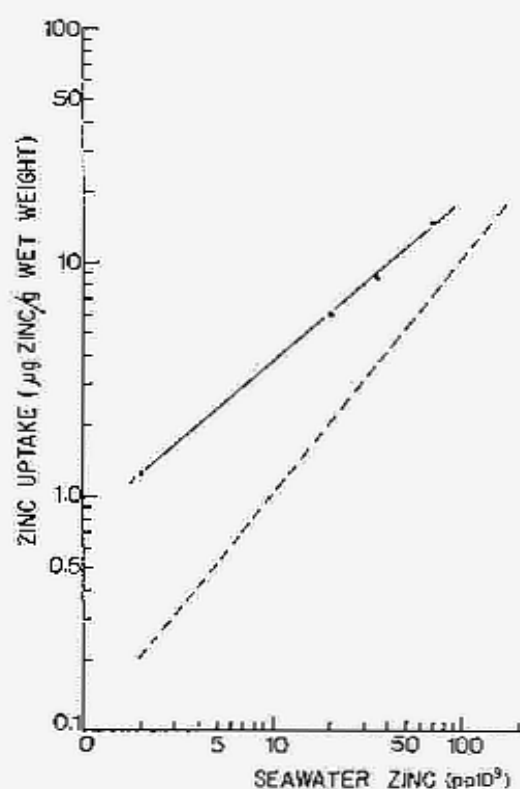
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FIG. 3. *Meganyctiphanes norvegica*: relationship between zinc uptake and zinc concentration in seawater after 6-day uptake of ^{65}Zn. The dashed line represents the slope of the line if uptake is proportional to concentration of zinc in seawater.
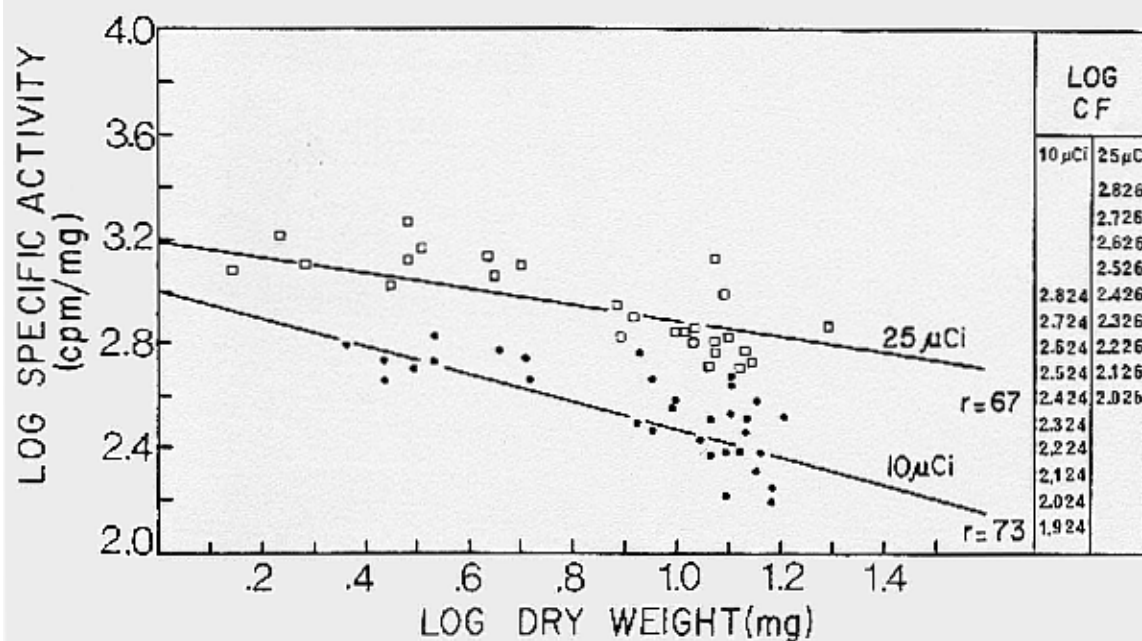

FIG. 4. *Euphausia pacifica*: relationship of weight-specific uptake and concentration factors (CF) to dry weight of euphausiids at 5°C and two concentrations of ^{65}Zn per litre. Uptake values and CF (based on animal dry weight) were determined at 20 hours before moulting began. Euphausiid weight : dry weight ratio was 5.5.
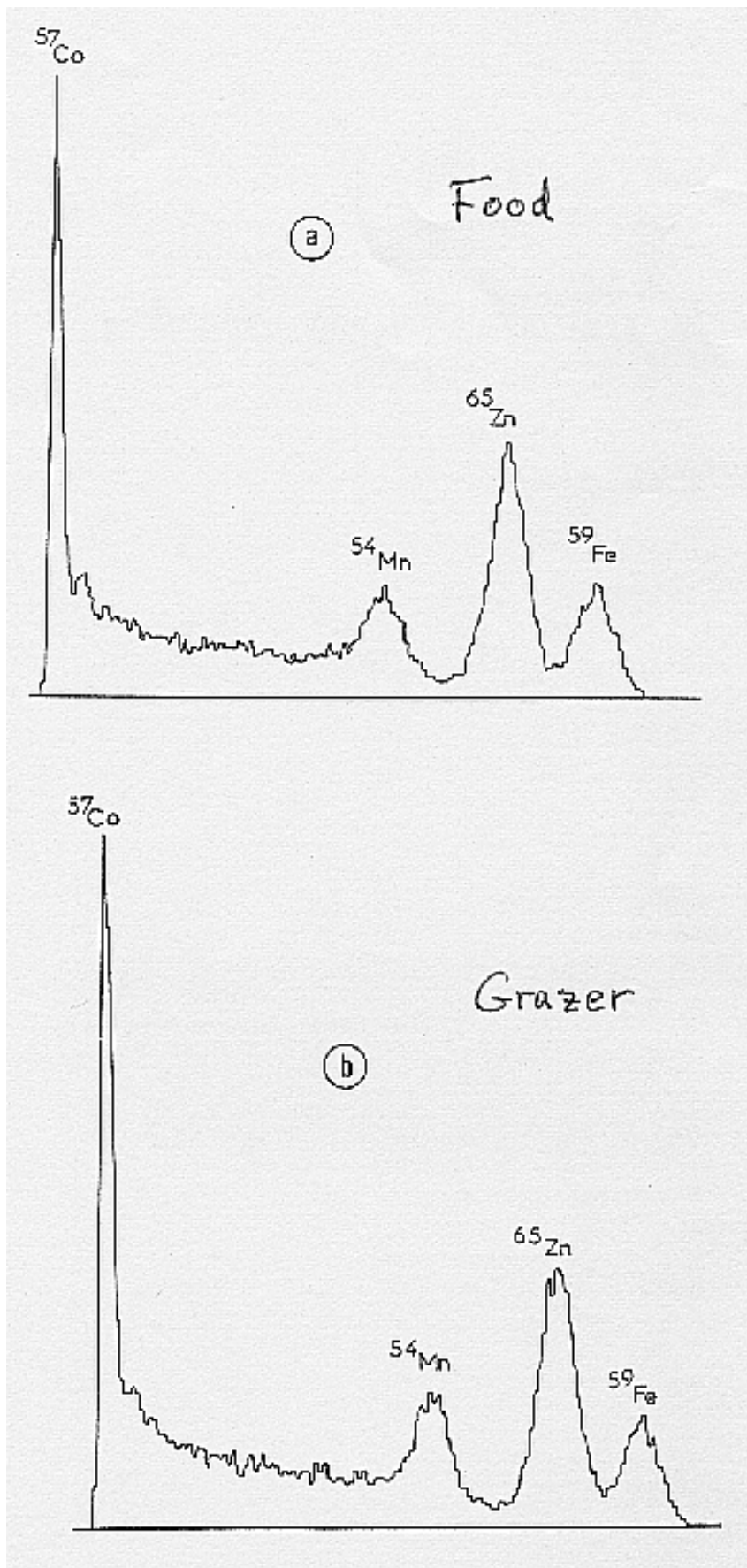
Fig. 5 (a & b)
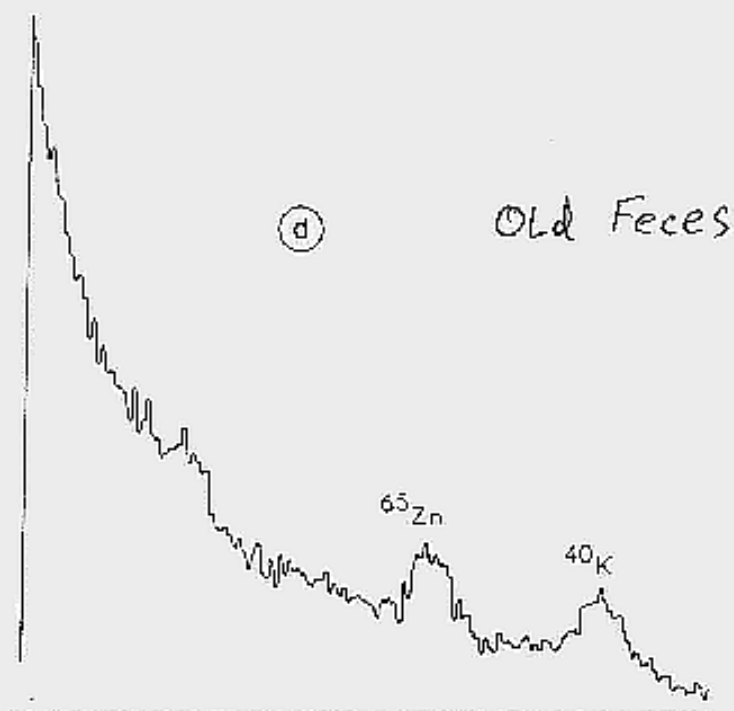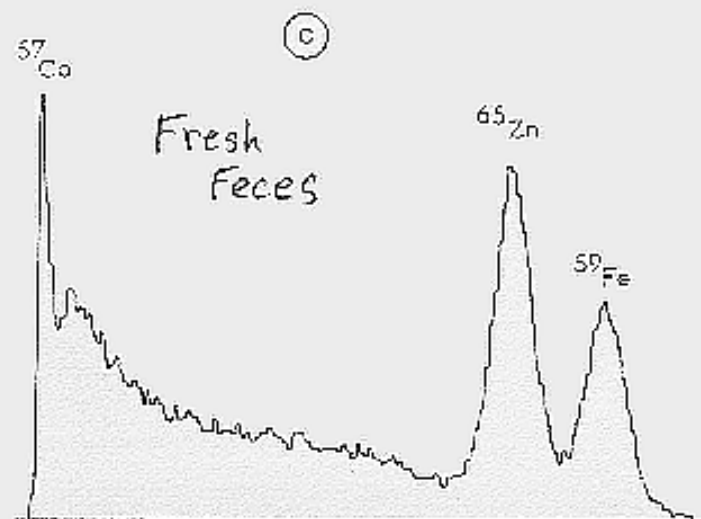
FIG. 5. Gamma spectra of (a) multiple isotope labelled Artemia that served as a food source for the euphausiid, Meganyctiphanes norvegica; (b) euphausiid immediately after ingesting radioactive Artemia (a) for 5 days; (c) euphausiid faeces collected 10 hours after the end of uptake (b); (d) euphausiid faeces collected 5 days after the end of uptake (b)
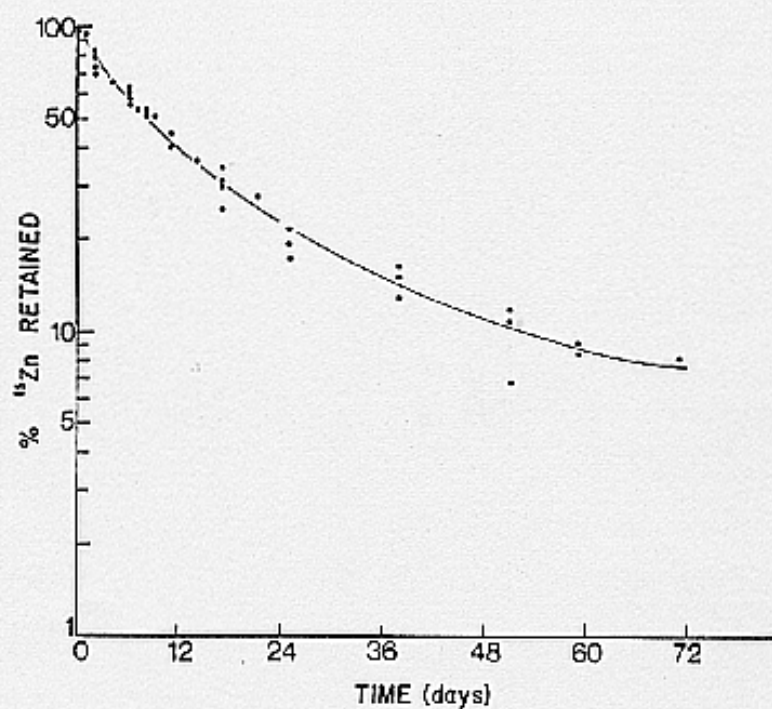
FIG.6. Meganyctiphanes norvegica: excretion of ^{55}Zn by euphausiids after 20 days of uptake from food and water. Values are corrected for ^{55}Zn loss due to faecal pellet production and moulting. Curve fit by inspection.

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12 Analysis of Alpha-Particle Spectra

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ABSTRACT

This paper presents the basic aspects of the analysis of alpha-particle spectra measured with semiconductor detectors. We discuss the methods and algorithms used in the optimization process, the influence of the statistical weights used in the fittings, the line shape models and the importance of the correct use of variances. The results of the 1997 IAEA intercomparison on alpha analysis packages and some future trends are also discussed.

1. Introduction

The analysis of alpha-particle spectra taken with semiconductor detectors relies on a combination of techniques whose aim is the extraction of the maximum available information from the spectra. Under standard conditions target values are the positions and areas of all peaks, from which the contributions of component elements in the measured source can be derived. But additional information as, for example, peak asymmetries and tailing contributions can be useful to identify and understand the basic phenomena taking place in the detector, to provide information about the source, to characterize the detector window, etc., and the complexity of the analysis depends on the amount and quality of the information that the user wants to obtain.

Several facts contribute to difficult the interpretation and analysis of alpha spectra. In first place, measurement systems with Si detectors have a limited energy resolution, about 8.5 keV in optimum conditions, and much poorer when the detector size increases or the source-to-detector distance decreases. Besides, there are only a few nuclides that decay by a single alpha branch and complex decay patterns are much more common. Therefore, the shapes and complexity of spectra are strongly dependent on the experimental conditions.

The spectrum of a source of monoenergetic alpha particles measured with Si detectors has a strong asymmetrical shape. If the sample being measured contains several alpha emitters, the contribution of the different nuclides and branches gives rise to alpha-particle spectra characterized by groups of lines in different degree of overlapping.
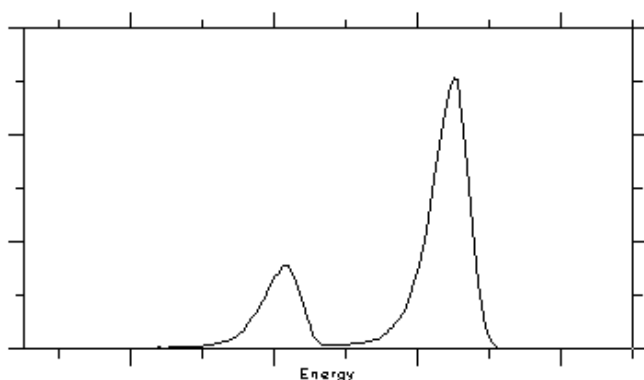
Figure 1. Alpha-particle spectra of ^{244}Cm, showing the two main lines

A full understanding of the shape of alpha peaks can only be reached by the study of the physical processes taking place inside the detector. Studies have been carried out to understand and describe the response of Si detectors to alpha particles, and, in general, to light ions. (See, among others, the contributions of L'Hoir 1984, Lennard et al 1986, Steibauer et al 1994). One of the practical consequences of the interaction is the lack of linearity of the detectors. Even with the thin windows (about 40 nm) of the new detectors, alpha particles loss about 6 keV before arriving to the depleted layer where they are detected. This and other effects contribute to the non-linearity of Si detectors which does not allow a precise measure-

ment of the energy of the structures in alpha-particle spectra unless a set of reference peak positions and energies are available from which the energy values can be interpolated.

2. Basic expressions for analysis

For a nuclide that decays by alpha emission, the number of alpha particles emitted in a time Δt is given by the expression:

$$\Delta N = N \frac{\ln(2)}{T} \Delta t$$

If the nuclide decays by more than one alpha branch, the number of particles emitted for each branch is obtained by including the corresponding alpha-particle emission probability in the second term of this expression.

Only a fraction ε of all emitted particles arrive to the detector, so that the number of detected particles is given by:

$$S = \varepsilon \Delta N = \varepsilon N \frac{\ln(2)}{T} \Delta t$$

For a sample containing two nuclides (1 and 2), it can easily be demonstrated that the ratio of the atomic contents between both nuclides in the source is given by the expression:

$$\frac{C_1}{C_2} = \frac{T_1}{T_2} \frac{\displaystyle\sum_i \frac{S_{1i}}{P_{1i}\,\varepsilon 1i}}{\displaystyle\sum_j \frac{S_{2j}}{P_{2j}\,\varepsilon 2j}}$$

Where P_{1i} and P_{2j} are the alpha-particle emission probabilities of the nuclides 1 and 2, T the half-lives, S the peak areas and ε are the efficiencies, which should include both the geometrical factors and the fraction of the peak areas calculated by the integration algorithm. If correctly defined, efficiencies are constant for all terms in the precedent expression, since the intrinsic efficiency of the detectors is very close to 1 and the calculation of the peak areas is carried out with the same procedure for all peaks in the spectrum.

Since the basic problem in spectral analysis is the determination of the peak positions and areas we shall discuss now the best way to obtain this information from the spectra. For spectra with non-overlapped peaks -a very infrequent situation- the analysis of the isolated lines can be done by adding the channel contents of all regions of interest after a careful extrapolation of the tails of the adjacent groups of lines. This technique requires a very good tail estimation and the use of precise values for the alpha-particle emission probabilities. Yet, it has been successfully used for the accurate estimation of the [238]Pu/ [239+240]Pu activity ratio in the frame of a multilaboratory EUROMET intercomparison [Bortels 1996], with total uncertainties of about 0.2%.

If the degree of overlapping of spectra is higher, complex algorithms are usually needed to determine spectral parameters. In the next section, we will discuss the general procedure to be used in the analysis.

3. Spectral analysis by functional minimization

When the peaks are overlapped, simple integration is no longer useful and other numerical procedures have to be considered. The fitting procedure involves three steps: a) the selection of a line shape model which represents the experimental behavior of an alpha peak; b) the

choice of an optimization criterion to fit the model to the experimental data; and c) the use of a numerical method to obtain the best values of the parameters, from which the magnitudes of interest, usually peak areas and positions, and the corresponding uncertainties can be derived.

The general formulation is the following: Consider a pulse height spectrum with n channels Y_x {x=1,n}, where Y_x is the number of counts accumulated in channel x. Let's suppose that the spectrum is formed by N peaks. We start by describing the peak shape by an analytical model, a function F_x, which is characterized by a set of parameters usually called "peak shape parameters". If we use, for example, a gaussian, the only shape parameter would be σ. If we admit that this model represents the experimental shape of a peak, it follows that any channel in the spectrum can be approximated by a linear combination of the values predicted by the model for the N component peaks:

$$S_x \approx \sum_{j=1}^{N} I_j F_x^j$$

Where F^j represents the contribution of the j-th peak and I_j its intensity. The function S depends on a set of parameters, which are the N peak positions and areas and the specific line shape parameters. The spectral analysis will be concluded when all peak parameters are determined. The process of obtaining the set of parameters that best satisfy the previous equation is known as optimization or fitting process.

Line shape models

A number of different peak models have been proposed for the analysis of alpha spectra. One of the basic assumptions is that all peaks in the same spectrum have similar shapes and therefore, the peak shape parameters are kept constant for a given spectrum. This is a reasonable hypothesis since most alpha peaks concentrate in an energy region of a few MeV and only in spectra taken in optimal conditions over an extended energy region could some differences be observed.

A good analytical peak model should closely follow the shape of real alpha peaks. Here, a compromise is mandatory between the complexity of the model and the performance that can be expected. A peak model with a large number of shape parameters will adapt very well to a variety of experimental situations, but the fitting process can become tedious or even impossible in some circumstances, e.g. in spectra with poor statistics

Considering the constant shape of the peaks all over the spectrum, it is not surprising that one of the first solutions were the use of a monoenergetic isolated peak as a model to which compare the others [García-Toraño and Aceña, 1976]. This can provide a good result although it is not very frequent to have a peak with the ideal characteristics in the spectrum. Additional problems are that the calculation of derivatives, usually needed in the optimization process, can make the fitting process unstable unless some extra cautions are taken.

Some of models proposed are based on functions with origin in the analysis of gamma spectra. They include gaussian-shaped peaks with functions to describe the asymmetry found in the low energy side of alpha peaks. The following model proposed by Baba [1978] uses two separate functions to describe the peak shape:

$$F_x = A \times \exp\left[-\frac{(x-m)^2}{2\sigma^2}\right]$$

In the central and high energy region

And

$$F_x = \exp\left(a(x-m)^3 + b(x-m)^2 + c(x-m) + d\right)$$

In the low energy region

Here, A is the peak amplitude, m the peak position and σ, a, b, c and d the shape parameters.

Watzig and Westmeier [1979] used a peak shape model described by:

$$F_x = A\left(\frac{\exp\left(-b(x-m)^2\right) + t\, ft(x,m)}{1 + HTAIL}\right)$$

Where t is a parameter that characterizes the tail amplitude and ft is a function describing the tailing structure of the peak, given by:

$$ft(x,m) = \frac{1}{\sqrt{b}}\exp\left(d(x-m) + \frac{d}{4b}\right) \times FI1\left(\sqrt{b}\left(x-m+\frac{d}{2b}\right)\right)$$

Where $b = \dfrac{4\ln(2)}{FWHM}$ and FI1 includes the error function.

More recently, Koskelo [1996] proposed a model with a gaussian plus and an exponential function of the form:

$$F_x = A\exp\left(\frac{T(2x - 2m + T)}{2\sigma^2}\right)$$

Here, T is the tailing parameter. The two branches of the model join at $x = m\text{-}T$.
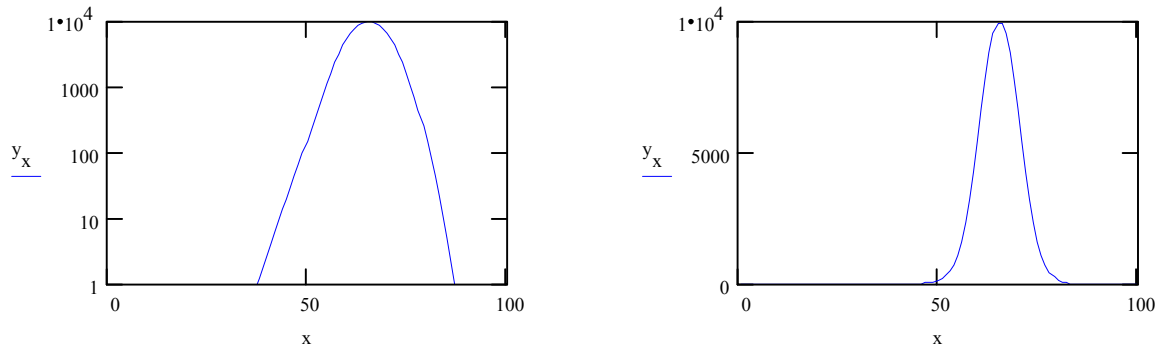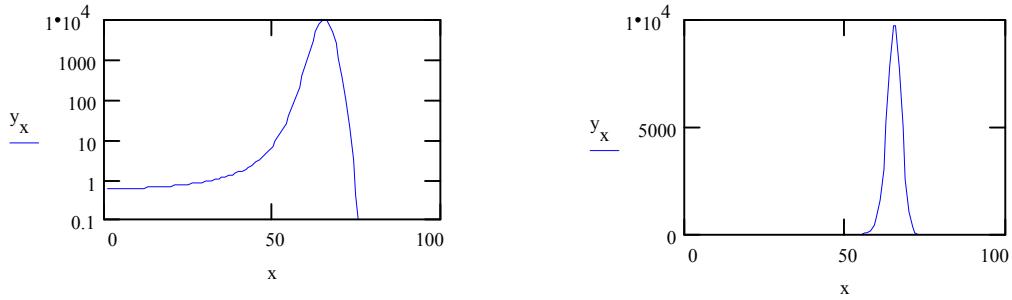

Figure 2. The line shape model of Koselo

Earlier in 1969, a more complex model was proposed by Trivedi, based on a modified gaussian:

$$F_x = A\exp\left(-\frac{\left(\dfrac{x-m}{\sigma}\right)^{t1}}{1 + \left((1 - \mathrm{sgn}\,(x-m)) \times (s(x-m))\right)^{t2}}\right)$$

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The parameter s is obtained by the use of the equation: $Q = \exp\left(\dfrac{1}{2\sigma^2 s^2}\right)$ that links the experimentally determined peak to valley ratio Q to σ and *s*. This is a complex line with several parameters that allow the modification of the line to adapt to many different condi-

tions.

L'Hoir [1984] studied the response of Si detectors to light ions including alpha particles and proposed a line model based on the convolution of two functions, a gaussian and a one-side exponential:

$$R(\eta) = \lambda \exp\left[\frac{(\eta - \bar{\eta})^2}{2\sigma^2}\right] \otimes \exp(\eta / \eta_0) Y(-\eta)$$

Figure 3. The line shape model proposed by Trivedi

Where Y(-η) the Heaviside unit step, η is the energy and λ is a constant factor. This model is the basis for ulterior developments by other authors. Bortels and Collaers [1987] added a second or third exponential to describe the peak asymmetry. The basic line is given by

:

$$E_x = \frac{S}{2\tau} \exp\left(\frac{x - m}{\tau} + \frac{c^2}{2\tau^2}\right) \times erfc\left(\frac{1}{\sqrt{2}}\left(\frac{x - m}{\sigma}\right) + \frac{\sigma}{\tau}\right)$$

Where *erfc* is the complementary error function and *S* is the peak area. The whole model uses a combination of functions with different exponential parameters τ and weights η:

$$F_x = (1 - \eta) E_1(x) + \eta E_2(x)$$

If the tailing structure of the peaks becomes more important, a third exponential function can be added.
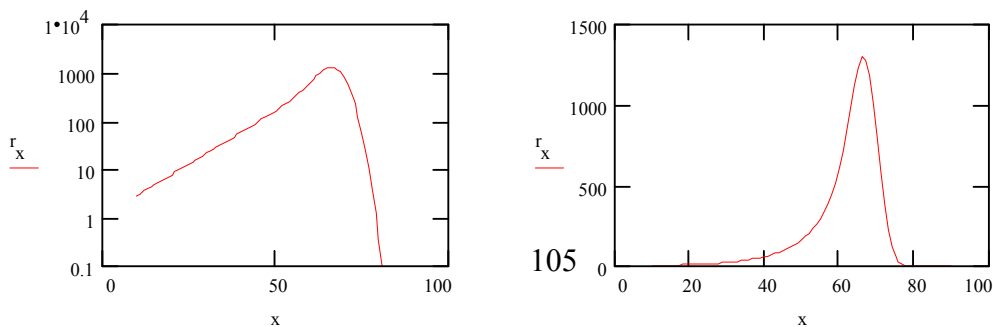

Figure 4. The line shape model proposed by Bortels and Collaers

Other models not described here have been proposed by Basova [1979], García-Toraño [1996]. Using a different approach Martin [1991] and Lozano[2000] describe the use of splines to model the peak shape, although their approach seems difficult to implement in spectra with overlapped peaks.

Optimization criteria and statistical weights

Once the peak shape model has been selected, the next step is the choice of an optimization criterion to obtain the optimal parameters, from which we will derive the data of interest, basically peak areas and energies. The most common criterion (but not the only one possible) is the minimization of the χ^2 statistic defined as:

$$\chi^2 = \sum_x w_x (Y_x - S_x)^2$$

Where w_x is the statistical weight assigned to Y_x.

There are several possible definitions of w_x that lead to a family of χ^2 statistics. Common definitions of w_x are $1/F_x$ (Pearson's definition) and $1/s_k^2$ (Neyman´s definition) where s_k^2 is the estimated variance for the channel contents. While the first definition is unambiguous, there is no general agreement for the second one, since s_k^2 can be defined in a variety of manners. If s_k^2 is taken as Y_x, the statistical weights are not defined for $Y_x=0$, and either this channel is excluded forn the fit or an average channel value must be used. The other alternative is to use the bayesian approach that indicates $s_k^2= Y+1$.

Phillips and Marlow [1978] studied the influence of the statistical weights in the fitting of spectra with low statistics and concluded that the use of $w_x= 1/Y_x$ leads to underestimate the areas of weak peaks. They suggest the use of an average channel contents as the best estimate for s_k^2. García-Toraño [1994] tested all previous definitions with a set of low statistics alpha spectra and found that the background under the peak plays an important role and that the only safe definition for any kind of experimental conditions is $w_x= 1/F_x$.

Baker and Cousins [1984] prpose an alternative χ^2 definition based on the maximum likelihood theory:

$$\chi^2_\lambda = 2\sum_x \left[F_x - Y_x - Y_x \ln\left(\frac{Y_x}{F_x}\right) \right]$$

While these authors found some advantages in the use of this definition for some nuclear spectra, others studied the application of the maximum likelihood definition of χ^2 to the analysis of alpha spectra and concluded that there was no significant difference [García-Toraño 1996].

Algorithms for functional minimization

To implement the functional optimization, we need to go one step further, and obtain a set of equations whose solution gives the values of the parameters. For an intuitive picture we can imagine that all possible values of χ^2 form a multidimensional surface, (with np dimensions). The numerical procedure must be able to find the global minimum of such surface, in which some local minima without physical significance are often present. A simplified picture

of this surface is presented in figure 5, where only 2 dimensions (peak positions) in the fitting of a doublet are considered.
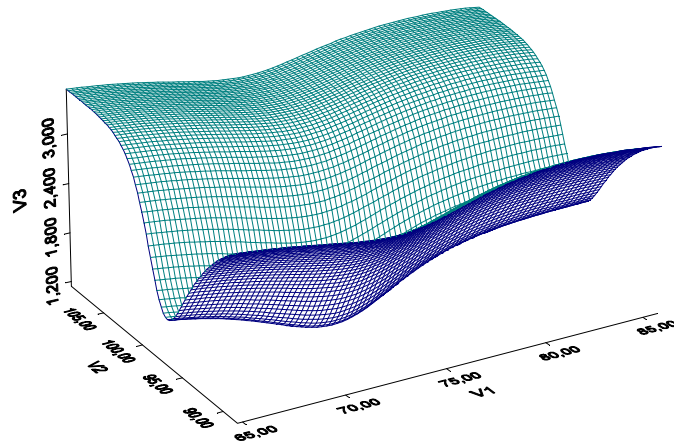

Figure 5. 3D plot of the values obtained for χ^2 in the fitting of a doublet as a function of the peak positions. This is a simplification of the complete 7-dimensional surface

The usual procedure involves the calculation of the partial derivatives of the χ^2 expression with respect to the parameters:

$$\left\{ \phi_i \equiv \frac{\partial \chi^2}{\partial p_i} = 0 \right\}_{i=1,np}$$

Where $\{p_i\}$ corresponds to the set of parameters that we are trying to determine. For each parameter, one equation (Φ_i) is obtained, thus leading to a *np x np* system of equations (*np = 2N* + peak shape parameters). Even for the simplest model shape that we can imagine - a gaussian peak- that gives rise to a set of non linear equations which are difficult to solve, specially when a large number of peaks has to be considered in the fitting. The numerical solution of such systems is carried out by iterative methods. Hence, a first approximation must be always provided for the values of the parameters before starting the process. If the initial values are not close enough to the optimal ones, convergence problems arise which will eventually produce the fail of the algorithm. For peak positions and areas, the experienced user can always provide a reasonable estimation. Yet, some other parameters have not a clear physical meaning that could be used to have "a priori" information on its values and a trial and error process is often required.

A number of different methods exist to solve systems of non linear equations equations but only a few can be used to fit complex alpha spectra. They can be divided into two big groups depending on whether they calculate the second derivatives matrix or not. The first group of methods are called Direct Search Methods, and are of special interest when the analytical calculation of the partial derivatives is difficult or not suitable. From these methods the most known is the one from Nelder and Mead, also known as Simplex. A simplex is a poly-

hedron with *np+1* vertices. A set of initial values is assigned to the vertices to form the initial simplex and some rules are given to derive new vertices by evaluating the function that is being optimized. A more efficient method was proposed by Powell. It is a gradient method in which an extensive use is made of line search procedures whose directions are changed by an efficient algorithm. Methods that do not use the information provided by the derivatives are usually less efficient in terms of convergence, but are very useful to provide a set of values to feed a more efficient algorithm. For a comprehensive discussion of these and other minimization methods, the book from Wolfe [1978] should be consulted.

While the direct search methods provide a simple procedure to obtain the peak areas and positions, they are computationally less efficient, and what is even most important, they can not be used to calculate the uncertainties in the parameters. These require the information of the covariance matrix, which can only be obtained from the partial derivatives matrix.

If the second derivatives of the χ^2 function to be minimized are available, some methods are available that exhibit a faster convergence provided that the initial values are adequate. Among them, the Newton-Raphson method is one of the most widely used. In the original Newton-Raphson algorithm, a set $\{Z_i\}$ of parameters is taken as a first approximation to the solution and the following sequence is implemented until convergence is reached:

$$\{Z\}^{k+1} = \{Z\}^P - H^{-1} (\{Z^k\}) \cdot \{Z\}^k$$

Here, *H* is the Hessian defined as:

$$H_{ij} = \frac{\partial \phi_i}{\partial Z_j}$$

Since the derivatives matrix is calculated as an integral part of the procedure, the method also allows a complete evaluation of uncertainties. A number of algorithms and methods are based on the Newton-Raphson procedure, with some modifications to allow a faster and stable convergence. For non-linear least squares, the Levenberg-Marquardt algorithm is the most popular, often combined with direct search methods to provide an initial set of values close to the final values. A comparison of fitting procedures has shown that this is probably one of the best approaches in the fitting of complex alpha spectra [García-Toraño 1996].

The method to derive the uncertainties of the parameters obtained in the minimization process is well established. The partial derivatives matrix contains all the information needed to obtain the covariance matrix. For linear fittings the method is straightforward; for non-linear systems, a Taylor expansion of the function also allows to obtain a good approximation to the covariance matrix, given by:

$$[L_{ij}] = \sum_{x=1}^{n} \left(\frac{1}{Y_x} \frac{\partial S_x}{\partial p_i} \frac{\partial S_x}{\partial p_j} - \frac{Y_x - S_x}{Y_x} \frac{\partial^2 S_x}{\partial p_i \partial p_j} \right) \approx$$

$$\approx \sum_{x=1}^{n} \frac{1}{Y_x} \frac{\partial S_x}{\partial p_i} \frac{\partial S_x}{\partial p_j}$$

Here, all partial derivatives are taken with respect to the parameters. The elements of this matrix are the components of the inverse of the Hessian matrix *H*; the diagonal elements contain the variances assigned to the parameters, and the covariances between parameters are

found in the corresponding row-column elements. More detailed information about uncertainty estimation is given by Isozumi [1985] and Sibbens [1998].

If the magnitude of interest is not a parameter, but can be written as a function F of the parameters, the uncertainty can be obtained with the covariance propagation law:

$$V(F) = \sum_{i=1}^{q} \sum_{j=1}^{q} (\sigma)_{ij} \frac{\partial F}{\partial p_i} \frac{\partial F}{\partial p_j}$$

The effect of the covariances can not be neglected in many cases. Let's consider one example. The multiplet formed by the three main lines of ^{239}Pu (5105.5, 5143.8 and 5156.7 keV) and the two of ^{240}Pu (5123.7 and 5168.3 keV) is a typical example of a group of lines that are strongly overlapped (see figure 6). The determination of the 239/240 activity ratio can only be obtained by a full deconvolution of the component peaks. The activity ratio is calculated with the intensities of the 5 peaks:

$$R = \frac{\sum A^{239}Pu}{\sum A^{240}Pu}$$

For the spectrum shown in the figure, the uncertainty in the result of the analysis (R=0.705) changes from ±0.016 without considering covariances to ±0.005 when the full calculation is done.
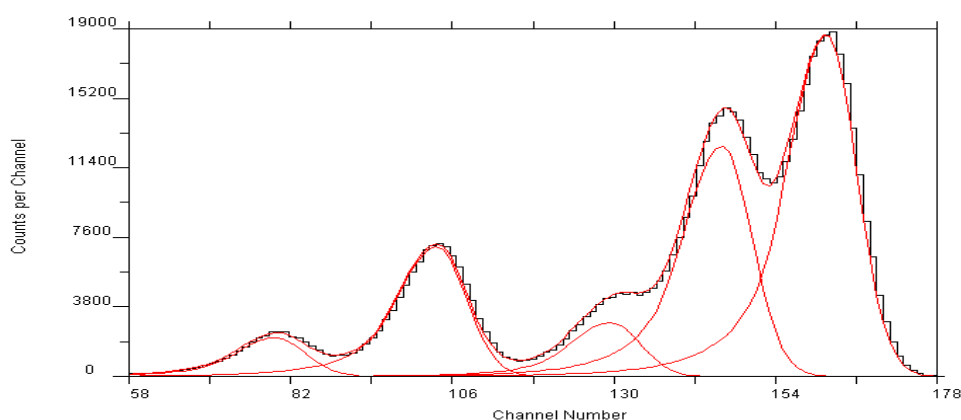
Figure 6. Fitting of the Pu-239+ Pu-240 multiplet

4. Commercial codes : the 1997 IAEA intercomparison

In 1997, several commercially available codes for the analysis of alpha spectra were tested in the frame of an intercomparison organized by the International Atomic Energy Agency. The main aspects considered for evaluation were: the ability of the programs to determine the peak areas and the statistical control and stability of the reported results. To this end, a set of refer-

ence spectra were acquired and fitted with the different programs. The results were expressed in tables and plots, and some indications were given about how to interpret the data to select the program that is best suited for a particular application. While some codes performed well for spectra deconvolution, others had a better statistical control or were easier to operate. One of the conclusions was that in the deconvolution of multiplets the uncertainties in the peak areas were underestimated, in some cases lower than the corresponding to Poisson statistics. As a general conclusion several test indicated that there is room for improvement. A complete description of the tests can be found in the references: [IAEA 1999, Blaauw et al. 1999].

5. The future

Non commercial codes also exist with a different approach, aiming at the obtention of the best analysis capabilities. They are based on complex peak models with more shape parameters and include algorithms and techniques that require some previous training. Therefore they can not be considered as practical tools for the routine analysis of the average alpha spectroscopist. Yet, the performances can be significantly better and in the future some of their capabilities will be adopted by commercial codes. The choice of a model shape according to the complexity of the problem; the "nuclide fitting" approach, in which all energies and emission probabilities for a given nuclide are kept constant; the selection of the optimal statistical weights for each particular problem and a full covariance analysis are some improvements that can be made available in the near future.

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13 New methods for Gamma Spectra Evaluation and Analysis

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Abstract

HPGe Gamma-ray spectrometry has been widely used for various applications over 30 years now. The method of analysis and peak evaluation has seen very little changes. However, the typical problems in the analysis do persist: how to determine the error estimates correctly, how to determine small peaks, what are the peaks left un-identified by the analysis software, how to make sure that the analysis result and spectra measured are of good quality.

Over the years many laboratories have made solutions of their own, many methods are available for peak determinations, calibrations and identifications. The difficulty is to minimize the need for human review and to make sure that the results presented by the analysis software is valid and reliable.

New methods for Gamma Spectra Evaluation and Analysis

Typical Analysis Scheme

Usually, the user of HPGe detector wants to know what is the origin of peaks seen in the spectrum. The second question is what are the activities of radionuclides causing the peaks. Before any analysis can start, the system has to be calibrated. At least three calibrations are needed: peak energy vs. channel, peak energy vs. efficiency and peak energy vs. FWHM. Additionally, peak energy vs. total efficiency calibration is needed to calculate the co-incidence corrections.

Assuming that the calibrations are present, the analysis is straightforward:
- The peaks are found using peak search method or by visual inspection
- Peak areas are quantified and peak intensities calculated using efficiency calibration
- Radionuclides are associated to peaks and activities calculated.

In this presentation some new methods used in this analysis scheme are elaborated and also checking the calibrations and analysis results discussed.
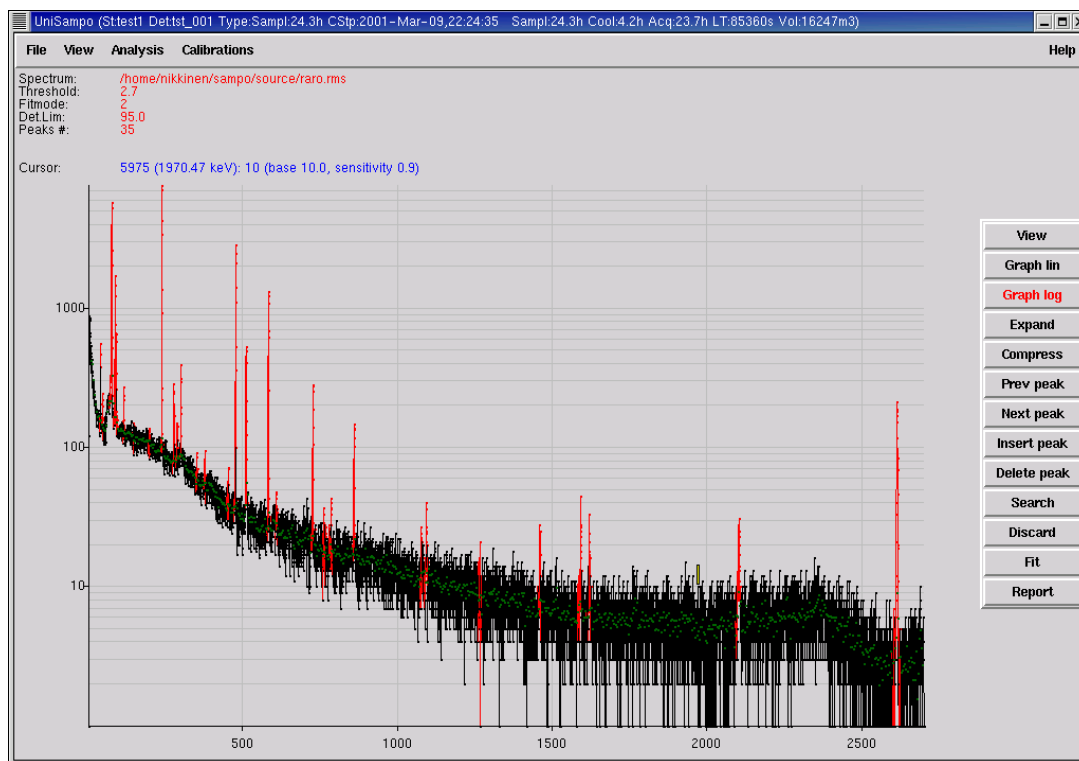
Figure 1. A typical environmental sample spectrum collected with HPGe detector. This is typical air filter spectrum, the next task is to find peaks, determine their areas, make radionuclide identification and report detected activities and detection limits for radionuclides of interest.

Peak Location

Usually, the most traditional method for peak location is based on smoothed second differences to detect the signal over the noise. In this method the signal search threshold is size of the peak in sigma's over the baseline. The method needs information on FWHM calibration

so that the peaks of correct shape are found. Some other method are using different kinds of filters or FFT in determining the peaks.

If the user is interested only on certain radionuclides, a library oriented search can be used. The list of peaks defined in library are tested and a confidence value of their existence is used to determine if the peak is present. This is a typical hypothesis testing: first we assume that the peak of interest is present in the spectrum and then we test if the peak area or shape are fitting well into the picture. A new method is the peak area based search: in a way we assume that all the channels have a peak and we are testing this hypothesis in practice for every channel. In this method the same question is asked for every channel: is there a peak on this channel. The peak candidates are tested using statistical criteria based on signal-to-noise ratio.

The peaks can be added also by hand, sometimes the experienced user can determine the essential peaks by eyes. The problem here is that small peaks over the high baseline are sometimes difficult to see in the spectrum. Sometimes the user may select spurious peak, because it is fitting the picture locally perfectly but in practice it is much below detection limit.

Peak Area Determination

After the peaks are found, the areas are determined. In practice this means the definition how many counts are present in the peaks over the continuum. Typically the peak area determination can be split into four different kinds of methods

- Summing over the channels and subtracting the baseline. This method can be used in simple cases but in case the spectrum has overlapping peaks this method can cause significant errors.
- Fitting a analytical function to the spectral data. The function shape is based on peak shape (FWHM etc.) calibration.
- Fitting a freely defined gaussian shape to the found peaks.
- Accurate determination of baseline and assuming the peaks to be the residual of this signal. In this case cubic splines are often used to determine the baseline.

Also analytical peak functions are different in different kind of solutions. Gaussian, tailed gaussian and lorenzian peak functions are generally used. Similary the baseline below the peak can be made of line, parabolic, or higher order polynomial, spline, or even simple average over the region of interest when dropping out the peaks. In some cases the peak is causing a large step below the peak, in these kinds of cases a step function (like erf, error function) is sometimes added to the baseline.

The peaks are in practice of different shape. The true gamma peaks have usually square-root like behaviour for the peak FWHM over the energy range. Some peaks usually do not fit into this pattern:
- X-ray peaks
- Annihilation peak (511 keV)
- Escape peaks
- Summing peaks
- Backscatter peak (In practice so wide in HPGe spectra that there are no problems)

Usually these peaks do not need to be determined accurately since they are not the primary target of our analysis, but the accurate information of peak areas of these peaks is useful

sometimes. Also, when a gamma peak of interest is partly shadowed by these peaks, the accurate definition of these peaks are needed.

The problems in the peak area determination are many times in the definition of baseline, where are the "control points" defining the baseline. In most cases the determination of baseline can be done automatically but in some cases there the baseline is harmed by other (non-found) peaks, Compton edge or other physical or non-physical phenomenum, all the known methods will fail. In these cases the user intervention is needed. It is important that the software is prompting the user on the issues that need help by user.
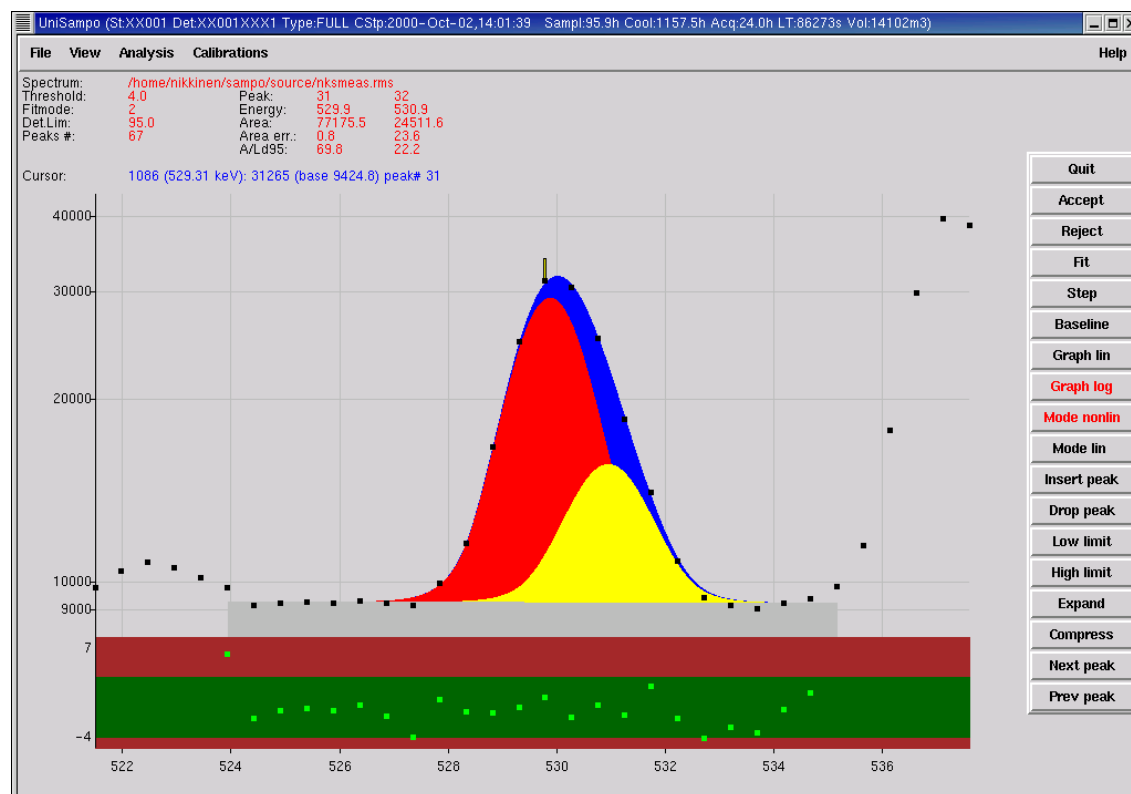
Figure 2. A difficult peak area definition, overlapping peaks has to be determined using true fitting procedure. This picture is the taken from ^{147}Nd and ^{133}I duplet.

Sometimes the peaks are so badly overlapping that the peak search routine cannot determine the small peak below the larger one. In these kinds of cases the residual between the fitted function and data points may be the way to determine the missing peak. Many software are prompting the user with a residual plot which is showing the user the size of the possibly missing peaks in sigma's.

Usual problem in peak determination is to make the decision when the peak is OK and when it is not. Specially, the small peaks over the high baseline are causing this kind of problems. One very useful method is to calculate peak based detection limit and compare it to the peak area. This method can be set very automatic and this way the peak search threshold can be lowered if the discarding procedure will drop out most of non-interesting peaks.

Figure 3. A peak sigma vs. significance (Area/Detection limit) plot for typical spectrum. The largest differences can be found from small peaks because a peak found by p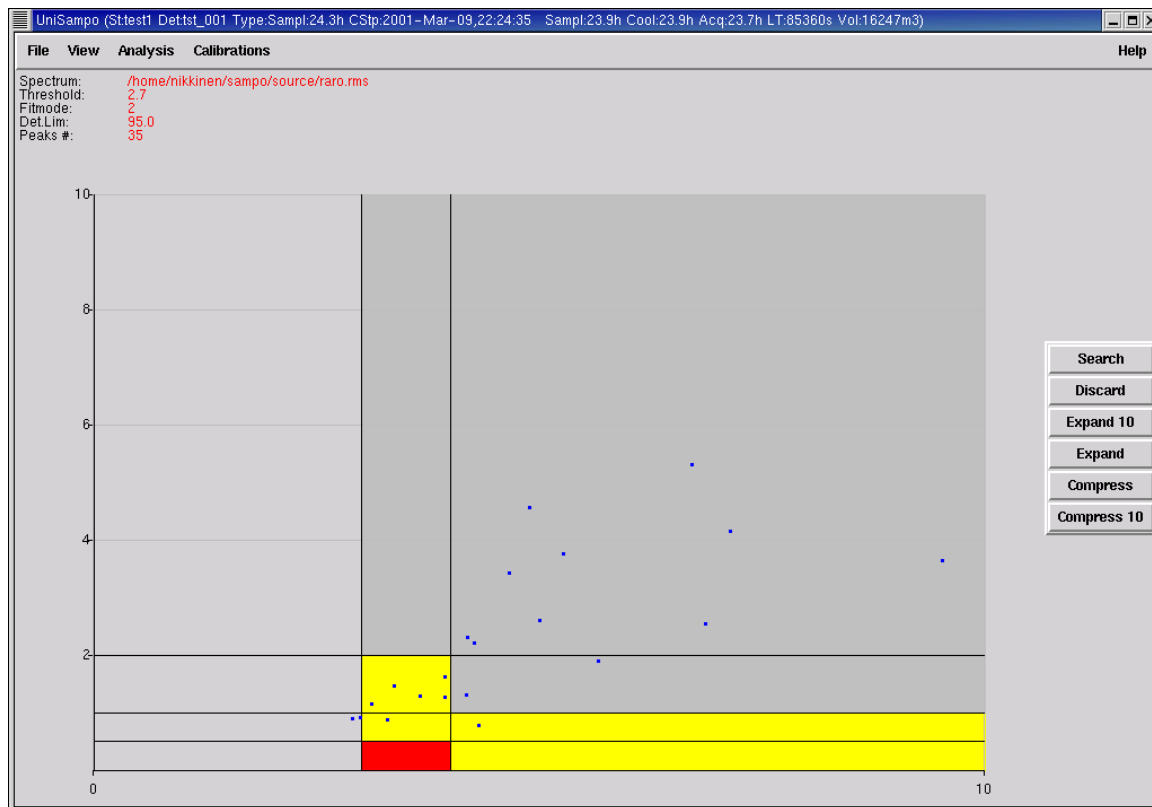eak search can be larger in practice due to intersecting peaks. After the peak area determination the true peaks are more easily distinguished from spurious ones.

Radionuclide Identification

List of peaks and their intensities are the main information for Radionuclide identification and activity calculations. The identification process can be simple if the radionuclides within the sample are very few and do not set up interferences for each other. There are, again, many methods that can be used for Radionuclide identification:

- Traditional, simple method is to select the largest, non-disturbed peak from each radionuclide of interest and calculate the activities based on main peak only. The problem of this method is that it is difficult to resolve the situation if the spectrum has overlapping peaks of different radionuclides.
- Simple much used balanced computational method, is taking the candidate radionuclides from the gamma-line library, associates the radionuclides with the found peaks, check how many lines are found within energy tolerance and how well the peaks are explained. The activity estimates are calculated using least-squares method to solve overlapping peaks.
- The most efficient way of doing the radionuclide identification is to let the expert system to decide the most optimum solution based on sample information (Shaman). This method is based on heuristical rules and it is mimicing the expert user in identification process.

```
44377 - Spectrum Data

[Close]  [To file]  [To printer]  [Help]

Spectrum file          : 44377.ids
Spectrum title         : St:tst2 Det:det1 Type:Sampl:744.0h CStp:1999-Mar-16,03:40:18   Sampl:24.3h Cool
Background spectrum     : NONE
Nuclide library        : /usr/local/gamma/shaman/lib/bnldat.glb
Start of sampling       : Mon Mar 15 03:19:39 1999
End of sampling         : Tue Mar 16 03:40:18 1999
Start of counting       : Tue Mar 16 07:52:47 1999
End of counting         : Wed Mar 17 03:22:47 1999
Reference date          : Wed Mar 17 03:22:47 1999
Sampling time           : 1.014 d
Decay time              : 4.208 h
Live counting time      : 19.48 h
Sample size (m^3)       : 12760
Energy ranges (keV)     : [0,2000.88]
User energy ranges (keV): [44,10000]
```

Peak Energy +- sigma (keV)		Emiss. rate +- sigma (gps)		Signific.	Expl. (%)	Status	Associated nuclides
3	75.0256 +- 0.422127	27.6502	+- 0.0858617	166.428	100.007	X	81Tl208 82Pb212 92U239
4	77.3186 +- 0.422806	41.4964	+- 0.098574	277.523	112.354	X	82Pb212 83Bi212
5	84.9823 +- 0.42514	0.85661	+- 0.0262657	7.17818	164.246	X	81Tl208 83Bi212
6	87.3996 +- 0.42588	13.9546	+- 0.0548197	112.953	122.153	X	81Tl208 82Pb212
7	90.0689 +- 0.426697	4.13048	+- 0.0343757	36.908	99.6372	X	82Pb212 83Bi212
8	115.346 +- 0.434792	1.37867	+- 0.023634	14.7114	92.0067		82Pb212
9	140.654 +- 0.443222	0.146525	+- 0.0188644	1.45289	100		43Tc99M
10	176.696 +- 0.455612	0.10043	+- 0.0181385	1.013	110.601	9	82Pb212
11	211.496 +- 0.467957	0.138856	+- 0.0208499	1.27644	91.4651		81Tl208
12	233.519 +- 0.475876	0.215415	+- 0.0267645	1.84528	112.499		81Tl208
13	238.623 +- 0.477722	124.041	+- 0.163142	1121.03	92.7144		82Pb212
14	252.526 +- 0.482819	0.595268	+- 0.0214988	6.44815	82.706		81Tl208
15	277.317 +- 0.491882	5.37707	+- 0.0405643	54.7874	99.988		81Tl208
16	288.068 +- 0.495819	1.07166	+- 0.0246208	10.8097	101.58		83Bi212
17	295.176 +- 0.498444	0.106616	+- 0.0219493	1.03802	60.6069	9	82Pb214
18	300.073 +- 0.500305	8.15318	+- 0.0502946	79.5961	88.13		82Pb212
19	327.948 +- 0.510651	0.414216	+- 0.0224057	3.86408	97.5681		83Bi212
20	351.796 +- 0.519623	0.117624	+- 0.0204993	1.06561	114.892		82Pb214
21	374.617 +- 0.528229	0.172071	+- 0.0221427	1.45962	100	K	
22	376.96 +- 0.529053	0.285799	+- 0.0231026	2.39977	100	K	
23	415.265 +- 0.543579	0.191457	+- 0.0218478	1.72066	274.249		82Pb212
24	452.714 +- 0.557861	1.0928	+- 0.0282873	10.0402	107.3		83Bi212
25	473.11 +- 0.565674	0.187974	+- 0.0207115	1.77166	85.9594		83Bi212
26	477.436 +- 0.567291	8.10095	+- 0.0591185	76.1067	100		4Be7
27	510.523 +- 0.580048	20.5105	+- 0.092327	132.023	100	A	*ANNI* 81Tl208
28	583.003 +- 0.607971	79.9406	+- 0.187913	569.588	99.7516		81Tl208
29	609.378 +- 0.618225	0.143517	+- 0.0195801	1.42314	100		83Bi214
30	657.764 +- 0.636963	0.209626	+- 0.0213935	1.97626	100	K	
31	722.103 +- 0.662048	0.224251	+- 0.0210044	2.21642	82.7793		81Tl208
32	727.113 +- 0.66394	20.1266	+- 0.10498	176.631	100.477		83Bi212
33	748.742 +- 0.672424	0.0713056	+- 0.0187049	0.740269	40.3911	G	81Tl208 92U239

Figure 4. Picture of expert system Shaman on process. Shaman is actually a combination on most advanced methods, a library browser and identification process control. The method of Shaman allows the full gamma line library to be used (ENSFD, 80000 lines, 3000 radionuclides), and it is using the information of radionuclide decay chains in the identification process. It also uses, for example, co-incidence correction, self-absorbtion correction, X-gamma summing effects, full half-life of the whole decay chain, estimation of sum- and escape peaks. The interface is actually hyperlinked between library data, identification results and spectrum peak results.

can2 - Graphical View

●Identified peak ●Not identified peak ○Explanation ○MDE

<<--	-->>
<-->	>--<
Xpnd Y	Cmpr Y
Reset View	
View Full	View Nucl
Peak Share	Peak Nucl
Prev Peak	Next Peak
Prev Nucl	Next Nucl
Prev Line	Next Line
Nrmlz Peaks	Nrmlz Off
Discr Up	Discr Down
Discr Off	
Help	Close

CURRENT PEAK (25/34)   Identified (status:)
Peak energy (keV):   968.7229   +-   0.8882
Peak emission rate (gps):   1496   +-   219.8369
Peak explanation (%):   96.08
Minimum Detectable Emiss. rate: 797.3

CURRENT NUCLIDE (1/1)   89 Ac 228   Background
Activity (Bq):   8578   +-   638.4
Half-life (h):   6.15   +-   0.3252 %
Genesis modes: (NAT 90Th232)

CURRENT NUCLIDE LINE (135/255) Status: F
Library energy (keV):   968.9711   +-   0.001032 %
Emission probability (%):   16.2   +-   2.469 %
Share (%):   96.08
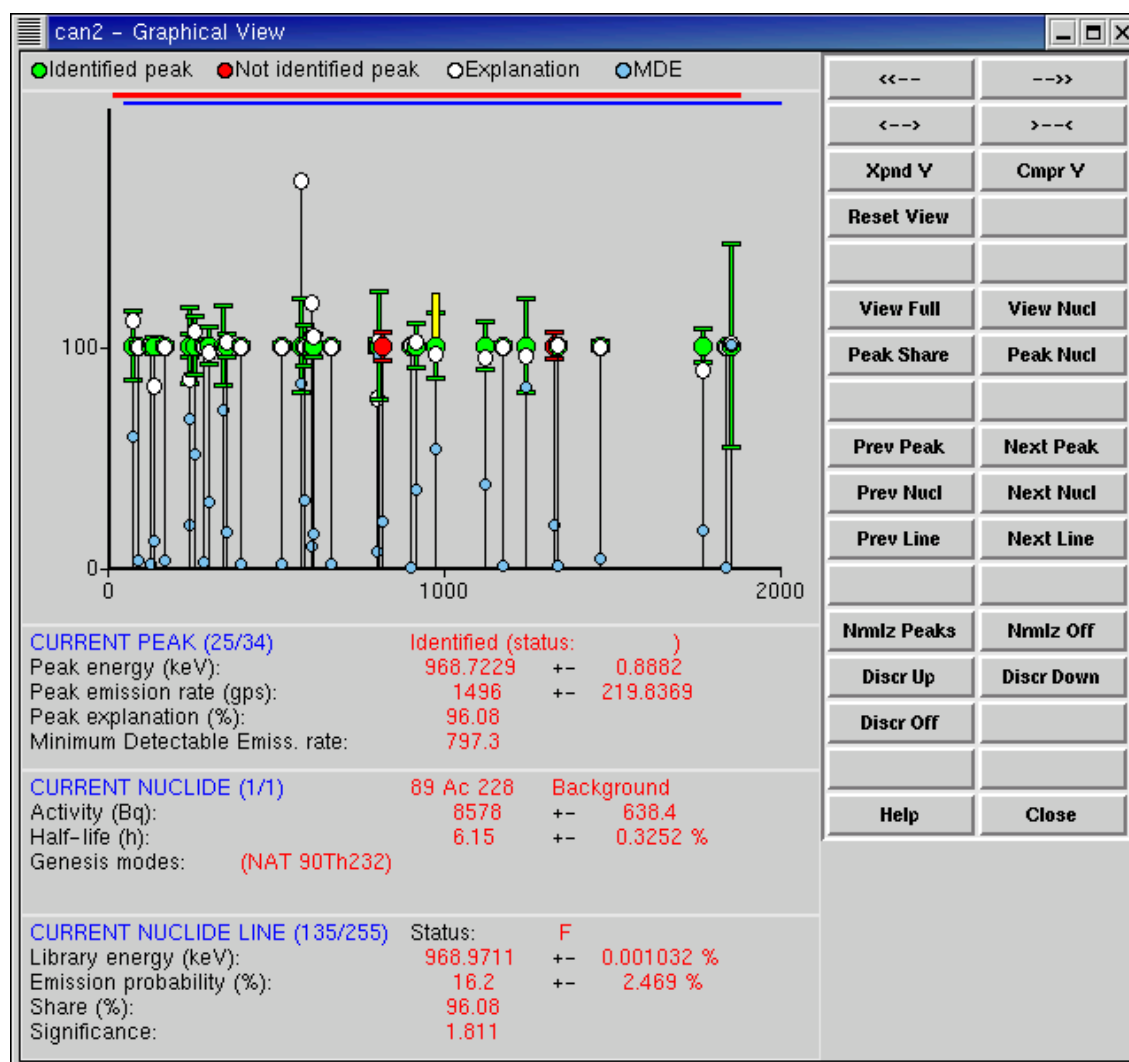Significance: 1.811

Figure 5. The quality checking using all the peaks. This graph is taken from Shaman, in this figure each peak area is 100%, the second point is the peak explanation percentage reported by Shaman and the lowest point in each line represent the peak based detection limit. This is a quick way to look that all the peaks are explained fine and that the peaks search threshold has not been too low and thus causing too many insignificant peaks to be used for identification process.

The verification of correctness of identification process is not necessarily easy task. Many times number of unknown peaks are causing uncertainties if the library data is not sufficient enough. The co-incidence correction factors need to be added if they are not calculated before, spuriously associated nuclides need to be discarded and small peaks checked if the peak there the radionuclide was associated is actually totally spurious. As an example following rules can be used for all the identification process estimations:

- Check that the peaks are explained close to 100% by all the radionuclides.
- Check that there are no negative activities in the radionuclides explaining the peaks.
- If there are too many false candidates, try to limit the energy tolerance for identification association process.
- Check that the most significant peaks of the radionuclides are above detection limits.

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- Check the calculated activity using the most significant peak, if the most significant peak is not visible or reporting completely different activity, check possible interferences.
- Check the activity error estimate, if the error estimate is large, be cautious of the result.

Detection limits

The most used method is the one referred by L.A. Currie ("Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry", 40 (3), 586-593 (1968), 95% probability level). As a rough rule the detection limit for a peak area at the 95% probability level (Currie) can be calculated as follows:

$$L_D = k^2 + 2L_C = 2.71 + 4.65\sqrt{B}.$$

Where the B is the number of counts at the baseline where the peak should be. There are number of definitions how to calculate the B itself and therefore the laboratories should also know themselves how wide region has been selected (preferably in FWHM's) for this calculation. Optimum value for this is +- 0.71 FWHM assuming that we are interested on peak width of +-2 sigma.

If somebody is interested in nuclear reactor or military releases, following isotopes are of high interest for calculating the detection limits:

Zr-95, Nb-95, Zr-97, Mo-99, Tc-99m, Ru-103, I-131, I-132, I-133, I-134, I-135, Te-132, Cs-134, Cs-137, Ba-140, La-140, Ce-141, Ce-143, Ce-144, Nd-147

Calibrations

Peak Energy calibration

Peak energy calibration is used to determine channel-energy relationship. Usually the relationship is close to linear line, so linear that it is very difficult to see if the calibration curve has some problems. Therefore, it is beneficial to see the non-linearity of the calibration (difference from linear line) and the distance from calibration point to calibration curve.

Other sources of errors for energy calibration are:
- Selection of false peaks for calibration
- Uncertainties in nuclear data
- Extrapolation of the calibration curve much beyond the calibration point range
- Too high or too low degree of the fitted calibration curve to the data points.
- Difference in assuming if the first channel in the calibration is 0 or 1.

There are three methods for energy calibration generation
- Traditional method: select at least two peaks, check their channels and add the energy-channel pair manually

- Assume that the calibration curve is somewhat ok, then search peaks and within certain accuracy that the found peaks are of known energy, make correction assuming that these peaks are corresponding.
- Check which selection of peaks will explain best the selection of known energies within the calibration source. This can be fully automatic and this procedure can be used also for the real sample spectrum assuming that the typical peak energies are known.
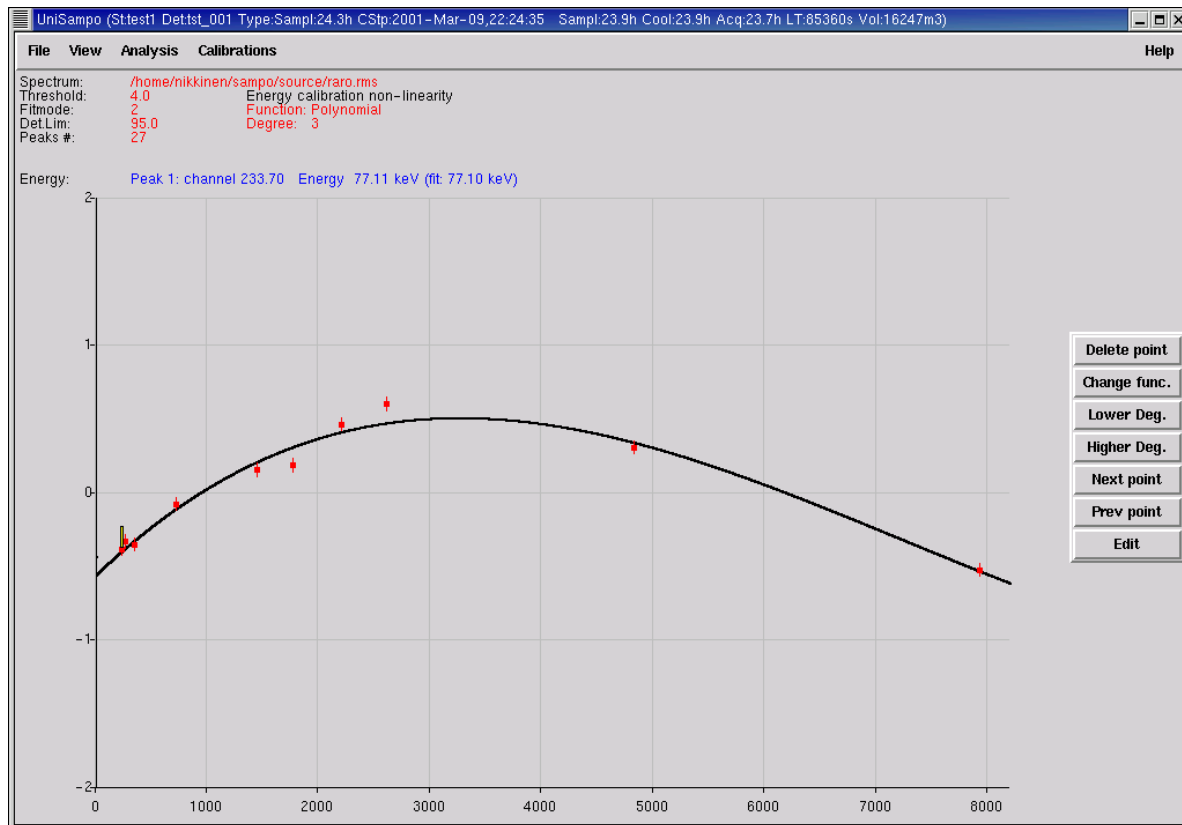

Figure 6. This is typical non-linearity plot of energy calibration. If we were using a straight line for this calibration, there would be systematic errors of more than 0.5 keV.

Peak Shape Calibration

Peak shape calibration usually means the Full-Width-Half-Maximum (FWHM). There are still number of other issues that can be calibrated over the energy for peak shape:
- FWHM or gaussian width of the peak.
- FWTM (tenth maximum).
- FWTM/FWHM, this ratio is 1.85 if the peak is purely gaussian
- Distance from peak center to the channel there the lower energy tailing will start.
- Distance from peak center to the channel there the higher energy tailing will start.
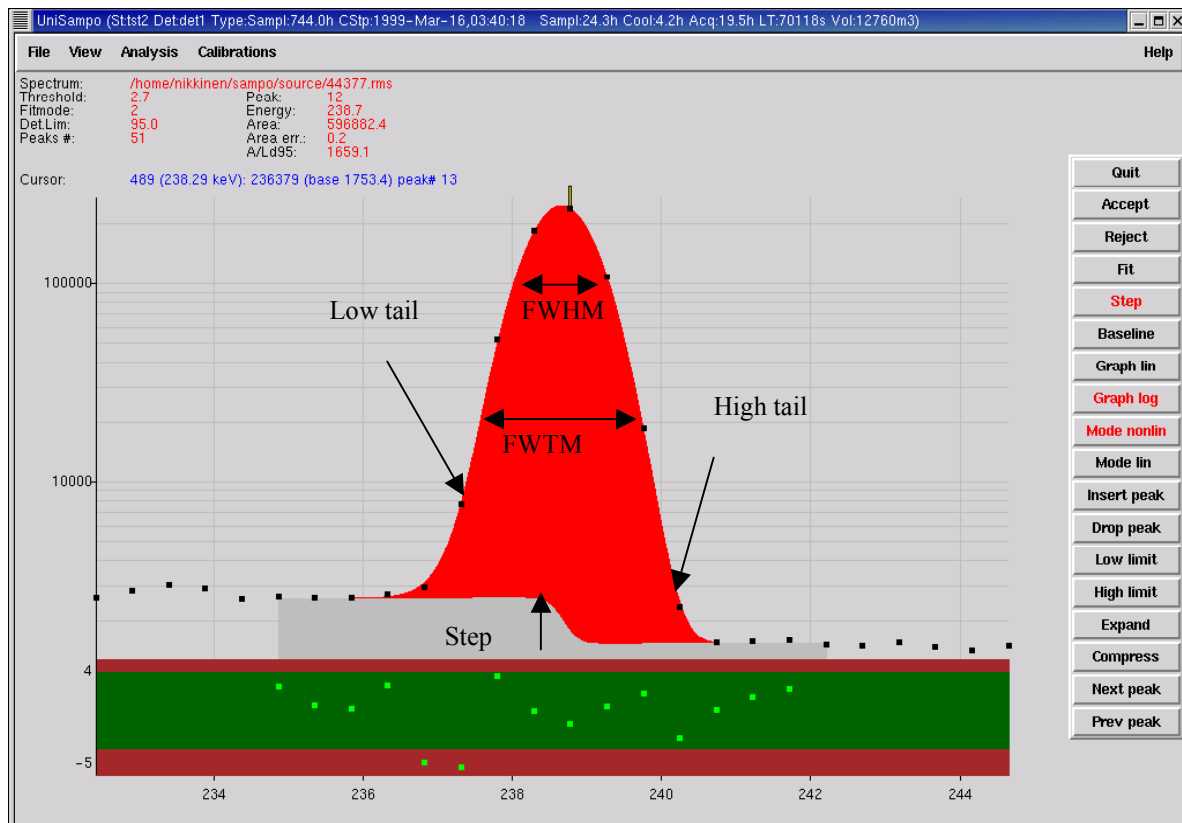- Peak height divided with height of the step below the peak

Figure 7. A typical gamma peak, in this figure the different calibrated issues are shown. The most essential parameter is FWHM, it is generally used in peak search procedure, peak area determination and detection limit calculations. Note that this peak is on log scale and therefore FWHM and FWTM levels are visually seen to be quite high position.

There are at least three methods to determine peak shape calibration:
- Traditional manual method: take each big peak and determine the half height of the peak and determine what is the peak width at that level.
- Same method as previous but allow the software to determine the peak shape. This is generally used in many commercial software packages.
- Use free width fitting with free parameters to the clear single peak. The parameters are defined by fitting procedure itself. Be careful of number of parameters fitted simultaneously, if the peaks are very narrow and there are many free parameters, it can occur that the fitting procedure start to compensate the peak shape functions with the baseline function.

Usual problems in peak shape calibrations are that:
- The peak shape is determined from too small peak,
- The peak selected for the calibration is actually a superposition of multiple peaks
- The peak selected for the calibration is not a gamma peak (X-ray, annihilation, escape)
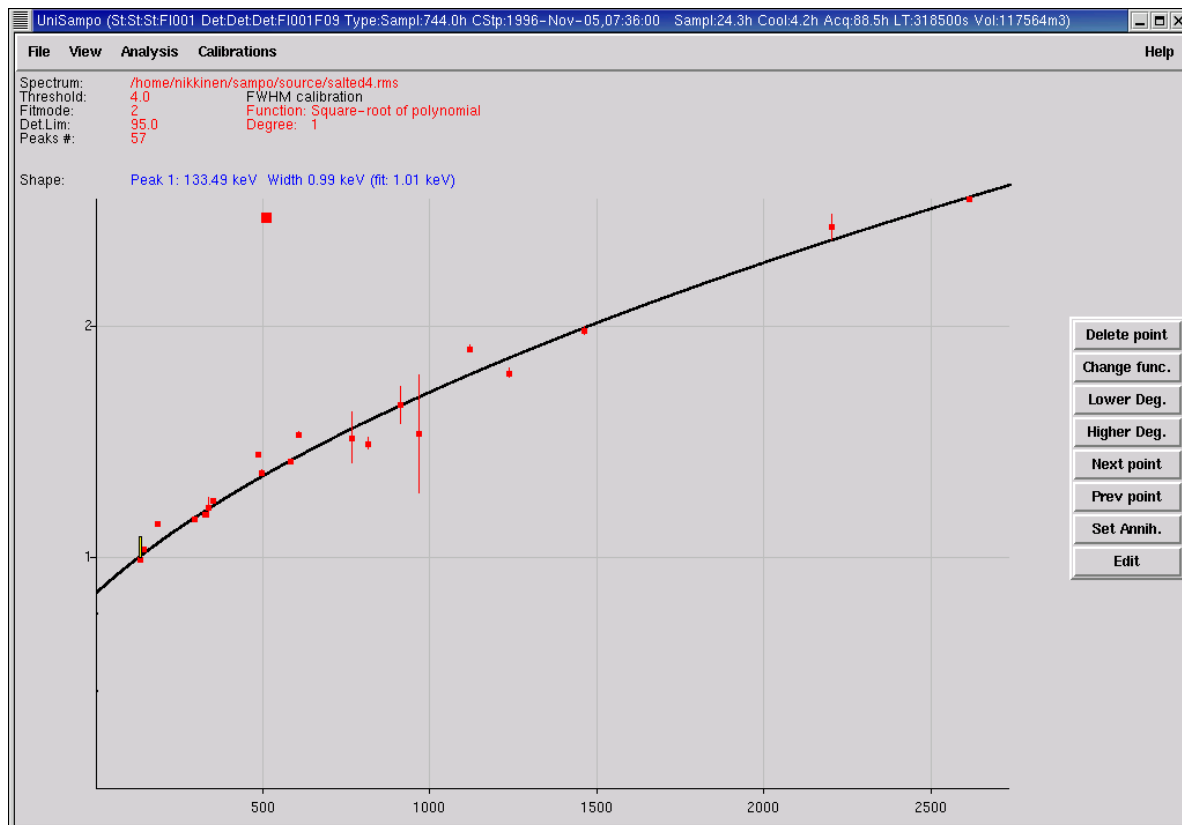
Figure 8. This is typical picture of FWHM calibration. The calibration function selected here is Squareroot of polynomial. This function is stable for wide range of energy and reasonably low degree of functions (1-3) can be used to determine the FWHM calibration. Annihilation peak (511 keV) is treated different way in this spectrum, this is important if the peaks close to annihilation peak need to be analyzed (like Kr-85, Sr-85 or Tl-208)

Checking the correctness of FWHM or other peak shape calibration is easy. Review the calibration, drop out the peaks which are not on the curve and check if annihilation peak needs different kind of calibration. X-ray peaks and escape peaks could be determined with different method (free width fitting or summing) if the peak shapes of these peaks are too far from calibration values.
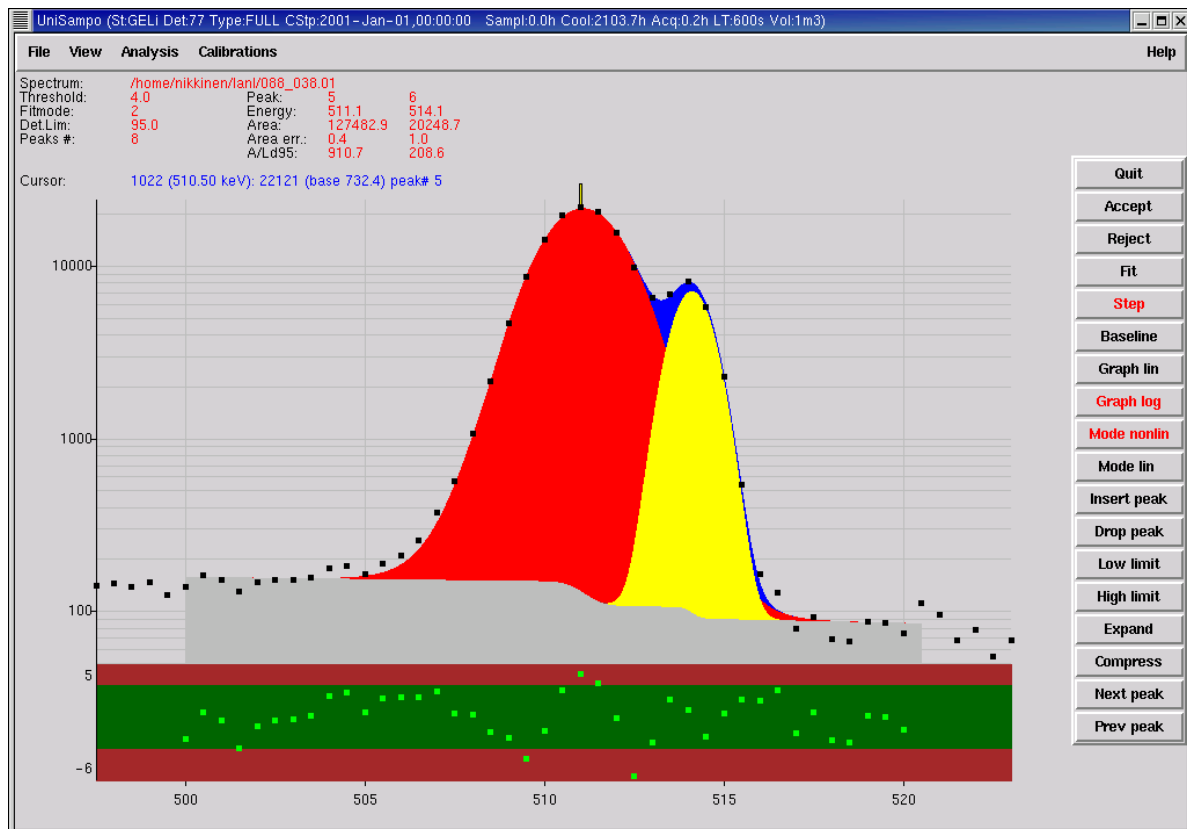
Figure 9. Annihilation peak analysis when having intersecting gamma peaks at the same energy region. This analysis is possible accurately only if annihilation line has separate peak shape calibration.

Peak Efficiency Calibration

Peak efficiency calibration is used to determine how large fraction of gammas emitted by the sample are detected completely within the detector. This means that the gamma coming to the detector may not interact with other material before emitting all the energy to the detector material. Usual problem in efficiency calibration are:

- True co-incidence summing
- Difficult geometries
- Self absorption
- Uncertainties of calibration sources
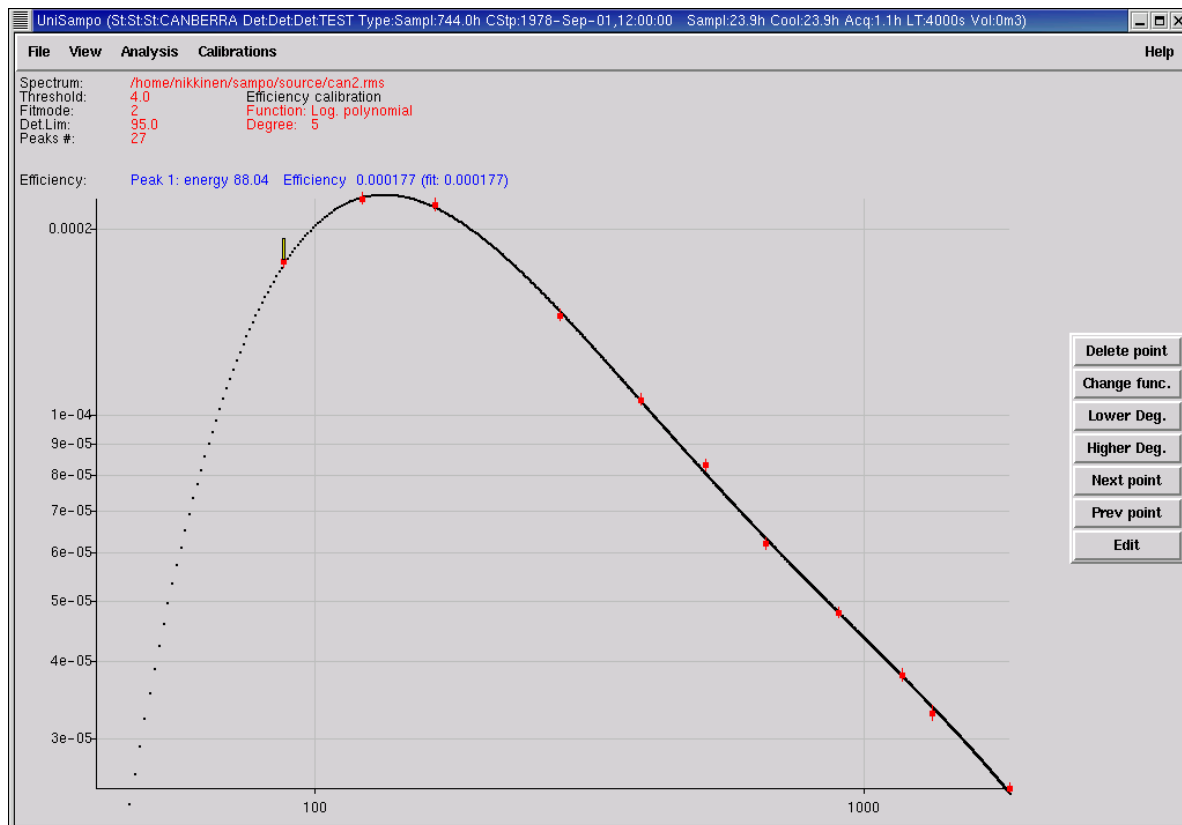- Sample activity vs. calibration source activity

Figure 10: Typical efficiency calibration of a calibration sample. The curve is close to perfect at high energy side of the curve.

There are three methods for efficiency calibration generation:
- Empirical method; a sample is measures in the same geometry as the calibration source. Then the found peak areas are calculated versus the known sample activities and as a final product the efficiency calibration is calculated. The problems are multi-gamma emitters and changes of sample matrix, which can result to significant error.
- Semi-empirical method; sample geometry changes are allowed, this range from density correction to point-source to volumetric sample corrections. To perform this type of calibration you will need both a simple calibration source and geometry information for sample and detector.
- True computational method. Usually this calculation is performed using Monte-Carlo method. There are many kinds of Monte-Carlo codes available for this calculation. The problem is that for fully computational approach you will need accurate information on both sample and detector geometry. Usually the problem is the dead layer of detector (few nm to several hundreds of µm of germanium) which will cause large uncertainties in low energy side of the calibration.
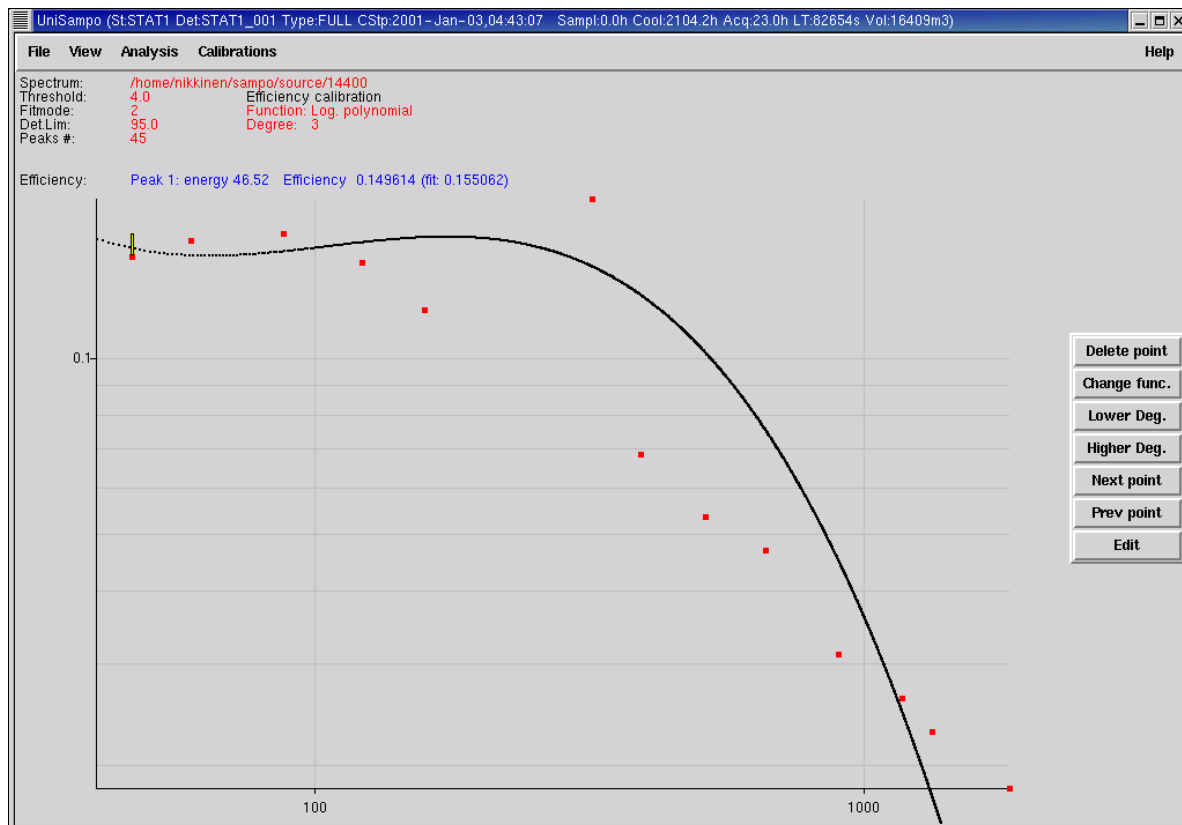
Figure 11: This efficiency calibration curve was developed without user intervention. The false calibration point was added accidentally to the calibration curve, because the calibration source did contain small amount of extra substance (^{51}Cr) as impurity and it was unintentionally associated to the calibration curve.

Verification of correctness of efficiency calibration is difficult since the efficiency calibration cannot be generated from sample spectrum as FWHM and energy calibrations. There are, however some possibilities for this determination:
-   Visual checking of the calibration curve. The high-energy side of the calibration (200-2000 keV) should usually be close to direct line on log-log –scale.
-   Assuming the co-incidence correction is not a big problem in the sample/detector geometry, the user can take one multi-gamma radionuclide to detect if all the peaks from one source are explained 100%.
-   Make a discrepancy plot on efficiency calibration, large difference from fitted curve to calibration data point pairs usually means that the accuracy of the calibration is not good.
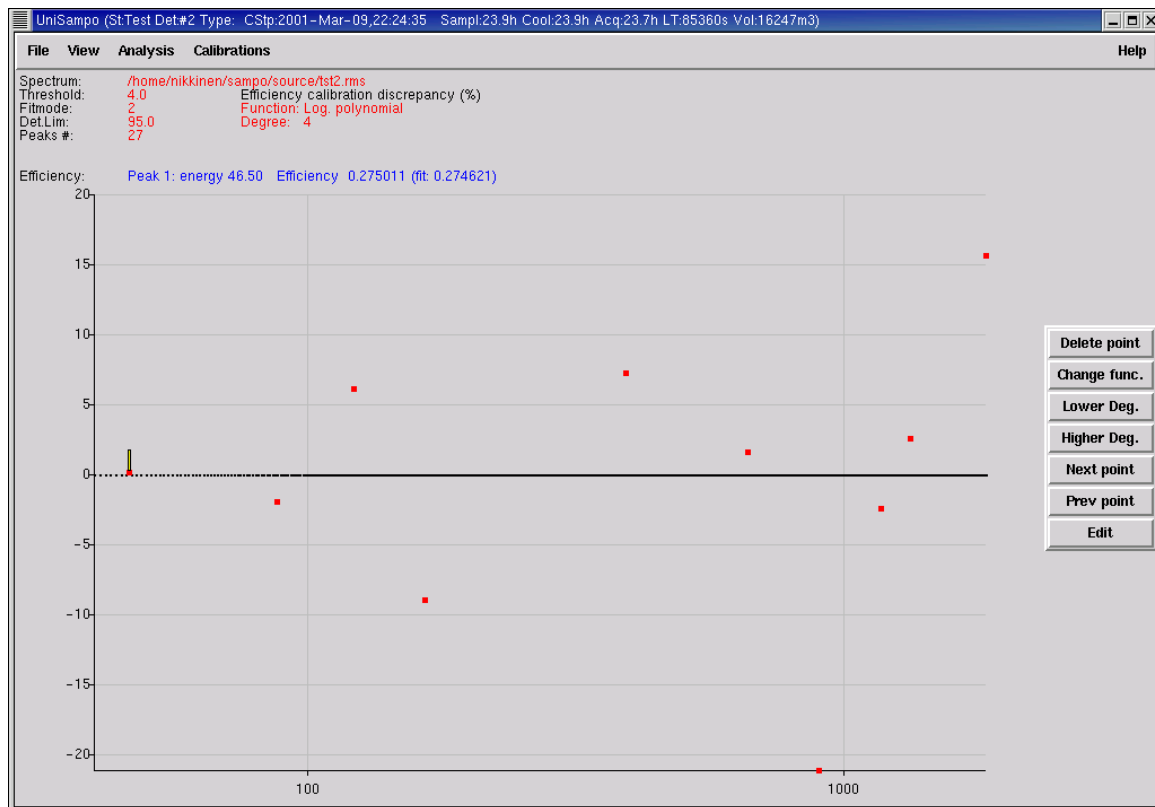
Figure 12. In this picture a calibration curve is suffering badly from co-incidence correction. Discrepancy at the higher energy side will show that large errors are assumed on calibration accuracy over 800 keV range.

Total Efficiency Calibration

Total efficiency calibration is describing how many gammas the detector is able to detect fully or partially (also within Compton continuum). There are three methods on determination of total efficiency calibration:

- Traditional manual method; find single-line gamma sources, prepare a true geometry calibration for each Radionuclide and check how many gammas are detected in the whole spectrum
- Computational method, assume certain detector geometry and calculate the total efficiency calibration from peak efficiency calibration. This method can be large source of error if the detector shape is substantially different from assumption.
- True computational method, calculate the total efficiency calibration using Monte-Carlo method.

As a rule the total efficiency calibration should be of same shape as peak efficiency calibration, it is approaching the peak efficiency calibration at energies but it should never be lower than peak efficiency calibration. For practical reasons it is wise to cut the integration range of total efficiency calibration using low lever discriminator. Otherwise, the noise in the measurement system will cause high concentration of counts to distort the calibration on lowest energy side.

Error estimates

It is relatively easy to detect the peaks and quantify the peaks and calculate the activities in simple cases. This is not enough for laboratory practices, also the error estimates for the Radionuclide activities has to be correct. We are usually talking about error budget, it is a combination of error estimates together, virtually all the significant errors has to be considered in the estimate. The sources of errors in gamma spectrum analysis are typically:
- Peak area error
- Peak location error
- Effciency calibration error
    - o Calibration source error or monte-carlo calculation error
    - o Calibration peak location and area errors
- Energy calibration error
    - o Calibration peak location error
- Peak shape calibration error
    - o Calibration peak shape parameters error
- Nuclear data uncertainties (branching ratio and line location error)

Then there are systematic errors, many times caused by sample handling uncertainties, geometry management problems, lack of co-incidence corrections within calibrations and sample spectra, self absorbtion correction error and sometimes even random error caused by the operator running the system.

Quality checking of the HPGe system

Although many of the problems presented in this paper may raise a feeling that the gamma spectrometric measurements will contain large uncertainties non-visible for the operators of the systems, the measurement system can be secure if a well established Quality Assurance system is in place and used systematically to detect the problems.
- Estimation of results based on expert view
- Check the spurious peaks and nuclides
- Check the missed peaks and nuclides
- Check the explanation level for gamma peaks
- Review all the peaks, all the calibrations and the activities in the reports

To help the maintenance of the HPGe system, a simple daily measurement can reveal if the measurement system is itself causing some problems. This can be performed using a very simple point source measurement daily. The issues to be checked are in this kinds of measurements are:
- FWHM over the time, widening of low energy peaks usually predict higher noise of the system. Generally widening peaks might predict the total brake-down of the system soon.
- Peak tailing using typical samples over the time.
- Energy calibration behavior over the time, slow shift may occur for example due to temperature changes of crystal
- Pulse rate of a simple QA source measured short time every day. This will ensure that the system efficiency is on equal level day-to-day.

Conclusions

The determination of gamma peak analysis correctness is not necessary easy task; multiple correction factors can correlate each others in the worst case. The review tools can be divided to two fields: automatic quality checking and hand review of the spectrum and calibrations.

Nearly all the calibration procedures can be automated, also the analysis of the spectra. In case the spectrum is difficult (badly overlapping peaks, high pulse rate or bad co-incidence corrections), the user guidance may be needed. There are tools to review the quality of the calibrations, the discrepancy plots for calibrations will easily show if some point pairs are incorrect.

The analysis procedure for searching the peaks, defining the peak areas and calculating activities has not changed in principle too much from 1960's, but the computer codes will calculate more than before and it makes the management of a laboratory analysis results convenient. Not too far from today is fully calibration source free calibration procedure, some Monte-Carlo systems are already on prduction use.

The pictures shown here in this presentation are based on UniSAMPO and Shaman software packages. UniSAMPO package can be tested freely. A limited time (6 month) full version will be available by sending email message to doletum@kolumbus.fi. UniSAMPO is the new version of Sampo software, it is run under Linux and Solaris environments. Linux is a free operating environment, it requires very little resources and inexpensive PC computers can be used. Linux and Windows can live nicely together in measurement laboratory, they can share same network, disc resources, printers etc. UniSAMPO supports also direct usage of some MCA´s linked to the computer.

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Title	Seminar on Detectors and Measurements Techniques 3-4 May 2001, Lund, Sweden
Author(s)	Elis Holm (editor)
Affiliation(s)	Risø National Laboratory, DK-4000 Roskilde, Denmark
ISBN	87-7893-106-1
Date	Januar 2002
Project	NKS/BOK-1.1
No. of pages	129

Abstract   A Nordic Seminar on detectors and radionuclide measurement techniques was held in Lund, Sweden, May 3-4, 2001. The objective was to highlight recent progress and problems for techniques to study environmental radioactivity. It covered the aspect of detector sample geometry's and methods for evaluation of gamma gamma pulse height distributions. Within the field of alpha-spectrometric techniques gridded ionisation chambers, semiconductor detectors and a general description for analysis of alpha-particle-spectra were presented. Recent development in mass spectrometric techniques, AMS (Accelerator Mass Spectrometry) and ICPMS (Inductively Coupled Plasma mass Spectrometry) for long-lived radionuclides was described. Principles for analysis of beta particle emitters, especially by liquid scintillation were presented. The seminar also covered radiochemistry such advantages and disadvantages between ion exchange, solvent extraction and extraction chromatography. The use of controlled laboratory conditions for discerning the dynamics of accumulation in organisms was demonstrated. Other techniques such as neutron activation were also shown to be useful analytical tool for certain long-lived radionuclides. The results of the intercalbration exercises within the Nordic countries showed the importance of such analytical quality control.

Key words   Gamma spectrometry, alpha spectrometry, spectra evaluation, mass spectrometry, radiochemistry, laboratory experiment, neutron activation, analytical quality control