RAPID INSTRUMENTAL AND SEPARATION METHODS

FOR MONITORING RADIONUCLIDES IN FOOD

AND ENVIRONMENTAL SAMPLES

Final Report
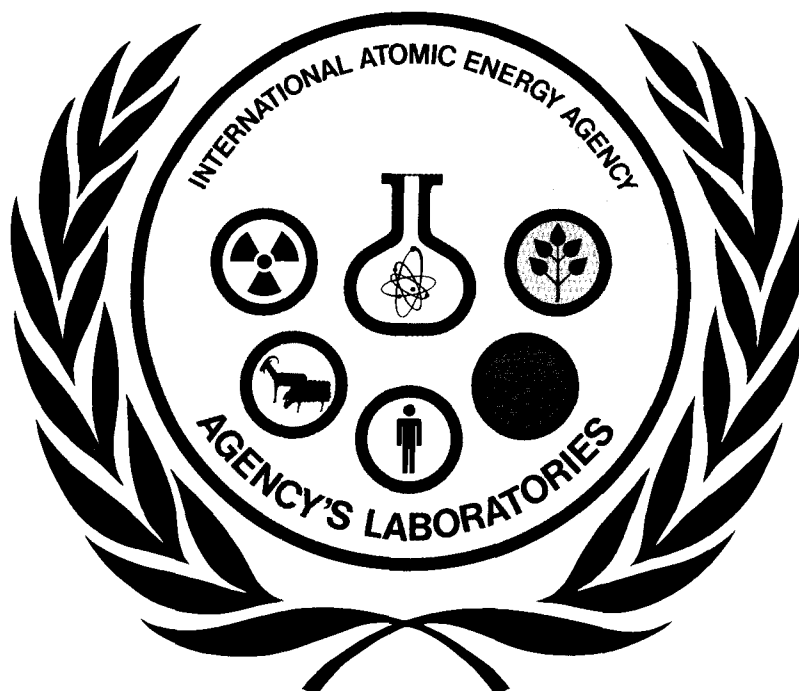on an IAEA Co-ordinated Research Programme

Vienna, Austria, 1995

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IAEA/AL/088, Vienna (1995)

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SUMMARY REPORT

1. INTRODUCTION

The Co-ordinated Research Programme (CRP) on Rapid Instrumental and Separation Methods for Monitoring Radionuclides in Food and Environmental Samples was established by the Agency following a Consultants' Meeting on the same topic, which was held 5-9 September 1988 in Vienna [1]. It was completed in 1992. At various times during its course it encompassed 15 participants from 14 countries. The scope of work and objectives of the CRP were established at the Consultants' Meeting [1]. It was agreed that the CRP should focus on the development of rapid methods for the determination of radionuclides in food and environmental samples during the intermediate and late post-accident phases. The rapid methods developed during the course of the CRP were intended to permit a timely and accurate determination of radionuclides at concentrations at least one order of magnitude below those specified for Derived Intervention Levels (DILs) for food by the WHO/FAO [2] and the IAEA [3].

Research Co-ordination meetings were held in Warsaw, Poland in September 1989 [4] and in Vienna, Austria in 1991 [5]. Reports of the meetings are available from the Agency on Request.

This document comprises copies of final reports from the participants and selected contributions presented by the participants at the meetings. The contributions were selected on the basis of being able to stand alone, without further explanation. Where there was an overlap in the information presented by a participant at both meetings, the most complete contribution was selected.

2. SUMMARY OF MAIN ACHIEVEMENTS

The main achievements of the CRP included both instrumental methods and chemical separations.

Instrumental Methods

A significant number of advances in instrumental methods were made during the course of the CRP. These advances are outlined below:

a. An efficiency calibration method for a gamma spectrometry system, consisting of a germanium detector and multichannel analyser, has been developed. This method was designed to provide very rapid quantitative results for samples of different sizes and densities in an emergency situation . A computer program and detailed information on detector type are required. A procedure was also proposed for the rapid interpolation of detector efficiency at precise energies for any sample with a density within a range of sample densities.

b. A rapid method has been developed for estimating the upper limit of ^{89}Sr and

^{90}Sr in thin deposition samples (eg. air filters and hot particles). It combined measurements of the ^{137}Cs/^{90}Sr ratio by beta spectrometry in 1987 and 1991 with a measurement of the ^{140}Ba/^{137}Cs ratio from a gamma spectrum taken in 1986 to obtain the Ba/Sr ratio in the reactor core. This ratio can be used to estimate the radiostrontium activity level in samples.

c.   A rapid method has been developed for separate determination of ^{89}Sr, ^{90}Sr and ^{90}Y by beta-spectrometry in air filters, fallout and chemically treated samples.

d.   A method has been developed for the rapid estimation of gamma-emitting radionuclides (e.g. ^{137}Cs) in near surface soil core profiles, using measurements by gamma spectrometry and exponential depth profile calculations. This procedure is a significant improvement over conventional core profile assessments, in that lengthy sampling and analysis are avoided.

e.   A method was described for the in-vivo assessment of ^{137}Cs in animals using a NaI detector. At a 95% confidence level, it was shown that the uncertainty in measuring the activity level in muscle tissue was 11% for cattle, 8% for sheep and 7% for reindeer.

f.   The applicability of using a "radwaste drum assayer" for the direct measurement of radionuclides in bulk food was assessed. This instrument can detect gamma emitters at 3.7 to 37 mBq/g levels and transuranic radionuclides at approximately 37 Bq/g. It can also detect ^{90}Sr, based on measurement of bremsstrahlung radiation from ^{90}Y, but not with the required sensitivity to meet the DIL.

g.   The applicability of using solid state detectors for the determination of ^{241}Am by gamma spectrometry was demonstrated and methods both with and without chemical separation were developed.

h.   The utility of inductively coupled plasma/mass spectrometry (ICP/MS) for the rapid, nearly complete isotopic analysis of any form of sample was described. Currently ICP/MS can detect 10^8 to 10^9 atoms of plutonium, uranium, and other radionuclides. Ongoing and future development, including efficient sample introduction techniques, single ion counting, and high resolution mass spectrometry may ultimately increase the sensitivity to 10^7 atoms, for radionuclides with a half-life of more than one year.

i.   The feasibility of designing a thin probe (2.5 cm diameter with a 1.25 cm diameter x 5 cm long NaI(Tl) detector) for monitoring ^{137}Cs in bulk food was described. Measurements with this detector are rapid and sufficiently sensitive to determine ^{137}Cs at levels in food which are below WHO limits.

j.   Simple, but specially designed spectrometric instrumentation for the rapid monitoring of gamma-emitters in food and environmental samples was described.

k.   A parallel grid ionization chamber was shown to be useful for determining α-

emitters in water, ashed grass, soil and air filters, without the need for prior chemical work-up.

One of the highlights of the second CRP meeting, was a presentation on designing a state-of-the-art mobile laboratory that can respond immediately after a nuclear accident. The primary purpose of this mobile radiological unit is to limit the radiation exposure to the general public by monitoring environmental samples and foodstuffs.

Chemical Separations

Rapid methods for radiochemical separation have now reached the state where results can be obtained within one working day. Some of the achievements related to rapid radiochemical separations are outlined below:

a.   A simple pre-concentration procedure for the rapid determination of ^{241}Am with greater sensitivity by gamma spectrometry was developed. This procedure has been applied to the analysis of Chernobyl soil samples.

b.   Several methods, utilizing either TBP or HDEHP, for the liquid extraction of ^{90}Y, have been developed to determine radiostrontium levels in a variety of sample matrices. Results for both ^{89}Sr and ^{90}Sr activity levels can be obtained during one working day. These methods have already been applied routinely to Chernobyl samples.

c.   It has been demonstrated that the application of crown ethers for radiostrontium determination is successfully competing with the more highly developed rapid liquid extraction procedures for ^{90}Y. Currently, the separation and determination of radiostrontium in soil can be carried out in about 8 hours. It is expected that radionuclide isolation using crown ethers may become a routine technique in the near future.

d.   An assembly has been constructed for the in-situ preconcentration of radionuclides from water. When the assembly contains Prussian blue impregnated ion-exchange resin, it can successfully pre-concentrate ^{137}Cs from volumes up to 10 liters at flow rates of 2 L/min. It has been demonstrated that the same assembly can be used to preconcentrate ^{234}Th and plutonium isotopes when it contains iron hydroxide impregnated resin.

e.   Several methods have been developed for streamlining the separation of transuranium elements.

3.   OTHER ACTIVITIES RELATING TO THE CRP

In October 1989 the Government of the USSR requested that the IAEA organise an assessment by international experts of "the concept which the USSR has evolved to enable the population to live safely in areas affected by radioactive contamination following the Chernobyl accident and an evaluation of the

effectiveness of the steps taken in these areas to safeguard the health of the Population". This request resulted in the International Chernobyl Project, which started in mid 1990 and was completed in 1991. One of the tasks under this project involved the corroboration of assessments of environmental contamination. This required an evaluation of the methodology used by scientists in the USSR and the validity of their data, as well as independent assessments of contamination in the environment and food in selected communities within the three most heavily affected regions in the USSR.

Although the Physics, Chemistry and Instrumentation Laboratory (PCI) of the Agency's Laboratories at Seibersdorf had the expertise to co-ordinate the project and actively participate in both sampling in the field and analytical work in the laboratory, it was clearly far beyond its limited resources to take on the entire job alone. Consequently, it was necessary to organise an international network of laboratories to do the bulk of the work on a volunteer basis. Some of the laboratories involved in this CRP formed the nucleus for this network of laboratories. They were joined by a number of Member States' laboratories which were approached by PCI to participate in the work. The assessment of environmental contamination, which required a concerted effort and a phenomenal amount of sampling and analytical work, was accomplished over a period of only about six months.

As the CRP on "Rapid Methods" was winding down, the participants realised that a new CRP would be needed to complement the work of the CRP and to maintain the connections in the network of laboratories. The scope of work of the new CRP was discussed at the second Research Co-ordination Meeting [5] and recommendations were made. The primary objectives for the new CRP were to:

1.   Maintain a network of cooperating analytical laboratories that are prepared to respond to requests for assistance.

2.   Improve and maintain the capabilities of these laboratories and provide training of individuals within Member States.

3.   Conduct research and development on applicable methodologies for response.

The new CRP on "Development and Selection of Analytical Techniques and Procedures for Measuring Accidentally Released Radionuclides in the Environment" started up in 1992.

REFERENCES

[1]   IAEA Report (IAEA/AL/019), "Report of the Consultants' Meeting on Rapid Instrumental and Separation Methods for Monitoring Radionuclides in Food and Environmental Samples", IAEA, Vienna. 1988.

[2]   FAO/WHO Supplement 1 to CODEX ALIMENTARIUS VOLUME XVII, WHO/FAO 1989.

[3]   INTERNATIONAL ATOMIC ENERGY AGENCY, "Derived Intervention Levels for Application in Controlling Radiation Doses to the Public in the Event of a Nuclear Accident or Radiological Emergency", Safety Series No. 81, p 90-91, IAEA, Vienna, 1986.

[4]   IAEA Report (IAEA/AL/043), "Report of the First Research Co-ordination Meeting on the Co-ordinated Research Programme: Rapid Instrumental and Separation Methods for Monitoring Radionuclides in Food and Environmental Samples", IAEA, Vienna, 1989.

[5]   IAEA Report (IAEA/AL/056), " "Report of the Second Research Co-ordination Meeting on the Co-ordinated Research Programme: Rapid Instrumental and Separation Methods for Monitoring Radionuclides in Food and Environmental Samples", IAEA, Vienna, 1991.

TABLE I. LIST OF PARTICIPANTS

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List of Participants cont'd.

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Coordinated Research Programme
on
"Rapid Instrumental and Separation Methods for Monitoring
Radionuclides in Food and Environmental Samples"

First Research Co-ordination Meeting

Rapid Separation and Liquid Scintillation Spectroscopic Determination of Sr-89, Sr-90.and Transuranium Elements of Interest

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Previous and ongoing work at the Atominstitute.

At the Atominstitute of the Austrian Universities investigations related to radioactivity in the environment have started around 1960 with monitoring of the site before and after operation of the reactor. Analysis schemes for fission nuclides had been worked out to determine nuclear weapons fallout. Food analysis had do be done, although on a very small scale, on Austrian export crops since 1970. In the seventies the Atominstitute participated in a Coordinated Research Programme on monitoring radioactivity in Danube river water. Radon and radon daughter products in various parts of Austria and radionuclides in construction materials were radioassayed by the Health Physics section. Since 1986 food and environmental radioactivity measurements are done for cooperating governmental and private institutions.

Equipment:

Sufficient laboratory space for radiochemical work can be provided and general radiochemical laboratory equipment is available. GeLi and HPGe detectors (40 - 100 cm^3), with adequate shielding are set up for gamma spectroscopy and can be used for food and environmental samples in the Health Physics (1), X-ray Physics (2} and Radiochemistry (2) Section. Alpha-detector and low level beta-counting systems are provided by the Health Physics Section. Multichannel analyzers are either hardware (ORTEC, CANBERRA, NUCLEAR DATA) or software MCA instrumentations. Computerized spectra evaluation and radionuclide analysis is done with programmes running on IBM AT personal computers or on the VAX data processing system. Two PACKARD liquid scintillation spectrometers are available at the Atominstitute, two LKB (QUANTULUS) LSC instruments are presently available at the closely cooperating

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Federal Food Research Institute. There is presently a shortage in manpower for radiochemical analysis work due to the low number of students and young scientists being interested in nuclear science in Austria.

Scope of Investigations within the framework of the CRP:

Investigations are focussed on fast radiochemical separation procedures to determine strontium-90, strontium-89, and alpha emitting materials from nuclear fallout in food and environmental samples. Special attention is paid to liquid scintillation spectrometry as radioassay method. It is tried to use digestion methods based on microwave heating under increased pressure in a teflon autoclave. There is no intention to develop purely instrumental methods (e.g. based on bremsstrahlung measurements) because of doubt in accuracy and reproducibility if these techniques are applied to complex mixtures of fission products and bulky samples.

Conventional radiochemical separation procedures are tailored to the need of rapid methods and optimized regarding sample size, equipment, and details of radiochemical processing.

Methods will be developed based on specific adsorption or ion exchange depending on complex compounds (e.g. Cyclohexanediaminetetraacetic acid).

The term "rapid method" is understood from two points of view:

- One sample will be analyzed within a short period of time (e.g. a few hours),

- A series of samples can be run in parallel to achieve a high number of sample throughput per day. Steps with little permanent handling (e.g. ion exchange separation procedures) have to be applied in parallel runs of samples.

Experimental Results.

Liquid scintillation Spectroscopy has been applied for measurement because sample preparation is simple and reproducible, a separation of strontium from calcium need not to be quantitatively, and both, strontium-90 and strontium-89, can be determined. LSC equipment seems to be more generally available than low level proportional counting equipment. Considerable progress has also been made in the field of low level liquid scintillation spectroscopy instrumentation.

In fig.1 and fig.2 flow sheets of the radiochemical separation procedures applied are presented. At first it has been tried to shorten the conventional "nitrate method" to obtain results within one working day. For some types of samples (calcium content lower than 300 mg) the strontium/calcium separation step could be omitted. By using centrifuges for precipitate separation, up to six samples can be run in parallel. In this case, the total analysis time is longer, but a sample throughput of six samples per working day can be achieved.

Time consumption for Strontium determination by shortened nitrate-method.

time (hours)

0	sample
1	microwave drying,
1.5	heating
	ashing
4	ashed sample
	dissolve in HNO_3
	add carriers
	add H_3PO_4, NH_4OH,
	boil, centrifuge
4.5	phosphate precipitation
	dissolve in HNO_3
	add 100 % HNO_3
5	Sr-nitrate precipitation
	centrifuge,
	dissolve in water
	adjust pH
	add CrO_4^{2-}, boil,
	centrifuge
	discard prec.
5.75	Ba-chromate precipitation
	add H_2O_2, Fe^{3+}, NH_4OH,
	centrifuge,
	discard precipitate
6.5	Cr,Y-precipitation
	add CO_3^{2-},
	centrifuge
7	Sr-precipitation
	dissolve in 0.5m HCl
	add LSC cocktail
7.5	count

Determination of strontium-90 in water without separation of strontium from calcium

time (hours)

0	sample
	add carriers
	add NH_4OH, CO_3^{2-},
	boil, centrifuge
0.45	carbonate precipitate
	dissolve in HCl,
	adjust pH,
	add CrO_4^{2-},
	boil, centrifuge
1.5	barium chromate precipitate (1)
	add Ba^{2+}, centrifuge
2.5	barium chromate precipitate (2)
	add Fe^{3+}, Y^{3+}-carrier
	add NH_4OH,
	centrifuge
3	Me^{3+}-precipitate
	add NH_4OH, CO_3^{2-},
	boil, centrifuge
3.5	Sr^{2+}-precipitate
	dissolve in 0.5 m HCl
	add LSC cocktail,
4	count.

Fig. 1 : Flow sheet of "shortened" nitrate-method, 15 - 65 g sample, counting by liquid scintillation spectroscopy. Average time consumption is indicated in hours.

Fig. 2 : Flow sheet of strontium-90 determination without separation of calcium. 0.1 - 0.5 l of aqueous sample. The procedure can also be applied for ashed and dissolved materials. The calcium content of the sample should be less than 300 mg. Counting by liquid scintillation spectroscopy. Average time consumption is indicated in hours.

IAEA-152	Milk Powder	90Sr
Recommended Value (Bq/kg)	Confidence Interval (Bq/kg)	Result of analysis (Bq/kg)
7.7	7.0 - 8.3	7.7 ±0.2 6.7±0.2

IAEA-154	Whey Powder	90Sr
Recommended Value (Bq/kg)	Confidence Interval (Bq/kg)	Result of analysis (Bq/kg)
6.9	6.0 - 8.0	6.4±0.2 5.8±0.2

IAEA-AG-B-1	Marine Algae	90Sr
Recommended Value (Bq/kg)	Confidence Interval (Bq/kg)	Result of analysis (Bq/kg)
10.2	9.7 - 11.5	10.2±0.3 8.9±0.3
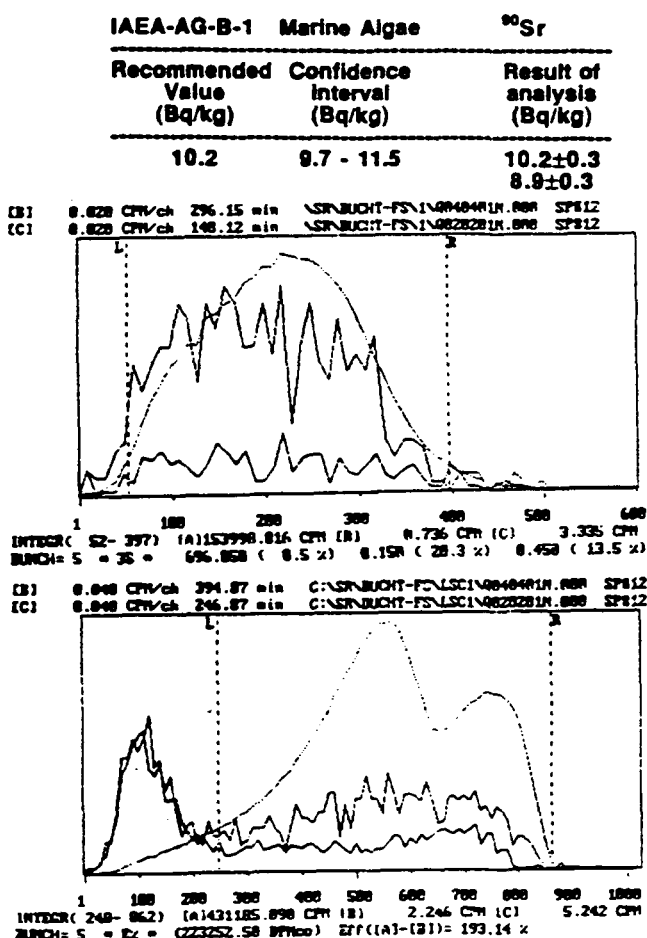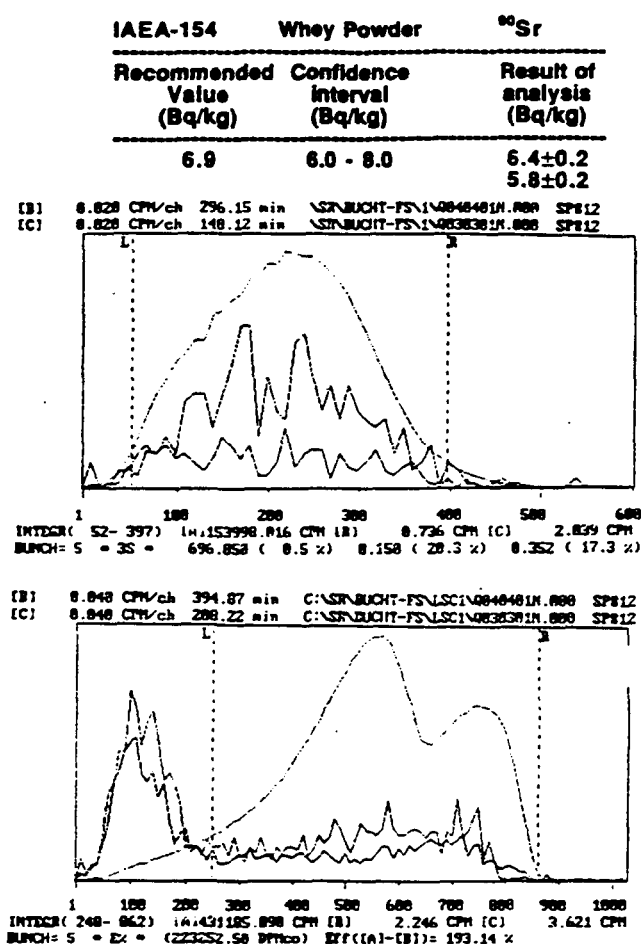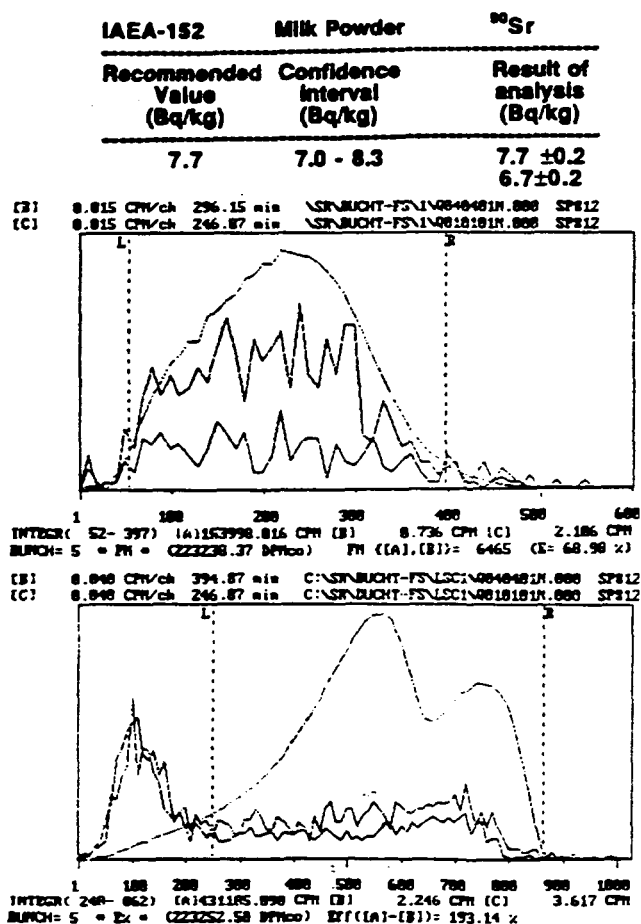
Fig. 3 : Sr - 90 - determination in IAEA certified reference materials (IAEA - 152, Milk Powder; IAEA - 154 Whey Powder; IAEA - AG - B - 1, Marine Algae), by "shortened" nitrate method. Measurements have been made using a LKB QUANTULUS liquid scintillation spectrometer at WALLAC OY company, Turku, Finland. Spectra of Sr-90 / Y-90 standard material, IAEA certified reference material and background are shown for Cerenkov counting and liquid scintillation spectroscopy. Chemical yield for Sr-90 separation was 60 - 65 %.

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Fig.3 shows examples for low level liquid scintillation counting using a LKB
QUANTULUS equipment (anticoincidence shield, background < 2cpm). The results
obtained are in fairly good agreement with the IAEA CRM recommended values.

A series of test runs had been made applying the "shortened nitrate method" and a
method omitting the calcium/strontium separation step. For these investigations samples

Fig. 4.

Fig. 4 (ctd)

Sr-90 in milk (nitrate method)

Sr-90 in cheese (nitrate method)
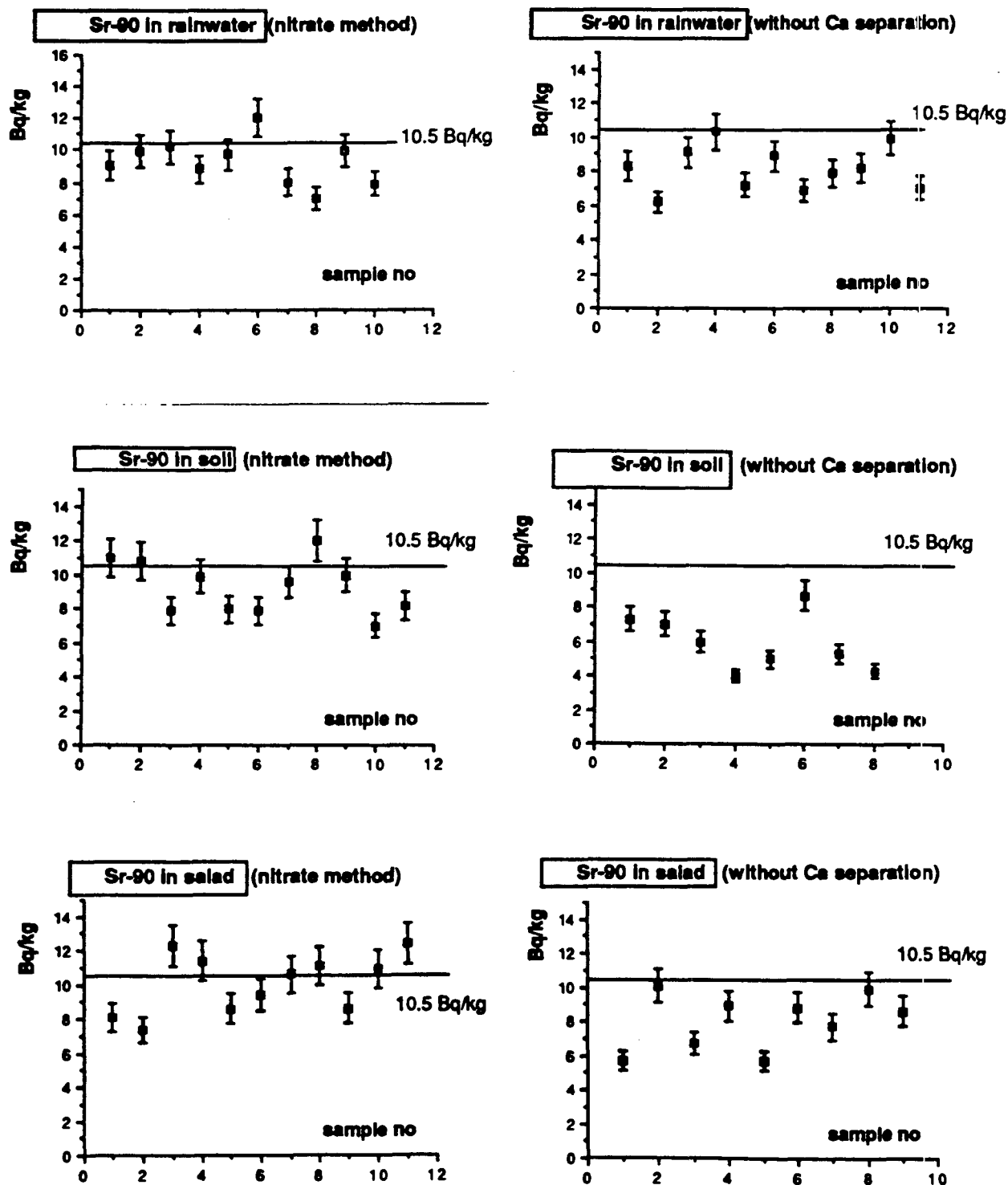
Sr-90 in meat (nitrate method)
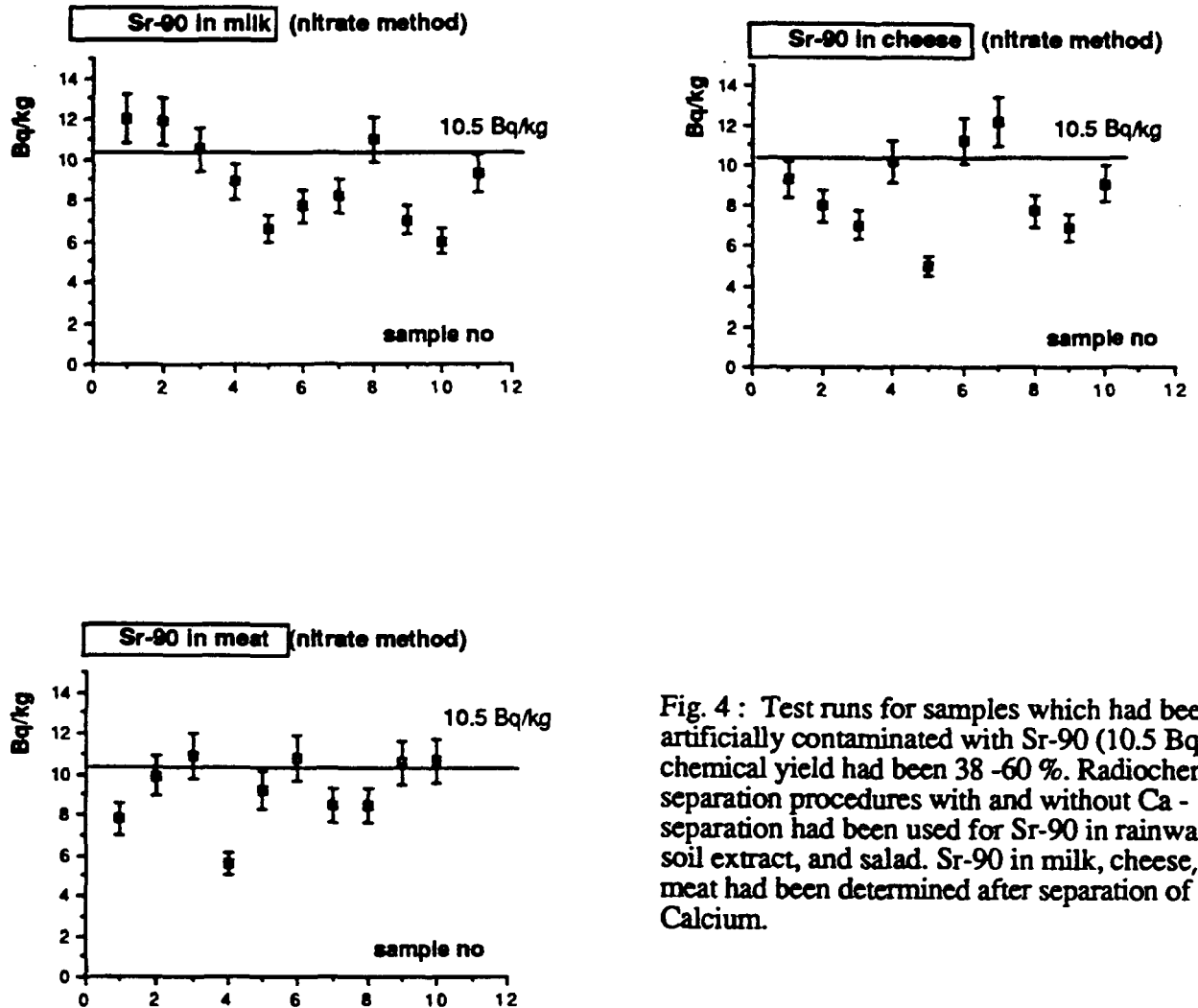
Fig. 4 : Test runs for samples which had been artificially contaminated with Sr-90 (10.5 Bq/kg), chemical yield had been 38 -60 %. Radiochemical separation procedures with and without Ca - separation had been used for Sr-90 in rainwater, soil extract, and salad. Sr-90 in milk, cheese, and meat had been determined after separation of Calcium.

had been artificially contaminated with strontium-90 (10.5 Bq/kg). At an average ten strontium-90 determinations were made from each contaminated sample preparation. In fig.4 the results obtained are summarized. Counting times were set to achieve a standard deviation of ±10% of the net count rate. In many cases too low values are obtained for strontium-90.

Relevance of the Institute's work within the Framework of Environmental monitoring and emergency preparedness of our Country.

In 1986 our laboratory provided the first Sr-90/Sr-89 data from environmental samples after the Chernobyl accident (rainwater, aerosol samples). Afterwards we had to analyze milk and vegetable and to train other people in radiochemical separation procedures. During this time manpower was provided by transferring staff members of the Institute of Pharmaceutical Research to our Radiochemistry Section. Whenever there will be a need of such type of investigation again, our Institute will have to serve the Governmental authorities also in the future. Rapid methods will be extremely helpful to fulfill the tasks the Institute has to do in this situation. Being also a University Institute and a training facility, such radiochemical procedures will be included in the practical education and training in the field of nuclear methods in environmental analysis.

Plans for future work.

Further test runs for microwave digestion should be performed, strontium-89 will be included into the investigations, cyclohexanediaminetetraacetic acid will be used as a complexing agent and calcium sulfate precipitates will be tested as an adsorbent for radiochemical separation of strontium. It will be tried to optimize the procedure without strontium/calcium separation steps. Less sophisticated low level liquid scintillation instrumentation (e.g. PACKARD 1050) will be tested. The possibility for applying liquid scintillation spectroscopy for the measurement of alpha emitting food and environmental samples will also be investigated.

Rapid Methods for Strontium Determination in Environmental Samples.

Karl Buchtela (Atominstitut of the Austrian Universities).

Presently available methods:

Until now two different approaches had been made to succeed in fast radiochemical separation procedures for the determination of strontium-90 in environmental samples:

- Investigations dealing with the extraction of yttrium-90,

- Investigations to tailor precipitation methods for strontium-90 separation to the needs of special sample types.

Optimal sample amounts:

Radiochemical procedures could be shortened considerably. The remaining bottle necks still are the sample pre-preparation, like drying, ashing, evaporation etc and of course the measurements. Large samples shorten the measurement process but increase the time consumption for sample pre-preparation and in many cases also for the radiochemical separation. Small samples facilitate sample handling but cause problems regarding detection limits and measurement time. Having some knowledge about the expected degree of contamination or just providing information that the contamination is lower than a given level may help to find an optimal sample size. As an example:

Low level Proportional Counting Tube			50 g sample
η = 35 %	Chem. yield = 90 %	t(measurement) = 100 min	2σ
background 0.5 cpm	LLD = 0.017 Bq		—
	MDA = 0.35 Bq/kg		
background 1.2 cpm	LLD = 0.027 Bq		
	MDA = 0.54 Bq/kg		

Cerenkov counting			50 g sample
η = 35 %	Chem. yield = 90 %	t(measurement) = 100 min	2σ
background 1.5 cpm	LLD = 0.030 Bq		
	MDA = 0.60 Bq/kg		
background 20 cpm	LLD = 0.11 Bq		
	MDA = 2.2 Bq/kg		

Such remarks can be considered being extremely trivial but thinking of planning something like a guide book for rapid methods, some guidelines how to start with a

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reasonable amout of sample material should be given. We are now dealing with such rules and we gladly accept advice from the group if it sems to be reasonable to continue.

Extraction method applied to soil samples:

The original schedule which had been discussed during the last meeting has its limitations. Equilibrium for strontium-90 and yttrium-90 has to be assumed; yttrium-91 can be determined by suitable measurement procedures. For application to soil samples additional separation steps have to be included to separate the uranium, thorium and daughter products. A coprecipitation step using iron hydroxide has little effect, it is not specific enough. If that procedure is applied e.g. to average Austrian soil samples (4.0 ± 2.0 Bq/kg), the contribution of radionuclides of the natural decay series is much higher than the yttrium-90 activity. Moreover due to the growth of daughter products the activity is increasing. By reextraction from the tributylphosphate phase using 3 M HNO_3 better separation of yttrium-90 and natural radionuclides is obtained, but still a rather high "background" due to natural occurring radionuclides is observed after the decay of yttrium-90. Much better results are obtained after a precipitation step with zirconium phosphate in acid medium. After that precipitation the activity of the yttrium oxalate show the correct half life of 64 hours. In other laboratories that separation from natural occurring radionuclides had been achieved by liquid extraction procedures. The flow sheet of the procedure is shown in Fig.1.

A very fast procedure using hexyldiethylhexylphosphate and hydrochloric acid medium has been developed in other laboratories, which will successfully compete with the above described method. This method has even found routine application in training courses.

We have made detailed investigation related to the decontamination of the yttrium-fraction from natural occurring radionuclides, zirconium and niobium.

If that method is applied for soil samples, the first step is a leaching process. This is now commonly in use for soil samples. In earlier described procedures one still may find the melting process using sodium and potassium carbonate to achieve total solution of the soil sample material. This is certainly not necessary. By the above mentioned leaching procedure all the strontium-90 which may be "available" for plants growing on that soil is certainly extracted.
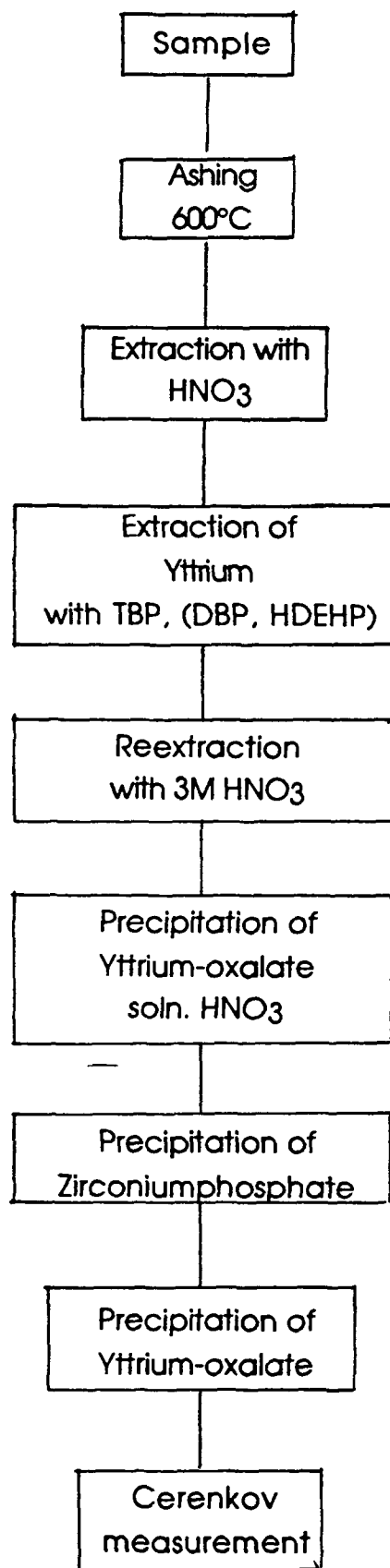
Fig.1 Flow sheet of extraction procedure with preciptiaion steps for the removal of natural occurring radionuclides

Leaching procedures to obtain "available strontium-90"

It should be discussed if leaching procedures extracting "available strontium" should also be applied for other environmental samples, like vegetables to avoid time consuming drying, ashing and dissolving procedures. Presently we are investigating such leaching procedures with plant materials. In these model experiments the strontium contamination is either caused by root uptake from a nutrient solution or by spraying the plant with a radioactive solution. The material is extracted by 6 M hydrochloric acid using a mixer. The main difficulty is the separation of a clear liquid phase from the suspension. Ending up with an aqueous solution of sample material any suitable separation procedure can be applied.

Precipitation methods for aqueous solutions:

Radiochemical procedures for the separation of strontium may have the advantage that also a strontium-89 determination can be done. So it may be worth while to investigate also rapid methods aiming at the separation of strontium. The nitrate method is the most common one. It can be applied for many type of sample material. The disadvantage is the rather high time consumption and the inconveniences related to the use of fuming nitric acid. At the last meeting a "shortened" nitrate method had been presented.

Fig. 2 shows the flow sheet of a procedure without the use of HNO_3. It was mainly designed for rainwater or drinking water investigations.

At the beginning a precipitation is done using a small amount of strontium carrier but a rather large amount of barium carrier. Barium serves also as a non isotopic carries for strontium. For precipitation from that large amount of liquid volume 20 mg strontium carrier is not enough, but a greater amount will be uncomfortable at later steps of the procedure. The bulk of barium together with radium is separated by chromate precipitation.

After some carbonate and hydroxide separation and purification steps the chemical yield is determined by taking a small aliquot before and after the last carbonate precipitation. The results obtained are compared and the strontium amount in the sample can be calculated. Not to lose time the AAS measurement can be done during the same time as the radioactivity measurement.

```
                    ┌─────────┐
                    │ 2 l water│
                    └─────────┘
                         │      addition of carriers:
                         │      100 mg Ba⁺⁺, 20 mg Sr⁺⁺,
                         │      10 mg Cs⁺, 10 mg I⁻.
                         │
                         │      CO₃⁻⁻ - precipitation
                         │
                  ┌──────────────┐
                  │ Carbonate-   │
                  │ precipitate  │
                  └──────────────┘
                         │      6M CH₃COOH, pH = 4.5
                         │      CrO₄⁻⁻
                         │
                         ├───────────────┤ BaCrO₄ │
                         │
                         │      CO₃⁻⁻ - precipitation
                         │
                  ┌──────────────┐
                  │ Carbonate-   │
                  │ precipitate  │
                  └──────────────┘
                         │
                         │      Fe⁺⁺⁺, (Ce, Zr-carrier)
                         │      NH₄OH,
                         │
                         ├───────────────┤ Fe(OH)₃ │
                         │
                         │───────────────────── 1 ml for AAS ─────►
                         │
                         │      CO₃⁻⁻ - precipitation
                         │
                  ┌──────────────┐
                  │ Carbonate-   │
                  │ precipitate  │
                  └──────────────┘
                         │
                         │───────────────────── 1 ml for AAS ─────►
                         │
                  ┌──────────────┐
                  │ Measurement  │
                  └──────────────┘
```
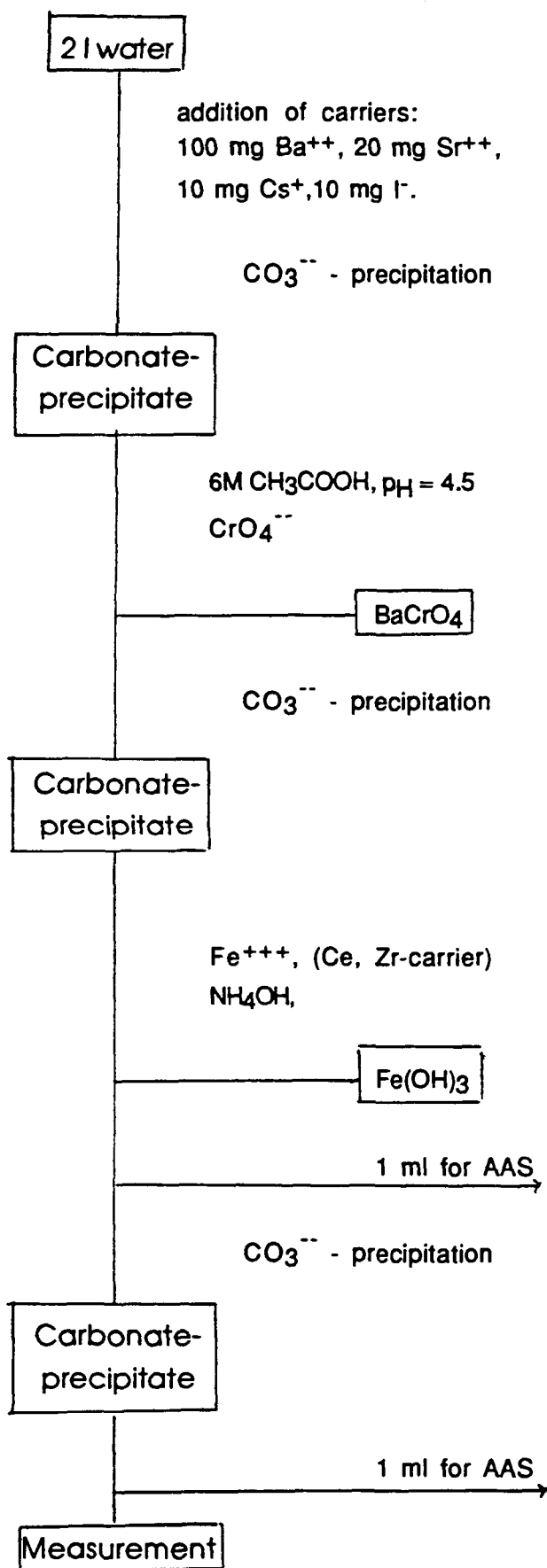
Fig.2. Flow sheet for strontium separation from aqueous solutions

Investigations using solutions of short living fission products.

It seems rather doubtful if these few purification steps are sufficient to remove the large number of short living fission products. We tried therefore to do investigations using a model solution containing short living fission products. This solution had been prepared by irradiation of natural uranium in our TRIGA reactor. The results of the decontamination regarding fission products had been much better than expected, but we consider that our investigation failed because of the high amounts of uranium which made it impossible to obtain a proper carbonate precipitation. Uranate compounds precipitating at lower p_H values caused unreliable results at the carbonate precipitation steps. Investigation have to be repeated either after removing the uranium from the model solution by liquid extraction or by using a fission product solution from a nuclear power reactor. A primary coolant solution will be a suitable sample.

The finally obtained strontium sample contained an excess activity of strontium-89 compared to that of strontium-90. We did not succeed in a reliable determination of strontium-90 using this model solution because of the short irradiation time.

Determination of strontium-89/90 and yttrium-90 in the same sample.

The simultaneous determination of strontium-90 and strontium-89 is usually done by separation of yttrium-90 after a suitable time for the growth of yttrium-90. Investigations are of interest to try a yttrium-90 measurement without separation by observing the increase of activity of the strontium sample due to the production and decay of the daughter nuclide yttrium-90.

Also it can be tried to use liquid scintillation spectroscopy to discriminate strontium-89 (1.46 MeV) from strontium-90 (0.55 MeV) immediately after the strontium precipitation. Until now all these determinations are only possible if the strontium-90 activity is not too low compared with the the strontium-89 content of the sample. Unfortunately regarding this possibility of determination but fortunately from the point of view of radiation protection immediately after a nuclear accident in most cases the activity of strontium-90 is much lower than that of strontium-89. Liquid scintillation spectroscopy does not give reliable results for low strontium-90 activity if a high strontium-89 activity is observed in a sample.

The growth of yttrium-90 in a sample of strontium-89/90 will increase the total activity. After a suitable period of time this increase might be sufficiently high to provide reliable information about the strontium-90 content. Due to statistics no reliable information will be provided for samples with an excess of strontium-89. If the strontium-89 activity is 20 times higher than the strontium-90 activity, no reliable information can be obtained, if it is 5 times higher, it is possible to provide a quantitative

information about the growth of yttrium-90 after 36 hours, and if twice the activity of strontium-89 compared to the strontium-90 were observed, there would be no difficulties for the simultaneous determination of both radionuclides. Dealing with the situation of high strontium-89 contribution an yttrium separation probably is unavoidable.

Economic considerations.

It might be of interest to compare the costs of chemicals necessary for nitrate separation procedures and TBP extraction method. The expenses for one strontium analysis using nitrate method is approximately three times higher than for the TBP extraction which costs about 2 US$ (based on FLUKA chemicals status 1991). Economic considerations regarding manpower and equipment is not included in these calculations. Cost of equipment are about the same for both methods, manpower costs may be higher for the nitrate method

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137Cs Pre-Concentration From Water Samples Using Prussian Blue Impregnated Ion-exchanger.

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1) Introduction

During the intermediate and the late phase of a nuclear accident, the water derived intervention levels can vary widely, depending on site-specific factors, integration time and intervention levels. If one considers 1% of the derived intervention level as the desired detection limit, large counting times or large sample volumes may be necessary.

In order to reduce both counting time and sample volume to be handled, sample concentration methods can be useful. For ^{137}Cs the use of hexa cyanoferrate compounds for this purpose is not new (1-3). The hexacyanoferrate compound can be used as it self or impregnated on ion-exchangers or silica-gel. The associated cation can be iron (III), nickel, cobalt or zinc. Using for seawater sampling purpose cupric hexacyanoferrate impregnated on an ion-exchanger, it was possible to sample up to thousand liters with a flow rate of 3 liter/min (5).

During the Goiania accident iron (III) hexacyanofenate impregnated ion-exchanger columns were used in the hospitals to avoid the discharge of contaminated urine, since the urine of the pacients had ^{137}Cs content up to 37 MBq/L (9). These columns (5 cm diameter and 50 cm height) could handle up to 100 liters urine with complete ^{137}Cs retention (10).

Based on this experience we decided to use the same impregnated resin in the analysis of ^{137}Cs river waters at Goiania. This work describes the experiments related to the adaptation of the method for this specific purpose.

2) Experimental

2.1) Preparation of the Impregnated Ion-Exchanger

To 1 liter resin (Dower 50WX8, 20-50 mesh) 1 liter of 1 M $FeCl_3$ was added and mechanically stirred for 30 minutes.

The aqueous solution was then removed and the resin was washed twice with distilled water. [To the resin it was added again 1 N FeCl$_3$, the process repeated and washed the resin with destilled water until get negative Prussian blue test]...

To the iron impregnated resin 1 liter 1 M K$_4$Fe(CN)$_6$ were added, mechanically stirred for 30 minutes, the aqueous phase aspirated off and the resin washed with destilled water until the obtention of a clear rinse solution.

2.2) The Column Assembly

The experimental assembly is shown in Fig. 1. The integrator flow meter (Liceu de Artes e Oficios; Micro hidrometro) and the filter Sartobran 5130&F9 (1.2 μm pre-filter and 0.45μm filter) are to be used only when collecting real samples. The lab experiments were carried out only with the glass column and the peristaltic pump (Sartorius SM 16&50). The glass column will latter on be replaced by a PVC one.

2.3) The Column Experiments

The first experiments were performed with a 2.5 cm diameter and 20 cm height column. The water volume pumped through was 50 liters and the flow rate 1 L/min. The ^{137}Cs content for each experiment was about 74 Bq/L. The first experiment was carried out with destilled water. Later on, K and Ca were added in concentrations similar to those found out on the Meia-Ponte River waters (Table 1).

The ^{137}Cs profile on each column was determined with a 3" x 3" NaI(Tl) detector (Fig. 2) and the ^{137}Cs content of the resin and of the resin-passed water were determined with a 15% relative efficiency intrisic germaniun detector. The results are shown on Fig. 3 and 4 and on Table 2.

Table 1 : Meia-Ponte River water composition at the Rochedo dam (Goiania, Brazil). N=6.

pH	7.3 +/- 0.1
K$^+$ (ppm)	1.6 +/- 0,5
Na$^+$ (ppm)	6.1 +/- 1,0
Ca^{+2} (ppm)	5.6 +/- 0,1
Mg^{+2} (ppm)	3.14 +/- 0,06
Al^{+3} (ppm)	< 3,0
Total Fe (ppm)	< 0.5
Mn^{+2} (ppm)	< 0,1

Table 2 : ^{137}Cs retention on Prussian blue impregnated resin (column 2.5 cm O x 20 cm height; water volume = 50L; flow rate = : 1/min).

Sample composition	Percentage of retertion	Percentagem of loss
Destilled water	(109,0 +/- 5,6)	< 0.1
Destilled water + K⁺ (10 ppm)	(105.0 +/- 4.5)	< 0.1
Seawater	(55.7 +/- 1.6)	(50.7 +/- 3.8)
Destilled water + K⁺ (10 ppm) + Ca⁺2 (10 ppm)	(103.7 +/- 4.3)	< 0.04

3) Discussion

The results have shown that the system can be sucessfully used for fresh water large volume samples. For seawater, by the other hand, some improvements are necessary. The problem origin seems to be the seawater pH(8,0). The iron (III) hexacyanofer- rate is soluble by alcali hydroxides. The seawater experiment eluate was turbid, yellow and with a pH = 6.0. This point out clearly for a dissolution of the column material. The eluate iron content, determined further, was 13.2 ppm, when the seawa- ter content is of tens of ppbs. One possible alternative can be the sample acidification to a pH about 5.

4) Proposal of further experiments.
In order to complement this study on the application of prus- sian-blue impregnated resins to environmental issues additional experiments are planned, such as:

i) Use of larger columns and higher flow rates.
ii) Field experiments to determine ^{137}Cs concentrations at the Rochedo reservoir, Goiania.
iii) Absorption characteristics of other radionuclides (ex: ^{60}Co).
iv) Field experiments at Angra dos Reis (Coastal Reactor Si- - te) aiming at the determination of radionuclides in local seawater.

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FIG.3-Cs-137 PROFILE ON A PRUSSIAN BLUE
IMPREGNATED ION-EXCHANGER COLUMN
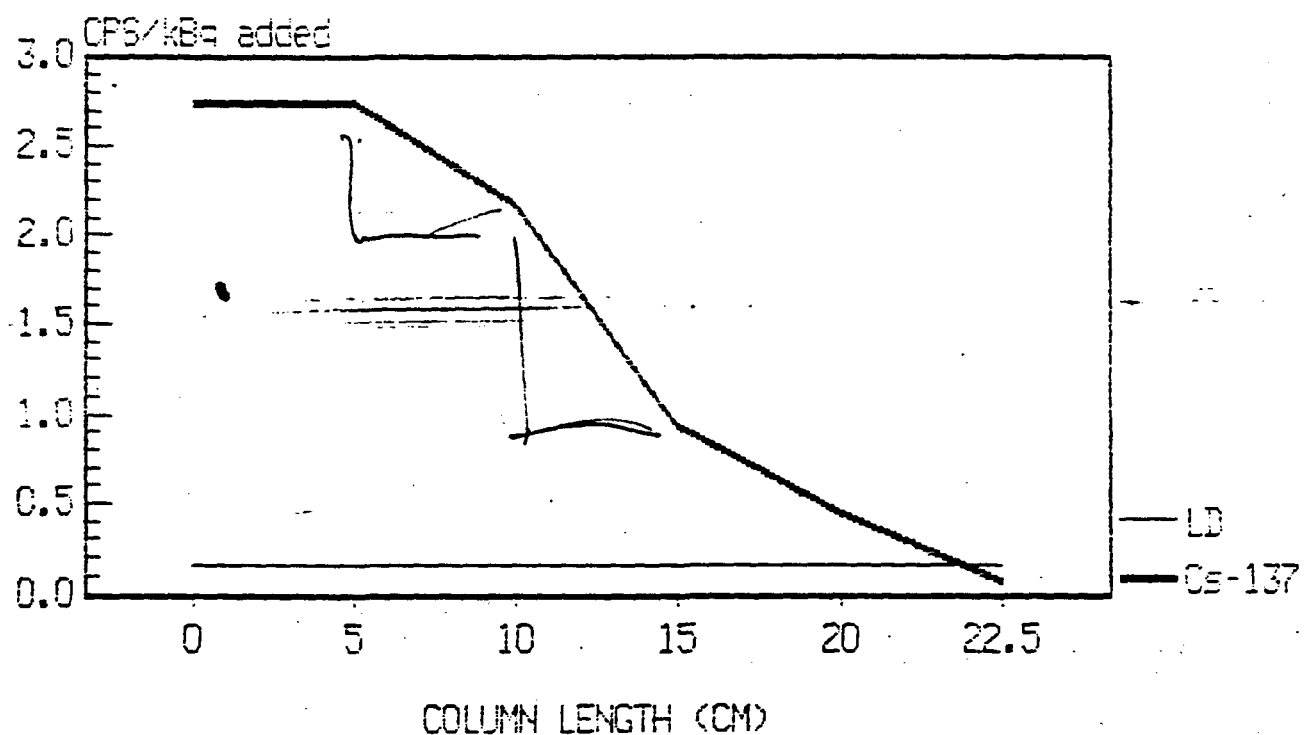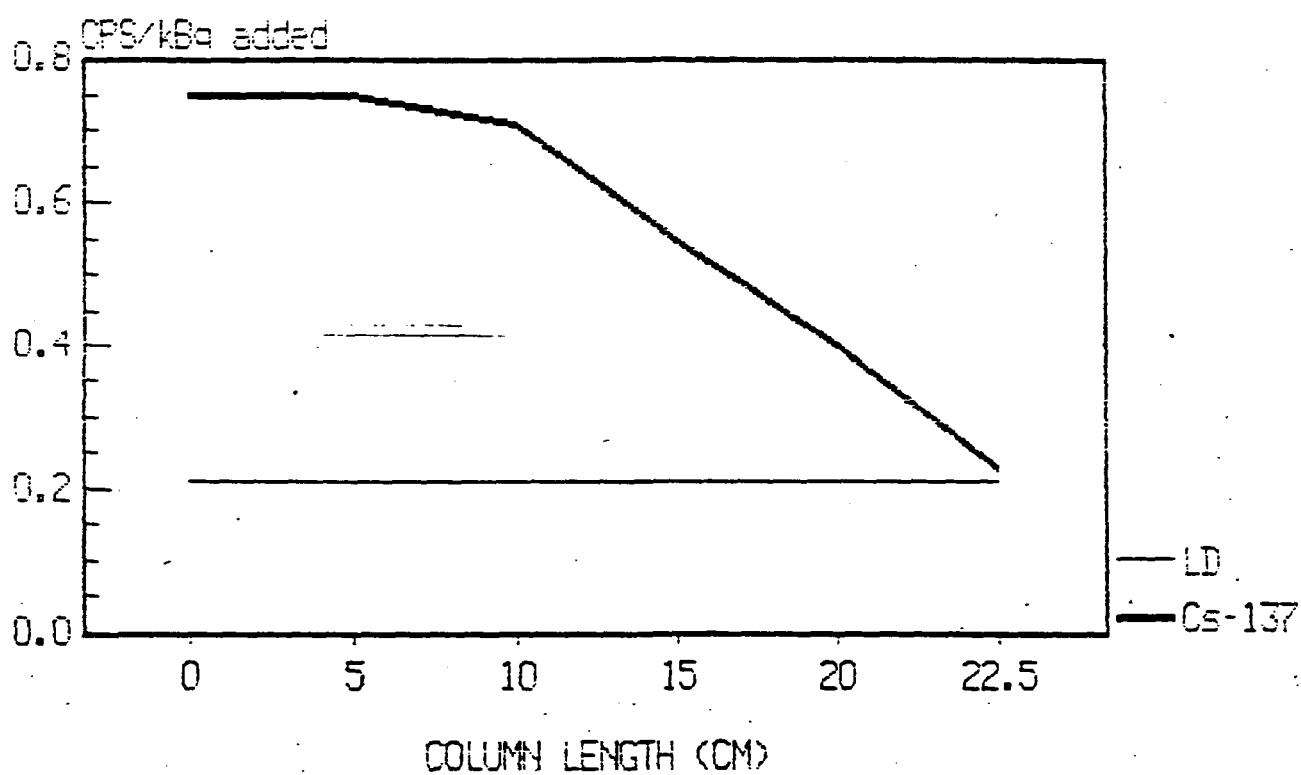AFTER THE PERCOLATION OF 50L WATER
CONTAINING 10 PPM K AND 10 PPM Ca

COLUMN LENGTH (CM)

FIG.4-Cs-137 PROFILE ON A PRUSSIAN BLUE
IMPREGNATED ION-EXCHANGER COLUMN
AFTER THE PERCOLATION OF 50L SEAWATER

QUANTITATIVE ANALYSIS OF β-EMITTING FISSION PRODUCTS

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1.Introduction

In the case of a civil nuclear accident γ-spectroscopy can provide nearly 90% of all necessary information. Still there are some questions which γ-spectroscopy cannot answer. Most of the questions are connected with β-emission and among them is the problem of pure β-emitters -^{90}Sr(Y), ^{89}Sr, ^{91}Y. Another question concerning mainly the personnel and the people present on the site of the accident is the surface β-beta contamination. As an example in Fig.1 the computer simulated total β-spectra for the Chernobyl mixture of nuclides for different periods after the accident are shown [1,2,3]. It is obvious that in the moments immediate after the accident the "soft" component of the β-spectrum up to approximately 200 keV prevails and so the error from a regular β-counter with a 5 mg/cm^2 window can reach up to 50% and more.

Those are some of the problems on which we are working - the "strontium problem" and β-dosimetry with Geiger counters. Our aim is to try to answer the following questions:

1.Is it possible to measure the absolute quantity of ^{89,90}Sr and their ratio over a large area within a short period (e.g. an week).

2.Is it possible to measure the absolute quantity of ^{89,90}Sr and their ratio in food immediately after the chemical

separation procedure.

3.Is it possible to measure the β-spectrum of a contaminated surface (soil,concrete.asphalt, etc.) within a short time (an hour) and what should the correction factors be for the regular β-counters.

We are trying to answer the above questions by a method for β-analysis of fission products. The method comprises a detector system and a processing procedure.

2.Detectors

Two detector systems were assembled and tested for the purpose of β-analysis. The detector of the first system is a planar HPGe detector with thickness 5mm, active surface approx. 30 mm^2 and a 75μ Be window. The second system includes a stylbene detector with an aluminized mylar widow (6 mg/cm^2). Special care is taken to avoid edge effects. The HP GE detector was chosen for its energy resolution and the stylbene detector for having the best energy resolution among the organic scintillators and also for its low Z (atomic number). The energy resolution of the plastic scintillators which we tested with conversion electron sources ^{137}Cs and ^{207}Bi (Amersham) varied from 12 to 20 % .

The importance of the low atomic number will be cleared later.

Additional details on the construction of the detectors and on measuring procedures will be reported later in our annual report of research contract 5633/R.

3.Approach

The experimental β-spectrum of a mixture of β-emitters $E(i)$ is a continuous one and is a result of the overlapping of the spectra of each of the nuclides with appropriate weight, here i is the channel number and corresponds to a certain energy. Then if $T(i)$ is the initial spectrum of the k-th nuclide, the problem for identification of the β-emitters is reduced to the mathematical minimization of the expression:

22

$$
(1) \qquad \sum_{i=1}^{n} \frac{1}{W_i} \left\{ E(i) - \sum_{k=1}^{m} a_k T_k(i) \right\}^2 = min[a]
$$

here a_k are the unknown quantities of each nuclide, n -channel number, m - number of all β-emitters, W_i - statistical weight of each channel. The most important problem is $T_k(i)$ and in practice in very few cases one can use the original β-spectrum for the corresponding transition (calculated or tabulated, e.g.[1]). Usually the β-spectra are distorted due to self-absorption and backscattering in the sample, backscattering in the detector and finite energy resolution of the detector.

There are two possible ways for solving the problem of the form of the β-spectra of each nuclide. The first approach is analytical. The initial theoretical spectrum is subjected to several procedures accounting for the various effects. The second approach is completely empirical. For each nuclide the corresponding spectrum is measured at the same conditions as when a complex spectrum is measured (for different conditions a set of spectra for each nuclide is necessary). Then the measured calibration spectrum is smoothed if necessary and is substituted in expression (1) instead of $T(i)$. The basic difference here is the necessity of radiochemical work for the source preparation, but the expected results are accuracy and reliability of the analysis.

In the present announcement we report results based on the first, theoretical approach since one of the developed detector system allows the analytical description of each effect and also some preliminary results of the second, empirical approach.

4.Experiment

4.1.Experimental test of the the two detector systems.

A β-spectrum is recorded in two consecutive measurements. During the first measurement β + γ + background are recorded, for the second measurement a 5 mm Al filter is inserted between the sample and the detector so only γ + background are measured. The difference is the β-spectrum.

Initially the detectors were tested with "thin" sources with less than 5 mg/cm^2 thickness and later using standard β-sources In fact the thin sources were mononuclide hot particles from the Chernobyl accident which had reached Bulgaria [4]. Fortunately some of the particles are purely mononuclide ^{106}Ru(Rh), ^{144}Ce(Pr), ^{90,89}Sr. Actually the last one is ^{140}Ba and strontium particle, but the barium has decayed long ago. The advantage of the particle sources is that the experimental spectra can be compared with the theoretical ones and any distortions should become evident.

In Fig.2a and 2b the experimental spectra of a mononuclide ^{106}Ru particle recorded with the two detectors are shown. The thick line is the theoretical spectrum of the ^{106}Rh β-transition. All problems which arise we shall illustrate with that source.

The stylbene spectrum coincides almost perfectly with the theoretical one except for the beginning of the spectrum. The rise of the experimental points at low energies is due to backscattering of the incident on the stylbene β-particles. Approximately 5% of the electrons leave back the crystal depositing nearly half of their initial energy. There is an way out even for that effect - there is experimental data on the energy distribution of backscattered electrons and for low Z targets the distribution can be analytically approximated.

The experimental spectrum recorded with the HPGe planar detector is quite distorted towards lower energies. That effect is due again to backscattering which for Ge is a considerable fraction ($\approx$ 30%) and the reflected electrons leave only 20 - 30% of their initial energy in the crystal. And something else - for high Z (higher than Al) there is no analytical function for the energy distribution of the reflected electrons, so the

theoretical spectrum cannot be transformed analytically to fit the experimental data.

The second correction accounts for the finite energy resolution. That is a simple procedure - a convolution of the theoretical spectrum over the apparatus function. That function is usually a Gaussian and for the simple case $\Delta E/E = const$, the integration is not a heavy problem. For time saving it is better to perform the convolution beforehand (for 8, 10, 12% energy resolution) and to keep the spectra on diskette. The energy convolution is actually necessary only for the stylbene detector. Our main conclusion is that the principle advantage of the Ge detector - better energy resolution is not of much importance for β-spectra. For γ-spectroscopy the aim is as good as possible energy resolution but for applied β-spectroscopy good resolution is not the main requirement since β-spectra are continuous.

The last correction for the initial theoretical spectra is the self-absorption and scattering in the sample. We have developed a semi-empirical method based on experimental data on scattering and theoretical calculation on dE/dx , so we can calculate what spectrum a thick sample emits. All initial and convoluted spectra are modified for samples up to 50 mg/cm^2 and stored on a diskette.

4.2.Experimental test of the method.

There are two possibilities for testing the method. The first one relies on data from γ-spectroscopy for $\beta-\gamma$ emitters, namely on ratios of Ru/Ce/Cs. Ru and Ce are determined from the β-spectra of Rh and Pr and Cs is measured from the electron conversion peak of 624 keV ($\approx$ 8%). Data from β-spectroscopy coincides within experimental errors with data from γ-spectroscopy.

The second method is somewhat artificial but with high reliability. Experimental mononuclide spectra are summed with known weights and then the resultant spectrum is decomposed into its constituents. When β-analysis was tested by this method the

importance of the precise detector calibration emerged.

In Fig.3 and 4 the spectra of a standard fuel hot particle detected with stylbene and HPGe detectors. The accuracy in the spectral decomposition of that particular sample is 20 - 25% for the different nuclides.

5.Applications of the method.

5.1.Determination of the Cs/Sr ratio of air filters.

The Cs/Sr ratio is a quantity necessary for the estimation of Sr over a large area by gamma-spectroscopy [6]. The knowledge of the absolute quantity and the chemical form of Sr are essential for the estimation of long term consequences. We measured that quantity by β-spectroscopy of air filters obtained from the department of Hydrology and Meteorology at the Bulgarian Academy of science. That department has a net of stations which among measuring other parameters,filter air through thin filters. Usually filters are changed daily but in the first days of May 86 they were changed at each 6 hours.

The quantity of Cs is measured by the area of the 624 keV conversion electron peak (7.78% of all transitions of the 662 keV level). The ^{90}Sr is measured by β-spectroscopy of Y and it can be measured either after the growth of Y (10-15) days, or after one or two days after the removal of the filter from the meteorological station - Fig.5. In Fig.6 the absolute quantity of Sr and Cs per equal amounts of filtered air is shown. The ratio of Cs/Sr for all days in which there was considerable fallout should be taken with its own weight proportional to the values of the quantities in each day.

The obtained value for Sofia is 5.4 ± 0.5 and that value is an initial guess for the actual ratio in soil. We believe that this figure is very close to the actual one.

In fission of ^{235}U with thermal neutrons the ratio of cesium and strontium is 1.06. The estimated value for USSR for the sixties is 1.6 - 2 [6] and this value is obtained through γ-spectroscopy and radiochemical procession of thousands of

samples. The estimation of the ratio of the blown out radioactivity of the Chernobyl reactor [3] is ~4 . Here we obtain a ratio of approximately 5, i.e. there is a certain enrichment of Cs. That is easy for understanding since Cs is more volatile and Sr is predominantly in the form of hot particles [4,5].

Our conclusion is that such a method can be applied for the measurement of Cs/Sr ratio and further for the estimation of the absolute quantity of Sr. The nuclides which interfere are $^{144}Ce(Pr)$ and $^{106}Ru(Rh)$ ($T_{1/2} \simeq 1y$ for both).

5.2.Analysis of Sr in food.

In 1987 our laboratory obtained a sample of radiochemically separated strontium from cheese and grass, the separation had been carried out in the radiochemical laboratory in the Agricultural Academy in Sofia. The aim was to watch the growth of Y in order to speed-up the measurement of Sr. In Fig.7 the results from one of the measurements is shown (6h run). ^{89}Sr and ^{90}Sr are clearly observed and their ratio and absolute quantity can be measured very quickly, e.g. 1 day after the separation.

The absolute quantity of each nuclide can be measured either by calculating the solid angles, or by calibrating the facility with a known activity (only ^{90}Sr is enough), or by measuring the absolute activity by another detector.

We are convinced that such a method will be very useful and very accurate for measuring both isotopes and their absolute quantity.The accuracy is much better than the method described in [6].

Some preliminary results on β-analysis and it applications were reported in [7].

5.3.Beta-spectroscopy of a contaminated surface.

In Fig.1. an estimation of the total β-spectrum for the Chernobyl accident is shown. Of course β-spectra can differ for different accidents and for different places The general feature

of all β-contamination mixtures is the relative abundance of low energy β-emitters with maximum energy up to 200 Kev. If a β-counter with a thin window ($\sim$5 mg/cm^2) is placed at a distance 1 - 5 cm then the total window thickness is 6 - 10 mg/cm^2. That window may cause up to 50% and more underestimation error when measuring surface contamination.

If the people know the energy distribution of the electrons emitted from a certain contaminated surface then corrections for the standard counters and recommendations for shielding can be made. Beta-spectroscopy with a stylbene detector of various samples (e.g. wipe test paper) can can give the energy distribution within less than an hour and no other corrections will be necessary. The error in the spectrum due to backscattering and self-absorption in the sample can be 10 - 20% but that is enough for estimations and recommendations.

We have calculated correction transmission factors for different average spectrum energy and also for different accidents and for different periods after the accident.

6. Conclusion

It is our belief that we have not discovered and tested all possibilities of the method of quantitative or computer β-analysis. The method itself needs additional efforts especially with HPGe detectors.
For the time being we can formulate some of the basic principles of quantitative β-spectroscopy:

1.A spectroscopic detector for electrons is necessary.

2.The energy resolution of the detector should be 10-12% or better.

3.The detector system must be stabilized.

4.The low Z detectors allow decomposition with modified theoretical spectra and also with experimental calibration spectra.

5.The high Z detectors allow decomposition only with experimental calibration spectra.

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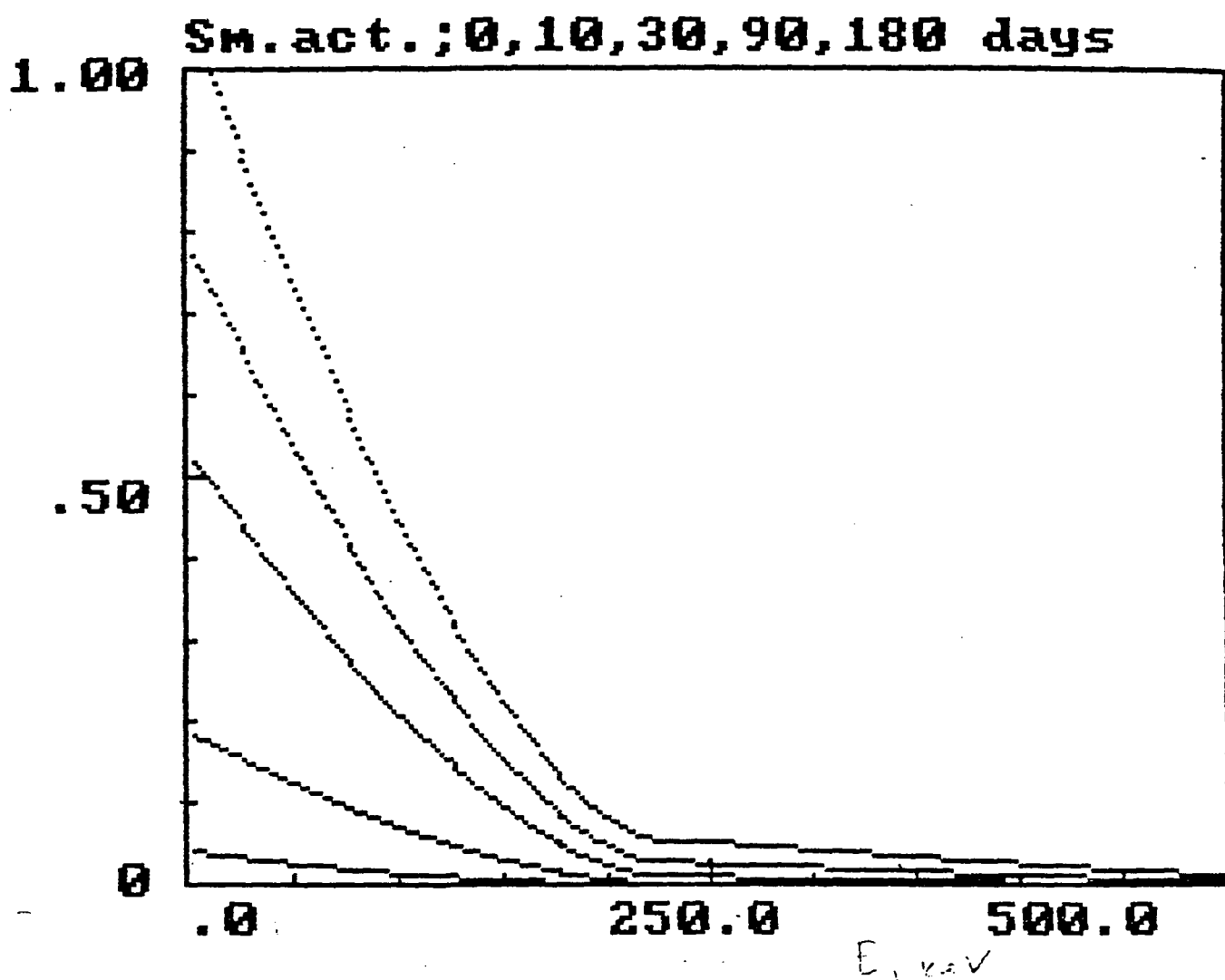
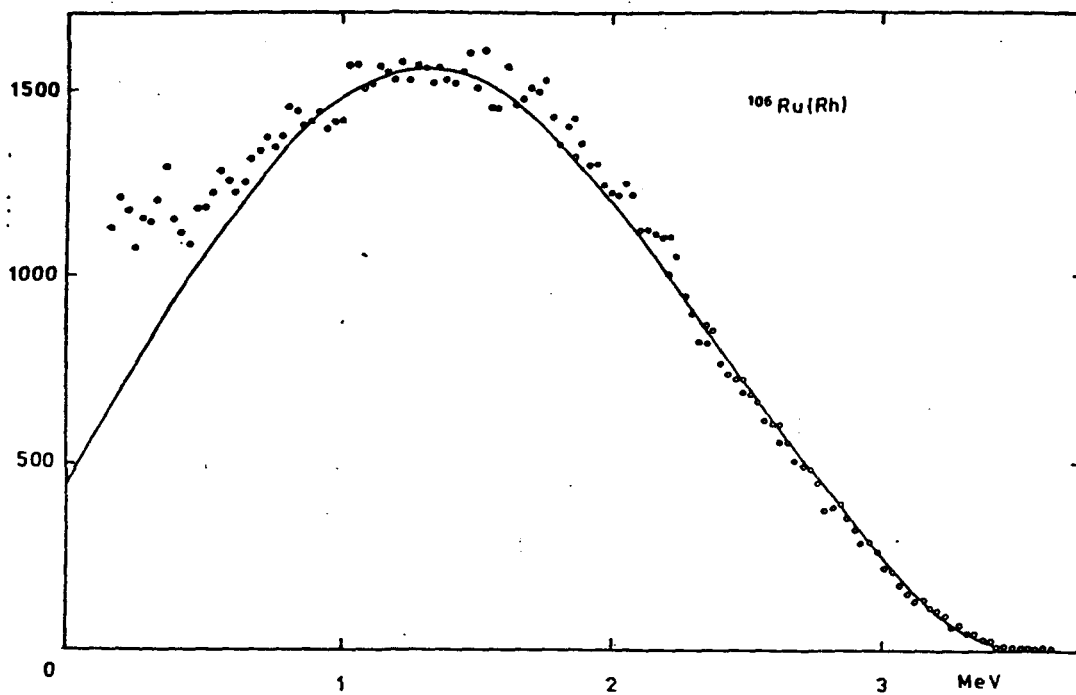Sm.act.;0,10,30,90,180 days
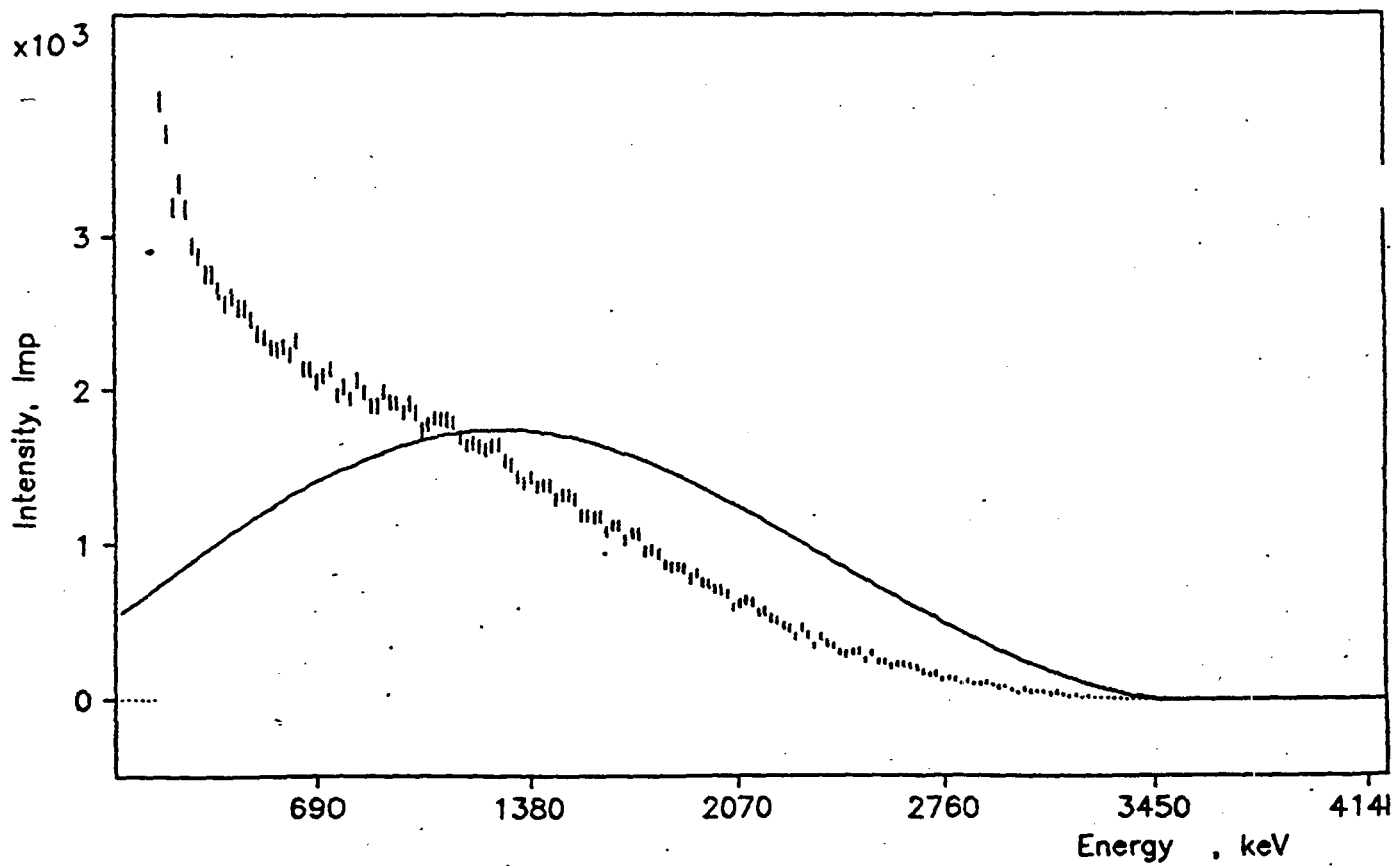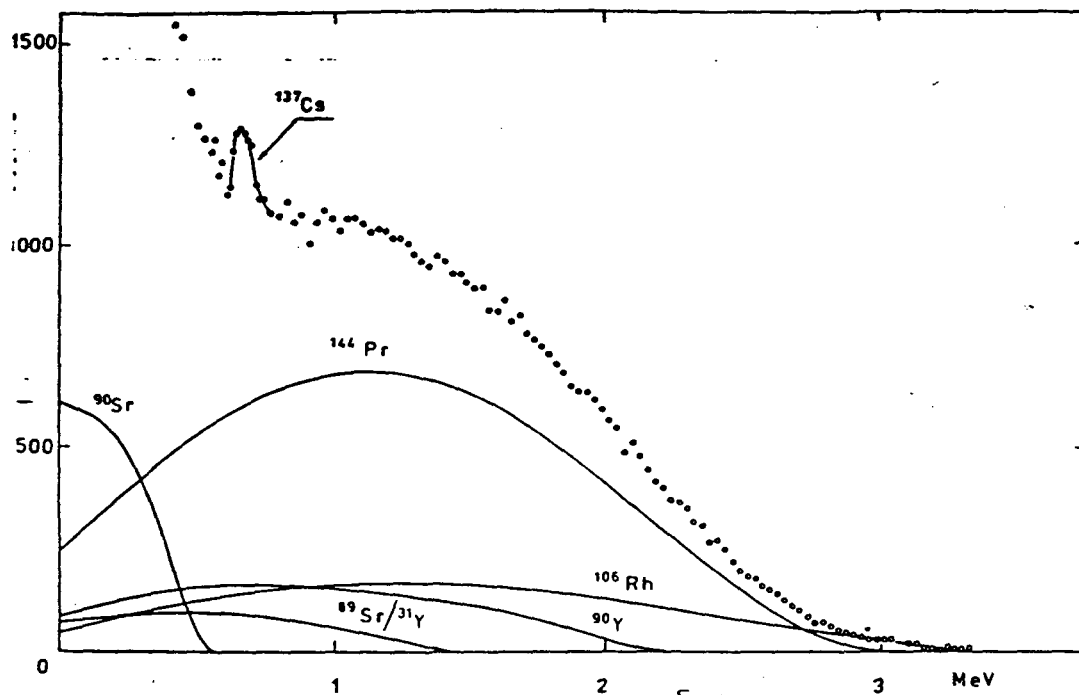
Fig. 4

^{106}Ru(Rh)

Fig 2a

Fig 2b

Fig. 3

Fig. 4

Fig 5

СОФИЯ 1.05 6.05
1986

○ ^{137}Cs

● ^{90}Sr

⊗ Cs/Sr

Cs/Sr = 5.4 ± 0,5

Cs/Sr

^{137}Cs

^{90}Sr

МАЙ 1986
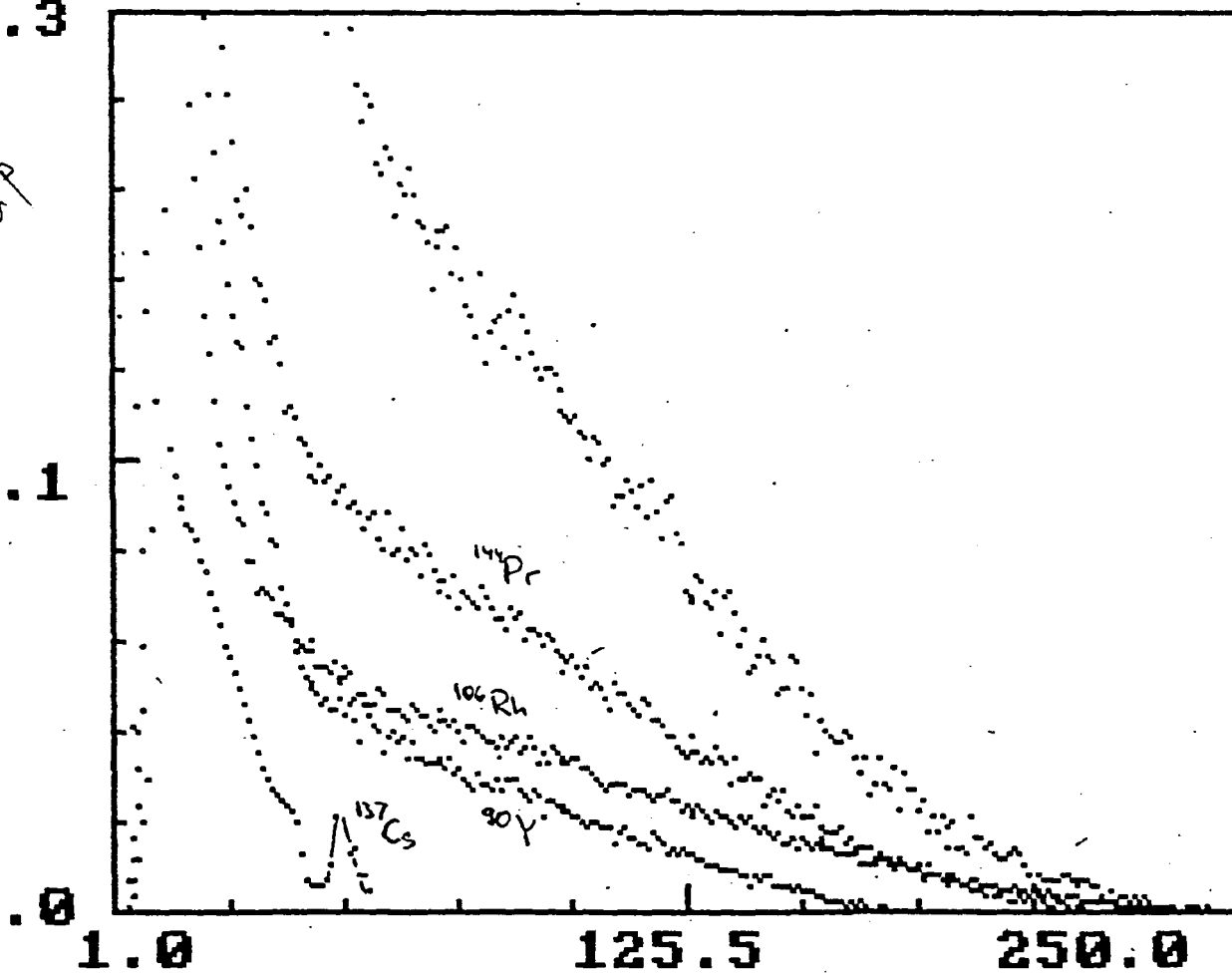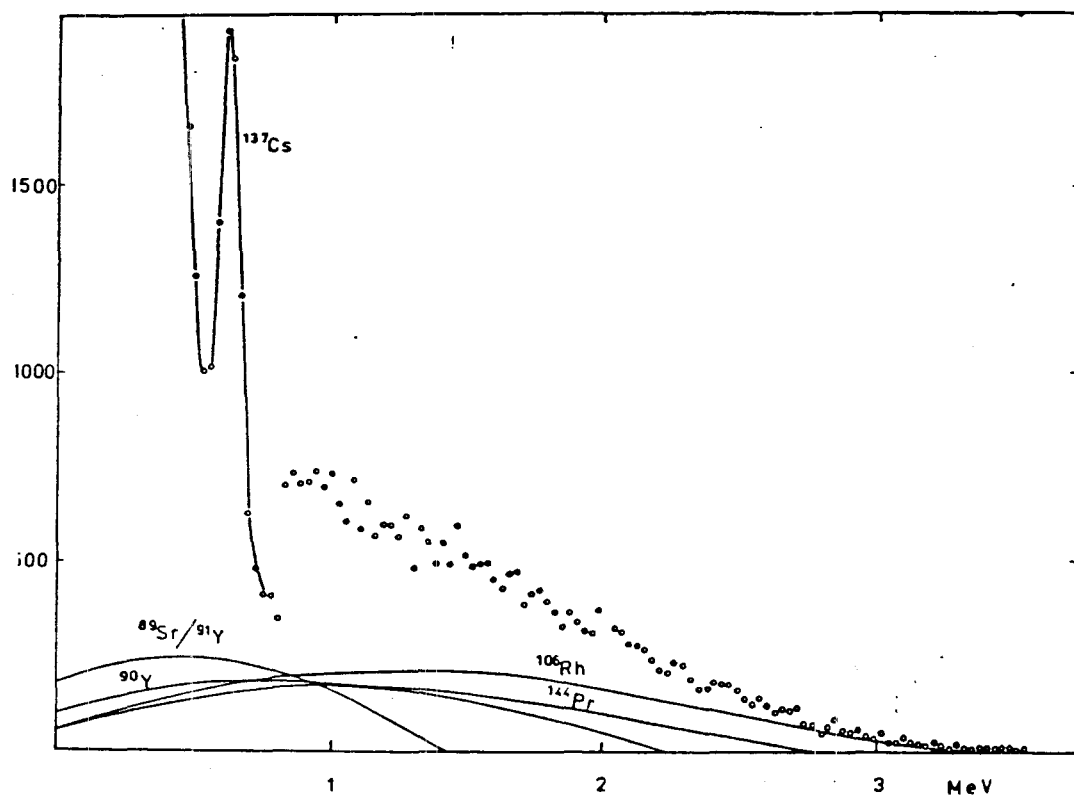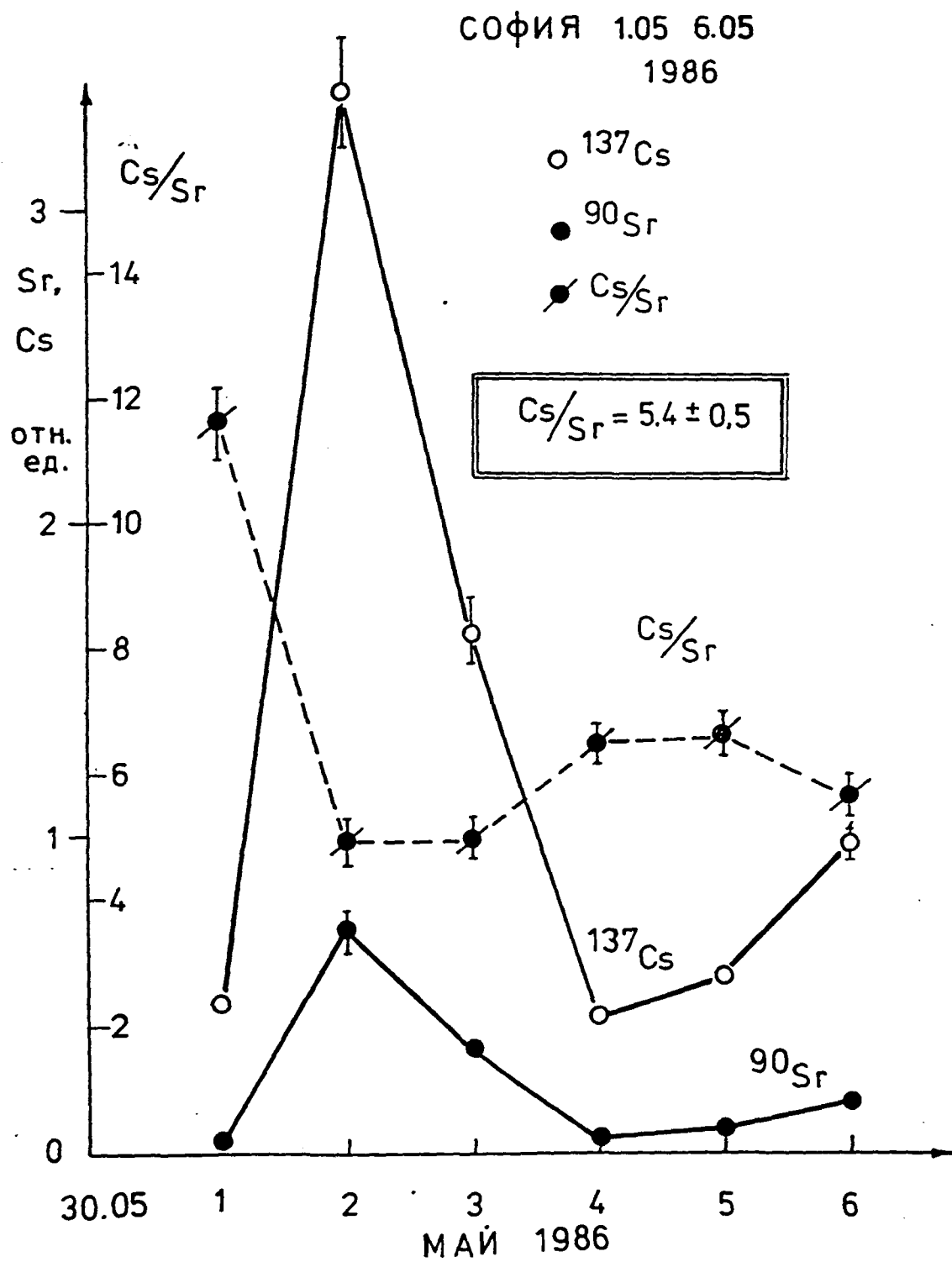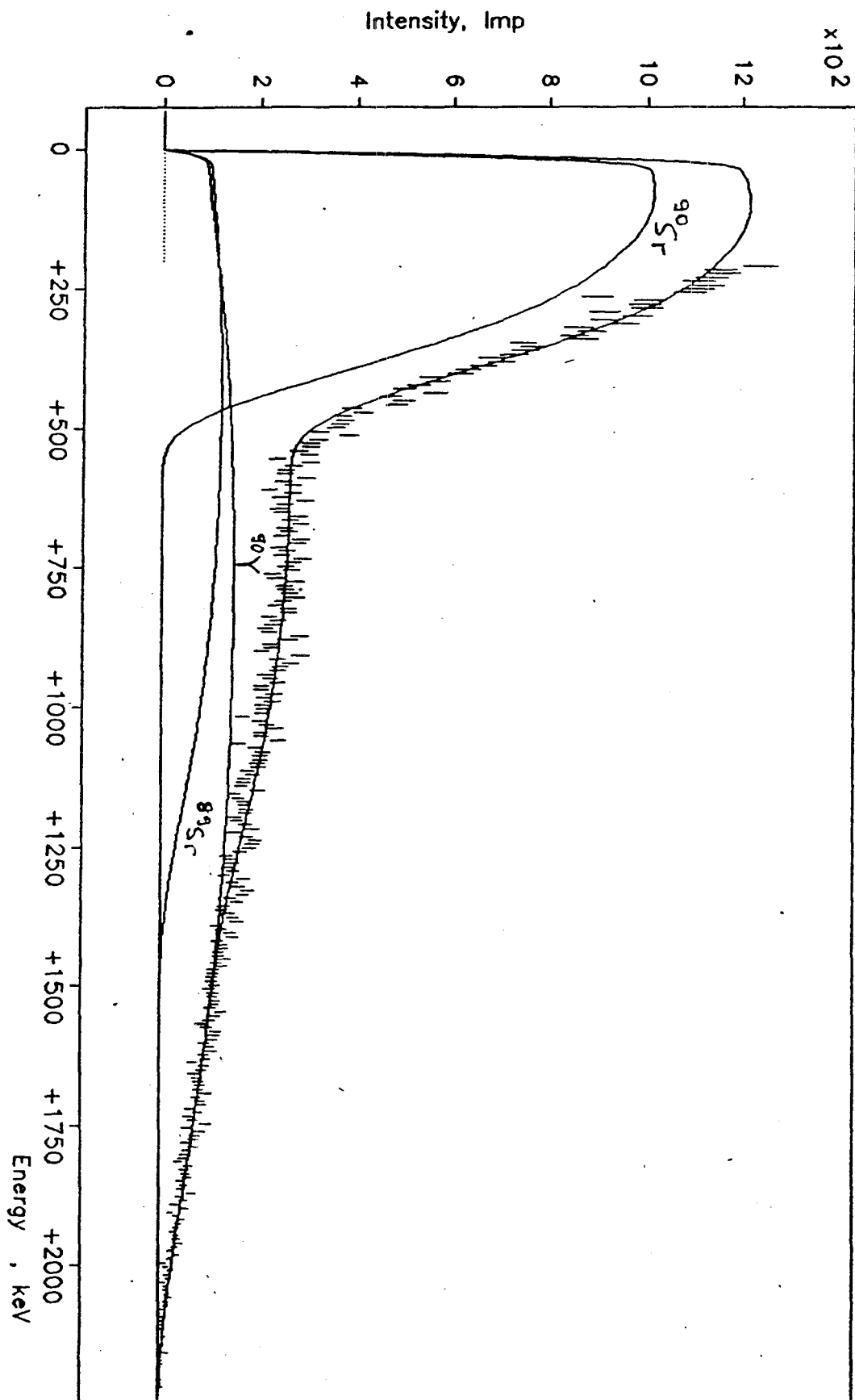
Fig. 6

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Rapid Correlation Assessment of Sr in Fallout by Gamma-Spectroscopy

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Note: The work is nearly completed.

Summary

Fallout samples, air filters and hot particles from the Chernobyl accident have been investigated by beta-analysis for the determination of the Cs/Sr ratio or the absolute Sr activity. Gamma-spectroscopic data from May 1986 gamma-measurements have been utilized for the calculation of the Ba/Sr ratio. The observed ratio in the samples is in close reference with the that ratio in the core of the damaged reactor but. It is concluded that the Ba/Sr reactor core ratio can be used for the estimation of the upper limit of the strontium activity in the fallout immediately after an accident. The Cs/Sr ratio can be used for the estimation of the strontium fallout in the late post-accident period.

Introduction

Most of the radioisotopes in the environment and food in the case of a nuclear accident can be reliably and quickly assayed by gamma-spectroscopy. There is a problem with some important isotopes which are pure beta- or alfa-emitters and which cannot be identified directly by gamma-spectroscopy. The activity of the isotopes of the strontium group ^{89}Sr, $^{90}Sr(Y)$, ^{91}Y after a three year reactor fuel cycle can reach approx.8% of the total in-core activity and one of them $(^{90}Sr(Y))$ is important for the long range health consequences.

In the post accident period the laboratories are faced with two major tasks - an estimation of the radioactivity in the fallout, and estimation of the radioactive contamination in food. The present research is attributed to the first class of tasks - rapid assessment of radioactivity in the fallout.

The purpose of the present investigation is to check the hypothesis that there is a correlation between Ba and Sr and the ratio of both isotopes in the fallout is in close relation with that ratio in the reactor core. Fallout samples, air filters and hot particles from the beginning of May 1986 from several sites in Bulgaria have been investigated by gamma-spectroscopy for Ba [1] in May 1986 and by beta-analysis for Sr [2] in 1987 and 1991.

Experimental

Samples from collected fallout, air filters and hot particles (HP) were investigated in May 1986 by gamma-spectroscopy. The 1986 data are used for the calculation of the $^{140}Ba/^{137}Cs$ ratio for each sample The samples were investigated also by beta-analysis, some of them twice — in 1987 [3] and in 1991. The second measurement increased the accuracy in strontium determination since Cs and Sr are now the two isotopes which radiation is dominant. The results from beta-analysis are used for the calculation of the $^{137}Cs/^{90}Sr$ ratio. The Ba/Sr ratio is obtained after the multiplication of the Ba/Cs and the Cs/Sr ratios. Cesium was chosen as a linking isotope since it is both a gamma-emitter and a beta-emitter with a $\alpha 10\%$ conversion electron line which is a very convenient internal standard. The 624 keV line (7.8%) and the 656 keV line (1.7%) [4] merge into one with total intensity 9.5% when detected with stilbene. The absolute activity of ^{137}Cs is usually known from γ-spectroscopy and the absolute activity of the β-emitters is estimated via the ^{137}Cs conversion line area and also the beta-spectrum area.

The fallout samples are collected on a $0.3\ m^2$ piece of cloth which afterwards is burned to ashes. The air radioactivity over Bulgaria is monitored in 5 stations by measuring the total beta-emission from air filters. The sampling is performed by filtering air through Synpor-2 filters (ϕ=2.5 cm) positioned at 2 m over the surface under a small cover for protection of direct deposition of dust. The air flow rate is 120 m^3 per 24 h and in 1986 at some stations the operators started changing the filters every 6 hours when they observed increased radioactivity (1 May).

Hot particles are also investigated for the Cs/Sr and Ba/Sr ratio since the particulate contamination over most of the

territory of Bulgaria was approximately 13% of the total radioactive deposition [5]. Two types of hot particles were investigated - standard ones which are pieces of the UO_2 fuel and Ba particles which are actually Ba-Sr particles [5]. Most of the hot particles are partially or totally depleted in reference to Cesium and therefore the Ba/Sr ratio was calculated by absolute measurements of Barium and Yttrium-90.

The method for decomposing a complex beta-spectrum into its constituents is described in [2]. The detector is a thin window stilbene crystal, 10 mm thick and with a 9 ÷ 10% energy resolution measured with conversion electron sources ^{137}Cs and ^{207}Bi. Briefly the method can be described as mathematical decomposition of an experimental beta-spectrum of a mixture of beta emitters into beta-spectra with known pre calculated form. The method accounts for distortions due to self-absorption and back-scattering in the sample, to passing through the detector window (and the air), to back-scattering in the detector and to the finite energy resolution of the detector.

The combination with γ-spectroscopy helps essentially in data processing. It is possible to fix the ratios of all $\beta-\gamma$ emitters in reference to a certain isotope, e.g. ^{137}Cs, thus reducing the free parameters in the fitting procedure. That option has been used in the data processing of the samples.

Results

Ba-Sr ratio in *fallout samples, air filters and hot particles.*

The beta-spectra of the measured samples are presented in Fig.1-4.

The beta-spectrum of one of the air filters is shown in Fig.1 and the spectrum of a fallout is shown in Fig.2.

The conversion electron peak in Fig.3 is very weak due to the Cs depletion and in Fig.4, for the Ba-Sr hot particle, it is completely missing. Two beta-spectra of one and the same HP are shown in Fig.4 - a spectrum recorded in 1987 when still traces of ^{90}Sr were observed and a second one recorded in 1991.

The Cs/Sr ratio in some of the standard hot particle was

determined by the described above method. For the Ba-Sr hot particle and for standard particles with very low Cs activity, the absolute Sr activity was determined by relative measurements of the counting rates of the Yttrium tail of the hot particle and a thin spectroscopic Sr source prepared by evaporation of a drop of Sr solution with known activity (Amersham) on a thin plastic substrata.

Some preliminary results from gamma-spectroscopy measurements and from beta-analysis are summarized in Table 1. The ratios of the isotopes of interest in the reactor core are calculated from [6,7].

Discussion

The measured Ba/Sr ratio in air filters and fallout samples is nearly twice higher than the ratio in the reactor core. There are two possible explanations for that observation - the first explanation is that Ba was more in the the radioactive release probably due to the higher volatility of BaO compared to that of SrO. The melting and boiling temperatures of BaO are $1920^\circ C$ and $2000^\circ C$ [8], the melting temperature of SrO is $2430^\circ C$ and the boiling temperature is missing in the cited handbook. The report of the INSAG meeting [9] also confirms a certain Ba enrichment in the release - the ratio of the activities of Ba and Sr in the release is approximately 1.5 times greater than activity ratio in the reactor core. The Ba depletion in the measured up to the moment hot particles backs up the supposition that the temperature during the accident has had a certain effect in the Ba release.

The ratios of Ba and ^{95}Zr in fallout samples and hot particles indicate that fallout samples are enriched in reference to Ba and that Ba is present also in the homogeneous activity [10]. Additional Sr depletion probably has occurred during the transfer since Sr has been observed only in the particulate radioactivity [5].

A second explanation for the observed high Ba/Sr ratio is that the fuel elements of the Chernobyl reactor had been with different burn up. Approximately 75% of the fuel elements were first-load rods and the rest of them were younger ones [11]. It is

quite difficult to calculated the effective reactor campaign which according to burn-up evidence (calculation and measurements) is 480-550 days although some 860 days have elapsed since the start of the reactor operation till the accident [11]. The authors of [11] attribute that discrepancy to the unknown in details history of the reactor - periodic and unplanned shut-downs and operation at lower power. It is possible but quite improbable that over the territory of Bulgaria the fallout deposition had been only from younger fuel rods.

It is a reasonable assumption that for an accident without extreme overheating as in the Chernobyl accident, the Ba-Sr ratio in an eventual release should preserve its core value. If overheating occurs, then Ba enrichment should be expected but in both cases the Ba-Sr core ratio can provide the upper limit for contamination with strontium.

From the measured Ba/Sr ratio and the comparison of the average value of many samples with the in-core ratio, one can draw a preliminary conclusion that in a case of a nuclear reactor accident it is possible to set an upper limit of the strontium environmental contamination if the Ba/Sr reactor core ratio is known. Immediately after a nuclear accident the isotope activities should be estimated very rapidly even with a considerable error - the error can be one or two fold, later more accurate measurements should be performed and hence the knowledge about the upper limit of Sr contamination may prove useful.

The Ba/Sr core ratio can be estimated by handbook data, e.g. [6,7] and some activity ratios for ^{140}Ba, ^{137}Cs, Sr^{89} and Sr^{90} for a thermal type of reactor are plotted in Fig.5. The Ba activity in the fallout is measured by routine gamma-spectroscopic investigation of fallout, air filters, samples of soil, grass etc.

If there is no *a priori* information about the reactor core one can use the $^{137}Cs/^{134}Cs$ or $^{144}Ce/^{141}Ce$ or $^{106}Ru/^{103}Ru$ ratios for the estimation of the duration of the reactor fuel cycle - that ratios, especially the $^{137}Cs/^{134}Cs$ ratio, are used for estimation of the fuel burn-up.

It is not a very simple problem to make an estimation of the core age even for reactors for which the core is partially

refueled each year with approximately 1/3 of fresh fuel rods. For other types of reactors with continuous refueling the problem is even more complex although some estimations are possible. As an alternative we propose a nomogram for calculation of the core Ba-Sr ratio via an isotope ratio, namely ^{144}Ce ^{103}Ce.

The fuel burn-up (and hence the core age) is routinely measured by the ^{134}Cs ^{137}Cs or ^{106}Ru ^{103}Ru or ^{144}Ce ^{103}Ce ratio.

The ^{134}Cs ^{137}Cs depends on the absolute value of the neutron flux Φ, and so it depends essentially on the type of reactor. That ratio cannot provide an universal dependence for the Ba-Sr estimation.

The yield of ^{106}Ru from ^{239}Pu is nearly 11 times greater than the yield from ^{235}U while the yield of ^{103}Ru is not so dependent on the type of the mother isotope. Therefore the ^{106}Ru ^{103}Ru ratio depends on the coefficient of Pu production for the particular type of reactor and on the initial Pu enrichment in the fuel rods. The conclusion is that the ^{106}Ru ^{103}Ru cannot be used for reliable estimation of the core age and hence of the Ba-Sr ratio. The data in the *Appendix* support the above conclusions for the ^{134}Cs ^{137}Cs and ^{106}Ru ^{103}Ru ratios.

The most suitable isotope ratio for the estimation of the reactor core age and for the core Ba-Sr ratio proved the ^{144}Ce ^{103}Ce ratio.

The proposed nomogram - Fig.5.- utilizes the ^{144}Ce ^{103}Ce ratio and although there are some uncertainties (the horizontal error bars) due to different types of reactors and fuel rods with different enrichment, the overall error for 1 - 3 year reactor campaign is 18 - 22% which is an acceptable accuracy.

The smooth curves for the Ba-Sr ratio were calculated according the expression:

$$\frac{^{140}Ba}{^{90}Sr} = R_o \frac{1 - e^{-t/\tau_{Ba}}}{1 - e^{-t/\tau_{Sr}}} (1 + \alpha t) \qquad /1/$$

where τ_{Ba} and τ_{Sr} are the mean lifetimes of Ba and Sr, R_o is the ratio of the equilibrium activities at $t=\infty$ and the factor $(1 + \alpha t)$ account for the Pu production and for the slight change of the Ba yield due to plutonium, $\alpha=0.05$.

The two thick curves are calculated for lines with ±5% deviation from /1/. That interval is enough for the the Ba-Sr ratio for WWER-440, WWER-1000 (both are PWR) and RBMK although there is very little data on the latter one.

The WWER-1000 is comparable as to core characteristics to Western types of reactors and therefore the Ba-Sr ratio for them either coincides or is very close to that in Fig.5. There is an uncertainty as to High temperature gas-graphite reactors (HTGR), graphite ball reactors (Germany) and the channel design reactor with heavy water of the CANDU type (Canada, Romania) and therefore additional study of the properties of the burned fuel of those reactors is necessary. The expected differences cannot deviate significantly from the values in Fig.5.

Conclusion

For more definite conclusions one needs a better and detailed picture of the Ba/Sr ratio for other regions on Europe. Samples of air filters and fallout are welcome to the laboratory. For the purpose of beta-analysis the samples should be relatively thin — up to 20 mg/cm^2– and at least 10 Bq in reference to ^{137}Cs. It is preferable if large area air filters and fallout samples are in ashes. If the sample had been measured during May 1986 by gamma-spectroscopy then it is possible to calculate and measure the Ba/Cs, the Cs/Sr and the Ba/Sr ratio, if no such data is available then only the Cs/Sr ratio can be measured. Additional data about the weight of the sample and other relevant information will be useful. Hot particles are also of interest, especially of the Ba-Sr type.

The Cs/Sr ratio is obtained as an intermediate result. That ratio can be used for the estimation of the Sr activity in the fallout [3] since for most of the countries in Europe the surface contamination with cesium has been studied in details and mapping and average values are published in most of the national reports on the accident.

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Note: Summaries in English of 3,5 and 10 will be supplied on request.

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Figure captions:

Fig.1.

Beta-spectrum of an air-filter (Sofia, 03.05.1986), measured 02.1991. The 624 keV Cs conversion electron peak is observed. The thick line is the theoretical beta-spectrum.

Fig.2.

Beta-spectrum of a fallout sample, (peak Rotev), 03.05.1986), measured 02.1991. The 624 keV Cs conversion electron peak is observed. The thick line is the theoretical beta-spectrum.

Fig.3.

Beta-spectrum of a standard UO_2 hot particle, measured 02.1991. Only traces of the 624 keV Cs conversion electron peak are observed. The thick line is the theoretical beta-spectrum.

Fig.4.

Beta-spectrum of a Ba-Sr particle, measured 10.1987 (a) and 02.1991 (b). No 624 keV Cs conversion electron peak is observed. The thick line is the theoretical beta-spectrum.

Fig.5.

Ratios of Ba, Cs and Sr isotopes for 1, 2 and 3 year reactor operation.

Table 1

ratio	core inventory		air filters			fallout		Hot particles	
	[6]	[7]	Sofia	Burgas		peak	Rotev	standard average of 6	Ba-Sr only one
			May 1986			May 1986			
			3,4,5	1,2,3,4	5	3			
Ba/Cs	18.2	20	5.6	3.7	–	7.9		–	–
Cs/Sr	1.44	1.35	11.4	16.3	9.7	7.1		–	–
Ba/Sr	26.3	32	64.5	60.5	40	56		23	6.8

Appendix

WWER-440 isotope ratios for different fuel rod enrichments – 3.6/2.4/1.6%:

	1 Y	2 Y	3 Y
$^{140}Ba/^{90}Sr$	55.4//61.3	29.6/35.6	21/23
$^{106}Ru/^{103}Ru$	0.148//0.175	0.19/0.26	0.34/0.39
$^{144}Ce/^{141}Ce$	0.5//0.484	0.686/0.64	0.755/0.735
$^{134}Cs/^{137}Cs$	0.57//0.68	0.974/1	1.34/1.484

WWER-1000 isotope ratios for fuel rod enrichment of 4%:

	Y	2 Y	3 Y
$^{140}Ba/^{90}Sr$	58.9	30.6	23.24
$^{106}Ru/^{103}Ru$	0.125	0.242	0.335
$^{144}Ce/^{141}Ce$	0.477	0.6675	0.7391
$^{134}Cs/^{137}Cs$	0.61	1.15	1.6

RBMK isotope ratios for 1100 days reactor campaign:

$^{140}Ba/^{90}Sr$	14
$^{106}Ru/^{103}Ru$	0.57
$^{144}Ce/^{141}Ce$	0.96
$^{134}Cs/^{137}Cs$	1.4

Air Filter. Sofia 3.05.1986 / March 1991

Energy, keV

Counts

×10²

46

Fallout peak Botev 3.05.1986 / April 1991

47

Hot Particle Ba-Sr / April 1991

Hot Particle UO2 / April 1991

Counts

x10¹

Energy, keV

49

51
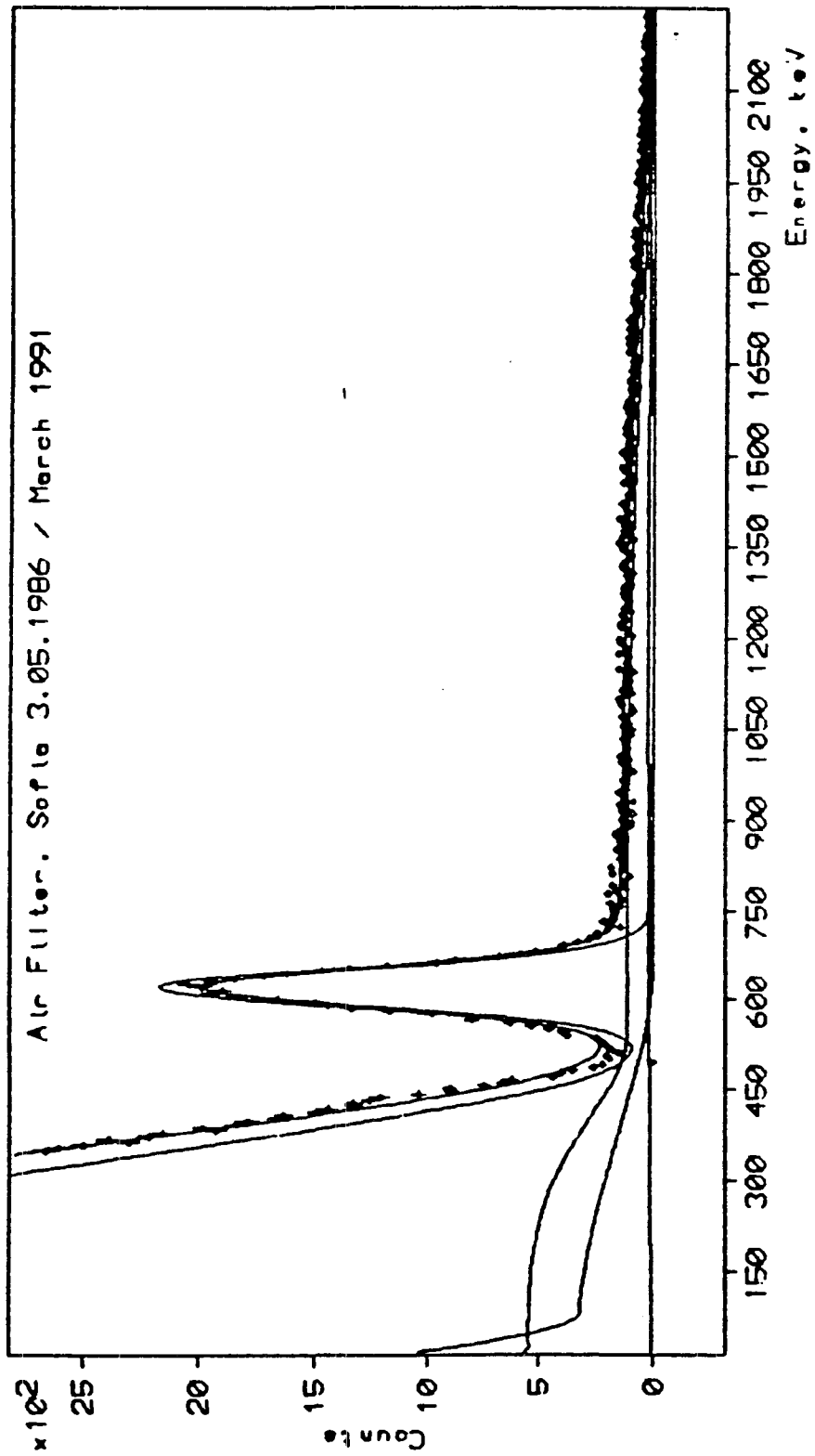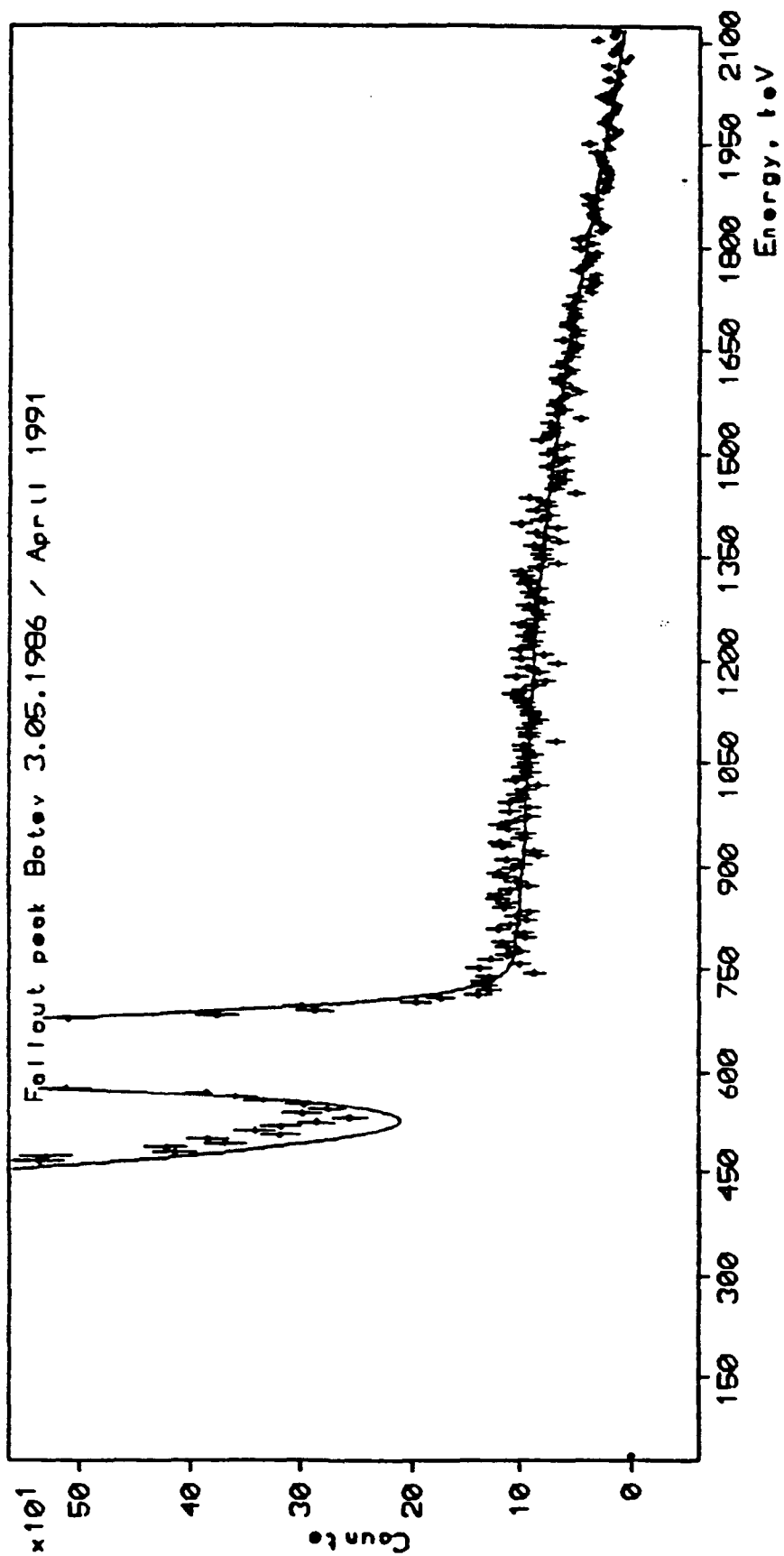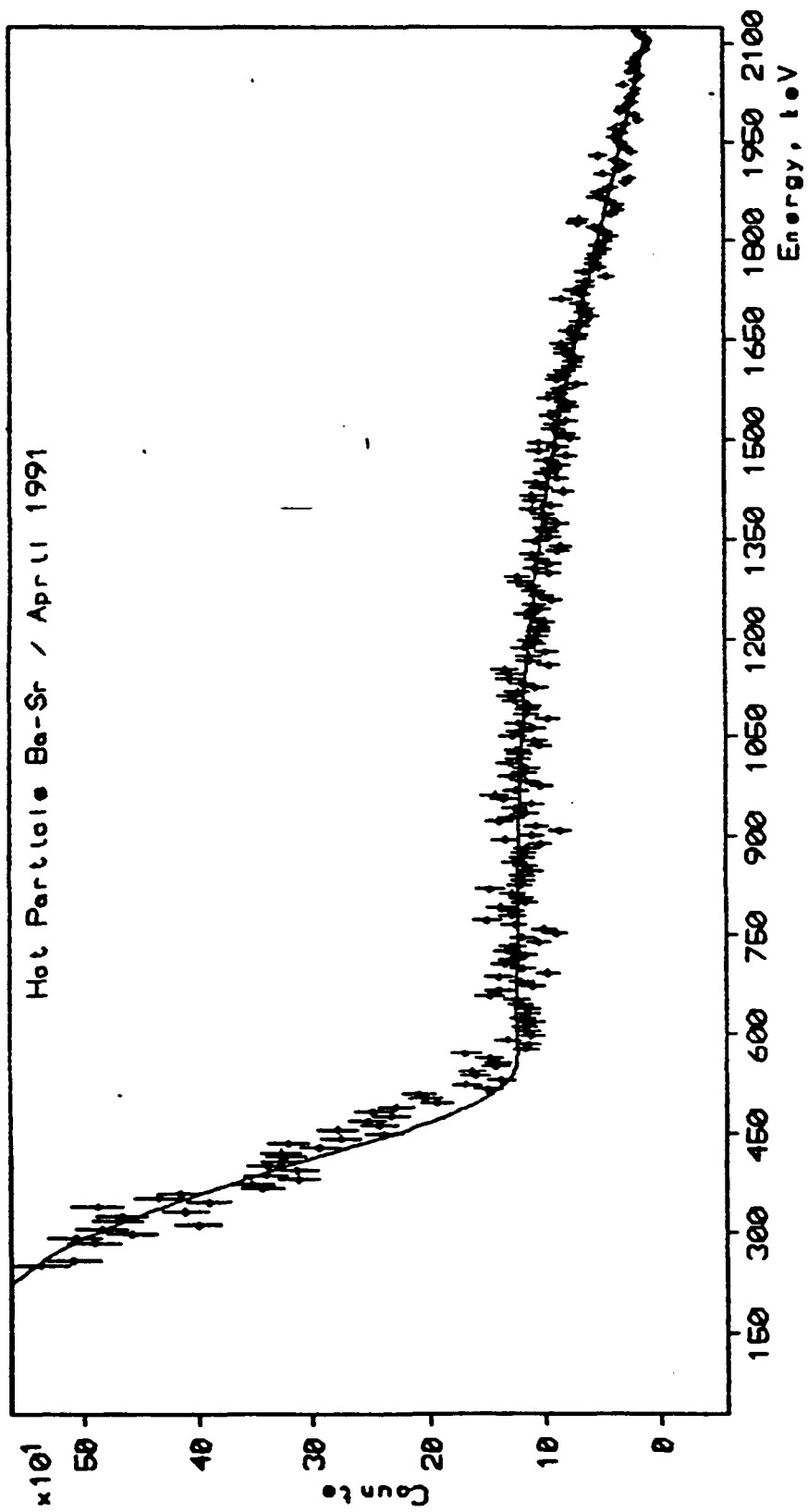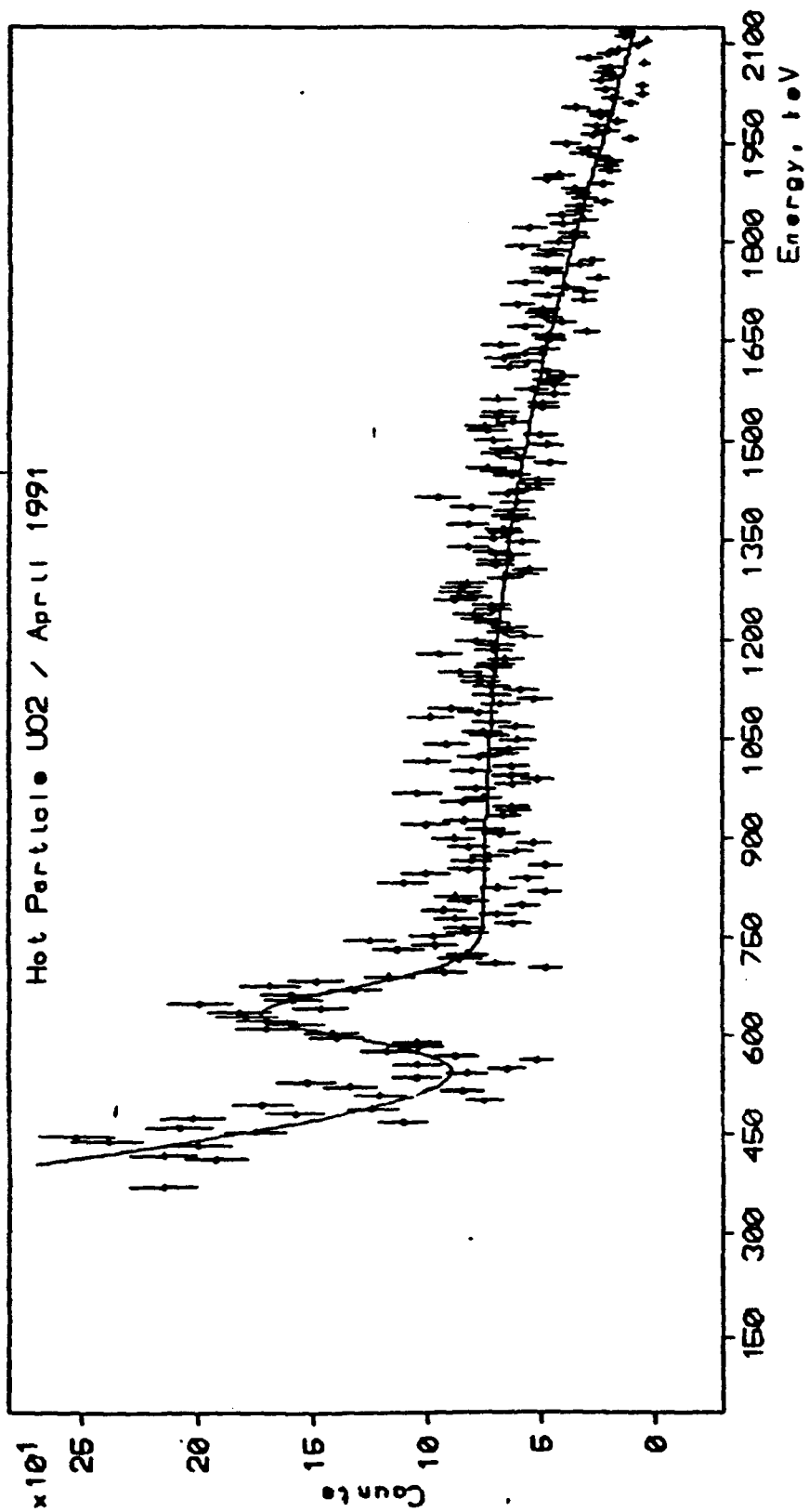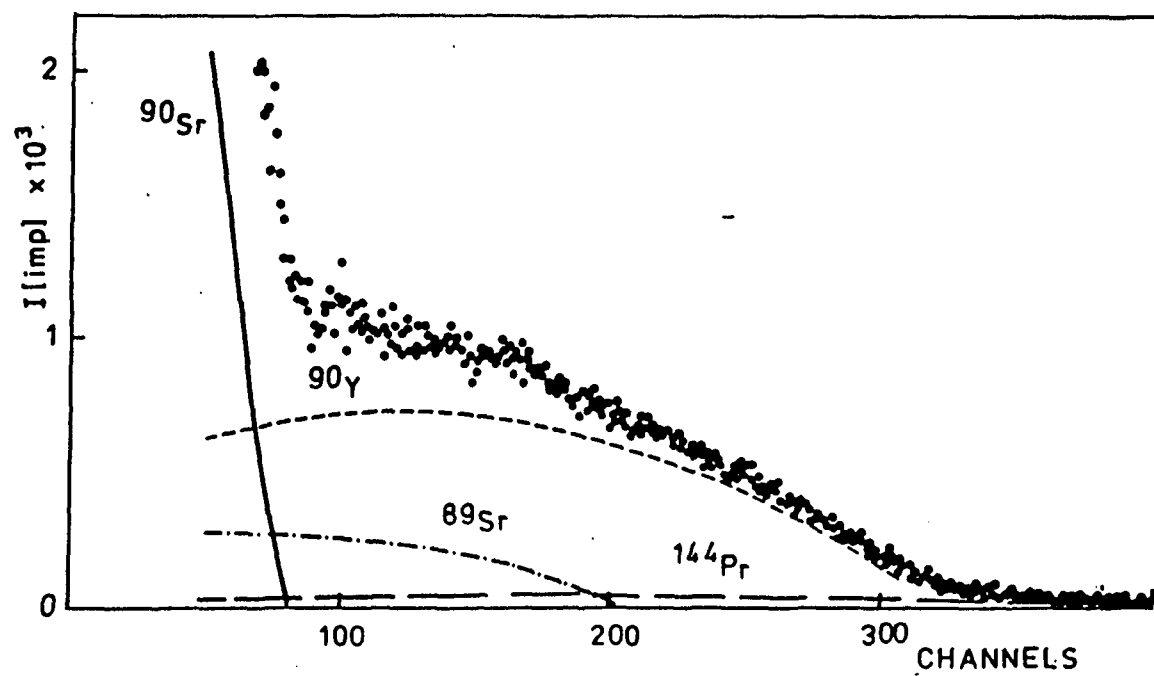
DEVELOPMENT OF RAPID ANALYTICAL METHODS FOR Sr—89/90 , Pu—239 /40 AND Pu— 238 ACTIVITY CONCENTRATIONS IN FALLOUT, SURFACE WATER, PLANTS AND AEROSOL FILTERS BASED ON MODIFIED ROUTINE USED ANALYTICAL PROCEDURES

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1. Introduction

In accordance with the tasks of the National Board for Atomic Safety and Radiation Protection in the system of nuclear environmental surveillance for many years there has existed a traditional spectrum of methods for the determination of radionuclides in environmental media. Due to the existing environmental monitoring programmes

- surveillance of GDR territory with respect to the impact of global radioactive fallout,
- surveillance of the environment of nuclear facilities and nuclear power plants,
- surveillance of the environment of mining facilities

and the involved necessity of analyzing a great number of samples, the following demants were made on the radionuclide determination methods:
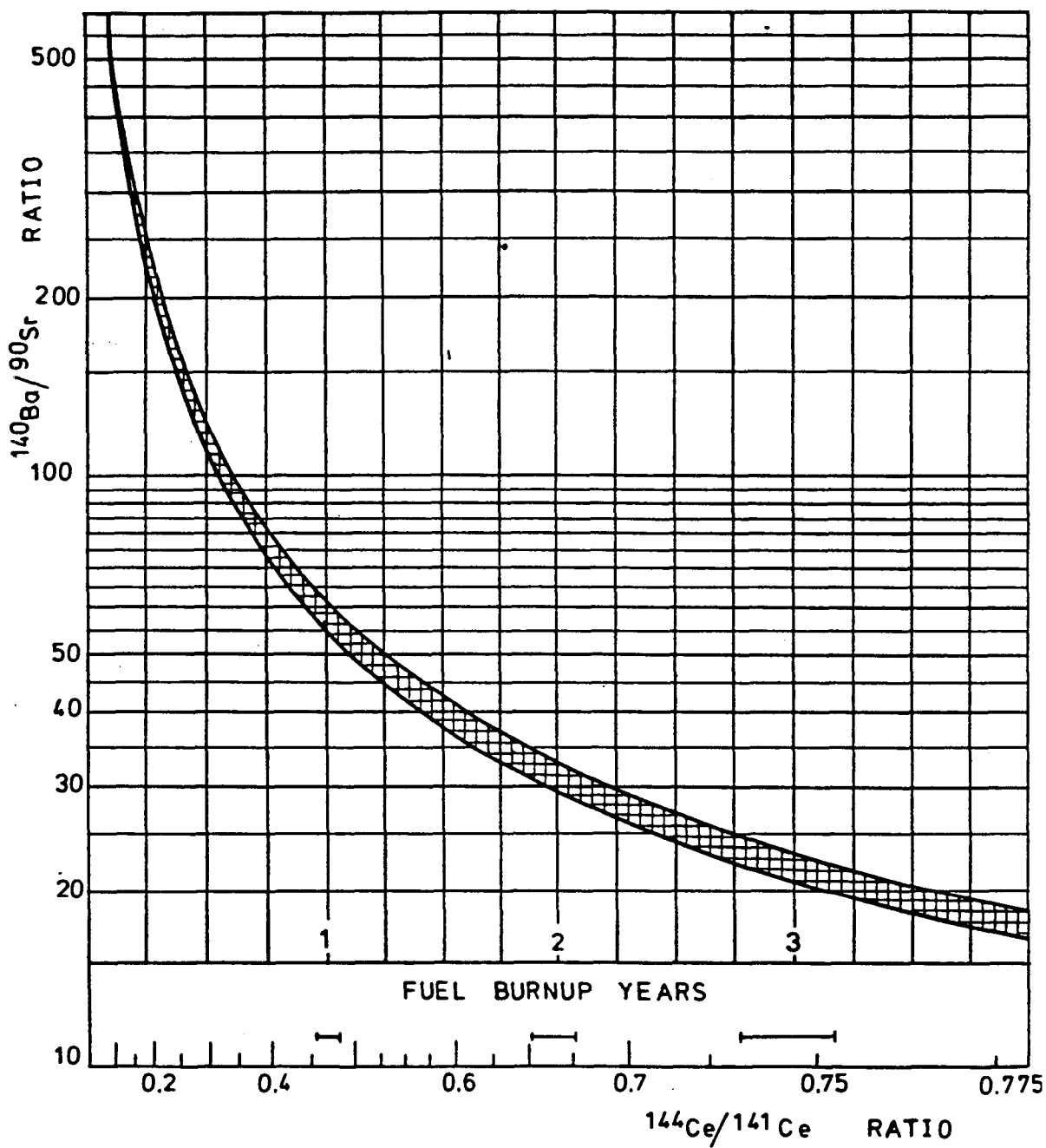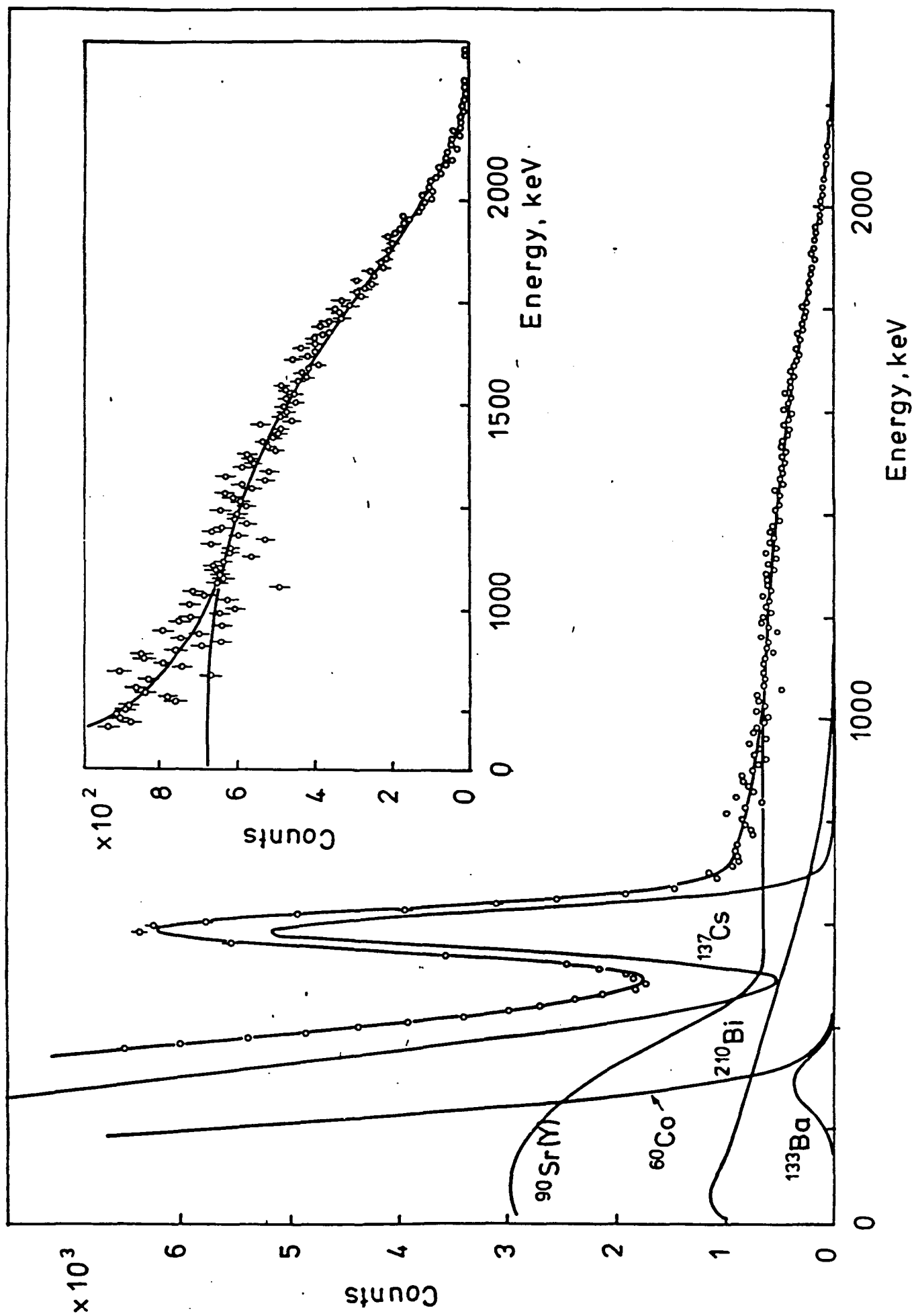
- as few as possible, simple and safe steps of analysis,
- use of effective nuclide selective activity measuring methods
- parallel processing of several samples,
- possible determination of several individual nuclides by one analytic approach,
- selective separation methods to produce pure element-specific measuring samples, due to the necessary use of gross activity measurements,
- using of same principal schemes of analysis for different sample media excluding methods of decomposition.

2. Survey of radiochemical analytic procedures and measuring methods

Table 1 gives a survey of the greater part of radionuclides to be determined in routine operation by radiochemical analytic procedures, the preparation and measuring procedure used and the detection limits attained. In this respect, in nearly all cases the following principal scheme applies:

- sample preparation (crushing, drying, dry or wet ashing),
- sample decomposition (in most cases total decomposition) for ash quantities between 1 g and 10 g,
- group separation for separating mass elements and interferring radionuclides,

- element-specific separation and preparation,
- measurement of activity.

Figure 1 gives a survey of the measuring methods and detection limits used in routine operation, both for direct gamma-spectrometric measurements and for alpha- and beta-activity determination.
So far, priorities in the development of methods have mainly been improvement of details of existing and routine used methods with the aim of

- eliminating particularly time-consuming and difficult steps in the analytical run (e.g. acceleration of decomposition methods),
- eliminating hazardous steps in the analytical run (e.g. work with fuming nitric acid),
- attaining a better reproducibility of the results of analysis,
- adaption of analytical method to changed radionuclid concentration levels in samples and use of more effective measuring devices.

3.   Work scheduled on the context of CRP

The National Board for Atomic Safety and Radiation Protection concluded the research contract No. 5633/RB with the IAEA which commenced on 1 August 1989.

It is the aim of the work scheduled to develop rapid methods allowing to determine Sr-89/90 and Pu nuclides in different environmental media within 24 hours modifying routine used analytical methods. The sample media in first place important in a nuclear accident such as fallout, rain, surface water, air filters and plants have been selected as sample media. Here, the problem consists in that one cannot necessarily assume high activity concentrations in these media because the radionuclide concentrations strongly depends on the type of accident, the operation time of a reactor and meteorological conditions. Therefore, sample preparation and sample decomposition involved has to be paid the same attention as to the separation of interferring fission products.

The tasks set comprise the following priorities which are subjects of investigation for the next years:

- quantitative enrichment of Sr-89/90 and of Pu radionuclides from solid samples; investigation of nuclide-specific enrichement,
- rapid and complete decomposition of the residues or ashes resulting from the enrichment procedure,
- quantitative separation of Sr-89/90 from Ca and interferring fission products
- quantitative separation of Pu nuclides from matrix-elements, uranium and thorium,
- optimization of the electrolytic production of measuring

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samples for alpha-activity determination with respect to a
minimum of time consumption, a maximum yield and a maximum
spectrometric resolution,
- development of a reliable measurement method for Sr-89/90
based on beta-anticoincidence counters using absorption
filters.

3.1. Sample preparation

Sample preparation hold a key rank in the development of analy-
tical methods because, as early as here, crucial limiting condi-
tions are set up for further processing of samples.

In accordance with the tasks and the detection limits of the
activity measuring devices, the following maximum sample amounts
can be assumed for the sample media considered:

- fallout, rain, surface water   1 - 5 l
- air filters (cellulose)   1 - 10 pieces
- air filters (cellulose nitrate,   1 - 2 pieces
              -acetate)
- plants (fodder, green vegetables)   0.5 kg (fresh mass)

With respect to the uniformity also of sample preparation methods
we start from the fact that the most efficient method also for
rapid methods to determine Sr-89/90 and Pu radionuclides is dry
ashing. Therefore, for liquid samples, preceding evaporation is
necessary.

From practical experience and preliminary tests made we can start
from the fact that the liquid samples will be evaporated to dry-
ness after about 1 hour, using large area evaporating dishes with
IR-radiatores, at an evaporation rate of 1-2 l/h. For the ashing
of the evaporation residue and the filter paper base, not more
than 1 hour is required. In contrast, a preparation time of not
more then 1 hour can be estimated for coprecipitation from the
same sample volume, including necessary heating and filtering.
Here a disadvantage, however, is the higher personal expenditure.

Cellulose air filters or such of cellulose nitrate or -acetate
take maximally 1 hour for ashing. A complete wet ashing of such
samples requires at least the same time. The advantage that,
afterwards, the sample is already in solution and can thus be
further processed is compensated by the higher personal expendi-
ture.

For plant samples dry ashing should be the only possible method,
directly starting with the fresh sample. An extensive mechanical
preparation of samples as in routine programmes, e.g. chopping of
fodder plants, crushing grass and green vegetables, is not advi-
sable in accidental situations due to their mainly surface conta-
mination and, therefore, activity losses and cross contaminations
will negatively affect the results of analysis. It can be estima-
ted that the time consumption necessary will not exceed 3 hours,

even for fodder plants having hard or big stalks (fodder rye, maize).

Since the radionuclides Sr-89/90 and the Pu nuclides are not highly volatile, the ashing temperature should not play any particular role at first sight. But this applies only to Sr nuclides. For Pu nuclides a regulation of ashing temperature is necessary, allowing for the following analytic procedure. The plutonium determined in environmental surveillance in the past had its origin mainly in nuclear weapon tests in the atmosphere. The plutonium oxide produced at the high temperatures involved in such tests is, to the present knowledge, a relatively freely soluble mixed oxide of the rough composition Pu_2O_3. This mixed oxide is produced when sparingly soluble Pu_2O_2 is heated beyond its melting point (Fp = 2,400 °C). In sample preparation, particularly at ashing temperatures of between 600 and 1,000 °C, the freely soluble mixed oxide can be converted to sparingly soluble Pu_2O_2, so that, for example, acid extracts do not yield to quantitative resolution of plutonium. Although it cannot be predicted with certainty to what thermal stresses released Pu particles were exposed and in what chemical compositions they are present, we should start from a similar behaviour, so that the ashing temperature should not exceed 600 °C.

To clear up the above-mentioned problems, the following working plan is proposed for the first year of the CRP contract:

- Checking the possibility of rapid ashing of fresh plant samples without expenditive mechanical pretreatment of samples. Taking of mass/time diagrams for 0.5 kg plant material (grass, lettuce, fodder rye) at 600 °C, determining the carbon content, checking the possibilities of complete ashing with addition of oxidants.
- Systematic investigation of maximum ashing temperature for plutonium on the basis of air filter spiked with Pu-239. Determination of Pu yield dependent from ashing temperature.

Preliminary results are presented in Table 2. Using various kinds of plants (red cabbage, head lettuce, spinach, grass and alfalfa), test of rapid drying at 300 °C and subsequent ashing at 600 °C were made. The results show that ashes are obtained within 1.5 hours.

3.2. Sample decomposition

What importance is attached to the complete detection of radionuclides in sample decomposition is shown, for the example of plutonium, by the great number of principally different or only partly varied decomposition and extraction methods. Mainly acid extractions and various melting and complete decompositions being applied. The fluoride-pyrosulfate melts or complete $HF/HNO_3/HClO_4$ decompositions of samples used, among others, are of course highly efficient decomposition methods but can be mostly used only for small sample amounts and are, in almost all cases, highly

time-consuming. In comparision, the acid extraction of ashes of environmental samples allows the use of greater sample amounts and requires only comparatively shorter processing times, but it has been often proved that, also depending on sample preparation, the plutonium contained in the sample was not quantitatively detected.

Under the given conditions ash amounts of up to 20 g are to be expected. These sample amounts can still be processed effectively by pressure decomposition with HNO_3. A complete decomposition of the sample ash can be obtained within 3 hours, at least quantitatively detect the radionuclides of interest.

The priority of work to be done in this field in the first year of CRP contract will comprise the following subjects:

- Time-optimized decomposition of air filter ashes and of ashes of evaporation residues of liquid samples, with the aim of a decomposition time of < 2 hours.
- Time-optimized decomposition of plant ashes (about 5 g per batch) with minimum use of HF.

First results show that a sample of 5 gramms of plant ash can be complete decomposited with a mixture of 30 ml HNO_3 and 5 ml HF in 3 hours using a pressure decomposition device. The whole decomposition process is more time consuming, because of the necessity of heating and cooling the device and of fuming the sample with a small amount of H_2SO_4 to displace HF. Further it is necessary to find the minimal amount of HF addition and a more efficient method of displacing or masking the HF residue.

3.3. Radiochemical separation and isolation

For the production of nuclide-pure measuring samples efficient separation methods are required both for the fission products occurring in a nuclear accident and for the mass elements contained in the sample that have a considerable effect on measuring conditions and measuring efficiency. For Sr-89/90 determinations, therefore, efficient separations of the other fission products to be expected are necessary because, here, a gross beta-activity measurement is used. Experiences show that a part of the interfering fission products, which can, above all, occur in great excess, are already volatile under the proposed ashing conditions and therfore do not play any decisive role in the sample material to be analyzed. Fission products like Ba/La-140 are separated at a sufficient separation step by $BaCrO_4$ precipitation.More problematic is the effect of the Ca content of the sample on the measuring sample because there may be disproportionately great measuring sample masses and, thus, technical problems may occur both in the measuring process itself (minimum distance between measuring sample and detector) and the greater area mass of the measuring sample may unjustifiably reduce measuring efficiency by absorption.

For Pu analyses, mainly an effective separation from other trans-

uranics and from the naturally occuring uranium isotopes is necessary. Otherwise, for example, accurate yield determinations using Pu-242 as a tracer will not be possible due to U-234 superposition.

3.3.1. Ca/Sr separation

Due to the chemical similarities of Sr and Ca, separation methods for these elements have been of great interest for long.

The Sr separation method still widespread today, by precipitation with fuming nitric acid, is not practicable for safety reasons in routine determinations, especially in case of limited time.

The separation of Ca and Sr by using the fact that $SrNO_3$ is sparingly soluble in anhydrous butanol cannot be applied for a rapid analyse due to the great expenditure in time (multiple butanol distillation).

Separation by complexing Ca with EDTA and cation exchange of Sr on a strong acid cation exchanger is not suitable either for rapid routine analyses, due to the small flow rate and the strong dependence of comlexation on pH within a very narrow range.

A practicable path requiring both small time expenditure and very good separation up to the 1,000-fold excess of Ca, is considered the extraction by crown ethers. Althrough these compounds are relatively expensive, their use can be justified by the fact that, first, they are used for a limited number of samples and only a relatively short period and, second, they are used in low concentrations, improving the price/performance relationship again.

Extraction by crown ethers is a selective element-specific separation method that has so far been investigated mainly for alkali and alkaline earth elements. The analytic importance of crown ethers lies in that they form complexes only with such cations, the ionic radii of which are adequat to the crown ether cavity diameter. In this way 1:1 complexes are formed via ion-dipole interactions. In literature, two crown ethers appear to be particularly suitable for Ca/Sr separation, namely the dibenzo-18-crown-6-ether and the dicyclohexyl-18-crown-6-ether. Especially for the later compount literature claims extraction yields of > 90 % for Sr, at an up to 1,000-fold Ca excess. A Sr/Ba separation using these crown ethers has not been successfully described in literature, so that here, classic precipitation methods have to be applied.

For the work to be done in the context of CPR for the first year, there will be the following priority

- Check and comparision of the separation behaviour of DB-18-crown-6 and DC-18-crown-6 from model solutions.

Derived from the results obtained, are the tasks for the follo-

wing years:

- Ch..ck of the separation behaviour of Ca/Sr model solutions
  and fission product solutions to better characterize the
  selectivity in carrier-free work.
- Check of the separation behaviour by simulating a sample
  matrix or using model samples and adaption cf the proposed
  separation scheme (Figure 2).

For the extraction of Sr in the presence of Ca, two crown ethers
presently available to us were tested. In first tests it could be
established that the system DC-10-crown-6/chloroform, extraction
yields of maximally 93 % have so far been attained, at a 500-
fold excess of Ca. When optimizing the working parameters, better
results can be obtained.

3.3.2. Pu separation

To separate the plutonium of the sample brought into solution
from the main components of sample material, chiefly three basic
variants are applied:

- Selective coprecipitation with sparingly soluble compounds
  of an element added or already present in excess in the
  sample.
- Adsorption or ion-exchange methods.
- Extraction methods.

Coprecipitations are the oldest methods applied for Pu separa-
tion. Their advantage of relatively simple and not very time-con-
suming performance is neutralized by the disadvantage that the
yield of this separation rarely ever exceeds 85 % and that, with
the inactive precipitate, one again obtains in the sample an
element to be separated and, moreover, in a sparingly soluble
form.

Adsorption and ion-exchange methods have the disadvantage of
frequently very small flow rates of exchanger columns that cannot
be completely compensated either by using several columns in
parallel. If these ion-exchangers could be effectively used in a
batch procedure a decisive reduction of time consumption would be
possible.

As before, extraction methods require the smallest time consump-
tion, even if waiting times for phase separation have to be ex-
pected. Here, the problem is, however, that plutonium usually has
to be present in an uniform oxidation stage in order to obtain
acceptable yields and that interferences by other elements can
easily occur.

The method so far used in the Board is based on the extraction by
Alamine-336 in xylene. Re-extraction is performed with a HCl/HF
mixture but it has the disadvantage that complete separation of
plutonium and uranium is not attained, so that yield determi-
nations using Pu-242 tracer are interferred by the U-234 fraction

and thus inaccurac. have to be accepted.

Therefore, for work in the CRP context, the following priority subjects are treated in the first year:

- Investigation o. the extraction/re-extraction run in the systcm Alami.2-336/xylene to enhance the selectiv.ty of the procedure. So, it should be tested to vary the re-extractant mixture HCl /HF and to charge the system from nitric media to hydrochloric media to obtain a better uranium/plutonium separation.
- Investigation of the applicability of Pu separation by means of ion exchangers (DOWEX 1) in the batch procedure to reduce processing time.

3.4. Producing measuring samples

Prerequisite to activity determination of Pu nuclides are measuring samples of minimum area mass and smallest possible diameter. Out of the preparation methods used like coprecipitations in submicrogram range, evaporation, vacuum sublimation and electro-lytic deposition, only the last method has prevailed to great extent. Principally, plutonium is electrolytically deposited as mixed hydroxide. Also in acid medium a thin hydroxide layer is cathodically produced, which is of course almost immediately destroyed when current is switched off. For this reason it is necessary to make the electrolyte alkaline before finishing elec-trolysis in order to avoid a dissolution of the Pu sample.

Mainly ammonium sulfate/sulfuric acid, ammonium chloride/hydro-cloric acid and ammonium oxalate/hydrocloric acid as electrolytic system are used. Quantity and quality of electrodeposition is depending on the electrolyte system, current strength and elec-trolysis time.

For work in the CRP context in the first year, the following task is to be met:

- Extended tests of the HN_4Cl/HCl electrolyte with the aim to short time of electrolytic deposition quoted from the literature.
- Tests of the $(NH_4)_2SO_4/H_2SO_4$ electrolyte to short time of electrolytic deposition substantial.

The work, done in the small time since starting the CRP showes the following results:

- The routine used electrolytic deposition from $(NH_4)_2SO_4/H_2SO_4$ electrolyte gives a mean yield of 94 % in an electo-lysis time of 90 minutes with an energy resolution of about 50 keV for matrix free standard solutions.
- Published results show that complete electrolytic deposi-tion of plutonium from NH_4Cl/HCl electrolyte was obtained within 20 to 40 minutes. Figure 3 shows the electrolytic deposition yield for a pure NH_4Cl electrolyte depending on

current and time. The bes. results were obtained for a current of 1.3 A and a time of 60 minutes. Figure 4 shows the electrolytic deposition yield for a NH_4Cl/HCl system. Here similarly results were obtained for the same current and a time of 40 minutes.

- The particularly high fluctuations within the groups of values are based on the small number of experiments and the counting error of 5 - 7 %. It is impossible to increase the current significant higher than 1.3 A, because of the possible beginning of electrolyte desintegration.
- The electrolytic cell allows an deposition diameter of 0.9 cm; the distance between the electrodes is about 7 mm. For the cathode steel discs are used. The energy resolution for both measuring series was 30 - 50 keV.

Measuring samples for activity determination of Sr-89/90 are exclusive prepared by precipitation of Sr_2CO_3.

3.5. Activity determination

The main work is directed to a rapid activity determination the beta-emitters Sr-89 and Sr-90 both present after producing the measuring sample by precipitation of $SrCO_3$. Here, the absorber method is to be applied, i.e. measurement of the activity of both radionuclides and the measurement of Sr-89 using an absorber (area mass 130 mg/cm^2). Then the individual activities can be determined by the ratio of individual pulse rates.

Therefore, the following tasks are to be met:

- Determination of the calibration parameters for the Sr-89/90 measurement.
- Investigation of the possible effect of aftergrowing Y-90 on the Sr-89/90 determination.

At present work on determination of the efficiency for Sr-89 activity measurement with and without absorber and for Sr-90 activity measurement without absorber depending on area mass is being performed for two detector sizes (diameter of counter window 25 mm and 50 mm, respectively).

For activity measurements of Pu samples an alpha-spectrometric system based on SB-Si detectors (area 400 mm^2) is used.

4. Summary

The presented procedure in meeting the tasks provided in the CRP is oriented towards

- the laboratory-technical equipment presently available to the Board,
- the methodical bases and experiences already existing in the Board and
- the present state of knowledge of international develop-

ments.

This is why we consider the modes of procedure presented here not
a rigid skeleton but we are striving to consider and utilize
recent insights and developments even if not yet contained as
such in the working plan.

Table 1: Separation and preparation methods used for individual radionuclide determinations

Radio-nuclides	Method of Separation and Determination	Kind of Samples	Lower Detection Limit
H-3	Electrolytical enrichment/LSC	water	0.2 Bq/l
C-14	$BaCO_3$-precipitation/LSC	air	1 Bq/m^3
Sr-89	$SrCO_3$-precipitation/ß-counting/sub-straction of Sr-90 activity	water plant soil	5 mBq/l 0.2 mBq/g 0.05 mBq/g
Sr-90	Y-90-extraction with HDEHP/$Y_2(COO)_3$-precipitation/ß-counting	water plant soil	0.5 mBq/l 0.2 mBq/l 0.04 mBq/g
I-131	AgI-precipitation/т-spectrometry	water	5 mBq/l
Cs-137	Ion exchange with AMP/Cs tCl_6-precipitation/ß-counting	water plant soil	0.1 mBq/l 0.2 mBq/g 0.5 mBq/g
Pb-210/ Bi-210/ Po-210	Spontaneous electrolytical deposition on Ni-discs/ß-counting/α-counting	water plant soil	10 mBq/l 1 mBq/g 10 mBq/g
Ra-224	Ra-coprecipitation with $BaSO_4$/α-counting/Rn-222-emanation/α-counting/substraction of Ra-226-activity	water plant soil	10 mBq/l 0.1 mBq/g 2 mBq/g
Ra-226	Ra-coprecipitation with $BaSO_4$/Rn-222-emanation/α-counting	water plant soil	10 mBq/l 0.1 mBq/g 2 mBq/g
Ra-228	Ra-coprecipitation with $BaSO_4$/Ac-228-extraction with DTPA/Ac-coprecipitation with $Ce_x(COO)_3$/ß-counting	water	20 mBq/l
Th-230, Th-232	Th-coprecipitation with Ca(COO)/Th-extraction with ALIQUAT/electrolytic deposition/α-spectrometry/Th-229-tracer	water plant soil	1 mBq/l 0.01 mBq/g 0.5 mBq/g
Uranium	Extraction with ethyl acetate/Na_2CO_3-K_2CO_3-NaF-fusion/fluorimetric determination	water plant soil	5 µg/l 0.01 µg/g 1 µg/g
U-234, U-235, U-238	Ion exchange on DOWEX 1x8/electrolytical deposition/α-spectrometry/U-232-tracer	water plant soil	0.6 mBq/l 2 µBq/g 15 µBq/g
Pu-238, Pu-239/40	Extraction with ALAMINE/electrolytical deposition/α-spectrometry/Pu-242-tracer	water plant soil	0.6 mBq/l 2 µBq/g 15 µBq/g

Table II: Results of ashing tests

Kind of Sample	Fresh Mass [g]	Drying Time [min.]	Loss of Mass [%]	Ashing Time [min.]	Ash Mass [g]
red cabbage	500	40	87	60	3.47
head lettuce	500	40	70	60	8.09
spinach	500	40	64	60	11.88
grass	500	40	59	60	14.03
alfalfa	500	40	51	60	12.33

Figure 1: Measuring methods used to det ~mine radionuclide concentrations

┌───┐
│   S A M P L E   P R O C E S S I N G   A N D   E N R I C H M E N T   │
└───┘
                                       ↓
        ┌──┐
        │   S E P A R A T I O N   A N D   P R E P A R A T I O N   │
        └──┘

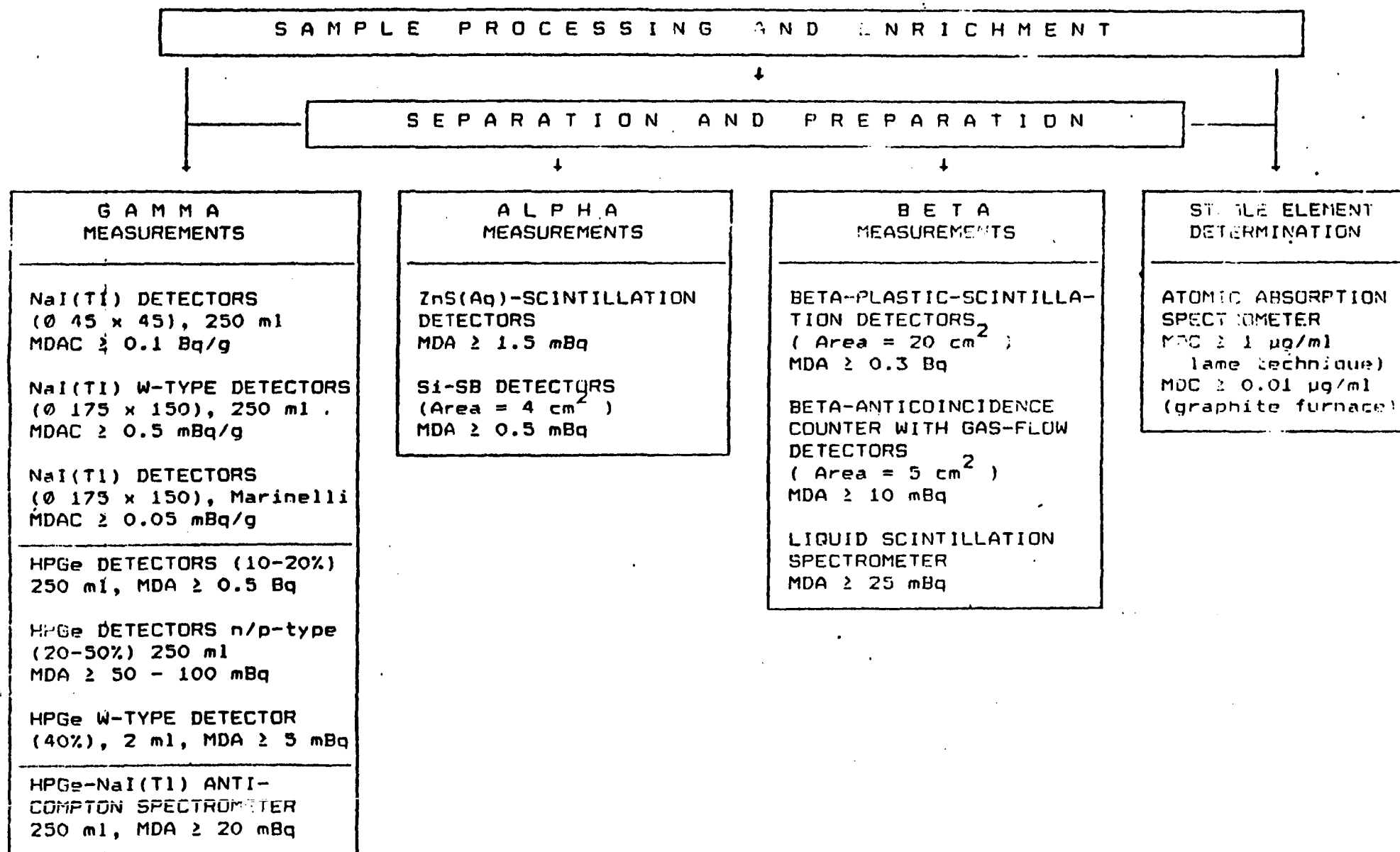| GAMMA MEASUREMENTS	ALPHA MEASUREMENTS	BETA MEASUREMENTS	STABLE ELEMENT DETERMINATION
NaI(Tl) DETECTORS (Ø 45 x 45), 250 ml MDAC ≥ 0.1 Bq/g NaI(Tl) W-TYPE DETECTORS (Ø 175 x 150), 250 ml . MDAC ≥ 0.5 mBq/g NaI(Tl) DETECTORS (Ø 175 x 150), Marinelli MDAC ≥ 0.05 mBq/g	ZnS(Ag)-SCINTILLATION DETECTORS MDA ≥ 1.5 mBq Si-SB DETECTORS (Area = 4 cm^2) MDA ≥ 0.5 mBq	BETA-PLASTIC-SCINTILLA-TION DETECTORS (Area = 20 cm^2) MDA ≥ 0.3 Bq BETA-ANTICOINCIDENCE COUNTER WITH GAS-FLOW DETECTORS (Area = 5 cm^2) MDA ≥ 10 mBq LIQUID SCINTILLATION SPECTROMETER MDA ≥ 25 mBq	ATOMIC ABSORPTION SPECTROMETER MDC ≥ 1 µg/ml lame technique) MDC ≥ 0.01 µg/ml (graphite furnace)
HPGe DETECTORS (10-20%) 250 ml, MDA ≥ 0.5 Bq			
HPGe DETECTORS n/p-type (20-50%) 250 ml MDA ≥ 50 - 100 mBq			
HPGe W-TYPE DETECTOR (40%), 2 ml, MDA ≥ 5 mBq			
HPGe-NaI(Tl) ANTI-COMPTON SPECTROMETER 250 ml, MDA ≥ 20 mBq			

Figure 2: Proposed Separation Scheme for Sr-89/90 Determination
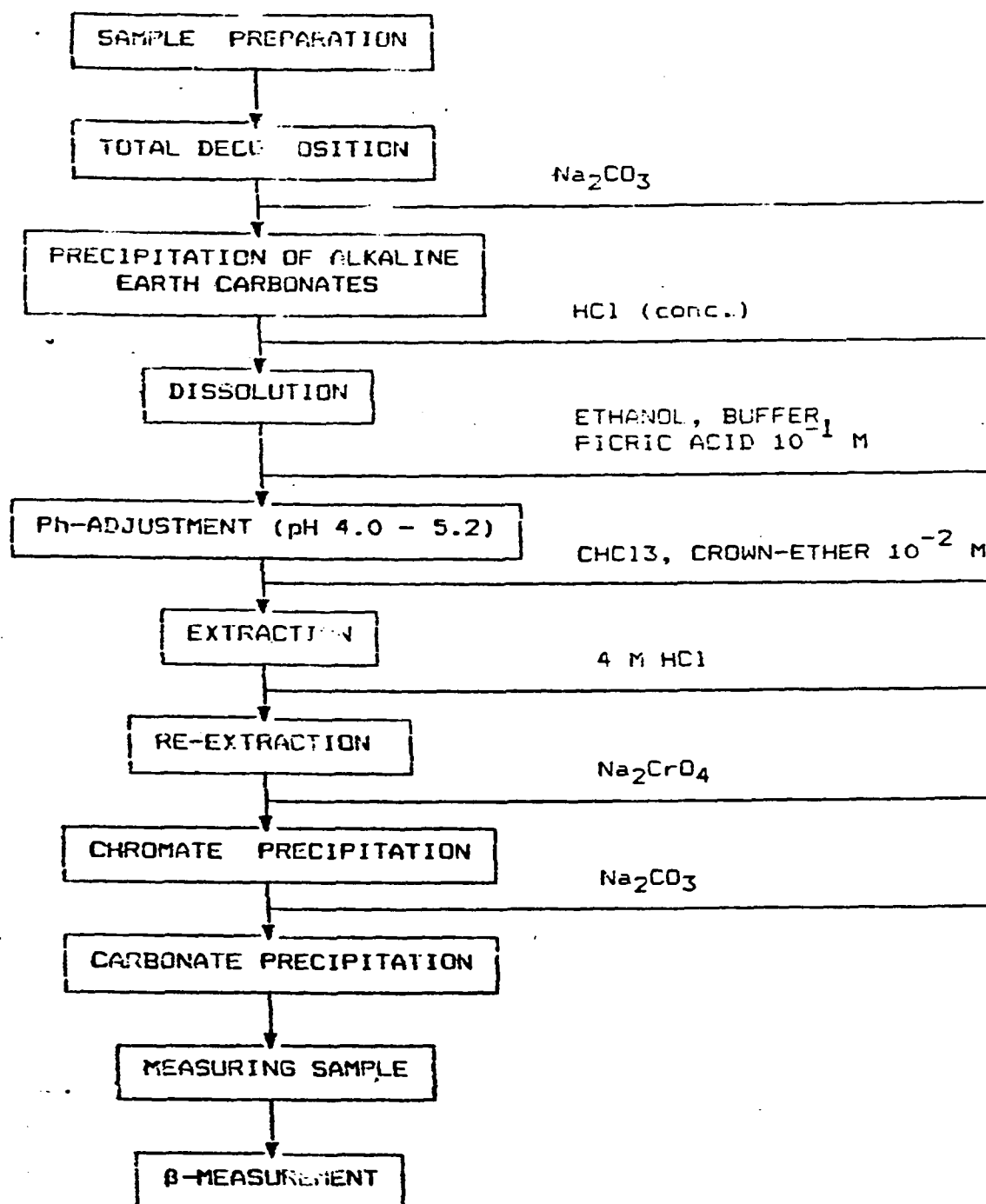
Figure 3: Optimization of electrolytic deposition of Pu-239 free ... electrolyte ... (0.1 M ... 01)
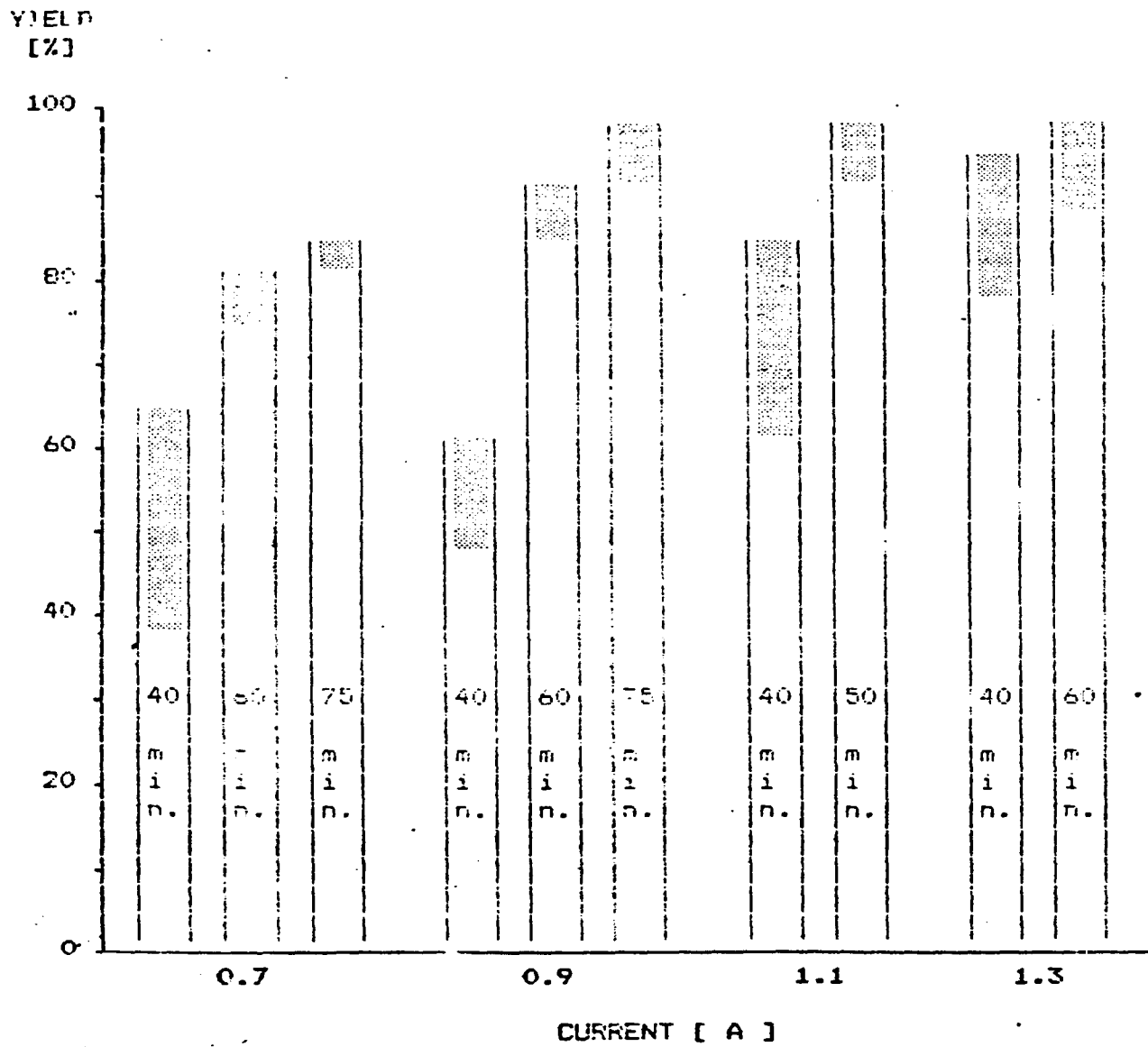
CURRENT [A]

Fig. 4: (figure — bar chart of YIELD [%] vs CURRENT [A])
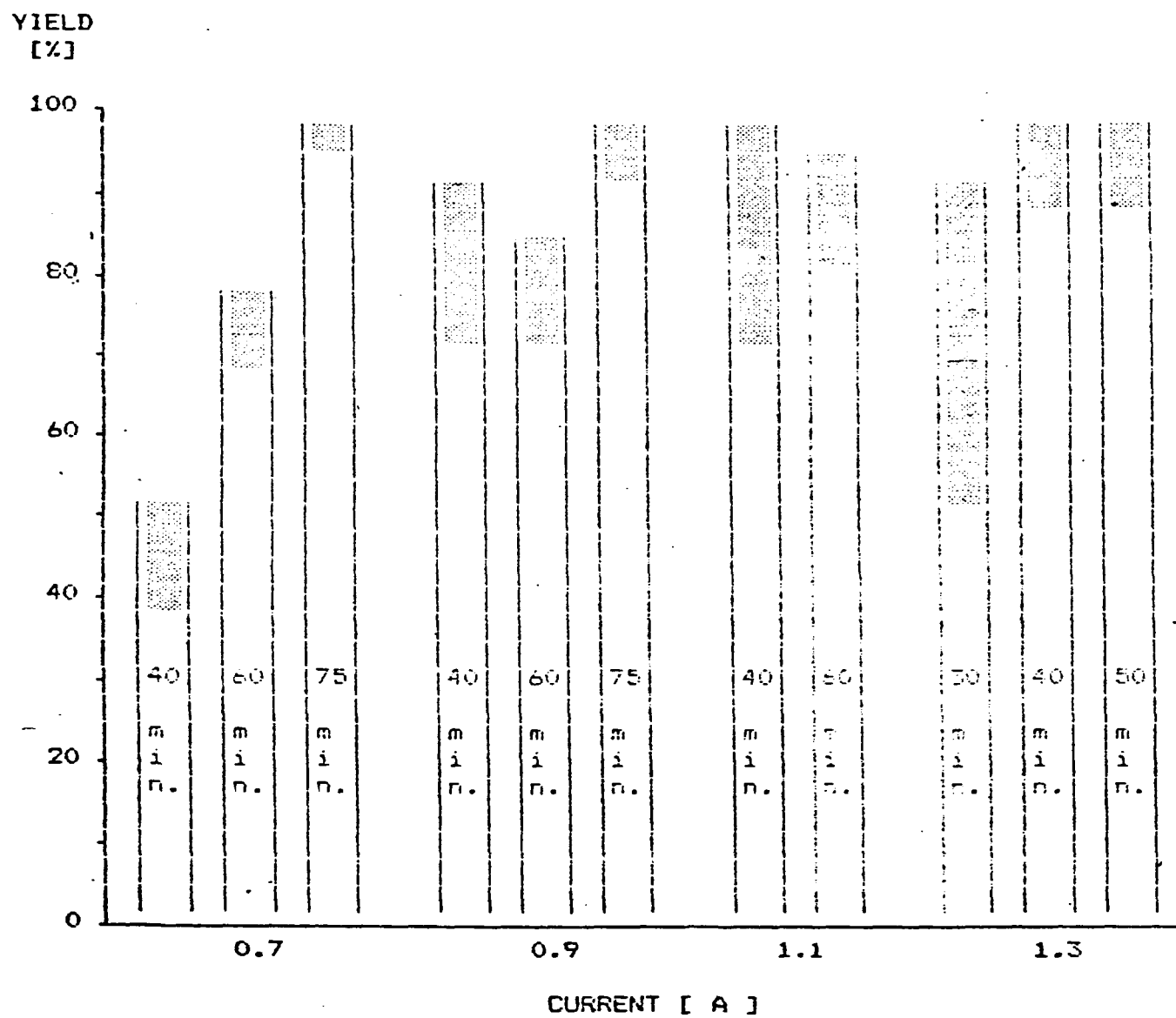
PROGRESS REPORT
on the studies carried out on the

Rapid In Situ Gamma Spectrometric Determination of Fallout
Radioactivity in the Environment

as a part of the co-ordinated research project G6 10 01:

Rapid Instrumental and Separation Methods for Monitoring
Radionuclides in Food and the Environment

Contract Number: 5452/RB
Institute: Central Research Institute for Physics, Budapest
Chief scientific investigator: Peter Zombori
Time period: 15 December 1988 - 31 August 1989

1. INTRODUCTION

The main aim of the present CRP is to identify the existing analytical methods and develop new ones, if possible, which provide rapid, reliable, and detailed information on the radioactive contamination of the environment after a major nuclear accident. Gamma spectrometry has long been regarded as one of the most applicable radioanalytical techniques but its use for environmental studies requires some further considerations. There are two possible approaches to measure environmental radioactivity: (a) taking samples of the different environmental media and measuring them in a laboratory or (b) taking the spectrometer to the place of interest and making in situ measurements. In the former case sampling is a crutial factor hindering the rapid analysis while the latter case is not always reliable due to the problems and uncertainities of the measurement interpretation.

The application of in situ gamma spectrometry for the determination of environmental radioactivity has become increasingly attractive since the advent of the high resolution semiconductor gamma detectors, especially, more recently, portable high purity Ge diodes (HpGe). In comparison with laboratory sample measurements, in situ gamma spectrometry has substantial advantages:

- The amount of 'sample' is much larger than in case of laboratory sample analysis.
- Work, time and money can be saved, representativity problems are avoided if sampling and sample preparation is not necessary.
- It is possible to determine the dose rate due to a single nuclide, in addition to its activity concentration, for different energies and radionuclide distributions in the soil.

The applicability of this technique was very well proved after the Chernobyl reactor accident when in situ spectrometry played an important role in the rapid evaluation of the fall-out situation. Our measurements provided information on the amount and composition of the radioactive contamination of the ground surface already in the first hours. These measurements enabled us to predict the time variation of the environmental radioactivity after the stabilization of the situation. The portability of the system was an important factor in performing a rapid and efficient survey in different parts of the country.

A serious disadvantage of this method is, however, that it requires some knowledge about the radionuclide distribution in the soil, which is normally determined by tedious and time consuming sample analysis of the different soil layers. Though fresh fallout is often assumed to be distributed completely on the ground surface recent studies revealed that a certain penetration of the radioactivity into the soil can occur already in the first instance. The improper estimation of the

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distribution parameter can result in a deviation of the determined activity concentration from the true value by a factor of 2 or more. This way the reliability of the method is limited due to the lack of information on the depth profile of the activity concentration.

The main objective of our study is to find a method (or more, if possible) to estimate the penetration character of the fallout radioactivity by using only spectral information obtained by the in situ spectrometric measurement thus avoiding the need for a long and tiresome sampling and sample analysis procedure.

II. METHOD and INSTRUMENTATION

The method of in situ gamma spectrometric determination of environmental radioactivity was elaborated by H.L. Beck at al. for NaI(Tl) detectors in 1964 [1] and developed for semiconductor detectors in the early seventies [2]. Since then many applications by various authors have been published [3-5].

The evaluation of environmental spectra measured by a detector situated 1m above the ground to be in a down looking position is based on the proportionality between the environmental concentration of a given gamma emitting radionuclide (S_A) and the count rate of the full energy peak of any of its gamma lines in the spectrum (N_f). According to Beck the determination of the calibration factor N_f/S_A can be divided into three parts, i.e.

$$\frac{N_f}{S_A} = \frac{N_f}{N_0} \; \frac{N_0}{\phi} \; \frac{\phi}{S_A}$$

Here N_f/N_0 is the angular correction factor, i.e. the angular dependence of the relative detector efficiency $R(\vartheta)$ (related to the efficiency at $\vartheta=0$) folded with the angular distribution of the photon flux, φ. N_0/ϕ is the photopeak count rate per unit flux of incoming photons parallel to the axis of symmetry of the detector (determined purely by the characteristics of the detector). ϕ/S_A is the unscattered photon flux at the height of the detector per unit activity concentration in/on the soil, S_A. The photon flux is given by

$$\phi = \int_V \frac{S(z)\exp[-\mu_a r_a -\mu_s(r-r_a)]}{4\pi r^2} \, dV$$

where μ_a and μ_s are the mass attenuation coefficients of air and soil, respectively, and $S(z)$ the activity concentration of the radionuclide in question at a depth z in soil.

N_0/ϕ is determined by calibration of detector efficiency using point sources of various gamma emitting nuclides. The angular correction factor N_f/N_0 is obtained by a combination of calibration measurement (determination of $R(\vartheta)$) and model calculation (determination of $\varphi(\vartheta)$). The quantity ϕ/S_A is not dependent on the detector characteristics and can be computed by using different model assumptions for the environmental source distribution.

In general calculations are performed by using an exponential radionuclide distribution in soil

$$S(z) = S_0 \, e^{-\alpha z}$$

with concentration per unit area

$$S = \int_0^\infty S(z) \, dz$$
$$= S_0 / \alpha$$

Using this expression, an equally distributed source ($\alpha = 0$) and a pure surface source ($\alpha = \infty$) can also be described. Besides the reasonable assumption, which is in accordance with measurements of depth profiles, the exponential distribution has the advantage that $d\varphi/d\vartheta$ as well as ϕ can be calculated analitically.

In principle any gamma-spectrometric measuring equipment can be applied for field measurement if the detector can be transported to the place of interest. In our investigation the following detectors were used:
- HpGe (p-type, 15% rel. eff.)
- HpGe (n-type, 25% rel. eff.)
- Phoswitch (NaI(Tl) + CsI(Tl))

III. DESCRIPTION of RESEARCH

A. Radionuclides of environmental relevance

In Annex VI of [6] a list of isotopes of expectable environmental appearance is given for several possible nuclear accident scenarios. From this list and also on the basis of our post-Chernobyl experience the main attention is to be paid to the Cs isotopes (Cs-134 and Cs-137) due to their yield and long half-life. Contamination of Cs-134 on/in the ground will diminish with a half-life of 754 days, if no other clearence or removal process than radioactive decay is expectable, while Cs-137 will be present in the environment for decades. There is a concern about other nuclides, as well, but they are not gamma emitters or their investigation with gamma spectrometry is of no use (Sr-90 and some transuranic radionuclides).

B. Study of their nuclear characteristics in using Ge detectors

A solution to the problem is given if the following two questions are answered:

- What are those spectral data (if at all), which are characteristically variable in the function of the source distribution?
- How to get the relevant conversion data for the actual spectrometric equipment? (Wether with calculation or by calibration measurements?)

The shape of the spectrum measured by a semiconductor detector is dependent on the energy and gamma yield of the gamma quanta emitted by the radionuclide in question and on the scattering processes in the media between the source and the detector. This scattering is a function of the photon energy and it depends on the characteristics of the media (composition, density etc.). These properties of the photon-matter interaction give the key to the characterization of the source distribution.

Cs-137 emits a single gamma photon of 661.6 keV energy with a 85.1% emission probability. There is, however, an additional X-ray line of the daughter product Ba-137m at 32 keV (This is actually a compound of a 32.2 keV K_{α_1} line with a 3.9% transition probability and a 31.8 keV K_{α_2} line with a 2.1% transition probability) and there is a cluster of K_β X-ray lines around 36 keV with a total transition probability of 2.3%. The 32 keV line will be observed with a 5.7% frequency compared to the decay of the parent Cs-137 and the total frequency of the 32 keV + 36 keV cluster is 7.9%.

Cs-134 has 9 lines with emission probability exceeding 1%:

Energy (keV)	Intensity (%)
475.4	1.46
563.3	8.38
569.3	15.4
604.7	97.6
795.8	85.4
801.8	8.73
1038.5	1.00
1167.9	1.80
1365.1	3.04

In case of Cs-134 the emission rate of the X-ray photons is less than 1%.

C. Identification of possible spectral dependence on the source distribution

If there is no matter between the source and the detector the shape of the spectrum is determined by the properties of the photon-detector interaction. If the space is filled with absorbing material then the gamma radiation field will be modified by two different effects, viz.:

- the attenuation of the primary (unscattered) photon flux
- the build-up of the scattered gamma radiation field.

The first effect will diminish the total energy peak intensities in an energy dependent way. The second phenomenon distorts the spectrum region below the total energy peak.

Since the unscattered flux per unit activity concentration ϕ/S_A is expressed as:

$$\frac{\phi}{S_A} = \frac{1}{2}[\, E_1(\mu_a \cdot h) - e^{\frac{\alpha \cdot h \, \mu_a}{\mu_s}} \cdot E_1(\mu_a \cdot h + \frac{\alpha \cdot h \cdot \mu_a}{\mu_s})\,] \qquad (1)$$

where

E_1 is the exponential integral of the first order and
h is the height of the detector above the ground,

therefore the energy dependence of ϕ/S_A can easily be computed, as is shown in Fig. 1 for different α exponential distribution parameters. If now we select two gamma quanta of different energies emitted by the same nuclide, than the ratio of their total energy peak intensities in the spectrum will be a function of the α value. The more distant are the energies the more pronounced is the effect. Thus the α source distribution parameter can be estimated from the ratio of total energy peak areas of different energy gamma photons emitted by the same nuclide. As an example the ratio of the primary (unscattered) fluxes per unit activity concentration at 662 keV and at 32 keV is shown in Fig. 2.

The drawback of the method is that it requires at least two, preferably distant energy gamma lines. This is a serious limitation for both Cs radionuclides. Most of the prominent lines of Cs-134 are closely situated in the 500-800 keV energy region, so only slight effect can be anticipated. Cs-137 has, on the other hand, a single gamma line at 661.6 keV, while the 32 keV X-ray is too low in energy to be detected by normal p-type HpGe detectors. The detection of this radiation requires n-type HpGe detector or an additional low energy photon (LEP) detector has to be applied.

Proceeding on the other line the build-up of the scattered gamma radiation field can offer another solution. When gamma radiation interacts with matter by Compton scattering the probability of forward (or small angle) scattering is a well defined non-zero quantity, which results in the appearance of a continuum in the gamma radiation field right on the low energy side of the primary (unscattered) gamma line. In the spectrum (i.e. the convolution of the energy distribution of the gamma flux and the detector response function) an increase in the continuum between the Compton edge and the total energy peak (the so called 'valley') can be observed. This way the size of the step in the spectrum when comparing the region below and above the total energy peak will be a function of the α source distribution parameter due to the scattering in the soil.

This method has the advantage that it is applicable also to single line isotopes. The probability of scattering in small angles is described by the Klein-Nishina expression [7].

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In principle the expectable change in the step size or its relation to the total energy peak area (i.e. the Peak-to-valley ratio) can be calculated. In practice, however, a proper experimental calibration is a more straightforward way of getting the necessary values.

The main disadvantage of the method is that its applicability is strongly dependent on the intensity of the gamma line and on the spectral environment of the total energy peak (whether there are interfering lines in the 'valley' or above the peak).

On the basis of the above considerations the following possible gamma spectrometric methods for the estimation of the source distribution parameter were investigated:

- Ratio of several lines measured by any Ge(Li) or HpGe detector (Cs-134)
- X-ray - main gamma line ratio measured by n-type HpGe (Cs-137)
- X-ray - main gamma line ratio measured by HpGe + LEP detectors (Cs-137)
- Peak-to-valley ratio measured by any Ge(Li) or HpGe detector (Cs-137, Cs-134)

D. Definition of the equivalent water thickness

The experimental investigation of the spectrum 'deformation' in the function of the α distribution parameter is rather difficult due to the fact that the creation of a standard source exponentially distributed in a semi-infinite space is practically impossible. But since the attenuation of the unscattered flux is attributable solely to the scattering described by Eq. (1) and because flux of a point source penetrating through a water volume is attenuated according to the law of exponentiality the equivalence of the two phenomenon provides the possibility for the definition of the equivalent water thickness thus giving a tool for experimental studies:

$$e^{-\mu_w d} = 1 - e^{\alpha h \frac{\mu_a}{\mu_s}} \cdot \frac{E_1(\mu_a h + \alpha h \frac{\mu_a}{\mu_s})}{E_1(\mu_a h)}$$

where
μ_w is the attenuation coefficient for water and
d   is the thickness of the water.

Solving the equation above for d the equivalent water thickness is plotted in the function of α in Fig. 3.

On the basis of the above considerations a series of measurement was carried out in the following experimental situation: Point sources of Cs-134 and Cs-137 isotopes were put 1m distant from the detector and spectrum measurements were made meanwhile filling up a container situated between the source and the detector with water to simulate the scattering properties of the soil. The result of the experiment are discussed in the next Section.

IV.   RESULTS and DISCUSSION

A. Ratio of different energy lines

In principle the energy dependence of ϕ/S_A makes the determination of the α distribution parameter possible if the nuclide to be measured has at least two different energy lines. This dependence is, however, a slowly changing function of the energy, so the expectable effect is significant only if the energy difference between the investigated lines is large.

Measurements were made to compare the peak intensities of the 563 keV + 569 keV doublet and the 796 keV + 802 keV doublet of Cs-134 at two different water thicknesses. The ratios obtained were as follows:

$$\frac{I~(796+802~keV)}{I~(563+569~keV)} = 3.00 \qquad at \qquad d = 0~cm$$

$$\frac{I~(796+802~keV)}{I~(563+569~keV)} = 3.50 \qquad at \qquad d = 14~cm$$

The difference between the two ratios is less than 20%. This means that the distribution can be estimated by this method only if the contamination is high enough to cause statistically significant peak intensities but the estimation is rather rough even in this case.

B. X-ray - main gamma line ratio (n-type HpGe)

Measurements were made to determine the X-ray to main gamma line ratio by n-type HpGe detector in the case of Cs-137 isotope. The water thickness changed from 0 to 14 cm by 1 cm steps. Fig. 4 shows the ratio of the peak areas at energies 32+36 keV and 662 keV. The ratios were: 0.33 at water thickness d=0 cm and 0.02 at d=14 cm. The difference between these ratios is very significant. The measuring uncertainities were less than 30% at the measuring time of 1000 - 2000 s. This means that the distribution of Cs-137 can be estimated in this manner.

C. X-ray - main gamma line ratio (HpGe + Phoswitch)

The ratios were also determined by another detector combination. A Phoswitch detector was used to detect the low energy peak and HpGe detector for photopeak at different water thicknesses. The attenuation of the main gamma line of Cs-137 in the function of the water thickness is much less than that of the X-ray line. It means that in case of the detector configurations investigated the ratio of the full energy peak areas of 662 keV gamma ray and 32+36 keV X-rays differs with a factor of about 6 depending on the water thickness ranging from d=0 cm to d=14 cm. This relatively high effect makes it principally possible to appy the method, nevertheless the application is limited because two different detector systems and sophisticated electronics are required.

The decrease of the X-ray to main gamma line ratio in the function of the water thickness (normalized to d=0 cm) is plotted in Fig. 5.

D. Peak-to-valley ratio (n-type HpGe)

Measurements were performed to determine the peak-to-valley ratio for Cs-137 isotope by n-type HpGe detector. Fig. 6 shows the ratios at different water thicknesses. The extermal values were as follows:

    115 at d=0 cm
    15   at d=14 cm

The uncertainities of the measurements were less than 30%. The method may be applicable - especially in the case of environmental distribution with equivalent water thickness ranging 0-5 cm - for the estimation of the Cs-137 ditribution.

V.   CONCLUSIONS

The following main conclusions cam be drawn at the present stage of investigations:

(1) In case of Cs-137 and Cs-134 the efficiency of the method using the different gamma line ratios (A) seems to be not satisfactory for describing the vertical activity distribution pattern in the soil.

(2) For Cs-137 isotope the X-ray - main gamma line ratio method using n-type HpGe detector (B) provides a promising means to determine the parameter of ta single exponential activity distribution profile in the full range of the expectable distribution patterns in the soil.

(3) The method of X-ray - main gamma line ratio by HpGe + Phoswitch detector combination (C) seems to be also effective enough to be applicable for the determination of Cs-137 activity distribution in the soil.

(4) The peak-to-valley ratio method (D) for the 662 keV gamma line of Cs-137 isotope proved to be applicable for the determination of the exponential source distribution parameter, α , first of all in the range of infinity (plane source) to about 3 cm^{-1} .

(5) We feel being encouraged by the promising preliminary results to continue these studies according to the following working plan:

    a/ Testing the applicability of the above methods (B-D) in environmental conditions, i. e. when the signal-to-noise ratio is much worse.

    b/ Determining the limits of applicability in terms of Cs-137 activity concentration and distribution pattern in realistic conditions.

c/ Finding methods and experimental conditions to
improve signal-to-noise ratio, for instance
reducing background by special shielding or by
pulse shape discrimination and coincidence
circuitry, etc.

d/ Investigating other detector systems having more
advanced feature for simultaneous and high
sensitive detection of both X-rays and gamma
radiation.

e/ Studying the disturbing effect of the presence of
other radionuclides in the determination of the
distribution characteristics of cesium isotopes.

f/ Extending the applicability of the methods for
other radionuclides and other possible source
distributions.

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FIGURE CAPTIONS

Fig. 1: Φ/S_A in the function of the photon energy for different $\propto$ exponential source distribution parameters

Fig. 2: The ratio of the primary (unscattered) fluxes per unit activity concentration at 662 keV and at 32 keV in the function of the exponential distribution parameter $\propto$

Fig. 3: The calculated equivalent water thickness in the function of the distribution parameter $\propto$

Fig. 4: Ratio of X-ray to gamma line areas measured by a n-type HpGe detector for Cs-137 versus the water thickness used for the calibration measurements

Fig. 5: Relative decrease of the X-ray line, i.e. the decrease of the X-ray (measured by Phoswitch) to main gamma line (measured by HpGe) ratio for Cs-137 in the function of the water thickness (normalized to d=0 cm)

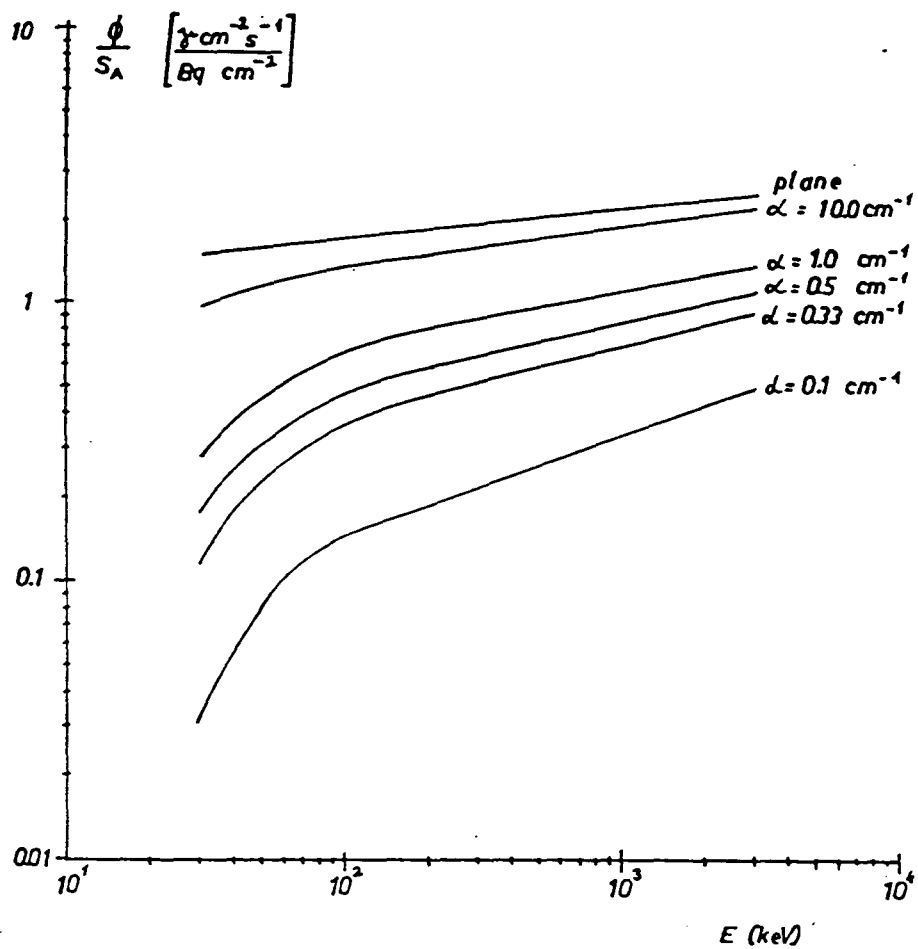Fig. 6: Peak - to - valley ratio measured by HpGe detector for the 662 keV peak of Cs-137 in the function of the water thickness
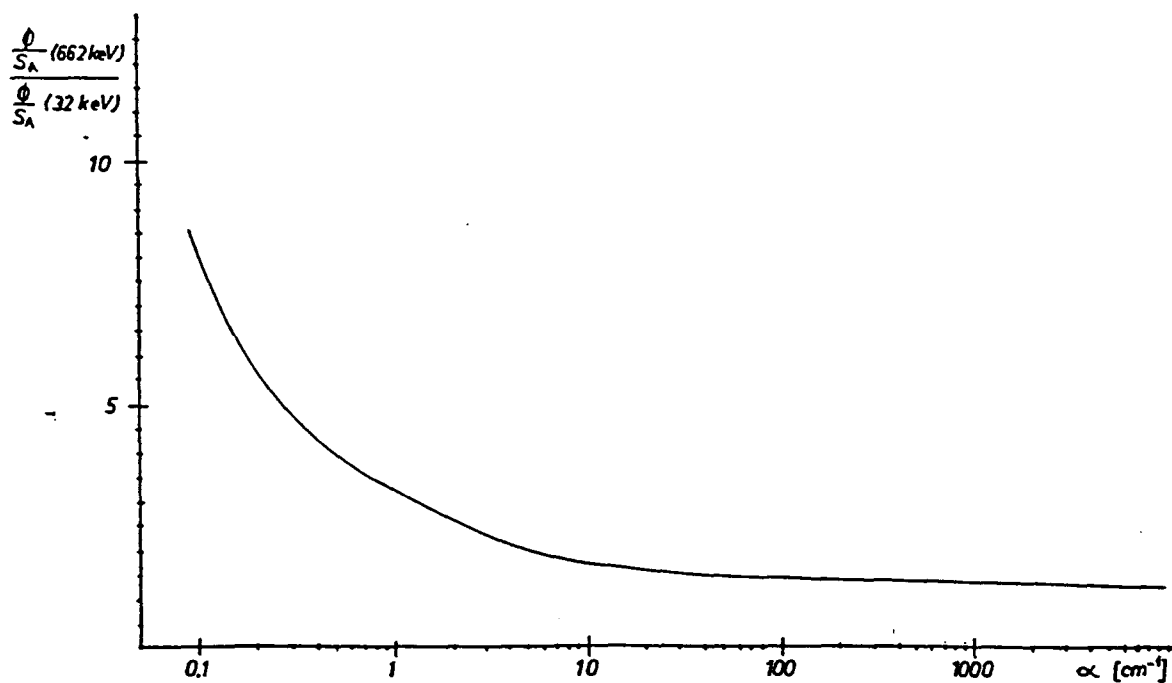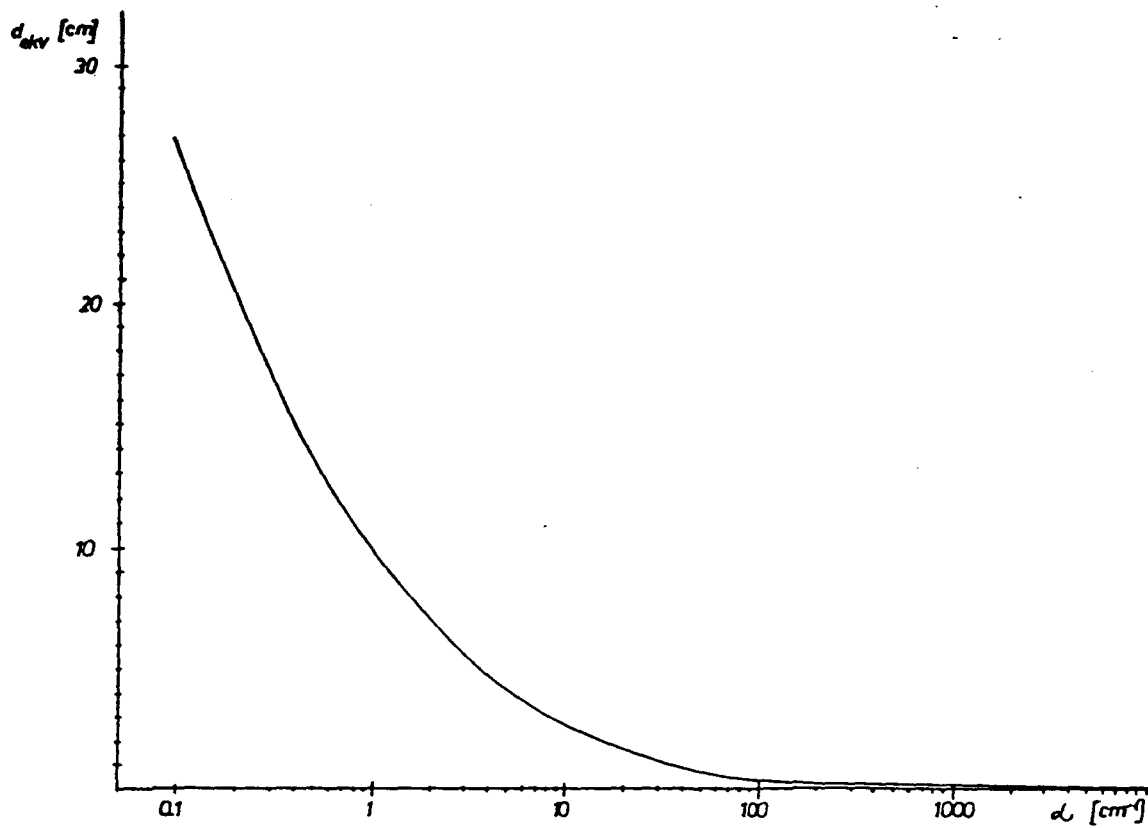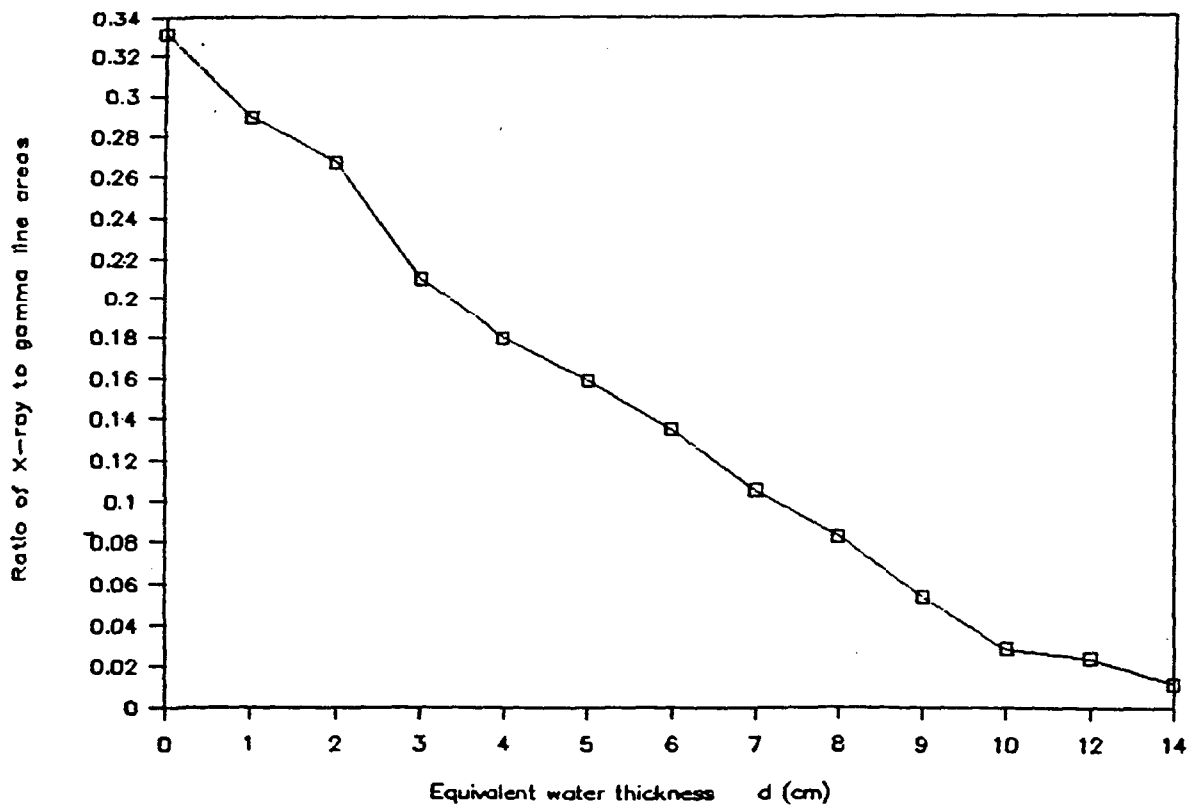
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 6

Peak – to – valley ratio

Equivalent water thickness   d (cm)

Fig. 5

Relative decrease of the X-ray line

Equivalent water thickness   d (cm)
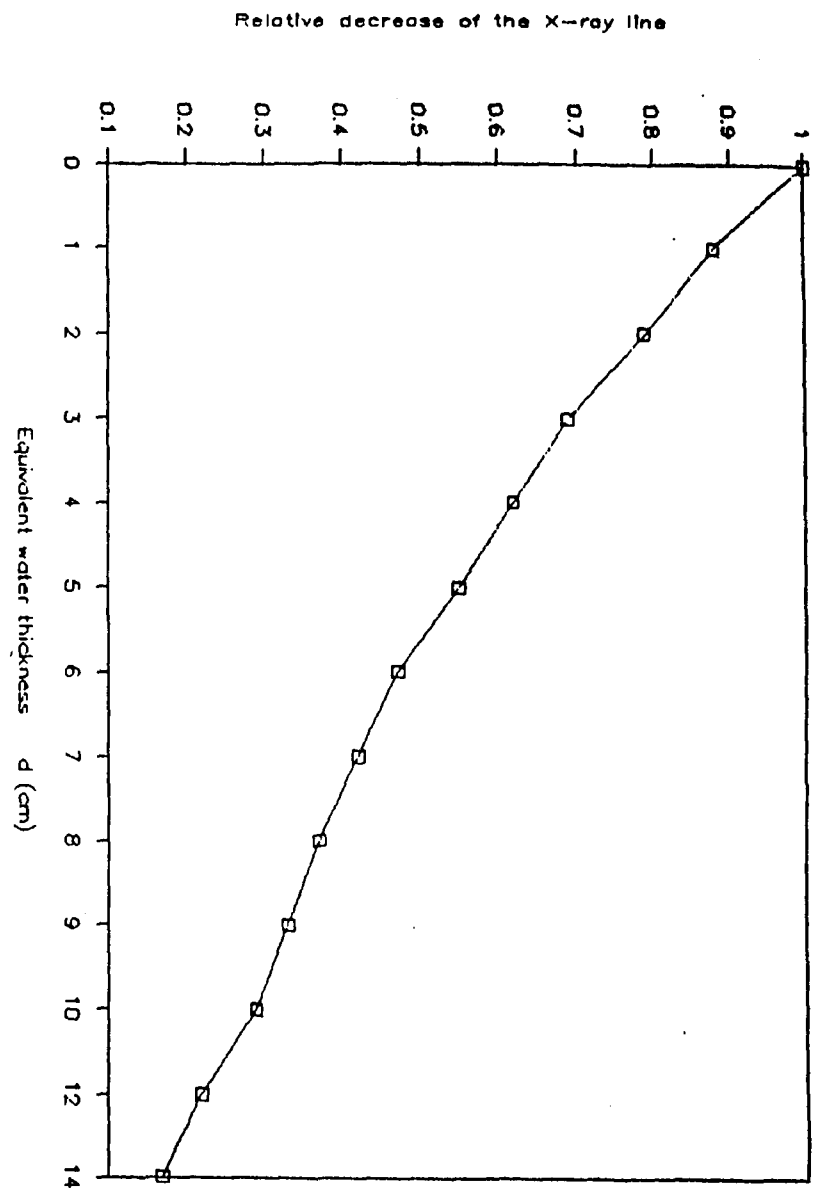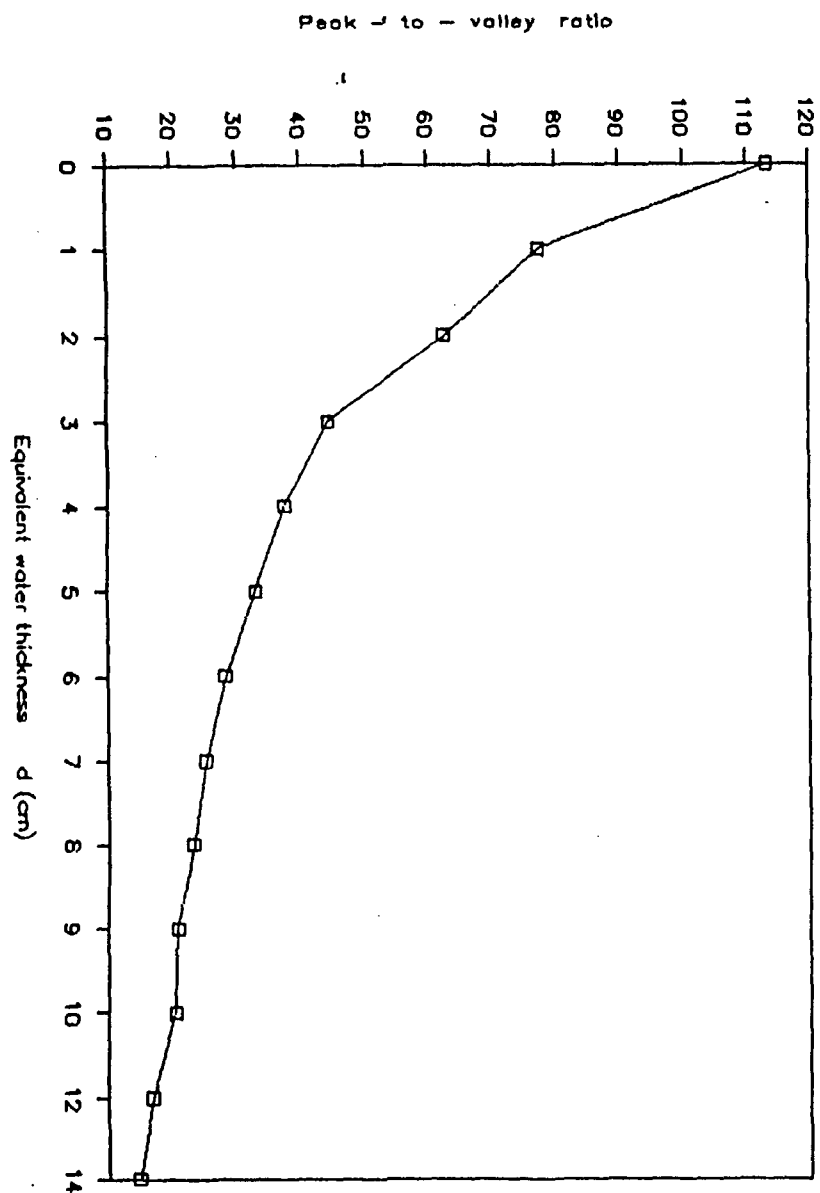
A New Method for the Determination of Radionuclide Distribution in the Soil by In Situ Gamma-Ray Spectrometry

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I.   INTRODUCTION

In case of major nuclear accidents when larger amount of radioactive material is released into the atmosphere vast areas can become contaminated by the nuclear fallout. The deposited radioactivity penetrates the soil in a complex manner: dry and wet deposition lead to different initial distribution patterns which are further modified by the later transport processes in the upper layers of the soil. The distribution is influenced by various factors (physico-chemical characteristics of the radioisotopes, soil type, weather conditions, environment etc.), the resulting soil profile is hardly predictable. An important lesson we learned from the Chernobyl reactor accident is the great variability of the contamination both in the extent of the deposition and in the penetration features.

In light of some recent studies the information on the radionuclide distribution in the soil has great importance in at least two different aspects:

a./ Some transfer coefficients describing the transport of the fallout radioactivity in different compartments of the environment are strongly dependent on the distribution pattern. A deeper penetration will decrease the resuspension of the radioactive material in the ground level air while radionuclides may become more available for root uptake by some plants. These competing processes influence the contamination of the vegetation in a manner not completely clarified, providing an important area for continuing research.

b./ The contamination of an area can efficiently be determined by the method of in situ gamma spectrometry. The conversion of the spectral information (line intensities) to surface contamination data is done by using factors, which are derived from model calculation

based on certain assumed radionuclide distribution profile. The conversion factors can be calculated and tabulated for different depth profiles but something must be known about the real distribution in order to select the appropriate factors in a given case.

The conventional way of assessing the distribution of the radioactivity is taking soil samples and analysing them layer by layer. This approach is rather time consuming, tiresome and it leads to results not necessarily representative for a larger area. The main disadvantage of the sample analysis is the long time necessary for getting the estimate of the radionuclide distribution though this parameter would promptly be needed for the proper conversion of environmental spectra measured in situ.

In recent years - following the reactor accident in Chernobyl - an increased interest for rapid methods of monitoring environmental radioactivity was expressed. The International Atomic Energy Agency initiated a research project to co-ordinate the activities carried out in various laboratories aiming at the development of rapid monitoring procedures. The Co-ordinated Research Project (CRP) G6 10 01 under the title Rapid Instrumental and Separation Methods for Monitoring Radionuclides in Food and the Environment has given a frame for 11 research programs. The Health Physics Department of the KFKI Institute for Atomic Energy Research (the former Central Research Institute for Physics) has taken a part in this CRP with a project titled: Rapid In Situ Gamma Spectrometric Determination of Fallout Radioactivity in the Environment.

The main objective of our study was to find a method to estimate the penetration characteristics of the fallout radioactivity by using only spectral information obtained by the in situ spectrometric measurement thus avoiding the need for a long and tiresome sampling and sample analysis procedure.

In our studies special attention was assigned to the two Cs isotopes (^{137}Cs and ^{134}Cs) being the predominant long-lived gamma-emitting contaminants after the Chernobyl accident: most of the considerations are based on the special nuclear characteristics of these isotopes. Nevertheless, the investigations are aimed at finding a procedure that can be generalized for the case of any isotope assessable by the method of gamma spectrometry.

II.   THEORETICAL BACKGROUND AND SPECTRAL INFLUENCE

The method of in situ gamma spectrometric determination of environmental radioactivity was elaborated by H.L. Beck et al. for NaI(Tl) detectors in 1964 [1] and developed for semiconductor detectors in the early seventies [2]. Since then many applications by various authors have been published [3-5].

The evaluation of environmental spectra measured by a detector situated 1m above the ground in a down-looking position is based on the proportionality between the environmental concentration of a given gamma emitting radionuclide (S_A) and the count rate of the full energy peak of any of its gamma lines in the spectrum $(\dot{N}_f)$. According to Beck the calibration factor $\dot{N}_f/S_A$ can be expressed as a product of three terms, i.e.

$$\frac{\dot{N}_f}{S_A} = \frac{\dot{N}_f}{\dot{N}_0} \frac{\dot{N}_0}{\Phi_0} \frac{\Phi_0}{S_A}$$

Here $\dot{N}_f/\dot{N}_0$ is the angular correction factor, i.e. the angular dependence of the relative detector efficiency $R(\vartheta)$ (related to the efficiency at $\vartheta=0$) folded with the angular distribution of the photon flux, $\varphi(\vartheta)$. $\dot{N}_0/\Phi_0$ is the photopeak count rate per unit flux of incoming photons parallel to the axis of symmetry of the detector (determined purely by the characteristics of the detector). Φ_0/S_A is the unscattered photon flux at the height of the detector per unit activity concentration in/on the soil, S_A. The photon flux is given by

$$\Phi_0 = \int_V \frac{S(z)}{4\pi r^2} e^{-\mu_a r_a - \mu_s (r - r_a)} \, dV$$

where μ_a and μ_s are the linear attenuation coefficients of air and soil, respectively, r is the distance between the detector and the volume element dV, r_a is the section of r in the air and S(z) is the activity concentration of the radionuclide in question at a depth z in soil.

$\dot{N}_0/\Phi_0$ is determined by calibration of detector efficiency using point sources of various gamma emitting nuclides. The angular correction factor $\dot{N}_f/\dot{N}_0$ is obtained by a combination of calibration measurement (determination of $R(\vartheta)$) and model calculation (determination of $\varphi(\vartheta)$). The quantity Φ_0/S_A is not dependent on the detector characteristics and can be computed by using different model assumptions for the environmental source distribution.

In general calculations are performed by assuming an exponential radionuclide distribution in soil

$$S(z)=S_0 \; e^{-\alpha z}$$

with concentration per unit area

$$S_A = \int_0^\infty S(z)dz = S_0/\alpha$$

Using this expression, an uniformly distributed source ($\alpha=0$) and a pure surface source ($\alpha \to \infty$) can also be described. Besides the reasonable assumption of exponential distribution (which is in accordance with many measurements of depth profiles) has the advantage that $\varphi(\vartheta)$ as well as Φ_0 can be calculated analitically. In this case the unscattered flux per unit activity concentration Φ_0/S_A is expressed as:

$$\frac{\Phi_0}{S_A} = \frac{1}{2}\left[E_1(\mu_a h) - e^{\frac{\alpha h \mu_a}{\mu_s}} \cdot E_1(\mu_a h + \frac{\alpha h \mu_a}{\mu_s})\right]$$

where

E_1 is the exponential integral of the first order and

h is the height of the detector above the ground,

therefore the energy dependence of Φ_0/S_A can easily be computed and is shown in Fig. 1 for different α parameters.

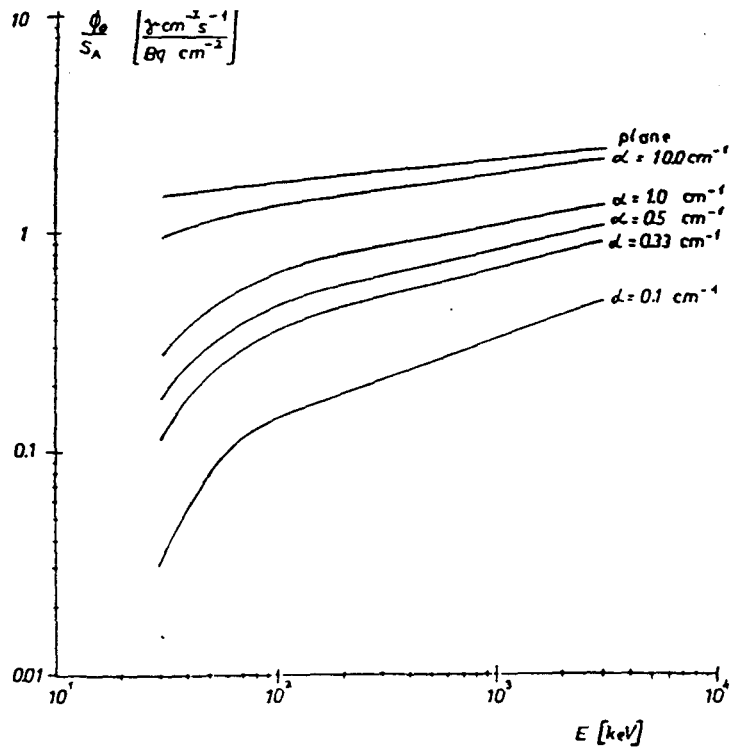**Fig. 1:** The primary (unscattered) flux per unit activity concentration (Φ_0/S_A) in the function of the photon energy for different α exponential source distribution parameters
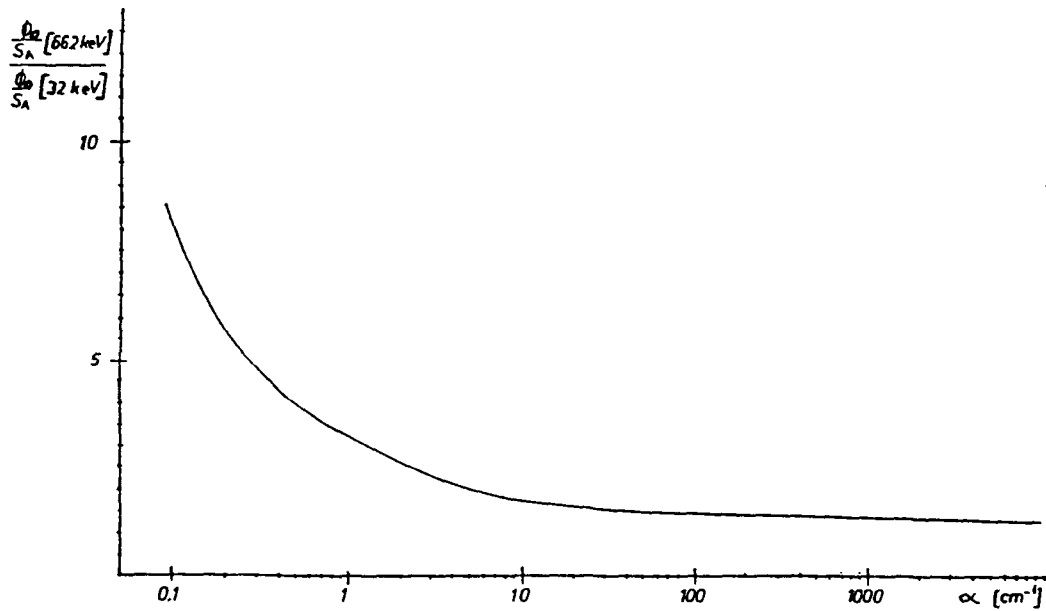

Fig. 2: The ratio of the primary (unscattered) flux per unit activity concentration (Φ_0/S_A) at 662 keV to that at 32 keV energy as a function of the exponential distribution parameter α

If there is no matter between the source and the detector the shape of the spectrum is determined by the properties of the photon-detector interaction. If the space is filled with absorbing material then the gamma radiation field is modified by two different effects, viz.:

- the attenuation of the primary (unscattered) photon flux,
- the build-up of the scattered gamma radiation field.

The α dependence of the unscattered flux vs. energy function offers a possibility for the estimation of the distribution parameter. If we select two gamma quanta of different energies emitted by the same nuclide, then the ratio of their primary (unscattered) fluxes will be a function of the α value. The more distant are the energies from each other the more pronounced is the effect. As an example the ratio of the primary (unscattered) fluxes per unit activity concentration at 662 keV and at 32 keV is shown in Fig. 2.

The drawback of the method is that it requires at least two, preferably distant energy gamma lines. This is a serious limitation for both Cs radionuclides. Most of the prominent lines of ^{134}Cs are closely situated in the 500-800 keV energy region, thus only a slight effect can be anticipated. ^{137}Cs has, on the other hand, a single gamma line at 661.6 keV, while the 32 keV X-ray is too low in energy to be detected by normal p-type HpGe detectors. The detection of this radiation requires n-type HpGe detector or an additional low energy photon (LEP) detector has to be applied.

So far only the peak intensities have been used, other possible information has not been extracted from the spectra. As it is obvious from the considerations above not only the characteristic lines but also the continuum of the energy distribution of the environmental radiation field undergoes considerable changes due to the photon-matter interaction processes. The scattered radiation forms a continuum between zero and the characteristic line as it is shown schematically in Fig. 3. The region on the low energy side of the characteristic line is a consequence of the forward photon scattering and its elevation is a function of the depth profile. The spectrum of a given line, measured by the detector, is the convolution of the energy distribution of the environmental radiation field and the

detector response function. The total spectrum is a superposition of the different spectrum components and, in general case, the 'discontinuous' peak regions sit on the 'continuous' background regions of other lines. The information on the amount of small angle scattering (and so, on the depth distribution) is inherited to the spectrum and is embedded in the step size (i.e. the difference between the counts in the region below and above the characteristic peak). The region adjoining the peak on the low energy side (a continuum between the Compton edge and the peak) is called the 'valley' and (since the 'valley' is increasing in the 'expence' of the decreasing peak during the scattering) the quantity defined as the peak area per 'valley' height (or 'peak-to-valley', in short) can be a good measure of the photon scattering of the gamma emitters distributed in the soil.
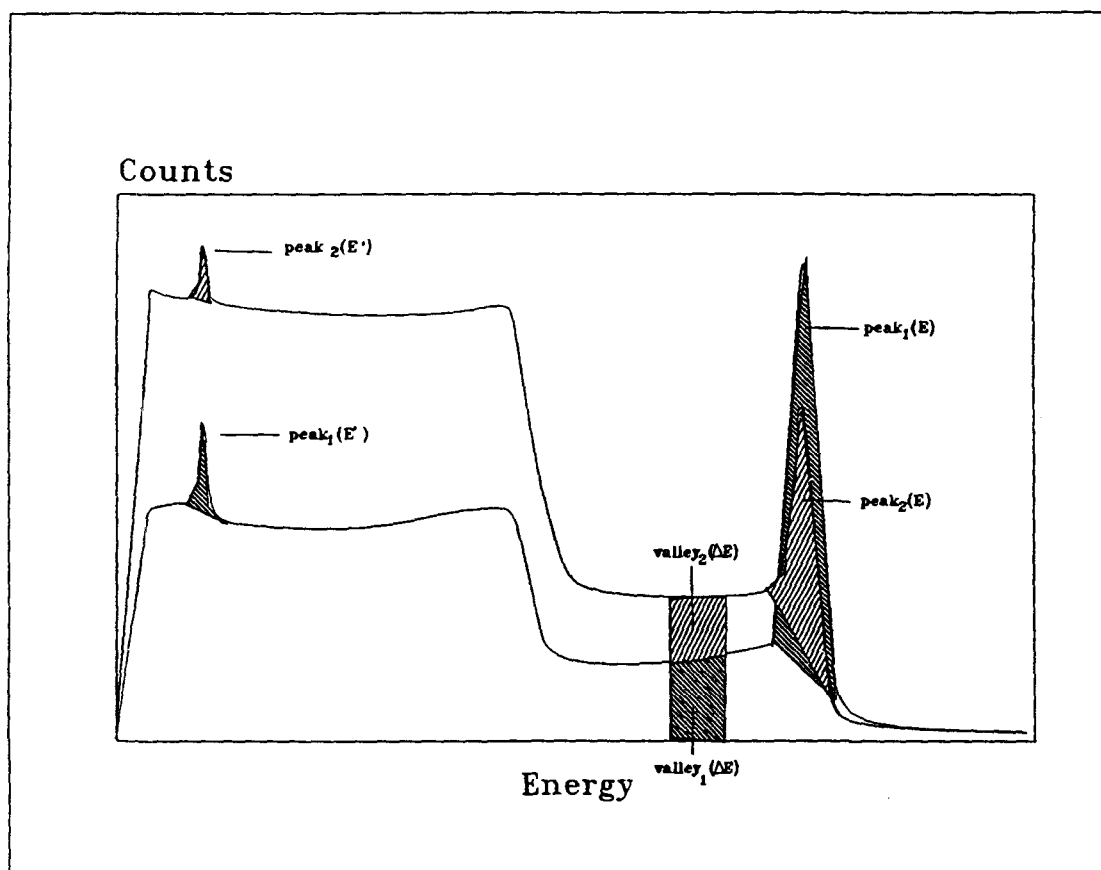
Fig. 3: A schematic presentation of the spectral distortion occuring due to photon scattering taking place in the matter between the source and the detector

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This method has the advantage that it is applicable also to single line isotopes. The probability of scattering in small angles is described by the Klein-Nishina expression [6]. In principle the expectable change in the step size or its relation to the total energy peak area (i.e. the 'peak-to-valley' ratio) can be calculated. In practice, however, a proper experimental calibration is a more straightforward way of getting the necessary values.

The main disadvantage of the method is that its applicability is strongly dependent on the intensity of the gamma line and on the spectral environment of the total energy peak (whether there are interfering lines in the 'valley' or above the peak).

On the basis of the above considerations the following possible gamma spectrometric methods for the estimation of the α source distribution parameter were investigated:

- Ratio of several lines measured by any Ge(Li) or HpGe detector (^{134}Cs)

- X-ray - main gamma line ratio measured by n-type HpGe (^{137}Cs)

- X-ray - main gamma line ratio measured by HpGe + LEP detectors (^{137}Cs)

- 'Peak-to-valley' ratio measured by any Ge(Li) or HpGe detector (^{134}Cs, ^{137}Cs).

The first three approaches are simply different technical realizations of the same basic method: the determination of the ratio of different energy lines in the spectrum. The fourth type of assessment is essentially different from the others and it requires some further considerations.

III. CALCULATIONS FOR THE 'PEAK-TO-VALLEY' RATIO

Let $N(E,\alpha)$ be the net peak area measured in the spectrum peak of energy E originating from a source distributed exponentially by depth in the soil with a distribution parameter α. Let us denote the 'valley' i.e. the elevation of the continuum in the properly selected ΔE energy interval on the low energy side of the peak by $I(\Delta E,\alpha)$. In fact

$$I(\Delta E,\alpha) = Int(\Delta E,\alpha) - Int(\Delta'E,\alpha)$$

where $Int(\Delta E,\alpha)$ and $Int(\Delta'E,\alpha)$ are the measured integral values in the energy intervals below (ΔE) and above $(\Delta'E)$ the peak energy E, so $I(\Delta E,\alpha)$ is the net step size on the presumably constant background continuum. Thus the 'peak-to-valley' ratio $Q(E,\alpha)$ can be defined as

$$Q(E,\alpha) = \frac{N(E,\alpha)}{I(\Delta E,\alpha)}$$

Since the 'valley' is not only due to the scattering in the matrices between the source and the detector but also a result of the interaction of the photons with the detector, it is necessary to define the initial value of the 'peak-to-valley' ratio, $Q_0(E)$:

$$Q_0(E) = \frac{N_0(E)}{I_0(\Delta E)}$$

Here $N_0(E)$ and $I_0(\Delta E)$ are the relevant quantities if only a monoenergetic parallel photon beam of energy E is applied.

a., The peak $N(E, \alpha)$

$N(E, \alpha)$ is the result of those photon transport cases when no interactions have taken place between the source and the detector, and the whole energy is absorbed in the detector. The probability P_0 of not being scattered is exponentially decreasing with the distance (r). If the matrix is homogeneous (e.g. air) then

$$P_0(\mu_a, r) = e^{-\mu_a r}$$

where μ_a is the linear attenuation coefficient of the air.

In case of a more realistic situation where the radionuclides are distributed in the soil as an exponential function of the depth z, i.e. the concentration $S(z)$ is

$$S(z) = S_0 \, e^{-\alpha z} \tag{1}$$

then the unscattered photon flux (Φ_0) can be calculated as

$$\Phi_0(E, \alpha) = \int_V \frac{S(z)}{4\pi r^2} \, P_0(\mu_a, \mu_s, r) \, dV$$

where r is the distance between the volume element dV and the detector

        P_0 is the probability of not being scattered during the transport from dV to the detector
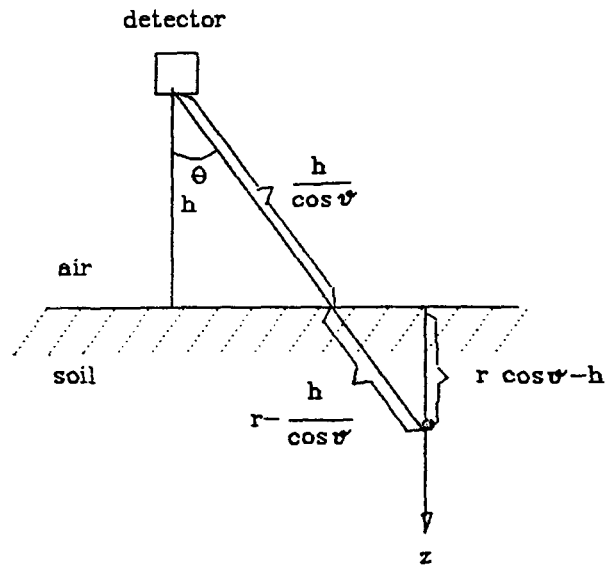
Fig. 4: Geometric parameters of the semi-infinite space model used for the calculation of the Φ/S_A conversion factors

Using the notations of Fig. 4, Φ_0 can be expressed as:

$$\Phi_0 = \int\limits_{0}^{\frac{\pi}{2}} \int\limits_{\frac{h}{\cos\vartheta}}^{\infty} \frac{S_0}{4\pi r^2}\, e^{-\alpha(r\cos\vartheta - h)} \cdot e^{-\left(\frac{\mu_a h}{\cos\vartheta} + \mu_s(r - \frac{h}{\cos\vartheta})\right)}\; 2\pi r^2 \sin\vartheta\; dr\; d\vartheta$$

Integrating the expression above we obtain

$$\Phi_0 = \frac{S_A}{2}\left[E_1(\mu_a h) - e^{\frac{\alpha h \mu_a}{\mu_s}} \cdot E_1\left(\mu_a h + \frac{\alpha h \mu_a}{\mu_s}\right)\right].$$

$N(E, \alpha)$ (collected during measuring time Δt) is calculated by using the full energy peak detection efficiency $\eta(E)$:

$$N(E, \alpha) = \eta(E) \cdot \Phi_0(E, \alpha) \cdot \Delta t \qquad (2)$$

(In this calculation the slight possible anisotropy of the detector response is ignored).

b., The 'valley' $I(\Delta E, \alpha)$

A photon of energy E emitted by the source may give a count in the energy region ΔE of the 'valley' if it interacted once with the matter between the source and the detector by forward scattering thus losing a small fraction of its initial energy. The probability (P_1) of interacting only once, if the matrix is air, is as follows:

$$P_1(\mu_a, r) = \int_0^r k \cdot \mu_a \, e^{-\mu_a x} \, dx \cdot e^{-\mu_a(r-x)} = k \, \mu_a \, r \, e^{-\mu_a r}$$

where k is the fraction of the interacted photons scattered into the energy interval ΔE and

x is the distance between the source and the point of interaction.

The flux of photons (Φ_1) reaching the detector having a single forward scattering during the transport from the exponentially distributed source (Eq. 1) is expressed as

$$\Phi_1(\Delta E, \alpha) = \int_V \frac{S(z)}{4\pi r^2} P_1(\mu_a, \mu_s, r) \, dV$$

where P is the probability of the photon being transported from dV to the detector having a single forward scattering to the energy interval ΔE.

With the notations of Fig. 4, P_1 reads

$$P_1 = \int_0^{r-\frac{h}{\cos\vartheta}} k\,\mu_s\,e^{-\mu_s x}\,dx\;e^{-\mu_s\left(r-\frac{h}{\cos\vartheta}-x\right)}\cdot e^{-\mu_a\frac{h}{\cos\vartheta}} +$$

$$+ \int_{r-\frac{h}{\cos\vartheta}}^{r} k\,\mu_a\,e^{-\mu_s\left(r-\frac{h}{\cos\vartheta}\right)}\cdot e^{-\mu_a\left(x-r+\frac{h}{\cos\vartheta}\right)}\cdot e^{-\mu_a(r-x)}dx =$$

$$= k\,e^{-\mu_s\left(r-\frac{h}{\cos\vartheta}\right)-\mu_a\frac{h}{\cos\vartheta}}\cdot\left(\mu_s\left(r-\frac{h}{\cos\vartheta}\right)+\mu_a\frac{h}{\cos\vartheta}\right).$$

Thus Φ_1 is

$$\Phi_1 = \int_0^{\frac{\pi}{2}}\int_{\frac{h}{\cos\vartheta}}^{\infty}\frac{kS_0}{4\pi r^2}\,e^{-\alpha(r\cos\vartheta-h)}\cdot e^{-\mu_a\frac{h}{\cos\vartheta}-\mu_s\left(r-\frac{h}{\cos\vartheta}\right)}\cdot\left[\mu_a\frac{h}{\cos\vartheta}+\mu_s\left(r-\frac{h}{\cos\vartheta}\right)\right]\cdot$$

$$\cdot\;2\pi r^2\sin\vartheta\;dr\;dV$$

The integration results in the following expression:

$$\Phi_1 = \frac{kS_0}{2\alpha}\frac{e^{-\mu_a h}}{1+\mu_s/\alpha} \tag{3}$$

By introducing the following variables:

$$A = \frac{\alpha}{\mu_s}\,,\quad B = \mu_a h\quad\text{and}\quad S_A = \frac{S_0}{\alpha}$$

Eq. (3) can be written as:

$$\Phi_1 = \frac{kS_A}{2} \frac{e^{-B}}{1+1/A}$$

In the special case of plane source distribution ($\alpha \to \infty$ i.e. $A \to \infty$) the flux of forward scattered photons is

$$\Phi_1 = \frac{kS_A}{2} \cdot e^{-B}$$

If the source is distributed uniformly in the ground ($S(z)=S_0$) then $\alpha = 0$ i.e. $A = 0$ and

$$\Phi_1 = \frac{kS_0}{2\mu_s} \cdot e^{-B} .$$

c., The 'peak-to-valley' ratio $Q(E,\alpha)$

The counts in the selected interval (ΔE) of the 'valley' (collected during the measuring time Δt) originate partly from the multiple scattering of the primary photons of energy E in the detector and partly from the full energy absorbtion of the forward scattered photons:

$$I(\Delta E, \alpha) = I_0(\Delta E) + \eta(E) \, \Phi_1(\Delta E, \alpha) \, \Delta t$$

(In this expression the slight difference of the full energy peak efficiencies at the energy position E and at the energy interval ΔE is neglected).

The 'peak-to-valley' ratio $Q(E,\alpha)$ is defined as:

$$Q(E,\alpha) = \frac{N(E,\alpha)}{I(\Delta E,\alpha)}$$

In the first step it is easier to express the reciprocal of $Q(E,\alpha)$, using Eq. (2):

$$\frac{1}{Q(E,\alpha)} = \frac{1}{Q_0(E)} + \frac{\Phi_1(E,\alpha)}{\Phi_0(E,\alpha)}$$

$$\frac{1}{Q(E,\alpha)} = \frac{1}{Q_0(E)} + k \cdot \frac{\dfrac{e^{-B}}{1+1/A}}{E_1(B) - e^{AB}E_1(AB+B)} \qquad (4)$$

In case of plane source distribution ($A \to \infty$) the following formula can be derived:

$$\frac{1}{Q(E,\infty)} = \frac{1}{Q_0(E)} + \frac{k\,e^{-B}}{E_1(B)}$$

For uniform source distribution Eq. (4) can be transformed to

$$\frac{1}{Q(E,0)} = \frac{1}{Q_0(E)} + k\,\frac{e^{-B}}{e^{-B} - B\backslash E_1(B)}$$

Up to this point the calculations were general enough to be valid for any primary energy E and energy interval ΔE. For the computation of $Q(E,\alpha)$ in the function of α for ^{137}Cs the numerical values of B, $Q_0(E)$ and k are needed. Further calculations will be made for the specific energy value E = 661.6 keV of ^{137}Cs, while the ΔE and Δ'E intervals were set for the energy regions 631–649 keV and 672–690 keV, respectively. Since B is defined as B = μ_ah its value for the standard detector height of 1m is

$$B = 0.010$$

$Q_0(E)$ is the 'peak-to-valley' ratio when no scattering between the source and the detector occurs. Its presence is a consequence of the multiple Compton scattering of the photons of energy E in the detector and thus is a quantity depending mainly on the geometrial characteristics of the semiconductor diode. The determination of $Q_0(E)$ is best done by experiment: a point source of ^{137}Cs positioned about 1m distant from the detector provides the required unscattered flux Φ_0 without having significant buildup of the forward scattered photon flux Φ_1. A typical value for a HpGe detector with relative efficiency of 20% used for in situ gamma-spectrometry is about 70.

The value of k was determined by calibration measurements. An experimental set-up, shown in Fig. 5, was used to measure Q in the function of the thickness of water between the source and the detector.
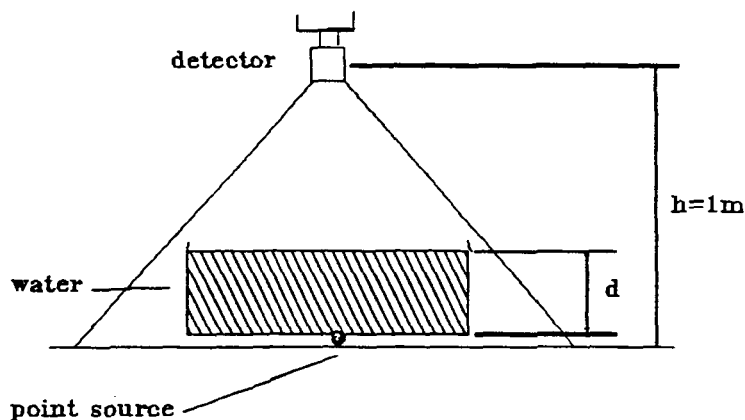
Fig. 5: S c heme of the calibration arrangement for determination of Q_0 and k

Since the relevant quantities in the calibration arrangement above are

$$\Phi_0 = \frac{S_0}{4\pi h^2} \cdot e^{-\mu_w d}$$

$$\Phi_1 = \frac{kS_0}{4\pi h^2} \mu_w d \, e^{-\mu_w d}$$

thus

$$\frac{1}{Q} = \frac{1}{Q_0} + \mu_w d$$

Using the measured values of Q (shown in Fig. 6) and the linear attenuation coefficient for water:

$$\mu_w = 0.085 \text{ cm}^{-1}$$

the following parameters were obtained by regression analysis:

$$Q_0 = 73.5$$
$$k = 0.052$$
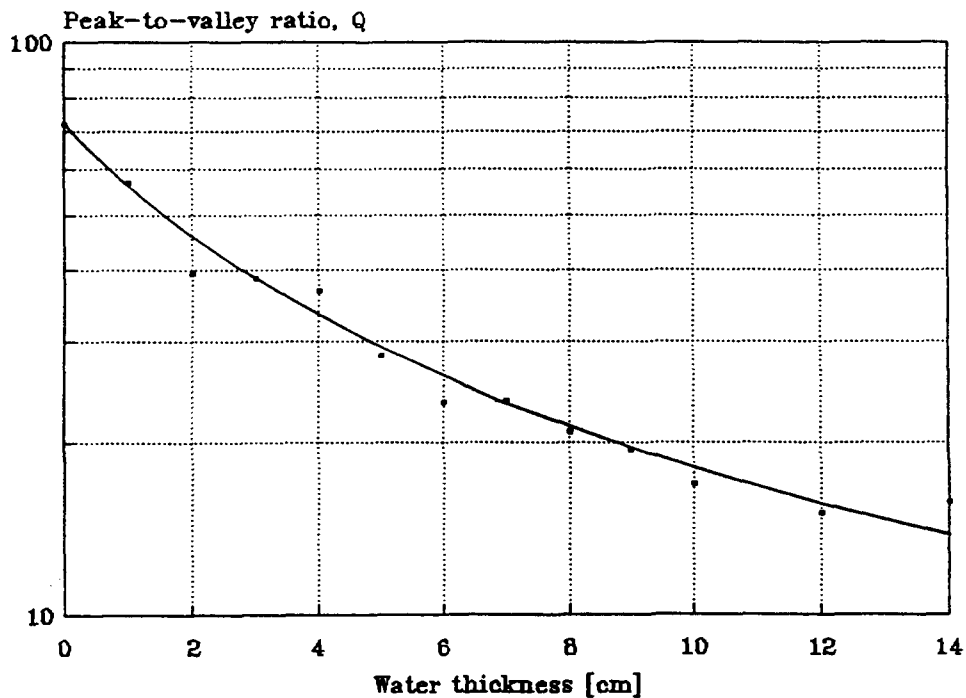
Fig. 6: 'Peak-to-valley' ratios (Q) in the function of water thickness, measured in the geometry of Fig. 5.

Substituting the numerical values of B, Q_0 and k in Eq. (4) $Q = Q(661.6 \text{ keV}, \alpha)$ can be calculated for any value of A, i.e. Q can be plotted in the function of α (for the calculations the value $\mu_s = 0.12$ cm^{-1} was used). Q is a monotonously increasing function of α between the extreme values of 14.6 for the uniform distribution ($\alpha \to 0$) and 37.0 for the plane distribution ($\alpha \to \infty$). (See curve (a) of Fig. 10 for the values of Q).

d., Modification of the exponential distribution model

Soil column measurements and compartment model calculations have shown that the simple exponential distribution is just a rough estimation of the real concentration profile. The departure from exponentiality is a function of time, soil structure, chemical composition, weather etc. Both theory and experiments prove that the migration of the radionuclides in the soil affects the distribution so, that the maximum concentration moves downwards and the uppermost layers become more and more depleted. Fig. 7 shows typical concentration profiles obtained by analysis of soil columns collected in the contaminated areas of the USSR, 4 years after the Chernobyl accident.
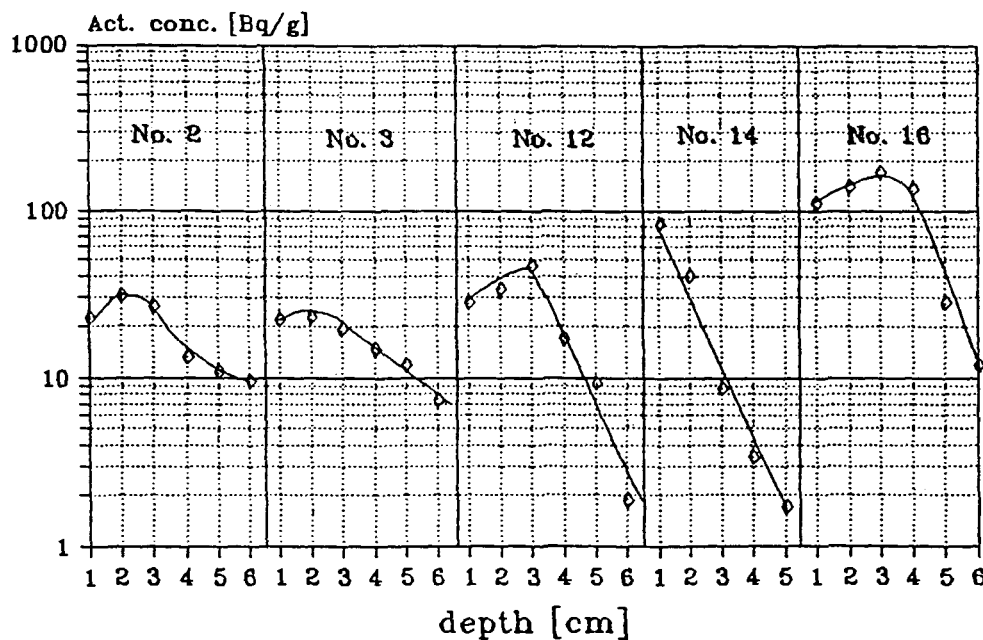
Fig. 7:   Concentration profiles of ^{137}Cs in the upper layers of soil in some samples originating from the contaminated areas of the USSR

Since the top layer of the soil plays an essential role in the attenuation of the unscattered flux and in the build-up of the scattered radiation field the model used for the calculation of Q has to be modified.

To allow for the depletion of the top layers while keeping the assumption of exponentiality for the underlying soil the following radionuclide concentration profile is proposed:

$$S(z) = S_0 e^{-\alpha z} - S_1 e^{-\beta z} = S_0 e^{-\alpha z} \cdot \left(1 - \frac{S_1}{S_0} e^{-(\frac{\beta}{\alpha} - 1)\alpha z} \right) \qquad (5)$$

In this model (beside the original parameters of S_0 and α) two additional parameters (S_1/S_0 and β/α) are introduced: S_1/S_0 setting the proportion of depletion and β/α describing the dynamics of approaching exponentiality.

Fig. 8 demonstrates the influence of the new parameters on the distibution pattern, while Fig. 9 shows the matching between measured data and values calculated on the basis of the modified exponential model.

Performing the calculations of Φ_0 and Φ_1 for the modified exponential distribution the following expressions can be obtained:

$$\Phi_0 = \frac{S_0}{2\alpha} \left[E_1(B) - e^{AB} E_1(AB+B) - \frac{S_1}{S_0} \frac{\alpha}{\beta} \left[E_1(B) - e^{\frac{\beta}{\alpha}AB} \cdot E_1(\frac{\beta}{\alpha}AB + B) \right] \right]$$

$$\Phi_1 = \frac{kS_0}{2\alpha} e^{-B} \left(\frac{1}{1 + \frac{1}{A}} - \frac{S_1}{S_0} \frac{1}{\frac{\beta}{\alpha} + \frac{1}{A}} \right)$$

By substituting Φ_0 and Φ_1 into Eq. (4) one gets:

$$\frac{1}{Q} = \frac{1}{Q_0} + k \cdot \frac{e^{-B} \left(\frac{1}{1 + 1/A} - \frac{S_1}{S_0} \frac{1}{\beta/\alpha + 1/A} \right)}{E_1(B) - e^{AB} E_1(AB+B) - \frac{S_1}{S_0} \frac{\alpha}{\beta} \left[E_1(B) - e^{\frac{\beta}{\alpha}AB} \cdot E_1(\frac{\beta}{\alpha}AB + B) \right]}$$
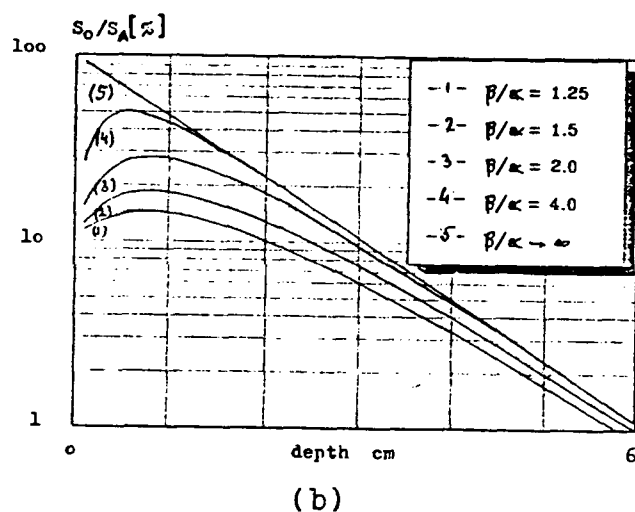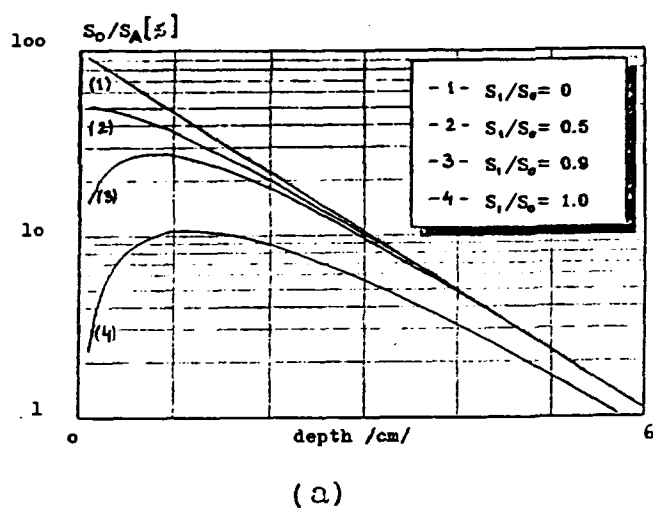
Fig. 8: Typical profiles of the modified exponential
distribution (α = 0.5), (a) for different S_1/S_0
values at β/α = 2.0 and (b) for different α/β
values at S_1/S_0 = 0.9
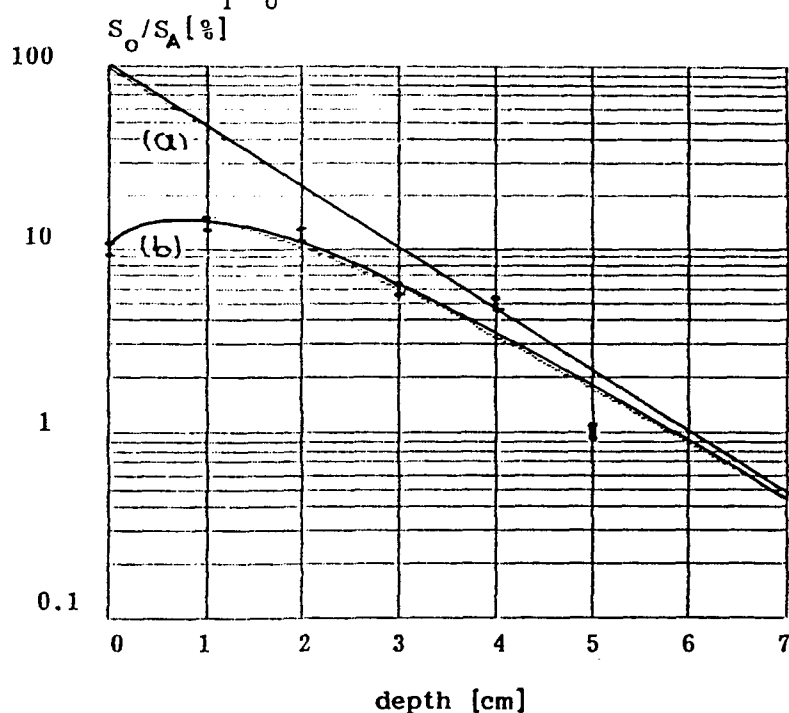
Fig. 9: Comparison of the measured depth distribution of
the Cs-137 concentration with the predicted values
of the simple (a) and the modified (b) exponential
model

The functions of Q versus α for different values of S_1/S_0 and β/α are plotted in Fig. 10 (curves (b)-(d)). A significant difference can be observed between the curves of the modified exponential distribution and that of the simple exponential model (curve (a)), especially in case of low α values. The proportion of depletion (S_1/S_0) has a primary importance, the influence of β/α is much more a smaller perturbation of the basic function characterized by the S_1/S_0 parameter.
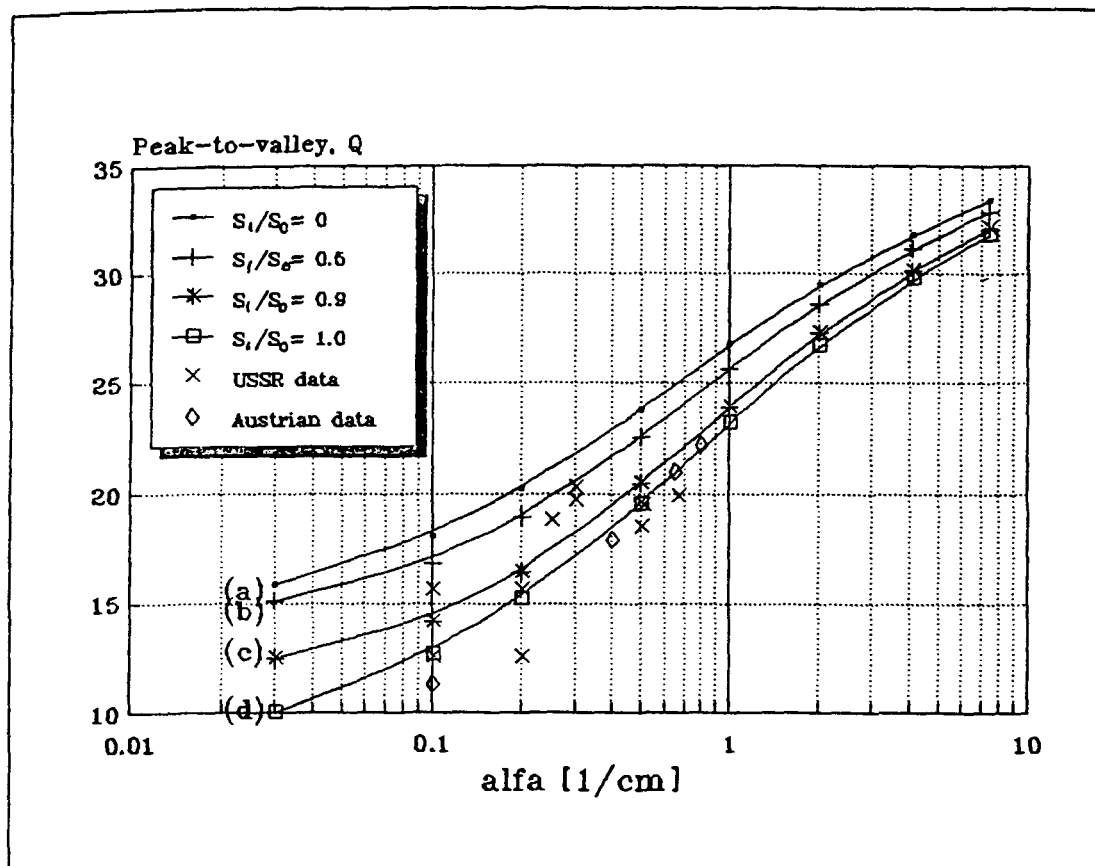
Fig. 10: Calculated values of the 'peak-to-valley' ratio (Q), for different S_1/S_0 parameters, in comparison with some experimentally determined Q values (β/α is set to 2.0)

It is to be emphasized that it is, in principle, impossible to determine α from a single measurement of Q, as long as S_1/S_0 and β/α are free parameters. It gives the possibility, however, that a range for possible values of α can be given. If further investigation of the transport processes of radionuclides in the soil can establish correlation between S_1/S_0, β/α and α, then a more accurate estimation of these distribution parameters will be obtainable.

To check the applicatibility of the model a set of measured data is also shown in Fig. 10. In these cases Q values obtained by in situ spectrometry are plotted versus α determined by laboratory gamma-spectrometric analysis of soil samples collected at the spot of the in situ measurements. Most of the measured data correlate well with the curves of perfect (100%) or substantial (90%) depletion, and even those data (e.g. set No. 12 in Fig. 7) which were close to exponentiality fell below the curve of the simple exponential model (curve (a)). A possible explanation for this phenomenon is that the relatively inactive vegetation acts as a depleted layer shifting the measured Q values towards the predictions of the modified exponential model.

Another consequence of the discussed departure from exponentiality is the slight change of Φ_0/S_A which is an essential quantity in calculating the $\dot{N}_f/S_A$ conversion factors. Here

$$S_A = \frac{S_0}{\alpha} \left(1 - \frac{S_1}{S_0} \frac{\alpha}{\beta} \right)$$

is the total activity per unit area, the quantity we are normally looking for. Thus

$$\frac{\Phi}{S_A} = \frac{E_1(B)-e^{AB}E_1(AB+B)- \dfrac{S_1}{S_0}\dfrac{\alpha}{\beta} \left[E_1(B)- e^{\frac{\beta}{\alpha}AB} E_1\left(\frac{\beta}{\alpha}AB+B\right)\right]}{2 \left(1 - \dfrac{S_1}{S_0}\dfrac{\alpha}{\beta} \right)}$$

This expression will give the usual definition of Φ/S_A if $S_1/S_0 = 0$ or $\beta/\alpha \to \infty$, i.e. the distribution is approaching exponentiality. Values of Φ/S_A for different S_1/S_0 values are presented in Fig. 11.

As it was pointed out only a range of possible α values can be given (if no other information on the distribution is available) on the basis of the Q measured. It is imperative, however, that whatever α is selected, the Φ/S_A value for the conversion is to be used accordingly. There is, fortunately, a compensating tendency in this procedure: though α may vary considerably depending on the S_1/S_0 and

β/α parameters the Φ/S_A factors will not differ so much if properly selected. As an example: if $Q=20.0$ is measured then α varies between 0.20 cm^{-1} (simple exponential case) and 0.55 cm^{-1} (modified exponential, $S_1/S_0 = 1.0$, $\beta/\alpha = 2.0$) meanwhile the Φ/S_A values are 0.46 and 0.53, respectively. It means that the uncertainty of the distribution does not affect strongly the in situ spectrometric determination of the contamination. There is, however, a potential risk to slightly overestimate the total deposition if the simple exponential model is used.
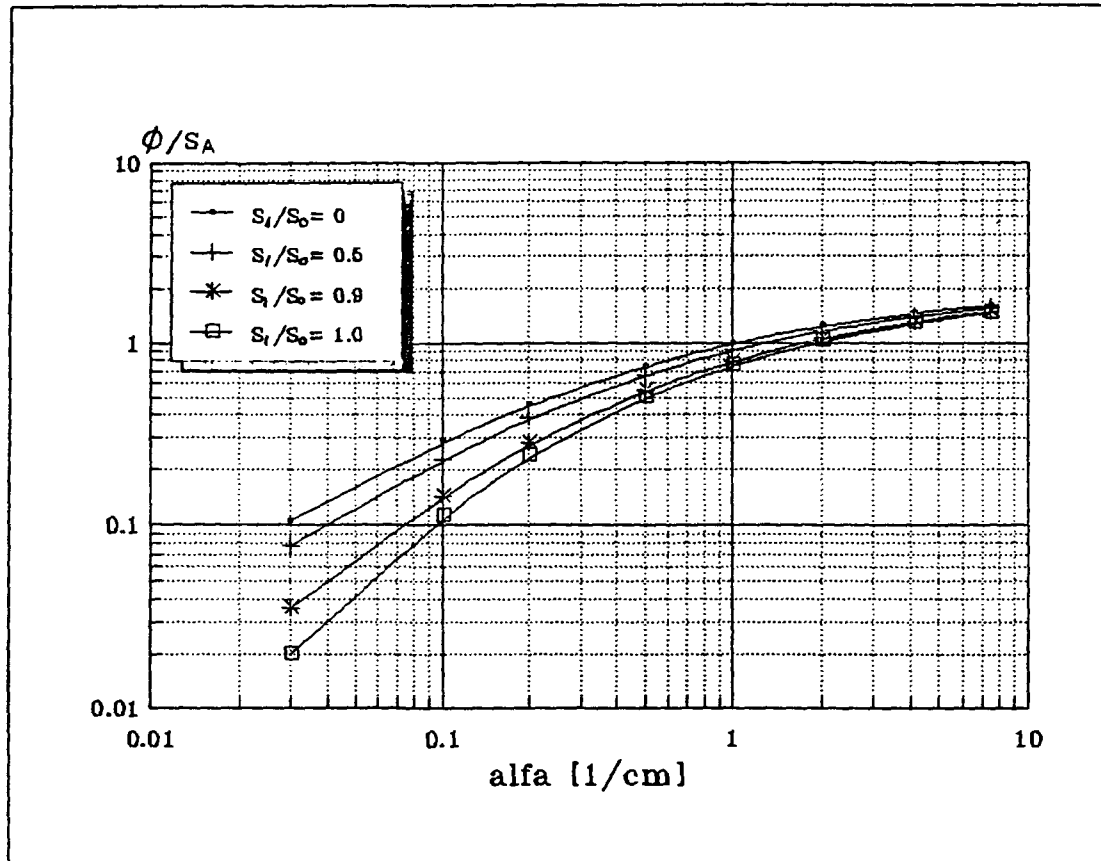
Fig. 11: Φ/S_A co n version factor for different S_1/S_0 parameter values (β/α is set to 2.0)

It is to be emphasized that the selection of the model function Eq. (5) of the modified exponential distribution is not based on theoretical consideration. Its use is justified since it can account for the top layer depletion and has the advantage of easy mathematical treatability. Eq. (5) has, however, a serious disadvantage: it cannot describe a deeper penetration of the maximum with high α value. With the passing of the time the migration of the concentration maximum may necessitate the further modification of the model.

IV. APPLICATIONS

During the recent years two expeditions were made to areas with high radioisotope contamination of Chernobyl origin:

a./ A measuring trip was organized to some selected parts of Austria, where the contamination was significantly higher than in Hungary and the distribution of the radionuclides in the soil was well known even before the measurements.

b./ In situ gamma spectrometric measurements were made in the USSR during an experts' mission to the most affected areas organized by the IAEA. In parallel with the in situ measurements soil samples were taken in order to determine the distribution profile by later laboratory analysis.

In the two missions two different measuring equipments were used so the calibrations for the spectrometers had to be performed twice. Both detectors were of the same type (reversed HpGe with extended sensitivity in the X-ray energy region) which condition enabled us to test both methods described in Section II.

As mentioned in Section III soil sample analyses showed that in most cases the exponential distribution model is just a rough approximation of the real soil profile. There are two major characteristic features which result in significant departure from exponentiality:

- In deeper layers of the soil the decrease of the radionuclide concentration is 'slower', a second exponential component with smaller α value below 10-15 cm is to be used to get a better fit to the distribution.

- A time-dependent desorption effect causes the concentration maximum to migrate from the surface to the deeper layers. The speed of the displacement is a function of the environmental parameters (soil structure and composition, chemical form of the contaminant, annual rainfall etc.) and it results in a 'hump' on the originally exponential distribution.

The first factor does not influence too much the in situ determination of the fallout radioactivity. The proportion of radioactivity below 15 cm to the total deposition is only a few

106

percent and its contribution to the primary flux measured by in situ gamma spectrometry is negligible in the whole energy region of interest. The second phenomenon, however, is certainly an explanation why the method of X-ray to main-gamma-line ratio did not work under real conditions. The X-ray line intensities were significantly less than expected and in some cases peak at 32 keV could not be detected at all, mostly because of the intense attenuation of the X-rays in the uppermost layers. The deviation of the 'X-ray to main gamma line' ratio from the expected values, however, can be an indication of the 'hump' in the soil profile so even the failure of the method can provide some information about the radionuclide distribution.

On the other hand the method of 'peak-to-valley' ratio provided results in good agreement with the soil sample measurements. Fig. 10 shows examples for the matching between the data of the two types of analysis, if the modified exponential distribution model is used.

The procedure works for ^{137}Cs (and as long as the isotopic ratio of the original contamination holds also for ^{134}Cs) with some limitations, however. At the present values are in the range of 0.1 - 1.0 cm^{-1} (relaxation length 1 - 10 cm) and we have no experience beyond this range. Interference of other nuclides can disturb the determination of the 'valley' (636 keV line of ^{125}Sb, for instance) or of the peak (658 keV line of ^{110m}Ag, etc). A further limit of the application is the level of contamination: pulse pile-up problems caused by high intensity radiation lead to distortions in the spectrum. A significant line broadening is expected in fields where the ^{137}Cs contamination is in the order of 10^3 kBq/m^2 when detectors of about 20% relative efficiency are used.

It is to be noted that the in situ measurements in the USSR provided information about the probable distribution much earlier than the soil sample analysis and this information was used to calculate a corrected value for the total deposition. This way these measurements can be considered as the first application of the methods developed under real field conditions and the method of the 'peak-to-valley' ratio proved to be very efficient. For this reason it is not worthless to give some further details of the measurements made during Mission 5 of Task 2 (devoted to the assessment of environmental contamination) within the framework of the International Chernobyl Project, coordinated by the IAEA [7].

The objectives of Mission 5 (part of the efforts to perform independent radiological survey to determine the contamination on selected sites of the affected areas in the USSR) gave an excellent opportunity to test and apply the method of 'peak-to-valley' ratio under realistic conditions. During the mission (in the summer of 1990) the international team of 8 experts visited 3 settlements in areas contaminated by the Chernobyl fallout: Bragin (BSSR) and Polesskoje (UkrSSR) in the controlled zone of higher contamination (15-40 Ci/km^2) and Daleta (UkrSSR) in a less contaminated area (< 5 Ci/km^2). (Former activity units are used in accordance with the official data provided by the USSR authorities). Two complete HpGe gamma spectrometric systems were operated by two groups of experts independently. Some measurements were made in the same place to give an opportunity for the comparison of the results but the groups usually worked separately. The experts of Working Group 1 (WG1) (I. Winkelmann and M. Schweigert from the Bundesamt fuer Strahlenschutz, Institute fuer Strahlenhygiene, Neuherberg and H. Sitter from Kernforschungszentrum Karlsruhe) operating one of the systems took soil samples for the determination of by later laboratory analysis, while Working Group 2 (WG2) (P. Zombori from the Central Research Institute for Physics, Budapest and H. Lettner from University of Salzburg) used the in situ spectra measured during the mission to determine the parameters of the radionuclide distribution. Some soil samples for laboratory analysis were also taken by WG2. The distribution parameters determined by the two different methods as well as the contamination values obtained by the two groups were later compared.

Nine spectra were available for the study of the radionuclide distribution by the method of 'peak-to-valley' ratio. Table 1 summarizes the Q values determined and sets of possible distribution parameter at different proportion of depletion S_1/S_0, in comparison with the the values provided by I. Winkelmann on the basis of his soil sample analyses. This comparison confirmed the concept of the modified exponential distribution: in general, parameters measured by sample gamma spectrometry were closer to those values derived from the 'peak-to-valley' ratio by assuming substantial depletion in the top soil layer.

Knowing the proper distribution parameters the corresponding value of Φ/S_A can be selected, thus the most appropriate conversion factor $\dot{N}_f/S_A$ is available. On the basis of the analysis outlined above the activity concentration and the dose rates at the selected measurement sites were determined (see Table 2) and the data were compared to the results of I. Winkelmann and his group (Fig. 12).
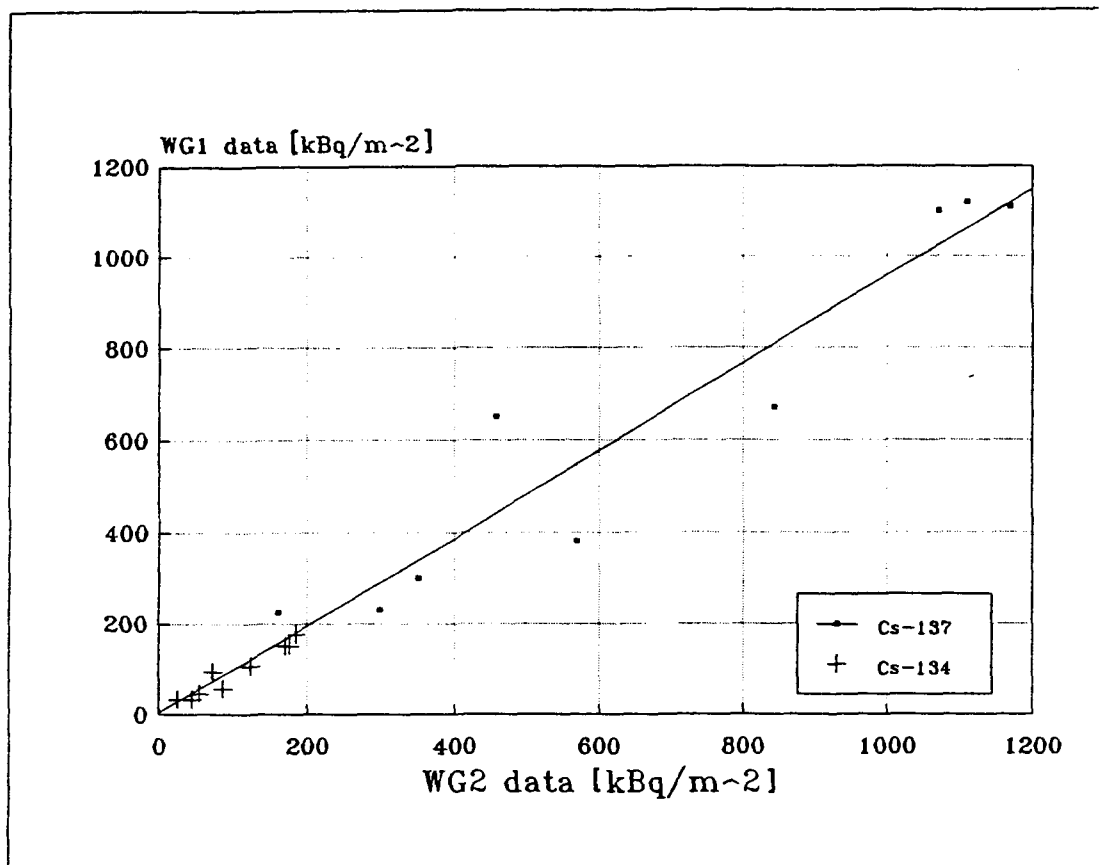
Fig. 12: Comparison of the Cs contamination data measured by
two in situ gamma spectrometric working groups (WG)
of Mission 5 in selected sites of the contaminated
areas of the USSR

Concerning the isotopic composition and the quantitative characterization of the contamination the following statements can be made:

As expected, ^{137}Cs was predominant in the composition, while ^{134}Cs was always found in a concentration 6-7 times less at the time of measurement (July-August 1990). Due to their nuclear characteristics ^{134}Cs had a relatively higher dose rate contribution (38 %), while 59% of the dose rate was attributable to ^{137}Cs. Because of the longer half life this relative contribution will increase in the future.

Beside the Cs-isotopes some other radionuclides (^{60}Co, ^{106}Ru, ^{125}Sb, ^{144}Ce) could also be detected in the environment, but their contribution to the total dose rate was in the order of 1 % or less. The ratio of ^{144}Ce concentration to ^{137}Cs concentration was not constant indicating a different type of contamination: while volatile Cs isotopes are more evenly distributed in the environment, ^{144}Ce may be contained in particles of the fuel element and so, distributed in a more discontinuous manner. (Fig. 13 shows a typical example for the isotopic composition of the contamination)

Rel. contribution

	Cs-137	Cs-134	Ce-144	Ru-106	Sb-125	Co-60
Dose rate	59.13%	38.261%	0.174%	1.565%	0.87%	0%
Act. conc.	76.984%	11.548%	5.065%	5.065%	1.317%	0.1%
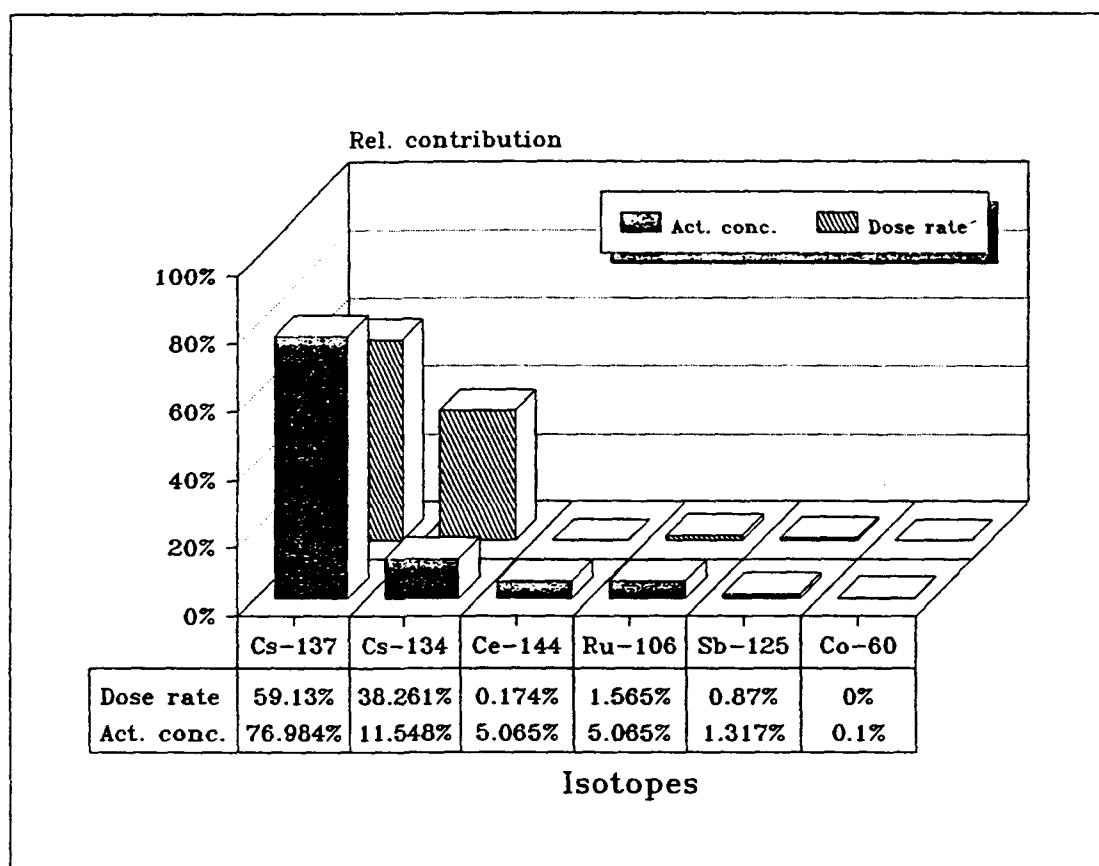
Isotopes

Fig. 13: Isotopic composition of the contamination measured by field gamma spectrometry in the contaminated areas of the USSR

^{137}Cs contamination data measured by in situ gamma spectrometry were again compared to the official data shown on the USSR contamination maps. In Fig. 14 measured ^{137}Cs activity concentrations generally lie within or below the range given by the soviet officials. Considering the great variability of the fallout and the random nature of the measurement site selection the agreement is very good.
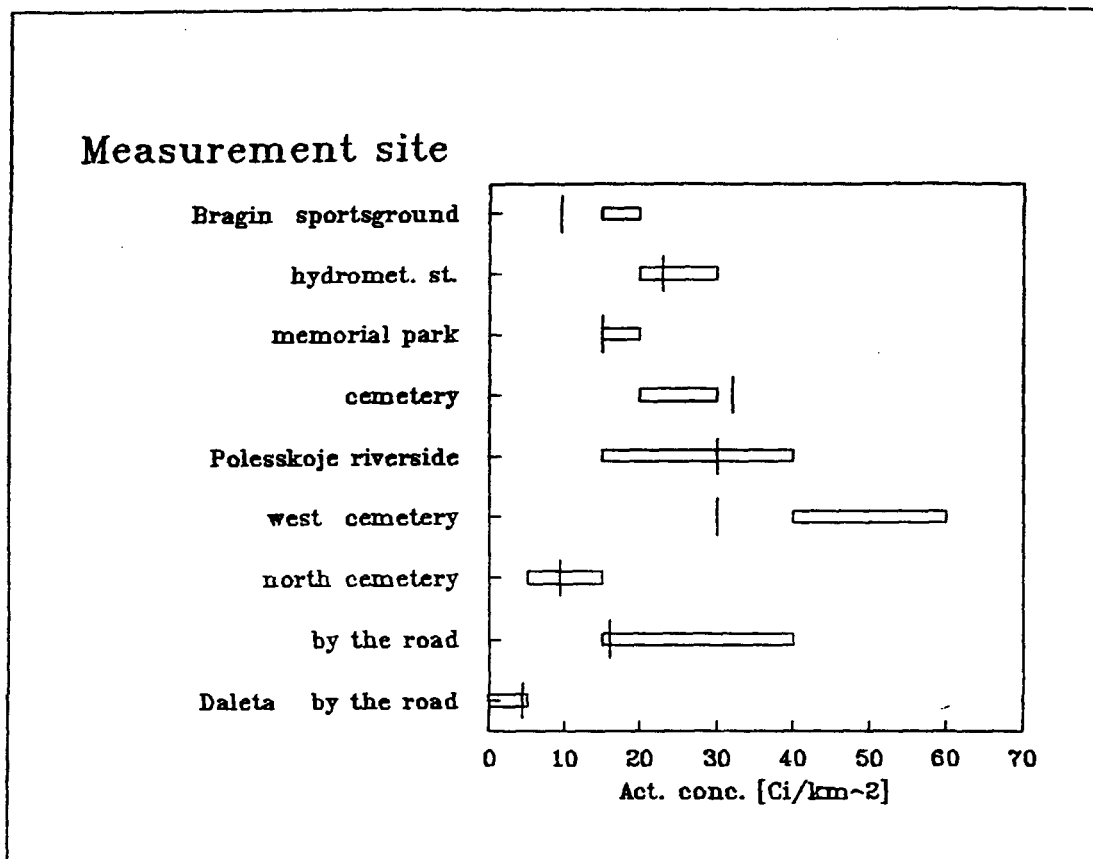
Fig. 14: Comparison of ^{137}Cs contamination data obtained by
field gamma spectrometry with official USSR data
($|$: in situ measurements, ▭ map categories)

V.   SUMMARY

The distribution of fall-out radioactivity in the upper layers of the soil has a strong effect on the ecology of the radionuclides and influences the conversion of the spectral information (peak intensities measured in situ) to surface contamination and dose rate contribution. The radionuclide concentration profile is usually determined by the time consuming soil sampling and sample analysis procedure which hinders the rapid evaluation of a larger scale environmental contamination. A growing interest in speeding up the radioanalytical work made this issue a major objective of coordinated research projects.

To obtain a fast and reliable estimation of the actual distribution pattern some new γ-spectrometric methods (based on the spectrum shape deformation due to scattering and absorbtion in matter) were investigated. The observation that deeper penetration correlate with higher 'valley' (i.e. the continuum on the lower energy side of a

characteristic peak in the in situ spectra) and some theoretical considerations and calculations concerning the small angle (forward) scattering of the photons provided a novel procedure (called the method of 'peak-to-valley' ratio) which proved to be efficient in accomplishing the objectives above.

The ratio of 'peak-to-valley' (Q) as a function of the radionuclide depth distribution parameter α was initially defined and calculated for the case of simple exponential concentration profile. Some calculations and experimental studies revealed, however, that the real distribution is different from the simple exponential one, and the distribution model used for the calculations had to be changed. The modified exponential model, given in the paper, has the potential to describe the real concentration profiles typical for most of the soil types a few years after a major nuclear accident (4-5 years after Chernobyl in the present case). Formulae and plotted graphs are given in the paper to convert the experimentally determined Q values to different sets of parameters.

The practical implementation of the method is very easy. Both peak areas and 'valley' integrals can be obtained immediately after the measurement and the 'peak-to-valley' ratios can be converted to α distribution parameters using the formulae or $Q(\alpha)$ plots given. The application can be disturbed, however, if the 'valley' or the peak interferes with other peaks, or if the intensities are too low to get statistically significant counts, especially for the 'valley'. It is also to be noted that only a range of possible parameter values can be given, but the consequent use of the distribution parameters and the corresponding conversion factors reduces the error of the contamination measurement by in situ γ-spectrometry.

The new method has been tested in measurements over areas of known high activity concentration in Austria and applied under realistic conditions during a mission to the contaminated areas of the Soviet Union. When compared to independent analyses a good agreement both for the distribution parameters as well as for the total contamination was obtained.

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Table 1

Comparison of the distribution parameters determined by the 'peak-to-valley' ratio and obtained by soil sample analysis (β/α parameter is fixed to be 2.0)

	Site		Parameters		
No.	description	Q	in situ		soil sample
			S_1/S_0	α	α
1	Bragin, sportsgound	17.9	0	0.06	–
			0.5	0.11	
			0.9	0.23	
			1.0	0.30	
2	Bragin, hydromet station	12.5	0	–	0.1 - 0.2
			0.5	–′	
			0.9	< 0.03	
			1.0	0.10	
3	Bragin, car training center	19.5	0	0.16	0.50
			0.5	0.23	
			0.9	0.41	
			1.0	0.49	
4	Bragin, cemetery	19.9	0	0.18	0.67
			0.5	0.26	
			0.9	0.44	
			1.0	0.55	
5	Bragin, memorial park	18.7	0	0.13	0.25
			0.5	0.19	
			0.9	0.34	
			1.0	0.42	
6	Daleta, by the road to Ovruch	18.5	0	0.12	0.30
			0.5	0.18	
			0.9	0.33	
			1.0	0.41	
7	Polesskoye, Park in front of the town hall	15.6	0	0.02	0.1 - 0.2
			0.5	0.05	
			0.9	0.16	
			1.0	0.22	
8	Polesskoye, cemetery, entrance area	19.7	0	0.17	0.30
			0.5	0.24	
			0.9	0.43	
			1.0	0.52	
9	Polesskoye, outside the town, by the river Uzh	20.3	0	0.21	0.30
			0.5	0.30	
			0.9	0.49	
			1.0	0.57	

Table 2

Results of the in situ gamma spectrometric measurements made in Bragin/Daleta/Polesskoye during Mission 5 (dose rates are compared to data measured by a dose rate meter SSM1)

Spectrum code	Location	Site description	Act. conc. ($k\,Bq/m^2$)		Dose rate ($\mu Sv/h$)
BRAGO0001	Bragin	Sportsground	Cs-134	54	0.19
			Cs-137	351	0.46
				Sum	0.65
				SSM1	0.68
BRAGO0002	Bragin	Hydromet. station	Cs-134	122	0.25
			Cs-137	844	0.59
				Sum	0.84
				SSM1	1.32
BRAGO03	Bragin	Car training center	Cs-134	44	0.17
			Cs-137	299	0.38
			Ru-106	44	0.002
			Ce-144	164	0.006
				Sum	0.56
				SSM1	0.51
BAGO004	Bragin	Memorial park	Cs-134	85	0.29
			Cs-137	569	0.73
			Ce-144	39	0.0015
				Sum	1.02
				SSM1	0.90
BRAGO0004	Bragin	Cemetery	Cs-134	169	0.60
			Cs-137	1170	1.52
			Ce-144	22	0.001
				Sum	2.12
				SSM1	2.20
DALETA01	Daleta	By the road to Ovruch	Cs-134	25	0.09
			Cs-137	159	0.21
			Ru-106	5	0.0002
				Sum	0.30
				SSM1	0.35
POLES01	Polesskoye	Park in front of the town hall	Cs-134	72	0.21
			Cs-137	458	0.48
				Sum	0.69
				SSM1	0.84
POLES02	Polesskoye	Cemetery, entrance area	Cs-134	175	0.62
			Cs-137	1071	1.39
				Sum	2.01
				SSM1	2.05
POLES03	Polesskoye	Outside the town, by the river Uzh	Cs-134	184	0.65
			Cs-137	1110	1.44
				Sum	2.09
				SSM1	2.30

Research Co-ordinating Meeting
Polen september 1989

Rapid Instrumental and Separation Methods for Monitoring
Radionuclides in Food and Environmental Samples

Live monitoring of cattle, reindeer and sheep.

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INTRODUCTION

After the Chernobyl accident the fallout differed consider-
ably from area to area in Norway and specially were found from
soil samples that the mountain pasture in Middle and South of
Norway were heavily contaminated. These natural ecosystem is
important in several nutrition pathways; notably sheep, goat,
reindeer and cattle.

In june 1986 the Health Directorate imposed action levels
for the nuclides Cs-134 and Cs-137. The action levels were 370
Bq/kg for milk and baby food and 600 Bq/kg for all other types
of food. In November 1986, the action level for reindeer meat
were increased to 6000 Bq/kg, and in June 1987 the level was
also increased to 6000 Bq/kg for wild freshwater fish.

The most effected meat production were reindeer, sheep and
cattle. Almost 20 to 35% of the sheep had activity levels
above the action limits. This fact initiated a broad program
to establish effective measure to increase the activity levels
and to sort out the animals which could be slaughtered. Tree
main approaches have been utilized in Norway in order to
achieve this and to limited the potentia health risk.

- action aimed at reducing uptake from soil to vegetation
  (plowing, use of fertilizing etc.)

- action aimed at reducing uptake from fodder to animals (use
  of cesium binder, change of slaughter time), or reducing
  unacceptable activity levels in animals (downfeeding).

- action aimed at reducing intake to humane (interdiction,
  dietary advice)

Live monitoring were in several of these action necessary
for and successful result.

METHOD

It was very important that the in vivo measurement could be
fast, accurate and simple. A 2" or 3" sodium iodide scintilla-
tion detector coupled to a multi channel analyzer was used for
the measurements. The detector was placed in different places
on the animal depending on the species. this was mostly due to
practical consideration. On sheep the detector was placed on
the back of the animal. On cattle the detector was placed on
the croupe of the animal. As to the reindeer, the animal was
put on its side, then the detector was firmly placed on the
basin (pelvis) between the hind legs.

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Before the in vivo measurements it were necessary to esti-
mate the background activity level of cesium. The detector was
placed in the same position that it would be if one should
measure an animal and the number of impulse in the energy area
for 134-Cs and 137-Cs were counted. The shielding factor for
each species was earlier estimated from monitoring animals
almost without activity on different sites with different
background levels of activity. The equipment was calibrated
for in vivo monitoring by using the function between the
registered number of net impulses in the energy intervals for
134-Cs and 137-Cs after the in vivo measurements and the
activity of the muscle tissue of the same animal after
slaughtering. In the first experiments we used 25 sheep, 40
reindeers and 20 cattle. We also developed a direct method
measurement on the carcasses of the same species.

RESULT

In fig. 1 is the plot of nett impulses per sec of in vivo
measurements is compared with the measurement on muscle tissue
from sheep.

The uncertainty in calculating the activity consideration
in meat from in vivo measurements was found to be less than 8%
at the 95% confidence level for sheep, 7% for reindeer and
11% for cattle.

DISCUSSION

The experiment and testing of the in vivo measurements was
made under controlled conditions, later measurements in the
field was also given good correlation between in laboratory
measurements of muscle tissue and in vivo measurements.

The uncertainty in the calculated activity levels from the
in vivo measurements have shown to be less than 10% at the 95%
confidence level. In sheep with activity level less than
400 Bq/kg the uncertainty may be some what higher than 10%
However, result from in vivo measurement seldom differ more
than $\pm$ 50 Bq/kg at these low activity levels. The in vivo
monitoring method has shown to be of great importance and the
dominating method has shown to be of great importance and the
dominating measurement method in Norway after the Chernobyl
accident.

Calibration of live monitoring on sheep

net impuls pr sec. from live monitoring

activity in muscle tissue (Bq/kg)x1000
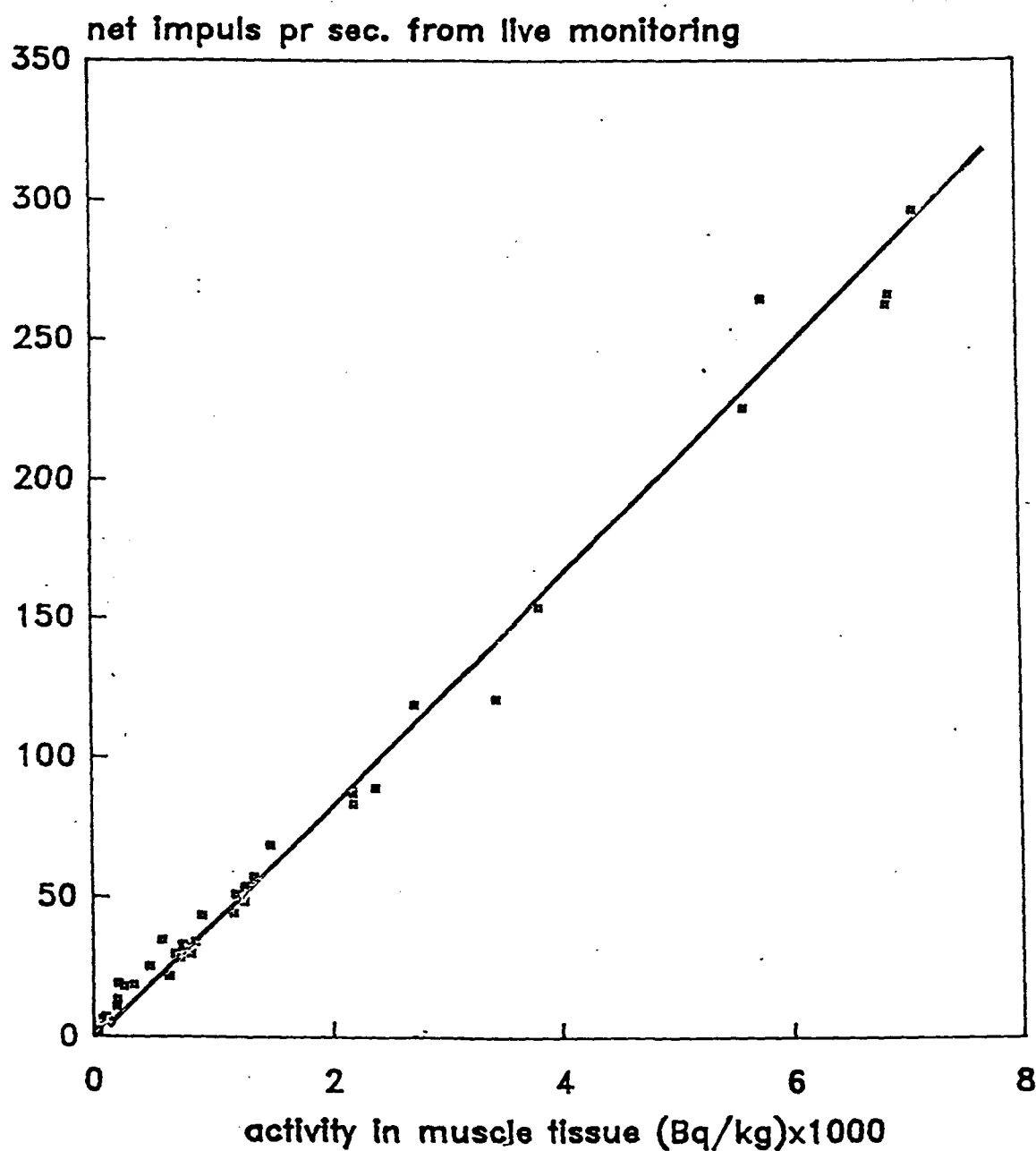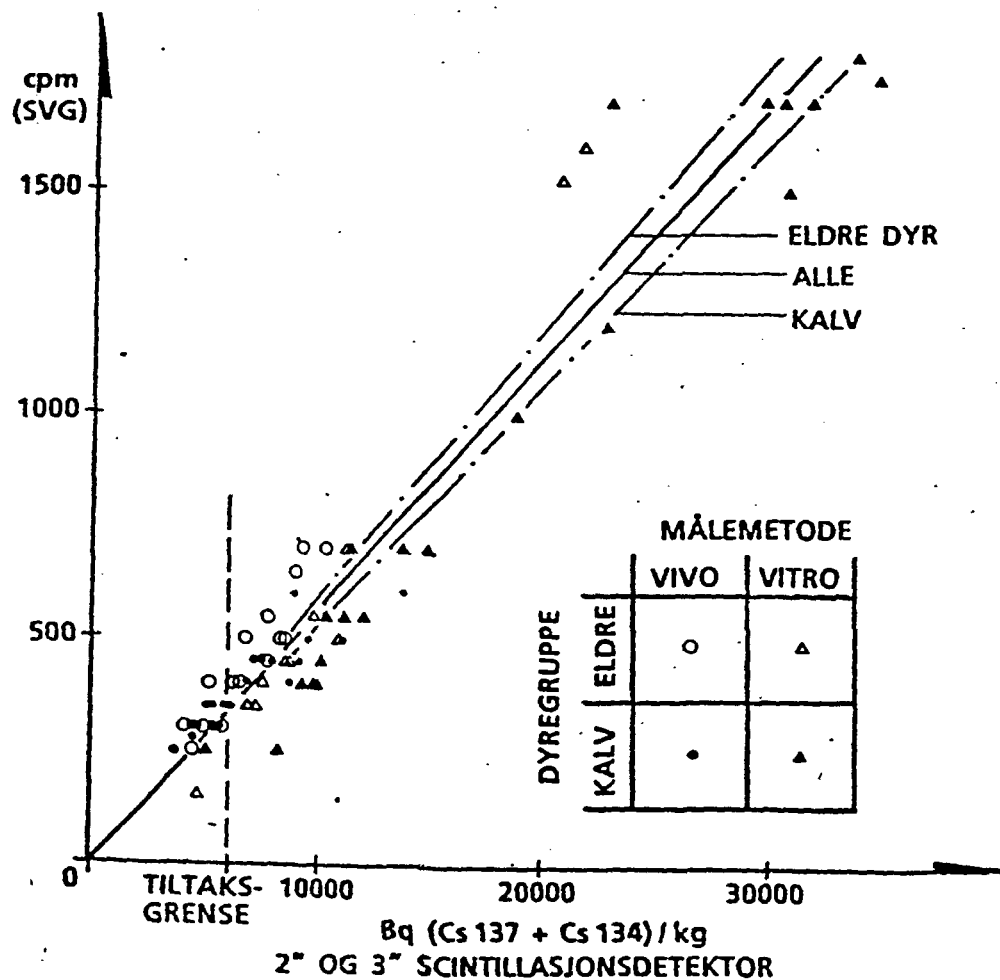
Fig 2

Correlation between cpm and measured activity levels
in muscle tissue with β- probe for the Radiometer SVG

CENTRAL LABORATORY FOR RADIOLOGICAL PROTECTION
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FINAL REPORT
ON RESEARCH CONTRACT No 5453

" QUICK ESTIMATION OF SEPARATE RADIONUCLIDES ACTIVITY
CONCENTRATION IN SPECTROMETRICALLY MEASURED SAMPLES "

Chief scientific investigator : ANDRZEJ PIETRUSZEWSKI

01.01.1990 - 31.05.1991

Scientific bacground and scope of project :
    Quick measurements of environmental and food samples
    of not predefined geometry and density.Quick calibra-
    tion procedures of germanium detectors efficiency.
    Errors range estimation.Recomendations on the quick
    spectrometrical measurements in the radiological
    emergency situation.

This research contract is the part of IAEA coordination
research programme G61001 on "Rapid instrumantal and
separation methods for monitoring radionuclides in food and
environmental samples".

WARSAW, 1991

on

"QUICK ESTIMATION OF SEPARATE RADIONUCLIDES ACTIVITY IN SPECTROMETRICALLY MEASURED SAMPLES"

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S U M M A R Y

This work carried under the IAEA/CLRP research contract No 5453 was performed in the framework of IAEA CRP on "Rapid instrumental and Separation Methods for Monitoring Radionuclides in Food and Environmental Samples" for the purpose of some practical guidelines elaboration which can be implemented for rapid estimation of separate radionuclides activity in spectrometricaly measured samples with germanium detectors under emergency situation.

The detector efficiency calibration for different types of environmental and food samples with different shapes and densities is identified as the most time consuming procedure in spectrometrical measurements. The research work under this project concentrated on the efficiency calibration of germanium detectors of different dimensions (of relative efficiency range from 7% to 30%) which are typically used for food and environmental samples control in spectrometrical laboratories. Each of detectors was calibrated for relatively small (~2g) and relatively big (~2kg) samples in total for 33 geometries and densities in the range from 1 to 2 g/cm^3.

It was assumed that spectrometical laboratory which utilise germanium detectors, and does not perform routine measurements of food and environmental samples control, as eg. University laboratories, medicine laboratories – can join quickly radiological protection services under emergency conditions if the calibration procedure of the detector will be simple and short.

Following recomendations for quick estimation of separate radionucles activity in samples of different shape and density, while measured with germanium detectors were elaborated as the result of research work under this project.

1. If you have your detector calibrated for your own container for one specified sample height you can put any bulk form sample you have got to measure, to this container fulfilling this container to any height, and do not hesitate to use your efficiency calibration for determination of this sample activity.

Realise that you will get accuracy below 3 fold and thats in the range of accuracy required for very rapid method of separate radionuclides activity measurements as specified by the requirements of IAEA CRP on rapid methods of activity measurements. Try to use table 4 for better estimation.

2. If you have no time for the preparation of voluminos reference standard source under emergency conditions than do your calibration with the point source located axially to the detector surface at two distances ~2-3 cm and ~5-6 cm. Then you can measure small and big samples with your detector.

Calibration curve on ~2-3 cm distance should be used for small < 200g samples. Calibration on ~5-6 cm should be used for samples > 200g and high density samples. Realize that such calibration enables you to achieve accuracy better then ± 50%.

3. You can quickly correct your results of activity estimation with the method described in p.2 calibrating your detector with point source at the distance of 5 cm from its surface and multiplying your results by cofficients factors which take under consideration your sample diameter and height. These factors are specified in tables 5 and are valid for typically used coaxial type germanium detectors. Utilising these factors you can get the accuracy better then ±30%.

4. Realize that sample density and its element composition
   influence your measurements. Use tables 6 for the estima-
   tion of the error caused by the difference in standard
   (typically water solution) and sample density. Anyway rea-
   lize that this error will be not higher than 100% even in
   the case of low energy region and the difference of 2 times
   in sample: standard density (the same geometry!)

Additionally to those recommendations there were two appendixes
elaborated for the needs of this and under this research
project:

1. Automatic IBM/PC computer programme on the efficiency curve
   determination with appropriate errors corridore as the function
   of energy. Efficiency data base can be created with his
   programme.

2. The "peak to total" method of detector efficiency calibration
   as desairbed by Moens [1] and [2] for voluminos samples was
   implemated and what can be interested to one performing spec-
   trometrical measurements detailed step by step stereometric
   solution of Moens [1] equations are elaborated and presented.
   Respective computer programme was also elaborated, checked and
   put in operation. This programme enables to calculate the de-
   tector efficiency for cylindrical samples after one calibration
   measurement with the point source. Anyway it requires the know-
   ledge of detector crystal parameter, what can be found not al-
   ways posible. X-ray photo of the detector capsule is then reco-
   mended for the determination of crystal size and its situating
   in capsule. Examples of programme utilisation and testing in
   comparison with experimental work are presented.

Presented recommendations, as elaborated basing on research
results, were checked at Chemistry Unit of PCI IAEA Seibersdorf
Laboratories. Results confirm the practical value of these recom-
mendations and are presented in appendix [3]. The paper on this
method was presented on IAEA symposium on "Environmental Contami-
nation folloving a major nuclear accident" 16-20 October, 1989 [4].

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RAPID METHOD OF ENVIRONMENTAL SAMPLES RADIOACTIVITY MEASUREMENTS WITH GAMMA SPECTROMETRY

1. INTRODUCTION

Spectrometrical laboratory which has to measure radioactivity of enviromental and food samples as well as all other types of different materials should be prepared for performing qualitative and quantitative analysis of samples with different isotopic composition and different activities of measured isotopes.

Dimensions of measured samples, their shape and magnitude can be very different. All that reasons influence the procedures of the efficiency calibration of typically used spectrometrical systems with germanium detectors, makes the calibration procedure time consuming and needs a big set of different voluminos calibration sources.

If during emergency situation the efficiency calibration for specific sample shape was not previously done, then the preparation of specific spectrometric calibration source - usually in form of solution of separate monoenergetic isotopes - lasts much longer and needs much more work than the measurement time of the sample itself. Therefore whenether there is the need of performing quick qualitative determination of separate radioisotopes activities, basing on the results of spectrometrical measurements, especially during the radiological emergency situation, troubles with not having specific efficiency calibration of germanium detector (for measured sample shape) limit the possibility of quick spectrum elaboration. As such precise calibration procedures are time consuming the necessity of their performing is not always purposefulness.

The goal of this research project was to propose simple method for the efficiency calibration which can be performed very rapidly in any laboratory which has in operation spectrometrical system with germanium detector and multichannel analyzer. Such calibration should enable measurements of the samples of different size and densities.

Proposed calibration procedure should be used only in emergency
conditions when the investigator is forced to give the results of
radioactivity measurements for samples very quickly what usually
requires to minimise the time spent for calibration. Proposed
method should also meet the requirements of the accuracy of
measurements as determined for the needs of radiological
protection in emergency situation, what means:

"To determine gamma emitting radionuclides at a concentra-
tion of at least one order of magnitude below the derived
intervention levels DIL-s for food as specified by WHO and
the IAEA and at least at the lover level of 100 Bq/kg"
in particular:

	Approximate accuracy	Approximate elapsed time
screening methods	10 fold	5 - 15 min
very rapid methods	2 ÷ 3 fold	1 ÷ 6 h
rapid methods	± 50 %	6 ÷ 24 h

This research project was concentrated on the problems of:

- achievable accuracy of voluminos bulk form sample measurements
  of any volume and density measured in cylindrical type contai-
  ners.

- quick efficiency calibration of germanium detector with one
  multielement point source and its utilisation for food and
  environmental samples measurement with.   •

The programme of work was as follows:

1. Efficiency calibration of different detectors with respect
   to volume, density (geometry factor). Application of these
   results where the parameters are not known and establishment
   of accuracy and precision. Starting to develop quick proce-
   dures to evaluate gamma-spectra with special references to
   short time measurements.

2. Determination of correction factors for different sample
   sizes and densities using Ge-detectors and point sources
   calibration.

3. Studying the possibility to use one set of correction fac-
   tors for Ge-detectors of different relative counting effi-
   ciency.

2. EFFICIENCY CALIBRATION METHOD OF GERMANIUM DETECTORS.

Activity A of radionuclide X which is present in measured sample of geometrical shape V and density ρ is determined as:

$$A_I = \frac{N_E^{\cdot I}}{F_{E,V}^* \, \eta_E^I \, * \, T} \qquad [\;1\;]$$

where :

N_E^I - is the number of counts in photopeak netto of the gamma line of photons with energy E which are emitted by radionuclide I

$F_{E,V}$ - is the coefficient of the detector efficiency for photons with energy E emitted by sample of geometrical shape V and density ρ.

η_E^I - is the coefficient of decay emission of photons with energy E of radionuclide X

T   - is the measurement time [s].

Activity measurement of separate radionuclides present in the sample with specific shape, volume and density requires the efficiency calibration of the detector with special voluminos reference source reflecting measured sample shape and volume.

Proposed in this work method for qualitative determination of separate radionuclides activities in samples of different volumes and densities requires the user of the spectrometrical system to perform only one efficiency calibration with point source placed in one specified distance from the detector surface.

The efficiency coefficient of spectrometer for the gamma radiation with photons energy E emitted by radionuclide present in reference point source can be determined as:

$$F_{E,W_P} = \frac{N_{E,W_P}^{I}}{A_{W_P}^{I} * \eta_{E}^{I} * T_{W}}$$ [2]

where :

$N_{W_P}^{I}$ — is the number of counts in photopeak netto of the gamma line with energy E emitted by radio-nuclide I present in the reference point source,

$A_{W_P}^{I}$ — is the activity of the radionuclide I present in the reference point source,

T_{W} — is the measurement time of the reference point source.

Multiplying the numerator and denominator of equation [1] by F_{E,W_P} we receive equation:

$$A_{I} = \frac{N_{E}^{I}}{F_{E,W_P}} \frac{F_{E,W_P}}{F_{E,V,P} * \eta_{E}^{I} * T}$$ [3]

Activity of the same radionuclide I present in voluminos reference standard of the shape and volume the same as the measured sample and with matrix density ρ_o is determined with equation [4]:

$$A_{Wo}^{I} = \frac{N_{Wo,E}^{I}}{F_{E,Wo} * \eta_{E}^{I} * T_{Wo}}$$ [4]

where from:

$$F_{E,Wo} = \frac{N_{Wo,E}^{I}}{A_{Wo}^{I} * \eta_E * T}$$

[5]

where:

F_{E,W_o} — is the coefficient of spectrometer efficiency for gamma photons with energy E emitted by radionuclide I present in voluminos reference standard,

N_{Wo}^{I} — is the number of counts netto in photopeak measured with spectrometer of the gamma line with photons energy E emitted by radionuclide I present in voluminos reference standard,

T — is the measurement time of voluminos reference standard

The difference in values of coefficients $F_{E,V,p}$ and $F_{E,Wo}$ is caused becouse of different densities and different composition of the matrix of measured sample and measured voluminos reference standard.

If $T_{E,V,p}$ and $T_{E,Wo}$ are the transmission coefficients of gamma radiation for photons with energy E for sample and the reference standard we can write:

$$F_{E,V,p} = F_{E,Wo} * \frac{T_{E,V,p}}{T_{E,Wo}} = F_{E,Wo} * q_E \qquad [6]$$

where :

$$q_E = \frac{T_{E,V,p}}{T_{E,WO}} \qquad - \qquad \text{is the relative transmis-}$$

is the relative transmission coefficient of gamma photons with energy E

Equation [3] can be also written as:

$$A_I = \frac{N_E^I}{F_{E,Wp}} * \frac{F_{E,Wp}}{F_{E,Wo} * q_E * \eta_E^I * T} =$$

$$= \frac{N_E^I}{F_{E,Wp} * \eta_E^I * T} * \frac{k_E}{q_E} \qquad [7]$$

where : $k_E = \dfrac{F_{E,Wp}}{F_{E,Wo}}$ is the coefficient of relative efficiency of the counts of gamma photons with energy E

If the coefficients k_E and q_E are known, then with the spectrometer, for which the calibration was performed only with point source placed on detector axis — it is possible to perform measurements of separate radionuclides concentrations in any voluminos sample.

3. EXPERIMENTAL PART

Six germanium detectors HPGe and Ge(Li) of different size, relative efficiences and resolution were used in experiment. Detectors parameters are presented in table 1.

Table 1.

Technical parameters of detectors used for efficiency calibration in research project.

Lp	Detector type (producer)	Detector material	Relative efficiency (%)	Resolution for 1332 keV
1	Coaxial HPGe (Canberra)	HPGe type P	30 %	1.78 keV
2	Coaxial GeLi (Kovo)	GeLi type P	10 %	4.10 keV
3	Coaxial HPGe (Canberra)	HPGe type P	15 %	1.75 keV
4	Coaxial HPGe (Canberra)	HPGe type P	17 %	1.75 keV
5	Coaxial GeLi (IBJ Świerk)	GeLi type P	7 %	4.5 keV
6	Coaxial HPGe (Tennelec)	HPGE type P	20 %	1.85 keV

Relative efficiency as presented in table 1 for each detector is the efficiency specified by manufacture in [%] with reference to the efficiency of NaJ(Tl) crystal of 3" x 3" dimensions for Co-60 gamma radiation of 1332 keV.

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Each detector was calibrated for 31 geometries with specially prepared multielement reference sources in the form of solution. Amersham QCY 48 reference source and multielement reference source produced ourselves in the Center for Isotope Production at Swierk in Poland were used for the preparation of voluminos reference sources.

Totally 33 reference voluminos sources were prepared in 6 different containers, five of which were of cylindrical -shape and one Marinelli type. The dimensions of prepared reference standards are presented on fig.1. Isotopic composition of prepared standards are enclosed in appendix 1. Efficiency calibration of each detector with point source was performed with sources produced ourselves and with multielement point source QCD-1 of Amersham. The density of voluminos sources was 1 g/cm^3. Additionally 4 standards were prepared with density of 2 g/cm^3 on the matrix of pure SiO_2. Two types of Marinelli standards with density 1 g/cm^3 and 2 g/cm^3 were also used for calibration. All certificates of used and prepared ourselves standards are presented in appendix 1.

volume = 150 ml

S-0.125/6
S-0.125/5
S-0.125/4
S-0.125/3
S-0.125/2
S-0.125/1

diameter = 5.6 cm
heights = 1,2,3,4,5,6 cm

volum = 70 ml

S-0.07/7
S-0.07/6
S-0.07/5
S-0.07/4
S-0.07/3
S-0.07/2
S-0.07/1

diameter = 3.5 cm
heights = 1,2,3,4,5,6,7

volume = 20 ml

S-0.02/5
S-0.02/4
S-0.02/3
S-0.02/2
S-0.02/1

diameter = 1.7 cm
heights = 1,2,3,4,5 cm
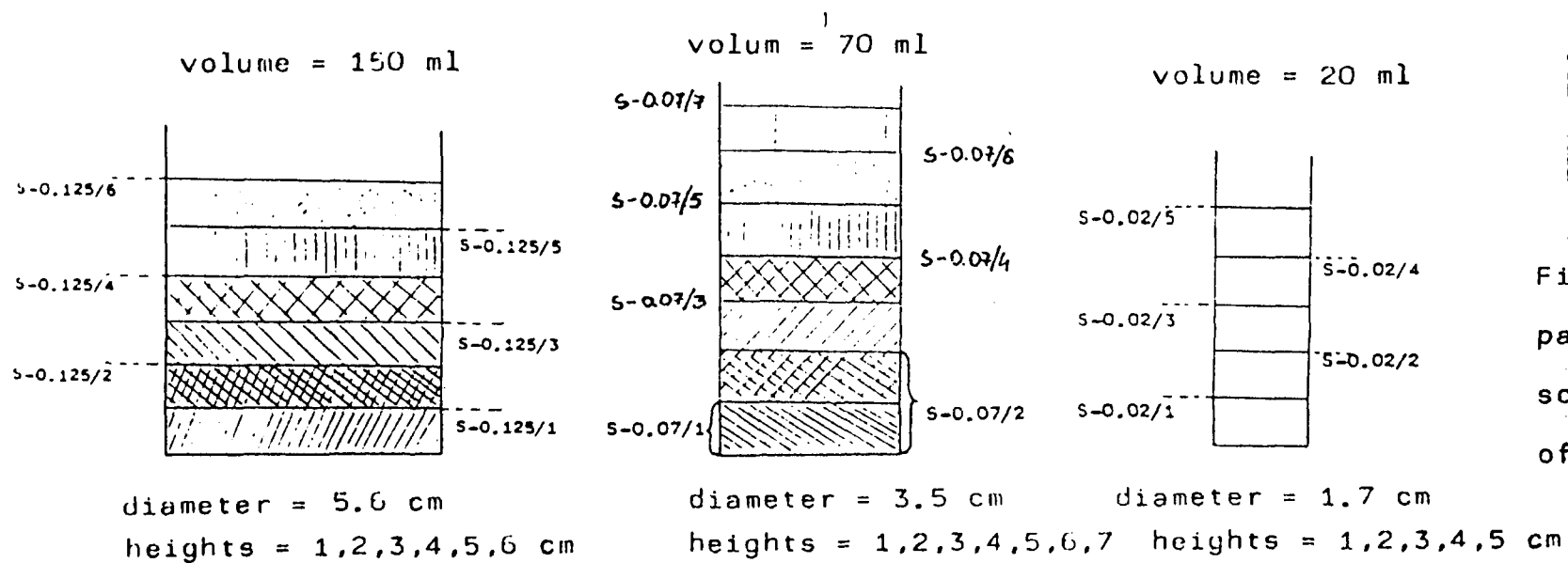
Fig. 1. Dimensions of prepared cylindrical reference sources for the calibration of detectors efficiency .

volume = 1000 ml

S-1.0/12
S-1.0/9
S-1.0/6
S-1.0/3
S-1.0/1

diameter = 9.5 cm
heights = 1,3,6,9,12 cm

volume = 500 ml

S-0.5/11
S-0.5/9
S-0.5/6
S-0.5/3
S-0.5/1

diameter = 7.5 cm
heights = 1,3,6,9,11 cm

56 mm

SP - 0.125/6

60 mm

SP - 0.125/1

SP - 0.5/11

110 mm

SP - 0.5/1
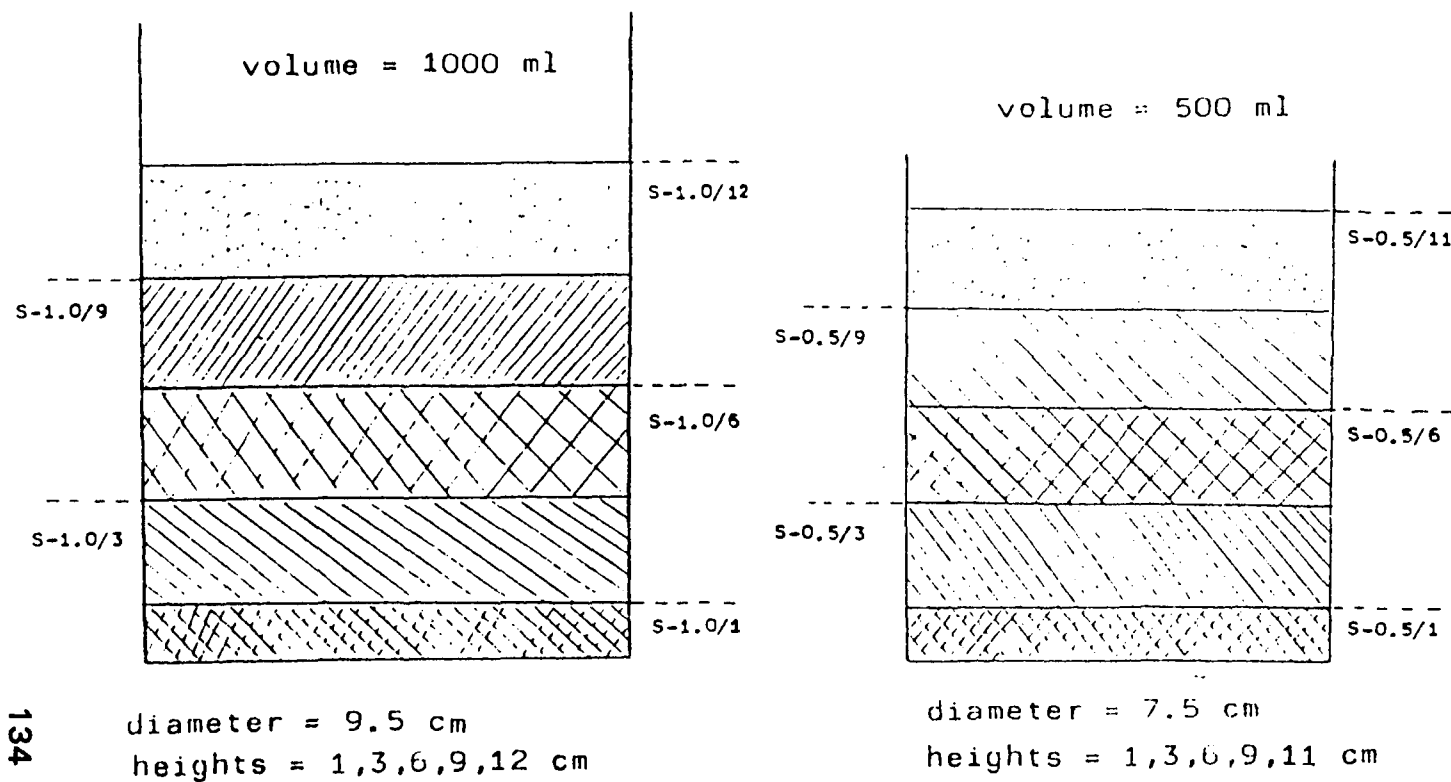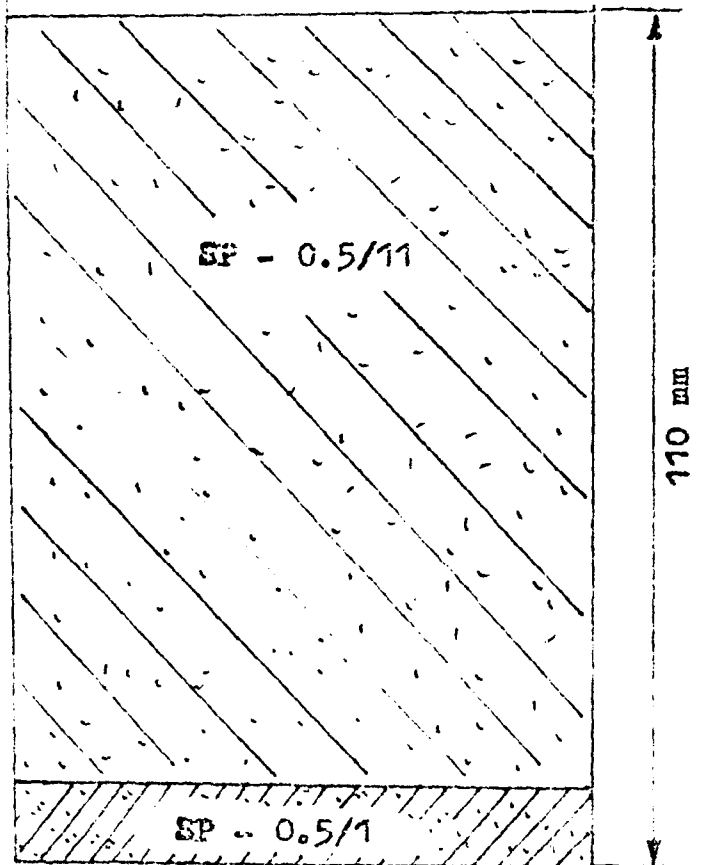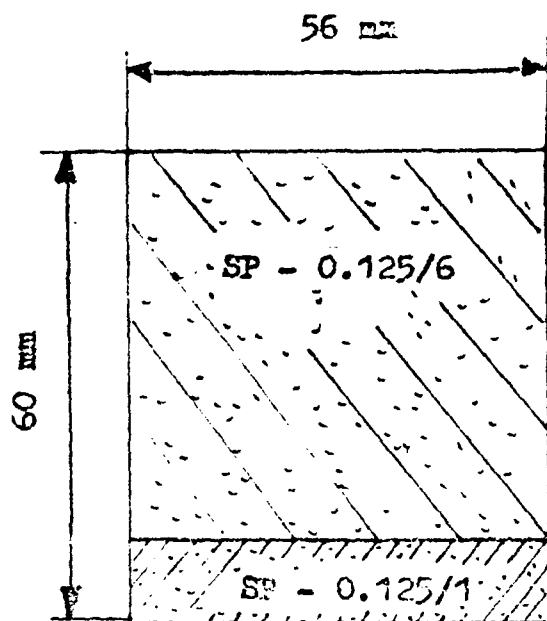
S A M P L E   D E N S I T Y = 2 g/cm^3

CONTAINERS :   0.125/1 , 0.125/6   /d= 5.6 cm/
0.5/1 , 0.5/11   /d= 7.5 cm/

104.1 mm

1.9

14.8

77.4

68.3

1.9   2.0

3.6
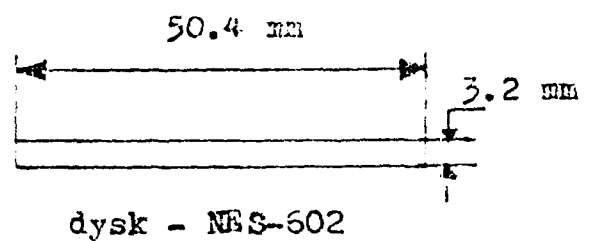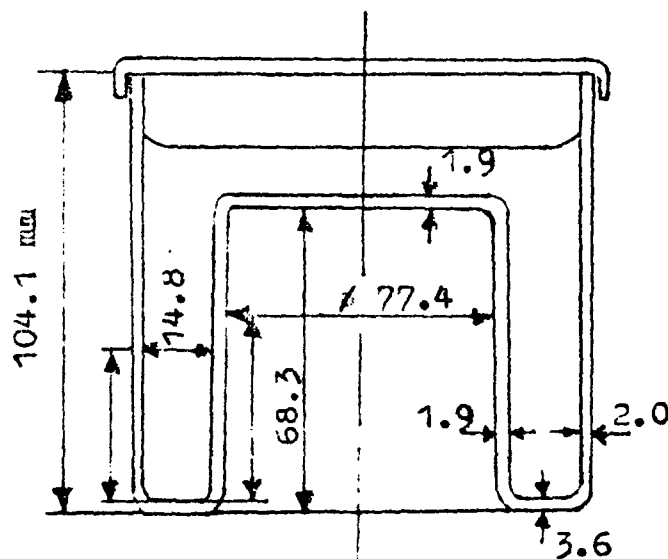
MARINELLI - 1 g/cm^3
2 g/cm^3

50.4 mm

3.2 mm

dysk - NBS-602

Table 3 present radionuclides used in prepared calibration standards and energy of gamma lines utilized in the calibration of the germanium detectors efficiency. The activity of prepared standards was determined with the accuracy better then ± 5%.

Table 3.

Radionuclides in prepared calibration standards used for the efficiency calibration of germanium spectrometers.

Radionuclide	^{241}Am	^{109}Cd	^{57}Co	^{57}Co	^{139}Ce	^{203}Hg
Energy (keV)	60	88	122	136	166	279

Radionuclide	^{51}Cr	^{113}Sn	^{85}Sr	^{134}Cs	^{137}Cs	^{134}Cs
Energy (keV)	320	392	514	604	661	795

Radionuclide	^{54}Mn	^{46}Sc	^{46}Sc	^{60}Co	^{60}Co	^{88}Y
Energy (keV)	834	889	1120	1173	1332	898, 1836

The detection efficiency curve was calculated according to the equation:

$$F_E = \frac{N * \exp (- 0.693 * t / T_{1/2})}{A * \eta * T} \qquad [8]$$

where: N - the number of counts registered in the photopeak of E [keV] energy

t - time [s] between the measurement and the reference date of the standard reference source activity

$T_{1/2}$ - decay time of particular isotope in the reference standard source [s]

A - activity of particular isotope [Bq]

η - decay efficiency of specified gamma line

T - the time of the reference standard source measurement [s].

Detection efficiency calculated with the equation [8] for each registered gamma line was approximated with least squared method to the logarithmic curve of 4th order as presented by equation:

$$Log \ (F_i) = b_j * (\ log \ (\ E_i))^{j-1} \qquad [\ 9 \ ]$$

For the automatic calculation and graphic presentation of detection efficiency curves there was special computer programme elaborated called "EFFCAL", which is described in appendix 2. This programme can be also utilized in each laboratory which uses the IBM PC computer. The copy of this programme is enclosed on the source diskette.

Calibration measurement were performed for 31 geometries of volume standards. Additionally each detector was calibrated for the point source geometry situated axially to the detector on the distance from 0 cm to 10 cm, each 1 cm.

4. RESULTS OF MEASUREMENTS.

The results of the measurements are presented in form of tables and diagrams in each of 6 calibration books for each of 6 calibrated detectors separately. Graphic set of calibration data for detector No 1 is enclosed as an example to this report(appendix 4).

5. THE ELABORATION OF MEASUREMENT RESULTS.

5.1. Quick estimation of any type and shape sample activity measured in the cylindrical container for which the one efficiency curve was determined.

Errors of the activity estimation while one reference calibration curve for cylindrical container is used for the activity determination of any voluminos sample in the container fulfilling this container to any height are presented in this chapter in forms of tables for each of calibrated detectors separately(appendix 5).

These errors were calculated for selected radionuclides covering the full energy range of interest in typical spectrometrical measurements used for food and environmental samples control.

$$^{141}Ce \quad - \quad 145.4 \text{ keV}$$

$$^{132}Te \quad - \quad 228.2 \text{ keV}$$

$$^{131}J \quad - \quad 364.5 \text{ keV}$$

$$^{103}Ru \quad - \quad 497.1 \text{ keV}$$

$$^{137}Cs \quad - \quad 661.6 \text{ keV}$$

$$^{134}Cs \quad - \quad 795.8 \text{ keV}$$

$$^{140}La \quad - \quad 1596.4 \text{ keV}$$

Errors were calculated according to the following equation:

$$\text{ERROR OF ACTIVITY ESTIMATION} = \frac{|A_i - A_{ji}|}{A_i} \times 100 \% =$$

$$= \frac{|F_{ji} - F_i|}{F_{ji}} \times 100 \% \qquad [11]$$

where.

A_i - real value of radionuclide activity in measured samples

$$A_i = \frac{N}{F_i * \eta * T * M} \qquad [12]$$

A_{ji} - activity value of the same radionuclide calculated using efficiency curve for j-type geometry

$$A_j = \frac{N}{F_j * \eta * T * M} \qquad [13]$$

Excluding extreme cases while e.g. when the detector is calibrated for the cylindrical container fulfilled with standard to 12 cm height and this calibration is used for the determination of 1 cm height sample, in all other practically meet cases, reffering the results of the calibration and calculations under this research project it can be applied the following formula for practical application in performing spectrometrical measurements:

```
IF YOU HAVE YOUR DETECTOR CALIBRATED FOR YOUR OWN
CONTAINER FOR ONE SPECIFIED SAMPLE HEIGHT YOU CAN USE
THIS CALIBRATION FOR ANY OTHER SAMPLE HEIGHT IN THIS
CONTAINER AND YOU WILL GET ACCURACY BELOW 3 FOLD FOR
VERY RAPID METHOD OF ACTIVITY DETERMINATION.
```

Table 4.

Comparison of results for the achievable accuracy of measuring and estimation of isotopes activities in bulk form samples full-filling the cylindrical containers to any height. Calibration of the detector efficiency is only for one specified geometry (eq. full container) in each ease. (graphic presentation of errors for each detector is presented in appendix 5).

Contai-ner type	Diame-ter [cm]	Height range [cm]	ERRORS RANGE [%]					
			Det.5	Det.2	Det.4	Det.3	Det.6	Det.1
			7 %	10 %	17 %	15 %	20 %	30 %
0.02	1.7	1÷5	14÷115	8÷94	16÷133	15÷136	20÷135	14÷117
0.07	3.5	1÷7	13÷195	3÷135	13÷200	14÷201	14÷204	13÷186
0.125	5.6	1÷6	14÷137	10÷105	13÷154	14÷158	14÷152	15÷144
0.5	7.5	1÷11	24÷238	25÷263	20÷308	15÷291	16÷291	19÷293
1.0	9.5	1÷12	26÷278	25÷312	32÷336	32÷339	30÷330	40÷333

These table present the extreme case for the low energy region of Ce-141 isotope energy range (145.4 keV). Errors range appro-ximate data for particular containers are presented in graphic form for each of detectors separately. These curves can be also used for approximation.(see appendix 5).

5.2. Quick calibration of germanium detector with reference point standard and its utilisation for the estimation of the activity of measured voluminos samples.

The efficiency for the point calibration reference source standard which was placed each 1 cm (0-10 cm) axially to the detector surface was wsed for the calculation of voluminos samples activity for each of 31 prepared and measured cylindrical standards. The errors of such activity estimation for separate radionuclides were calculated es follows:

$$\text{ERROR OF ACTIVITY ESTIMATION} = \frac{| A_i - A_{ipj} |}{A_i} \times 100 \% \qquad [14]$$

where:

A_i – the real activity of specified radionuclide i in measured voluminos sample

A_{ipj} – the estimated activity of radionuclide i in voluminos sample calculated using efficiency curve of point source olaced of the distance j (1-10 cm) axially over the detector surface.

These errors of the activity estimation were determined for 3 isotopes emitting the gamma radiation in energy range 120÷1332 keV:

$$^{57}\text{Co} - 122 \text{ keV}$$

$$^{137}\text{Cs} - 661 \text{ keV}$$

$$^{60}\text{Co} - 1332 \text{ keV}$$

For each of cylindrical containers fulfilled to the minimal (1 cm) and maximal (see fig.1) height errors as determined with equation [14] were determined and olotted as the function of the height of point source over the detector surface. Results are oresented in graphic form. for each of detectors seoarately.

Analysis of results for all of the detectors use for calibration, allows for the formulation of the following practical guideline that can be applied in practical quick measurements of the radionuclides activity in spectrometrically measured voluminos samples of environmental and food type with semiconductor germanium detectors:

Quick efficiency calibration of germanium detector with reference point calibration source placed axially over the detector surface can be utilised for quick activity estimation of separate radionuclides in small ~ 2 g and big ~ 2 kg voluminous samples.

To achieve in such estimation the accurency of ~ 50% the detectors should be calibrated at two distances from the detector

2-3 cm   and   5-6 cm

The calibration performed at the distance 2-3 cm should be utilized for small samples (below 200 g)

The calibration performed of the distance of 5-6 cm should be utilized for big samples (over 200 g) and for samples of relatively high density.

In appendix 6 graphic presentations of experimental results are enclosed.

5.3. Correction factors - relative efficiency coefficients for typical voluminous samples measured with germanium detectors k_E

Relative efficiency coefficients k_E as presented in chapter 2 were determined basing on experimental results of the efficiency calibration for 6 of calibrated detectors as described in table 1.

The value of the coefficient k_E was determined for all of detectors using the reference efficiency curve of point source placed 5 cm axially over the detector surface. Voluminous reference standards were measured on the detector surface. The distance of 5 cm between the point source and the detector was found to be optimal (see results of chapter 5.2).

Values of the relative efficiency coefficients were determined for each of calibrated geometries of cylindrical reference samples. Presented in table 4 values of coefficients k_E are mean arithmetical values for 6 detectors as described in table 1.

Table 4 presents also standard deviations for calculated values of k_E coefficients. Presented in table 5 coefficients k_E are mean values for 3 of selected energies of gamma radiation (122 keV - [57]Co, 662 keV - [137]Cs, 1332 keV - [60]Co).

Table 5. Values of correction factors - relative efficiency
coefficients for germanium detectors :

$$k_E = \frac{F_{E,W\rho}}{F_{E,Wo}}$$

as determined for voluminous cylindrical standards of the
ρ_o = 1 g/cm^3 density. The distance of the point reference stan-
dard from the detector surface = 50 mm. σ_{kE} is the standard
deviation of the mean arythmetical volume of k_E for gamma lines -
122 keV, 661 keV and 1332 keV.

Container type	Diameter = 17 mm				
height [mm]	10	20	30	40	50
coefficient k_E	0.20	0.26	0.31	0.37	0.45
σ_{kE}	0.03	0.03	0.03	0.04	0.05

Container type	Diameter = 35 mm						
height [mm]	10	20	30	40	50	60	70
coefficient k_E	0.25	0.31	0.36	0.43	0.50	0.57	0.65
σ_{kE}	0.04	0.05	0.04	0.05	0.06	0.07	0.09

Container type	Diameter = 56 mm					
height [mm]	10	20	30	40	50	60
coefficient k_E	0.31	0.38	0.44	0.52	0.60	0.69
σ_{kE}	0.03	0.03	0.03	0.03	0.04	0.06

Container type	Diameter = 75 mm				
height [mm]	10	30	60	90	110
coefficient k_E	0.37	0.51	0.74	1.07	1.27
σ_{k_E}	0.04	0.04	0.13	0.13	0.17

Container type	Diameter = 95 mm				
height [mm]	10	30	60	90	120
coefficient k_E	0.44	0.63	0.95	1.31	1.67
σ_{k_E}	0.04	0.07	0.12	0.20	0.28

Determination of the activity of radionuclide present in measu-
red sample requires to know the value of the relative gamma ra-
diation transmission q_E (see [6]). The value of this coefficient
is influenced by the composition of elements of sample matrix and
of its density. Qualitative determination of element composition
of measured sample is time consuming and in the case of necessity
of quick determination of radionuclides activity is not usually
practiced. Reference voluminous standards used for the determina-
tion of the coefficient k_E were water solution samples of $\rho_0 = 1$
g/cm^3. Values of mass attenuation coefficient μ_E [cm^2/g] of
environmental and food origin samples, can vary from μ_E as for
water, for different energy range of gamma radiation, from few to
several tenths of percent. This causes, that values of relative
transmission coefficient q_E of environmental samples of matrix
density $\rho \sim 1$ g/cm^3 and of different element composition, while
the thickness of the sample is in order of 10 cm, vary signifi-
cantly from q_E value of a water sample of the same thickness.

The factor which decides of the q_E coefficient value for typi-
cal environmental and food samples is the sample thickness.
Sample of ~ 10 cm thickness, which densities are of 0.8 and 2.4
g/cm^3, depending on the gamma radiation energy, differs in their
q_E coefficients from few to 100 %. That's why, if the sample
material density and its element composition are explicity diffe-
rent than those of water, then utilization of appropriate proper
coefficients q_E for determination of radionuclide activity using
equation [6] is necessary.

In [...] 6 [...] related transmission [...] for gamma radiation of photons energy in energy range 80 - 2000 keV are calculated according to equation [15] for samples of 0.8 to 2.35 g/cm^3 density. Calculations were performed assuming that element composition of those samples is those of typical soil, building materials, fly ash samples. Following element composition was used for calculations:

H (0.56 %) , O (49.6 %) , Si (31.5 %) , Al (4.8 %) ,

Ca (8.3 %) , Fe (1.2 %) , Mg (0.24 %) , Na (1.7 %) ,

K (1.9 %) , S (0.12 %)

$$q_E = \frac{T_{E,V}}{T_{E,Wo}} = \frac{\left[1 - \exp\left(-\mu_{m_\rho, E} * d_\rho\right)\right] * \mu_{H_2O} * d_{H_2O}}{\mu_{m_\rho, E} * d_\rho * \left[1 - \exp\left(-\mu_{m_{H_2O}, E} * d_{H_2O}\right)\right]} \qquad [15]$$

where $\mu_{m_\rho, E}$ [cm^2/g]   – is the effective mass attenuation coefficient for gamma radiation with energy E as for above defined element composition of the sample,

$\mu_{m_{H_2O}}$ [cm^2/g]   – is the effective mass attenuation coefficient for gamma radiation with energy E by water,

d_ρ [g/cm^2]   – is the surface density of the sample

d_{H_2O} [g/cm^2]   – is the surface density of the water sample

Table 6. Values of the relative transmission coefficients for gamma energy [from 100 to 2000 keV] for samples of 10, 40 and 110 cm thickness.

$$q_E = \frac{T_{E,V,\rho}}{T_{E,Wo}} \qquad [\ 16\ ]$$

H (mm)	ρ $\frac{g}{cm^3}$	Energy (keV)						
		100	200	600	800	1000	1500	2000
10	0.8	1.02	1.02	1.01	1.01	1.01	1.01	1.00
	1.0	1.00	1.01	1.00	1.01	1.00	1.00	1.00
	1.2	0.98	1.00	0.99	1.00	0.99	1.00	1.00
	1.4	0.97	0.99	0.98	0.99	0.98	0.99	0.99
	1.6	0.95	0.98	0.98	0.99	0.98	0.99	0.99
	1.8	0.93	0.97	0.97	0.98	0.97	0.98	0.98
	2.0	0.92	0.96	0.96	0.97	0.97	0.98	0.98
	2.35	0.90	0.94	0.95	0.96	0.96	0.97	0.97

H (mm)	ρ $\frac{g}{cm^3}$	Energy (keV)						
		100	200	600	800	1000	1500	2000
	0.8	1.04	1.05	1.04	1.02	1.02	1.02	1.02
	1.0	1.01	1.03	1.02	1.01	1.01	1.01	1.01
	1.2	0.96	0.99	0.99	0.99	0.99	0.99	0.99
40	1.4	0.90	0.95	0.96	0.96	0.96	0.98	0.98
	1.6	0.85	0.90	0.93	0.94	0.94	0.96	0.96
	1.8	0.81	0.86	0.90	0.91	0.92	0.94	0.95
	2.0	0.76	0.82	0.88	0.88	0.90	0.92	0.92
	2.35	0.69	0.77	0.83	0.85	0.86	0.89	0.90

H (mm)	ρ $\frac{g}{cm^3}$	Energy (keV)						
		100	200	600	800	1000	1500	2000
	0.8	1.16	1.17	1.13	1.10	1.09	1.08	1.06
	1.0	1.00	1.06	1.03	1.04	1.03	1.02	1.03
	1.2	0.89	0.96	0.97	0.97	0.97	0.99	0.99
110	1.4	0.80	0.85	0.89	0.91	0.90	0.93	0.95
	1.6	0.65	0.79	0.84	0.85	0.86	0.89	0.90
	1.8	0.64	0.71	0.78	0.81	0.81	0.84	0.86
	2.0	0.58	0.65	0.73	0.76	0.77	0.81	0.83
	2.35	0.49	0.58	0.66	0.69	0.70	0.74	0.77

Equation [7] assumes the simplification that gamma rays penetrate the sample perpendicularly to its surface. The error which is the result of this simplification is of small importance in the total error of sample activity determination.

The practical utilization of presented tables can be as follows:

Data from table 7 can be utilized by each spectrometrical laboratory for quick estimation of the measurement errors in the measurements of samples varying greatly from the reference standard density (usually ~ $1g/cm^3$).
It must be realized that in extreme cases for the low gamma energy range and the difference in density of 2 times the error can be of up to 100 %.

Experimental confirmation of data in table 7 is presented for each of detectors in diagrams for containers:

$$
\begin{array}{lll}
0.125 \ 1 & - (\ h = 1 \ cm \ and \ 6 \ cm, \ \phi = 5.6 \ cm \ ) \\
0.5 \quad 1 & - (\ h = 1 \ cm \ and \ 11 \ cm, \ \phi = 7.5 \ cm \ ) \\
0.5 \quad 1 & - \ Marinelli \ type \ container.
\end{array}
$$

Enclosed set of diagrams as for detector No 1 present detection efficiency curves for samples of 1 g/cm^3 and 2 g/cm^3. (appendix 4).

Rapid determination of strontium-89 and strontium-90 in food and environmental samples by Cerenkov counting.

by
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SUMMARY

The method has been developed for emergency situations. Minimum detectable concentrations of 5 Bq/liter, kilogram of strontium-89 and strontium-90 respectively is achievable in the presence of nuclides considered to be released under accidental conditions. Result on the strontium-89 and strontium-90 content in a sample can be obtained within 12 hours. One technician can easily handle 8-10 samples during a working day of eight hours.

The determination of the strontium isotopes is accomplished by monitoring the Cerenkov radiation from strontium-89 and yttrium-90 in a liquid scintillation counter. The later is the daughter product of strontium-90. Prior to the Cerenkov counting the sample is separated from interfering nuclides by oxalate precipitation, chromate precipitation and HDEHP-extraction.

The method has to be futher improved and evaluated with respect to different soiltypes such as forest mineral soil layers, agricultural soils and pastures. Futhermore, the decontamination procedure should be evaluated for a sample containing frechly irradiated uranium.

OUTLINE OF THE METHOD

Sample quantity

The sampling, the transportation and the sample preparation (drying and ashing) is, for the most part, the time limiting step in the procedure. Small sample quantities are therefore preferable. In order to meet the requirements of the detection limit the following sample quantities are recommended ; milk and water 100 ml; other food, vegetation and soil 100 gram fresh weight.

Sample preparation

All samples are prepared in the presence of a carrier solution containing strontium,yttrium and barium.

Samples of milk, vegetation and other foods are dried and ashed before decontamination of interfering nuclides. The ashes are dissolved in dilute hydrochloric acid.

Radionuclides in the soil are extracted by diluted hydrochloric acid were after the extract has to be decontaminated from interfering nuclides.

Concerning water no sample preparation is needed before the decontamination procedure.

Decontamination of interfering nuclides

Nuclides decaying with high beta energies are considered to cause Cerenkov radiation and with that interfere in the determination of the strontium isotopes (Table 1). These nuclides have to be separated from the matrix before Cerencov counting of strontium-89 and yttrium-90, the daughter nuclide of strontium-90 (Figure 1).

Table 1. Nuclides considered to be present in the sample matrix after an accidental release of radioactive matherial.

NUCLIDES		HALFLIVES	VALENCE	SEPARATED BY
Rb-86	*	18.7d	+1	oxalate precipitation
Sr-89	*	52d	+2	
Y-90	*	64h	+3	HDEHP-extraction
Sr-90		28.7y		
Y-91	*	59d	+3	HDEHP-extraction
Nb-95		35d		
Zr-95		65d		
Nb-96		23h	+3, +5	HDEHP-extraction
Mo-99	*	66.7h	+6	HDEHP-extraction
Ru-103		40d		
Ru-106		1.02y		
Rh-105		35.9h		
Ag-111	*	7.5d	+1	oxalate precipitation
Pd-112		21h		
Cd-115	*	53.5d	+2	?
Cd-115m	*	43d	+2	
Sn-121		27h		
Sn-123	*	42m		?
Sb-124	*	60d	+3,+5	HDEHP-extraction
Sb-125		2.76y		
Sn-125	*	9.4d	+2, +4	?
Sb-127	*	93h	+3, +5	HDEHP-extraction
I-131	(*)	8.7d	+1,+5,+7.	ashing, oxalate precipitation
Te-131m	(*)	30h	+4,+6,-2.	HDEHP-extraction
Te-132		78h		
I-133	*	21h	+1,+5,+7.	ashing, oxalate precipitation
Cs-134	*	2.1y	+1	oxalate precipitation
Cs-136		13d		
Cs-137	*	30y	+1	oxalate precipitation
Ba-140	*	12.8d	+2	chromate precipitation
La-140	*	40h	+3	HDEHP-extraction
Ce-141		33d		
Ce-143	*	33h	+3,+4	HDEHP-extraction
Ce-144		0.8y		
Pr-143	*	13.7d	+3	HDEHP-extraction
Nd-147	*	11.1d	+3	HDEHP-extraction
Pm-147		2.5y		
Pm-149	*	53.1h	+3	HDEHP-extraction
Pm-151	*	28h	+3	HDEHP-extraction
Sm-153	*	46.8h	+2,+3	
Np-239	(*)	2.35d	+3,+4,+5,+6	HDEHP-extraction
Tb-160		73d		
Actinides				
Th,U decay prc*				chromate precipitation, HDEHP-extraction

* nuclide is expected to give Cerenkov radiation

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Figure 1. Decontamination of interferring nuclides for determination of Sr-89 and Sr-90 in food and environmental samples
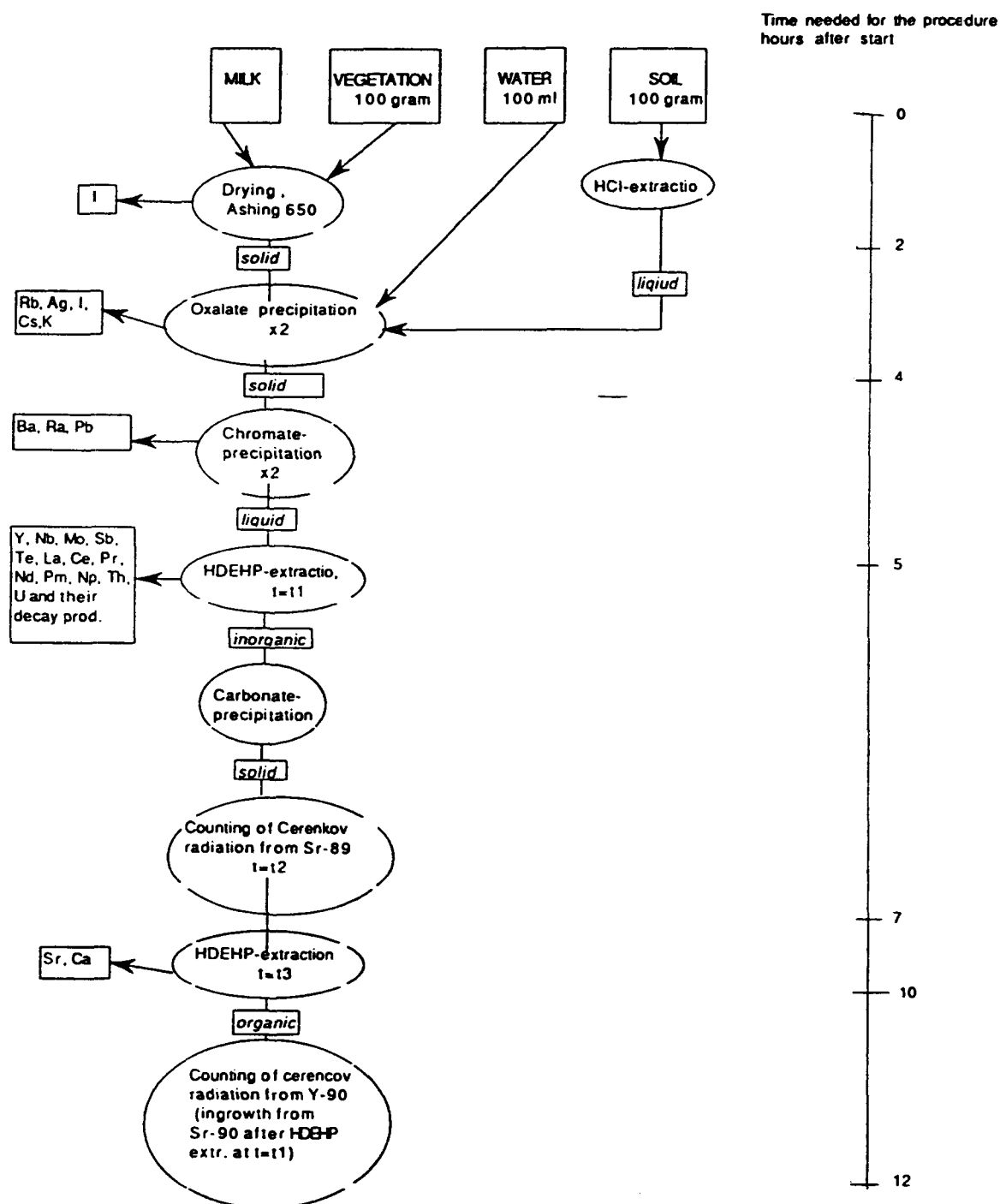
Strontium and other multivalent ions (e g barium, yttrium, cerium) are concentrated by precipitation as oxalates. Monovalent cations (e g potassium and cesium) will remain in the solution. (Table 2, Sunderman & Townley 1960).

Table 2. Decontamination of interferring nuclides in a water sample
Mean of four replicates.

	inital activity Bq/sample	remaining initial activity (%) in the sample after	
		oxalate precipitation (x2)	oxalate precipitation (x2)+ chromate precipitation (x2) + HDEHP- extraction (x1)
		mean (sd)	mean (sd)
Cs-137	90	<1 (0)	<1 (0)
Ba-133	40	100 (0)	<1 (0)
Sr-85	35	100 (0)	96 (3)
Y-88	55	88 (2)	<1 (0)
Ce-139	15	78 (5)	<1 (0)

The oxalates are ignited and the residue dissolved in dilute acid.

Ions of Barium, Radium and Lead are separated from strontium by precipitation as chromates.

Tri and tetra valent ions such as yttrium, cerium and lantane as well as uran and thorium and their decay products are separated from strontium by extraction with HDEHP (Di(2-ethyl-hexyl)phosphoric acid) (Table 2). The capacity of HDEHP of separating strontium from tri and tetra valent ions has been demonstrated by Peppard et al 1957.

After separation the inorganic phase will contain isotopes of strontium (strontium-89 and strontium-90) and yttrium-90 growing in from strontium-90. The inorganic phase is considered to be decontaminated from any substantial amounts of interfering nuclides.

The amount of strontium-89 is determined by monitoring the Cerencov radiation in a liquid scintillation counter. If large amounts of strontium-90 compared to strontium-89 are present in the sample, the ingrowth of yttrium-90 has to be taken into consideration in calculating the amount strontium-89 based on the Cerencov counting (Figure 2).

Strontium-90 is determined by Cerenkov counting of yttrium-90. Yttrium-90 is the decay product of strontium-90 and has been growing into the sample since the first HDEHP-extraction(t=t1 in Figure 1). After a sufficient time of ingrowth, about 5 hours (Figure 3), yttrium-90 is separated from strontium-89 by an additional HDEHP extraction and monitored by Cerenkov counting.

Figure 2. Part of Cerencov counts orginating from strontium-89 (%)
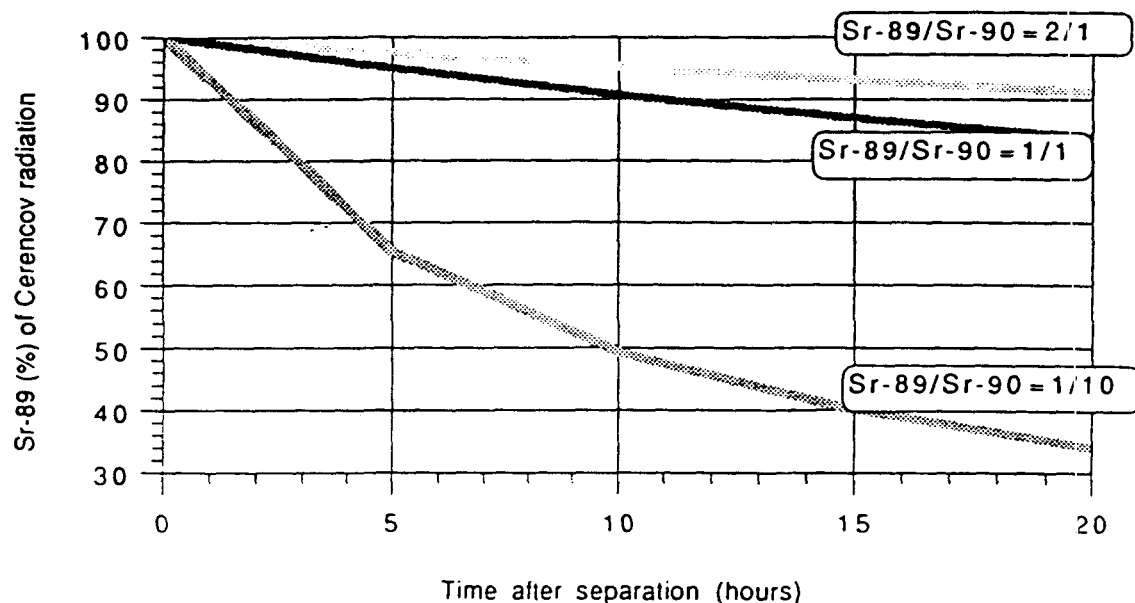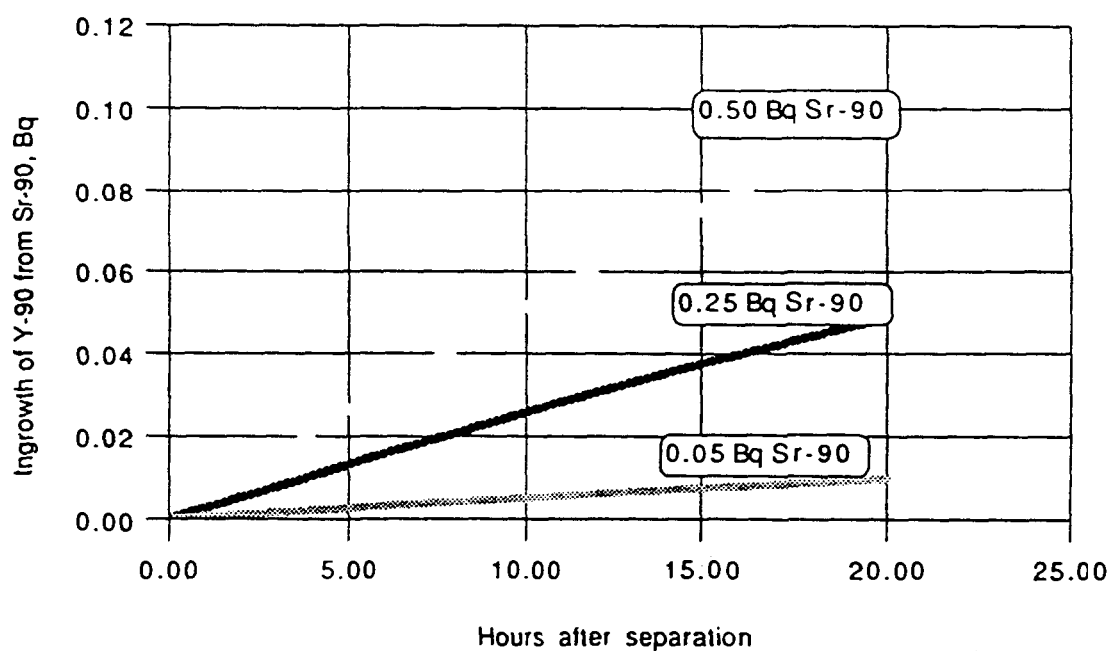in relation to the time after separation with HDEHP at t=t1 (Figure 1).

Figure 3. Ingrowth of Y-90 from Sr-90 after separation with HDEHP (Figure 1)

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Recovery (yield)

The recovery of strontium or yttrium, for strontium-90 determination, was evaluated in different sample matrixes by using strontium-85 as an internal tracer (Table 2) as well as by titrimetric and grvimetric procedures (Table 3). The recovery of strontium and yttrium varies between 80 and 95% exept for acid mineral forest soil layers where the recovery varied between 0-20 %. For emergency situations where an accuracy of ±10%-50% is required an average figure of recovery can probably be used. The determination of recovery can therefore in most occasions be excluded in the routine procedure under emergency conditions. It must however be stressed that the recovery of strontium (yttrium) will vary between the different laboratories and technicians as well as for different sample types. It is therefore necessary to determine an average figure of recovery on each laboratory to be used in the routine procedure of strontium determination. It is also important to evaluate the method for different soil types in order to obtain reliable average figures of recovery.

Table 3. Recovery of Y-90 for determination of Sr-90 after decontamination and concentration procedure according to Figure 1. Mean of 10 replicates

sample	initial concentration, Bq/liter,kg mean (sd)	recovery, % mean (sd)
milk	0.09(0.03)	0.88(0.02)
water, effluents from nuclear power plants	7.3(22.6)	0.85(0.03)
soil, litter and humus layers of forest soils	62.5(19.7)	0.82(0.05)
soil, acid mineral soil layers of forest soils		0.00-0.28
vegetation, herbs,grass)	36.2(30.4)	0.91(0.2)

CALCULATIONS

Strontium-89

$$\frac{Cer(t=t_2)}{Eff} = R \times (Sr^{89} + Y^{90})$$ Ekv 1

The contribution of yttrium-90 (Y^{90}) to the Cerencov counting at $t=t_2$ is caused by the ingrowth from strontium-90 (Sr^{90}) after the HDEHP-extraction at $t=t_1$ (Figure 3). The Cerenkov radiation from yttrium-90 at $t=t_2$ can in general be disregarded as the Cerenkov counting will be carried out within a couple of hours after the separation step at $t=t_1$ (Figure 2)) . Furthermore, the proportion between strontium-89 and strontium-90 can be considered to be higher than 1 during the early phase after an accidental release of radioactive matherial. Ekv 1 can therefore be simplified :

$$Sr^{89} = \frac{Cer(t=t2)}{Eff \times R}$$ Ekv 2

Strontium-90

$$\frac{Cer(t=t3)}{Eff} = R \times Y^{90} \qquad \text{Ekv 3}$$

After separation of yttrium with HDEHP at t=t1 yttrium-90 has been growing into the sample from strontium-90. The amount yttrium-90 in the sample will increase according to:

$$Y^{90}=Sr^{90} \times (1-e^{-((\ln 2)/T_{1/2}) \times (t_3-t_1)}) \qquad \text{Ekv 4}$$

From Ekv 3 and Ekv 4 the amount of strontium-90 in the sample can be calculated according to:

$$Sr^{90} = \frac{Cer(t=t3)}{R \times Eff \times (1-e^{-((\ln 2)/T_{1/2}) \times (t_3-t_1)})} \qquad \text{Ekv 5}$$

—

Cer = Cerenkov counts corrected for background, cps

Eff = Counting efficiency, <1

R = Recovery of Sr^{89} and Y^{90}
   an average value of R can be used for rapid determination under emergency conditions.

Sr^{89} = Activity of strontium-89 in the sample, Bq/sample

Sr^{90} = Activity of strontium-90 in the sample, Bq/sample

Y^{90} = Activity of yttrium-90 in the sample, Bq/sample

$T_{1/2}$ = halflife for yttrium-90 = 64 hours

$(t=t_1)$ = time at the first HDEHP separation, hours (Figure 1)

$(t=t_2)$ = time at the first Cerencov counting, hours (Figure 1)

$(t=t_3)$ = time at the second Cerencov counting, hours (Figure 1)

DETECTION LIMIT

$$DLSR^{89} = \frac{DL}{Sq \times T \times Eff \times R} \qquad \text{Ekv 6}$$

$$DLSR^{90} = \frac{DL}{Sq \times T \times Eff \times R \times (1-e^{-((\ln 2)/T_{1/2}) \times (t_3-t_1)})} \qquad \text{Ekv 7}$$

DL = detection limit: $3 \times \sqrt{background}$, counts

Sq = sample quantity , liter or kg

$DLSR^{89}$ = Detection limit for Sr^{89}, Bq/liter or Bq/kg

$DLSR^{90}$ = Detection limit for Sr^{90}, Bq/liter or Bq/kg

T = counting time , seconds

Δt = time for ingrowth of yttrium-90 = t3-t1, hours

Eff = Counting efficiency, <1

R = Recovery of Sr^{89} and Y^{90}

Making the following assumptions:
    Background 5cpm
    Counting time 60 min
    Sample quantity; liquid: 100 ml
                      solid: 100 gram
    Recovery 0.8
    Counting efficiency 0.6

$DLSR^{89}$= 0.30 Bq/liter or kilogram

$$DLSR^{90}= \frac{0.30}{(1-e^{-0.011\Delta t})} \quad \text{Bq/liter or kilogram}$$

In addition to the sample quantity, counting time and prestanda of the instrument (background), the detection limit for strontium-90 will depend on the time during which yttrium-90 is allowed to grow into the sample (Figure 4)., Yttrium-90 should be allowed to grow into the sample for at least five hours in order to meet the requirements of a detection limit of 5 Bq/liter or kilogram at a sample quantity of 100 gram (or 100 ml), a counting time of one hour in a liquid scintillation counter with a background of 5 cpm.

Figure 4. Detection limit for strontium-90 (Bq/liter,Bq/kilogram) as a function of the time of ingrowth of yttrium-90.
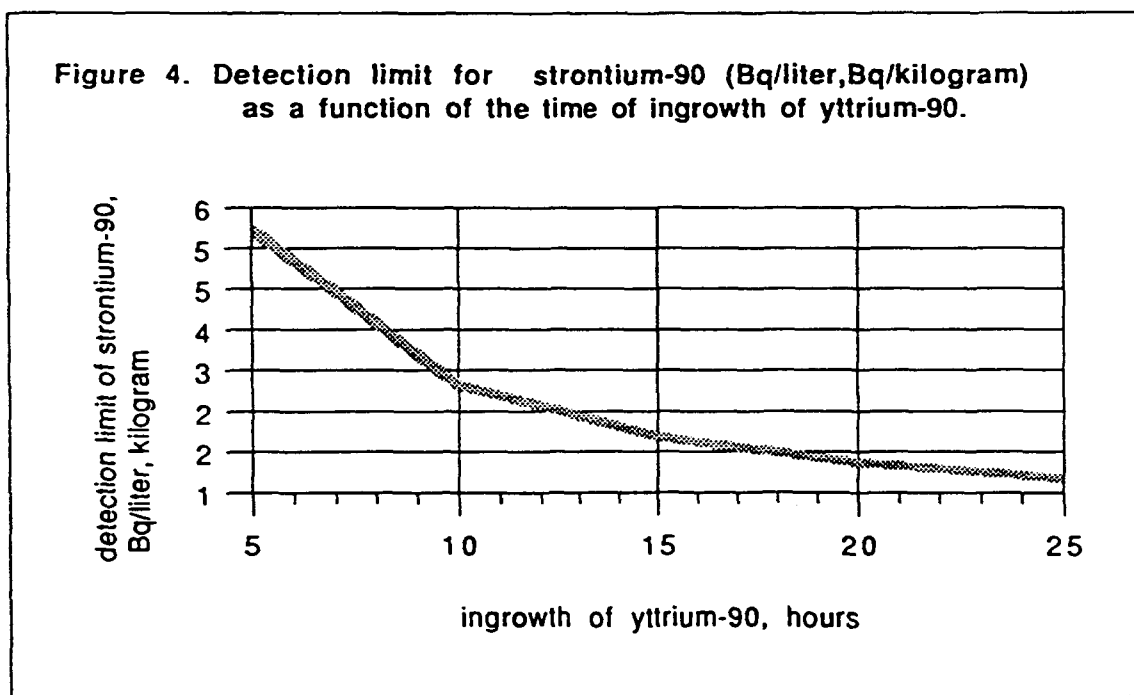
CONCLUSIONS

The method has been shown to be reliable for samples of milk, vegetation, organic soil layers and water. It is however important to futher evaluate the method for mineral soils as the method has been shown to give very low and variable values of recovery for this sample matrix.

Second Research Coordination Meeting
of
Coordinated Research Programme
on

Rapid Instrumentation And Separation Methods For Monitoring Radionuclides In Food And Environmental Samples

M.H. Beach

IAEA Headquarters, Vienna   Meeting Room C07-V
12-16 August 1991

Ministry of Agriculture, Fisheries and Food
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UNITED KINGDOM ACTIVITY REPORT

1 Introduction

Radioactivity studies by the Ministry's (MAFF) Directorate of Fisheries Research at Lowestoft, England have continued as outlined in the Working Paper submitted at the first CRP in Warsaw, Poland during 4-8 September 1989. The principle aim is to measure the radioactive dose to man (using food as the indicator and investigating external pathways). Approximately 10,000 environmental samples are analysed each year for radioactive content (includes about 1200 biota and 400 water samples) and the results published in a comprehensive Report entitled "Radioactivity in Surface and Coastal Waters of the British Isles". (Copies of the 1989 Report are available here, and publication of the 1990 Report is imminent).

Our radiometric systems continue to be improved and updated. The least-efficent (18.2%) GeLi gamma detector has been replaced with a pure Germanium detector (68%), and a low-level large-area beta counter (127mm) with automatic sample-changer and another 10-place alpha/beta counter have been purchased. The alpha radiometric suite has been extended to 128 detectors with the addition of an improved 16-detector module designed and constructed in-house. Also, the controlling computer hardware and software has been extended to enable greater flexibility, reliability and fuller integration with the gamma radiometric system (a new facility is the greater security of the data and the ability to control remotely an assigned bank of alpha detectors).

2 CRP Activities

At the end of the last CRP Meeting the agreed research contribution from MAFF, United Kingdom was as follows:

(a)   Sample Preparation Programme. Detail of our current sample preparation programme with particular attention to the preparational effort for each of the various types of sample prepared and the MHD time-scales. Also, a brief description of the methodology employed.

(b)   Sample Density/Efficiency Algorithm. The development of an algorithm to enable interpolation between counter efficiency curves for a range of sample densities at constant volume to provide greater accuracy. (At present a small number of preset geometry calibration curves are employed and the closest available curve for each sample is used). Errors are small but could be reduced further by an interpolation algorithm.

(c)   Inter-comparison Exercises. Liaise with other Institute's participants for inter-comparison exercises (Sr-90 estimates were mentioned as a possibility).

3 Sample Preparation Programme

A large range of aquatic samples is received which includes fish (particularly the commercial edible species), crustacea, molluscs and sediments, flora and waters. A precise preparational procedure is documented for all samples with the principle considerations being the preservation of the critical nuclide, adequate sample to ensure acceptable counting precision, attention to edible fractions where relevant, and repeatability of technique. Examples are given of the various procedures employed:

3.1   Fish are usually received whole although fillets are not uncommon. Whole fish are washed, gutted, and filleted. The gut flaps are removed from the fillets and discarded along with the bone, head and tail. The edible fraction is obtained from the whole and the fillet weights. This information is necessary for data on the relationship between nuclide uptake and fish age/species, and to enable more meaningful data to be obtained in the "rapid count situation" where whole fish are counted wet. Usually the fillets are dried by mincing onto a pre-weighed aluminium tray in an oven at 90-100°C for a minimum of two days or until completely dry. Wet counting uses a "tub" counting geometry (8cm diameter by 5cm height or 5.1cm diameter by 4.1cm height) according to sample availability, whereas the dried samples are counted using a either of the two tub geometries or the compressed "biscuit" geometry (5cm diameter by 1cm thick)

3.2   Crustacea and Molluscs take considerably longer to prepare since the edible fraction only is counted. For example, due to the declining discharges from Sellafield, in 1985 only 350 winkles were required to give a sufficiently large sample whereas now 1200 are required and can take several hours to prepare. Similar geometries and wet/dry counting is undertaken as described for fish samples.

3.3 Sediments comprise turf, saltmarsh and peat and combinations of mud, sand, and coal. Kilogram sample quantities are received in 0.5 litre plastic mud pots which are then spread into pre-weighed aluminium trays and dried. Mud samples are first frozen and then freeze-dried for about two days. Freeze-dried samples remain friable, whereas dried mud samples produce solid bricks which are useless for further dry preparation. Turf or saltmarsh samples are received in slab form. These are examined carefully to decide whether an oven-drying or freeze-drying procedure is more appropriate.

3.4 Water samples are regularly analysed for radiocaesium. 25 or 50 litre volumes of fresh or salt water are first filtered through a 0.45μm paper and then acidified with concentrated nitric acid. The radiocaesium is extracted by passing the water through an absorbing cartridge of molybdophosphate on a silica gel substrate (C W Baker, 1975). The cartridges are counted subsequently using a 125 x 125mm NaI(Tl) well crystal with automatic sample-changer.

3.5 Core samples are collected either manually or using mechanical devices with release messengers. The manual method requires a 10cm diameter plastic tube to be driven into the substrate; and then dug out whilst ensuring that the sample remains undisturbed inside the tube. Both ends are sealed and the surface end of the substrate clearly marked. Cores are typically mud, sand or peat and are received frozen; lengths range from 20cm upwards. Core slices are obtained using a piston, slice former and cutter (slices range between 2-5cm thick). Mud slices are freeze-dried and sand and peat slices oven-dried.

3.6 Preparation time for the various categories of samples is summarised in the table below. (Molluscs include mussels, winkles, cockles and oysters; crustacea include crabs lobsters, nephrops and shrimps; round fish include salmon, cod, herring, haddock and mackerel; flat fish include plaice, sole, halibut, turbot and brill; and small fish include white bait). The M, H, and D categories refer to 1-60 minutes, 1-6 hours, and 6-24 hours respectively as designated at the first CRP Meeting in 1989.

	Clerical entry time (m)	Prep time (m)	System Header (m)	Counting time (m)	Total Process time (m)	No of samples 1 detector			No of samples 8 detectors		
						M	H	D	M	H	D
Molluscs	2	60	2	10	74	-	5	19	-	40	152
Crustacea	2	30	2	10	44	1	8	33	8	64	192
Fillets	2	2	2	10	16	4	24	96	32	192	768
Round Fish	2	-5	2	10	19	3	18	76	24	144	608
Flat Fish	2	5	2	10	19	3	18	76	24	144	608
Small Fish	2	2	2	10	16	4	24	96	32	192	768
Weed	2	2	2	10	16	4	24	96	32	192	768
Sediments	2	2	2	10	16	4	24	96	32	192	768

The above sample throughputs are based on counting Cs-137 (662 keV) for the minimum time to achieve a 20% 1σ error. Since Cs-137 is a mid-range energy, it is estimated that nuclides with different energies (eg Am-241) would decrease the throughput of sample by a factor of about two; Iodine-131 is counted very efficiently and would allow a slight increase in sample throughput. Also, to achieve these times would require three teams to cover the 24-hour day for sample

preparation and to continuously supply the 8 detectors (efficiencies ranging from 25 to 68% relative to a NaI detector at 25cm). Minimum drying time is 48 hours and minimum ashing time is 60 hours.

4 Rapid counting - errors

As discussed above, the standard counting geometries employ the disc or "biscuit" geometry (5cm diameter by 1cm thick) and the tub geometries (8cm diameter by 5cm height and 5.1cm by 4.1cm height). The geometry used depends on the amount of sample available. Corrections for self-absorption are achieved by calibrating the expected density range using a multi-nuclide source (eg QCY 48 from Amersham International).

An indication of the errors to be expected is presented in the graphs below. In each case the error is based on a 1σ confidence limit.

4.1 50g of fish muscle (wet) with a specific activity of $100Bq.kg^{-1}$ Cs-137 on a GeLi detector with a relative efficiency of 29.1% using the small tub geometry.

50g fish muscle (wet) containing 100 Bq/kg Cs-137
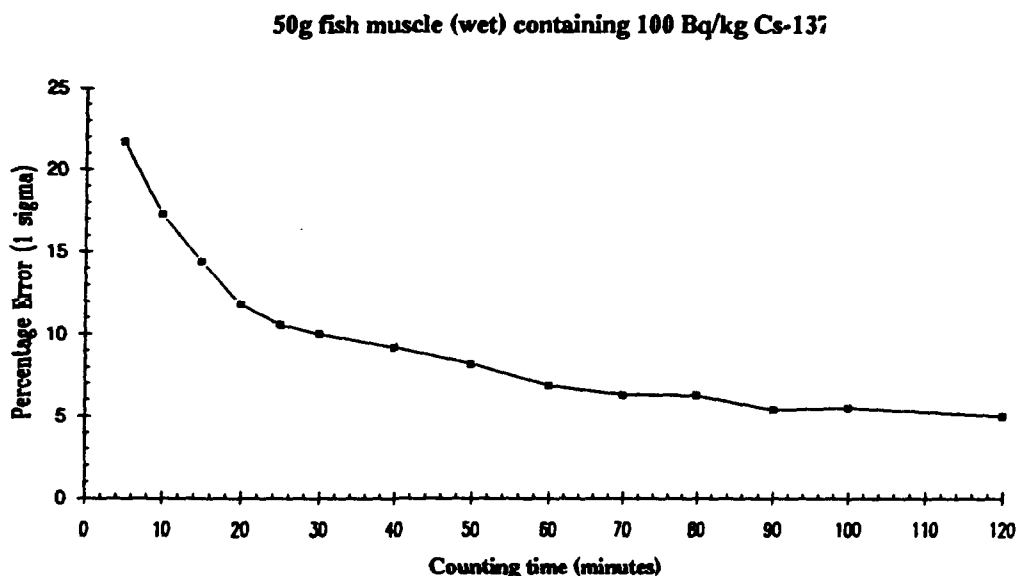
4.2 <u>Comparison between 20g disc and 287g tub geometries</u> for a dry material containing <u>Am-241</u> (59.54keV) on a GeLi detector with a relative efficiency of 24.6%.

Percentage count error for Am-241. Disc and Tub geometries
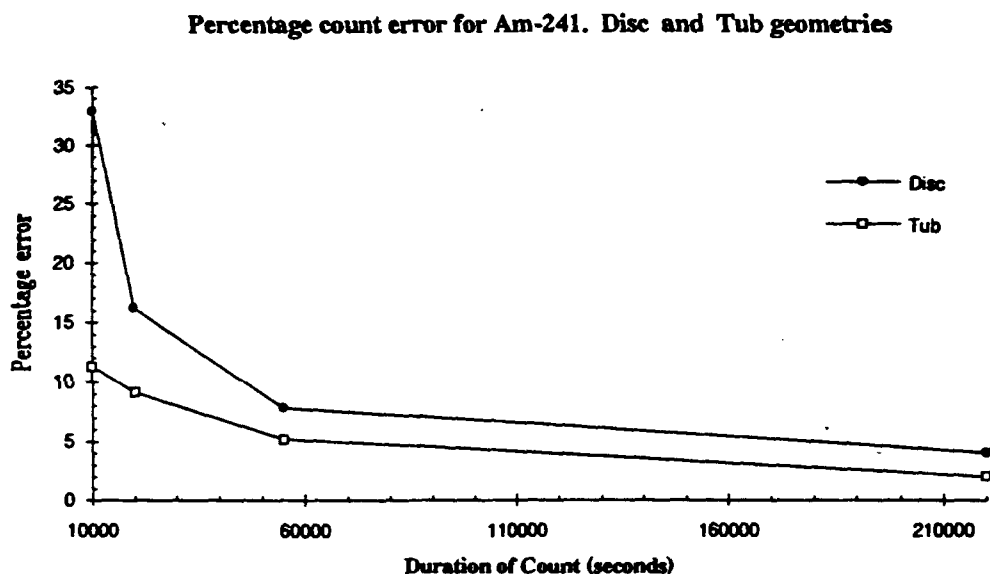
4.3 <u>Comparison between 20g disc and 287g tub geometries</u> for a dry material containing <u>Cs-137</u> (661.65keV) on a GeLi detector with a relative efficiency of 24.6%.

Percentage count error for Cs-137. Disc and Tub geometries

164
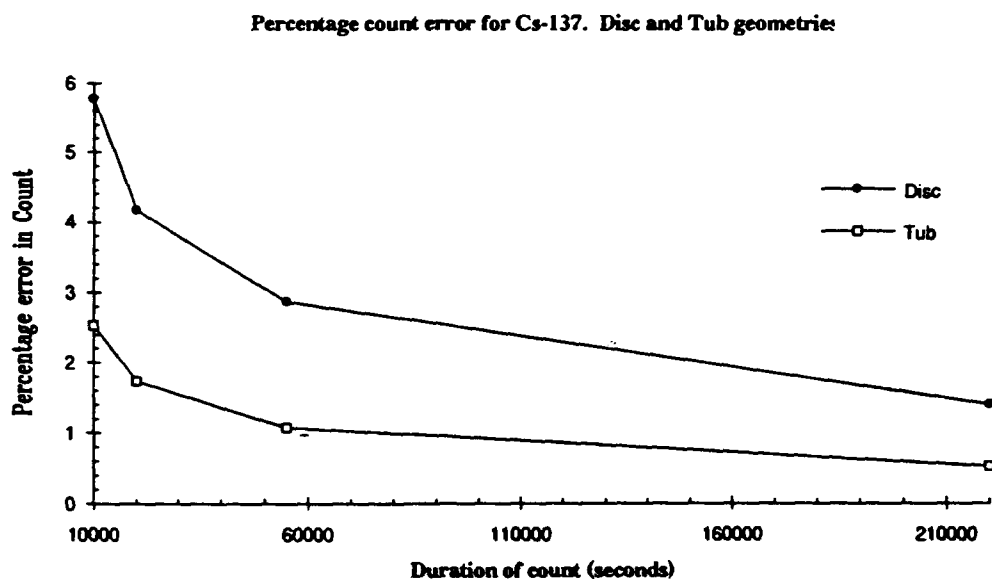
4.4 Comparison between 20g disc and 287g tub geometries for a dry material containing K-40 (1460keV) on a GeLi detector with a relative efficiency of 24.6%.

Percentage count error for K-40. Disc and Tub geometries.

5 Correction of cascade gamma-ray summing effects

Cascade summing is due to the simultaneous detection of two or more gamma rays occurring in cascade from the decay of an excited nucleus in which the life-times of intermediate levels are short relative to the integration time of the amplifier. It results in the removal of counts from the channels at which the individual digitised peaks would occur and places these counts in channels equivalent to the energy of the summed pulses. At th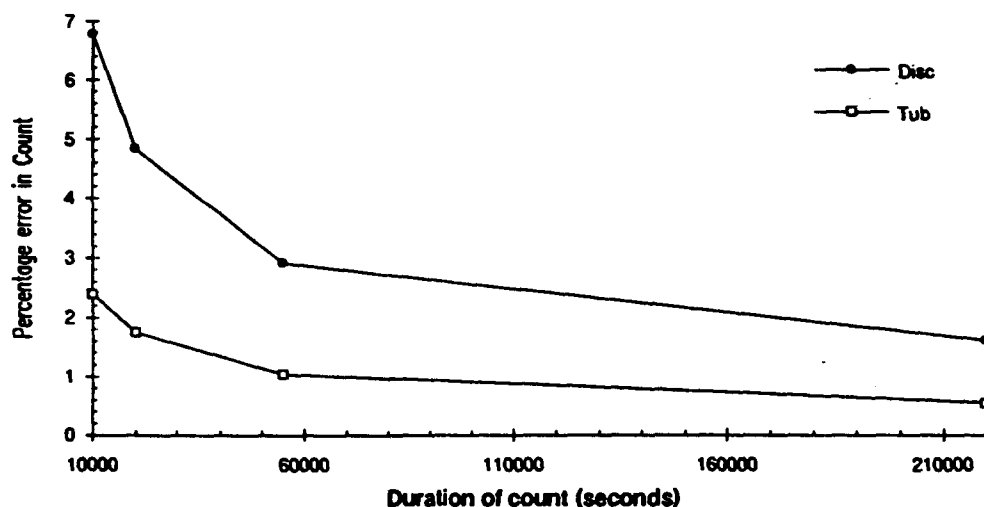e very low levels of environmental activity the errors due to these coincidence effects are small and reduced further by moving the sample further away from the detector.

However, should a correction be necessary, and assuming j gamma rays to be in cascade, then the fractional loss C_C to the first order is given by:

$$C_C = 1/\{\sum_{i=1}^{i=j} (1-f_i \varepsilon_{t(i)}\}$$

where f_i = fraction of coincidence photons of energy i in coincidence with the gamma
   ray of interest, and

   ε_t = total efficiency of the coincidence photon of energy i.

6 Sample Density/Efficiency Algorithm

The aim is to generate a mathematical relationship that will enable counter efficiency to be determined at a precise gamma energy for any given sample density in a preset range.

At present a suite of four calibration curves spans the four relative densities of 0.7, 1.0, 1.22 and 1.6 (relative to water) for the 287ml tub geometry A sample with intermediate density would be calibrated using the most adjacent curve; this introduces errors that could be reduced by mathematical interpolation.

Four samples were prepared with relative densities of 0.7, 1.0, 1.22 and 1.6, each "spiked" with a multi-nuclide prepared standard, and counted in the 287ml tub geometry on one of our GeLi detectors. The following data were obtained:

Relative Density v Efficiency

Nuclide	Energy	200g 0.70	287g 1.00	372g 1.22	462g 1.60
Am-241	59.54	4.17	4.03	3.58	3.31
Cd-109	88.00	4.29	3.56	3.64	3.04
Co-57	122.10	4.19	3.50	3.60	3.03
Ce-139	165.90	3.57	2.97	3.13	2.65
Hg-203	279.20	2.48	2.07	2.22	1.86
Sn-113	391.00	1.82	1.54	1.64	1.40
Sr-85	514.00	1.42	1.21	1.29	1.14
Cs-137	661.00	1.19	1.02	1.13	0.94
Y-88	898.00	0.89	0.77	0.82	0.72
Co-60	1173.00	0.71	0.62	0.66	0.58
Co-60	1332.50	0.63	0.55	0.59	0.52
Y-88	1836.00	0.49	0.43	0.46	0.41

A preliminary examination of the data showed that Efficiency could not be predicted by a linear combination of energy and density (ie multiple regression). See curves below:

Efficiency Curves for Four different Densities
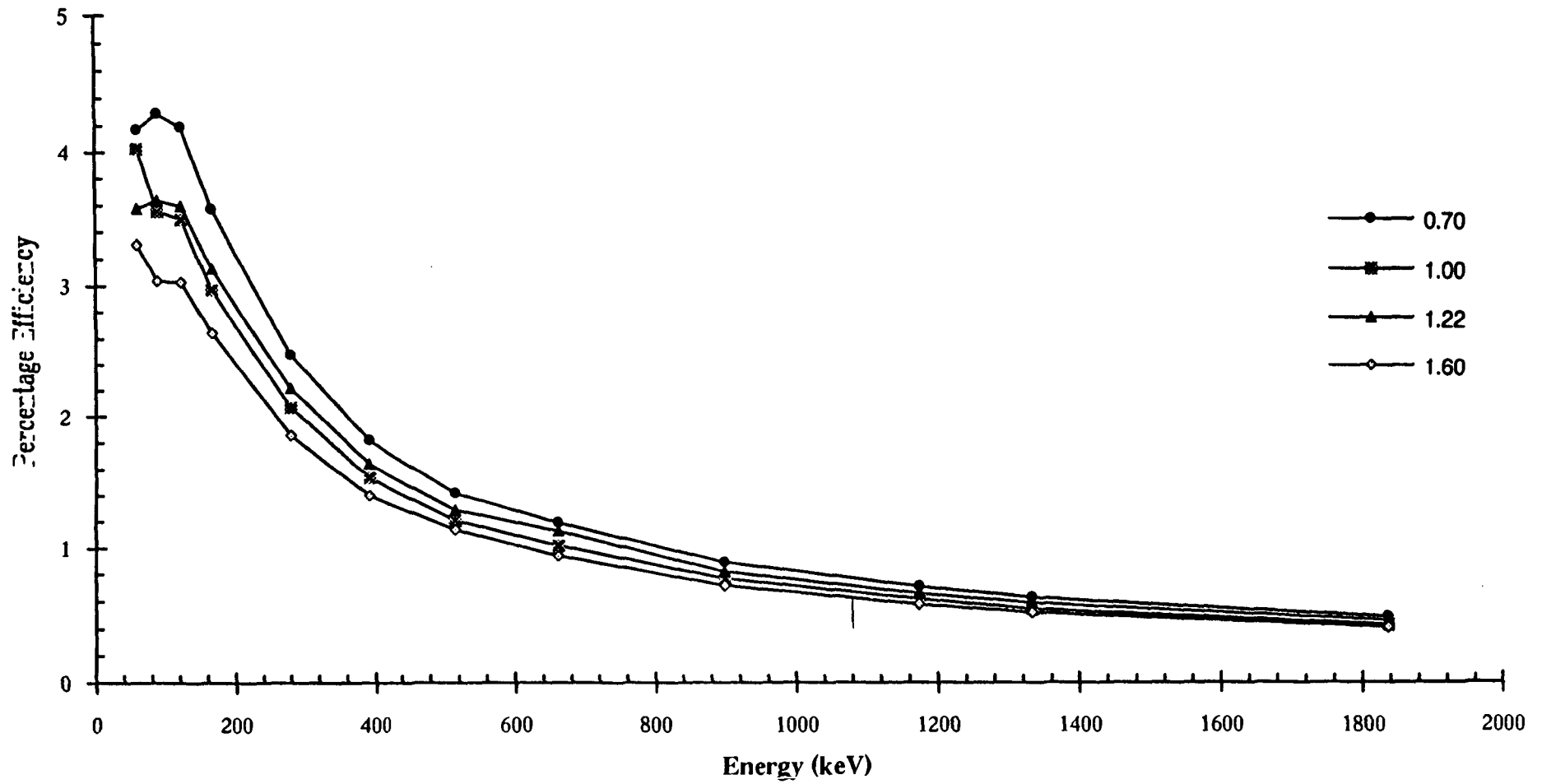
Various emperical curves were assessed, the most effective being a family of curves of the form:

$$\text{Efficiency}^{-1.35} = a_0 + a_1 * \text{Energy}$$

fitted separately for each of the four relative densities to three ranges of energy. The curves were:

Relative Density 0.7

Energy range (keV)	Equation
59 - 122	$\text{Efficiency}^{-1.35} = 0.143$
122 - 661	$\text{Efficiency}^{-1.35} = -0.043 + 0.00126 * \text{Energy}$
661 - 1835	$\text{Efficiency}^{-1.35} = -0.217 + 0.00155 * \text{Energy}$

Relative Density 1.0

Energy range (keV)	Equation
59 - 122	$\text{Efficiency}^{-1.35} = 0.172$
122 - 661	$\text{Efficiency}^{-1.35} = -0.037 + 0.00154 * \text{Energy}$
661 - 1835	$\text{Efficiency}^{-1.35} = -0.210 + 0.00182 * \text{Energy}$

Relative Density 1.22

Energy range (keV)	Equation
59 - 122	$\text{Efficiency}^{-1.35} = 0.177$
122 - 661	$\text{Efficiency}^{-1.35} = -0.010 + 0.00133 * \text{Energy}$
661 - 1835	$\text{Efficiency}^{-1.35} = -0.217 + 0.00165 * \text{Energy}$

Relative Density 1.6

Energy range (keV)	Equation
59 - 122	$\text{Efficiency}^{-1.35} = 0.215$
122 - 661	$\text{Efficiency}^{-1.35} = -0.019 + 0.00167 * \text{Energy}$
661 - 1835	$\text{Efficiency}^{-1.35} = -0.128 + 0.00189 * \text{Energy}$

These fitted lines are shown plotted below for each relative density with the observed efficiencies superimposed.

DENSITY=0.7

DENSITY=1.0

DENSITY=1.22
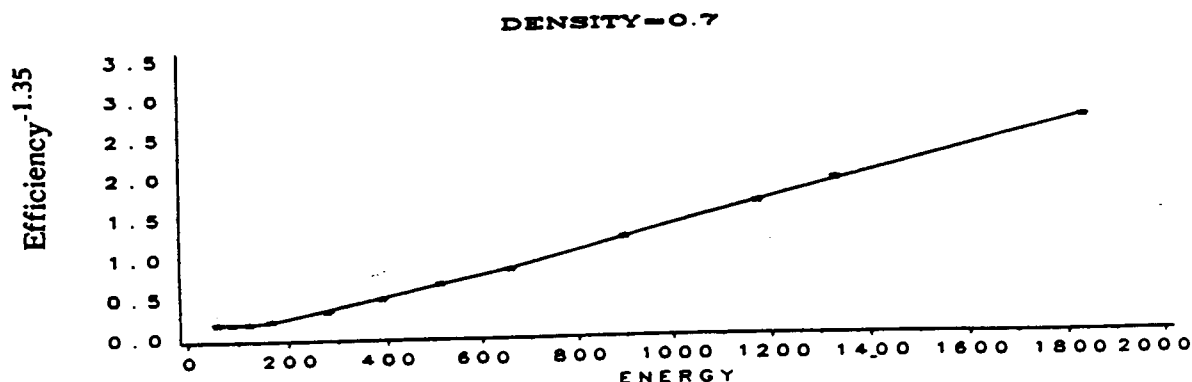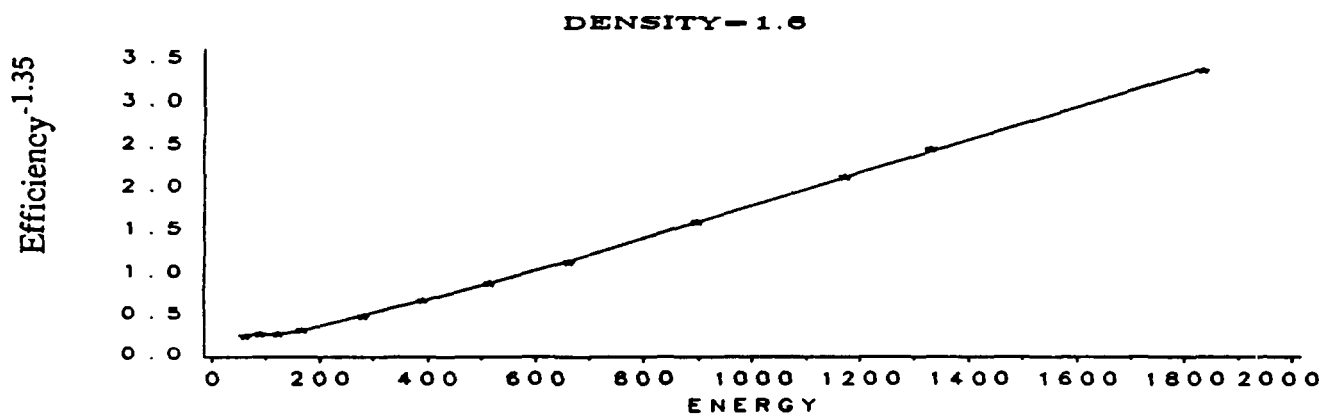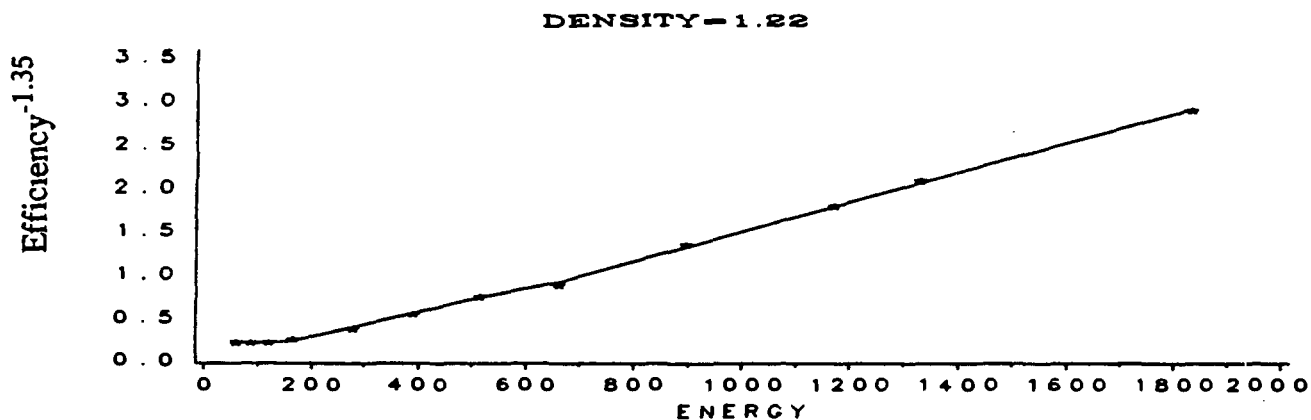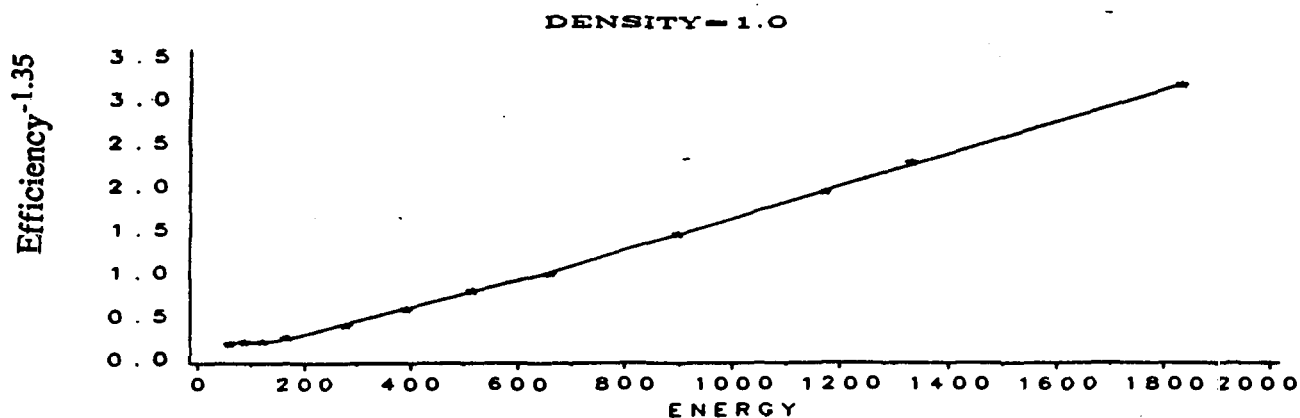
DENSITY=1.6

The curves above can be used to predict efficiency at intermediate densities to those observed by interpolating from the pair of equations on either side of the required density. This extra computation could be avoided if a series of curves of the form

$$\text{Efficiency}^{-1.35} = a_0 + a_1 * \text{Energy} + a_2 * \text{Density} + a_3 * \text{Energy} * \text{Density}$$

- provided an adequate fit to the data. Curves fitted to this data fitted the data less well and a comparison of residual standard deviations (on an Efficiency$^{-1.35}$ scale) shows a progressively worse fit as energy increases.

Interpolation equations have been generated which require an initial decision of such as: 0.7 < density < 1.0 and 59keV < energy < 122keV, and then a corresponding equation of the form:

$$Efficiency = \{b_0 + b_1 * Energy + (b_3 + b_4 * Density)\}^{-0.74}$$

These equations provide a good fit and are being currently tested with intermediate sample densities.

7 Other Aquatic Research Programmes

7.1 <u>Gamma counting of Strontium-89/90</u> was investigated. Since no gamma emissions or X-rays from the decay of Sr-90 or its daughter Y-90 are detectable by our radiometric systems, the possibility of detection by the generation of Bremsstrahlung form beta emissions was investigated . A series of water samples (50ml containers) was prepared with specific activities ranging from 100Bq.ml^{-1} to 1681 Bq.ml^{-1}. Peak counts occurred about 100keV and are shown in the graph below against specific activity.

Gamma Response from Sr-90 Water Samples
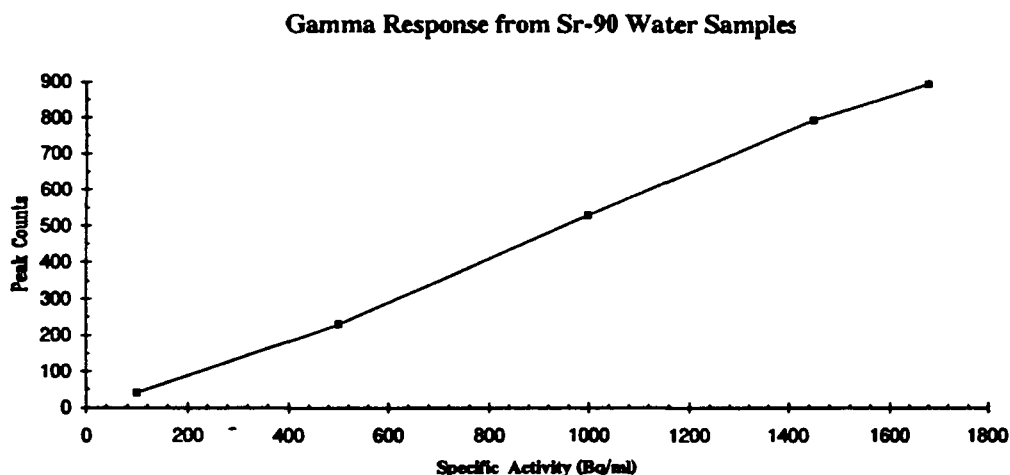
The aim was to detect an activity of 160Bq.l^{-1} of Sr-90 (the derived intervention level for infants - WHO, 1988). However, as can be seen form the graph above, the measurement of Bremsstrahlung from Sr-90 becomes unrealistic at about 100Bq.ml^{-1} which is about 3 orders of magnitude higher specific activity than the recommended intervention level.

7.2 <u>Monitoring of Chernobyl contamination</u> continues with a wide range of projects. The transfer of Cs-137 through freshwater lakes has been studied with the observed

diversity of specific radioactivity in fish resulting from particular stocking programmes (indigenous population versus pellet-fed put-and-take stock).

7.3   Polonium-210 has been shown to be significant in the assessment of individual doses, effects are enhanced by various industrial treatment processes. Studies have taken place to elucidate the gut-transfer factor necessary to calculate individual doses.

7.4   An analysis of Protactinium-234m in silt samples indicated a discrepancy in the expected secular equilibrium with Th-234. Subsequent work between MAFF and BNFL (British Nuclear Fuels Ltd), involving mass spectrometry and an investigation of coincidence summing effects, concluded that sample density has a significant effect on the quoted emission probabilities of Th-234 for the low energy photo peaks. Values of 3.99% were determined for the 63.29keV peak (ICRP value 3.81keV) and 0.91% for the 1001keV peak (ICRP value 0.589).

7.5   Considerable data on the radioecology of Lake Trawsfynydd and the dose to the local critical group has been obtained and is being worked up for publication.

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M H Beach
8 August 1991

PACIFIC NORTHWEST LABORATORY
OF
THE U. S. DEPARTMENT OF ENERGY

Richland, W.A.

U.S.A.

RICHARD W. PERKINS

COORDINATED RESEARCH PROGRAMME ON
RAPID INSTRUMENTAL AND SEPARATION METHODS
FOR MONITORING RADIONUCLIDES
IN FOOD AND ENVIRONMENTAL SAMPLES

12-16 AUGUST 1991

VIENNA, AUSTRIA

RAPID METHODS
FOR MEASURING RADIONUCLIDES

There are continuing programs at the U. S. Department of Energy's Pacific Northwest Laboratory aimed at improving techniques for the measurement of radionuclides. Three of them that seem to be of particular interest are:

1. ICP/MS methods for long-lived radionuclides

2. The barrel counter for measurement of radionuclides in bulk samples

3. Rapid methods for transuranic radionuclide measurements

Work is continuing in all of these areas and technologies for their use have proceeded to the point where they can be applied to many problems. A discussion of each of these methods follows.

APPLICATION OF ICP/MS TECHNIQUES
TO
RADIONUCLIDE ANALYSES

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As mass spectrometry has continued to gain sensitivity and reliability, inductively coupled plasma/mass spectrometry (ICP/MS) has become increaingly useful in the measurement of radionuclides. The optimization of ICP/MS is improving our ability to use atomic detection of radionuclides in that it allows the near complete isotopic analysis of any form of sample. While aqueous samples are generally introduced into the plasma source, solids or individual particles and organic solutions may be atomized and continuously introduced into the plasma source.

We are presently developing laser ablation and electrothermal vaporization (ETV), as well as other nebulization techniques for the direct analysis of geologic materials, glasses, biological substances, and foods. Detection sensitivity of 10^{11} atoms are routinely achieved by solution nebulization, and 2 to 3 orders of magnitude in sensitivity can be gained using ETV sample introduction and other improvements (i.e., background reduction).

Our studies indicate that concentrations of less than a disintegration per minute per sample (assuming a sample can be 1 ml or less) of Tc-99, I-129, Np-237, U-234, U-235, U-236, U-238, and Th-232 can be observed in a single one-minute scan. Subnanogram quantities of I-129, Tc-99, U-234, U-236, and U-238 represent a small fraction of a disintegration per minute.

Work at our Laboratory is aimed at development of enhanced sensitivity by a combination of improved technology. The application should greatly improve our capabilities in radionuclide and isotopic measurement in a wide range of sample materials. The following viewgraphs indicate the status and the direction of the research program at our laboratory.

DETECTION OF RADIONUCLIDES USING INDUCTIVELY COUPLED PLASMA/ MASS SPECTROMETRY

RADIONUCLIDE DETECTION vs HALF-LIFE

Figure: Log-log plot of Activity (dpm) versus t1/2 (years). Vertical axis "Activity (dpm)" ranges from 10^{-6} to 10^{5}. Horizontal axis "t1/2 (years)" ranges from 10^{-1} to 10^{11}. Labeled reference features include "10 Pg/ml Reference Line", "0.01 Pg/ml", "10CFR20", "RADIOACTIVE", and "BACKGROUND RADIATION". Plotted radionuclides: Sr-90, C-14, Ra-226, Cl-36, Se-79, Al-26, Nb-94, Sb-126, Am-243, Np-236, Cs-135, Cm-245, Pu-239, Tc-99, Bi-210, Zr-93, I-129, U-233, Pd-107, Np-237, Pb-205, Cm-247, U-236, Sm-146, Pu-244, U-235, U-238, Th-232.

ULTRA-TRACE RADIONUCLIDE DETERMINATION USING ICP/MS

INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY SCHEMATIC
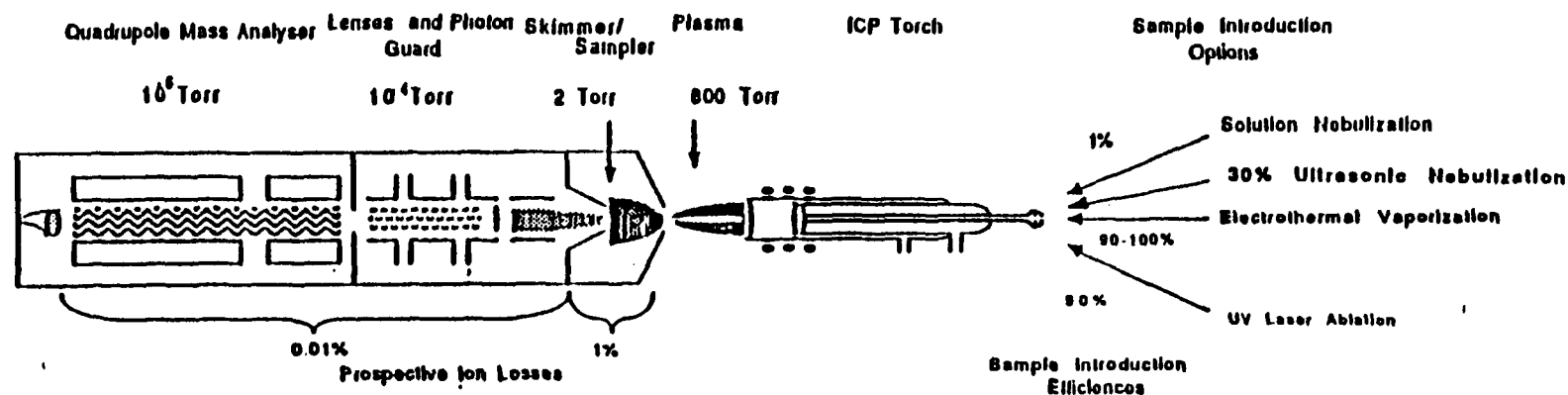
ICP/MS Sensitivity (currently 8 to 10^9 atoms) can be improved by:

* use of more efficient sample introduction techniques
* understanding basic principles of ion and gas dynamics in the ICP/M interface interface
* use of high-resolution mass spectrometers (with higher ion transmission)

Ultimate sensitivity should approach 10^7 atoms, resulting in a superior design capability for all radionuclides with half lives > t yr

~10ppt

64 c/s FULL SCALE
0.5 second DWELL TIME

Th-232

Np-237

U-238

Pu-242

232   234   236   238   240   242   244
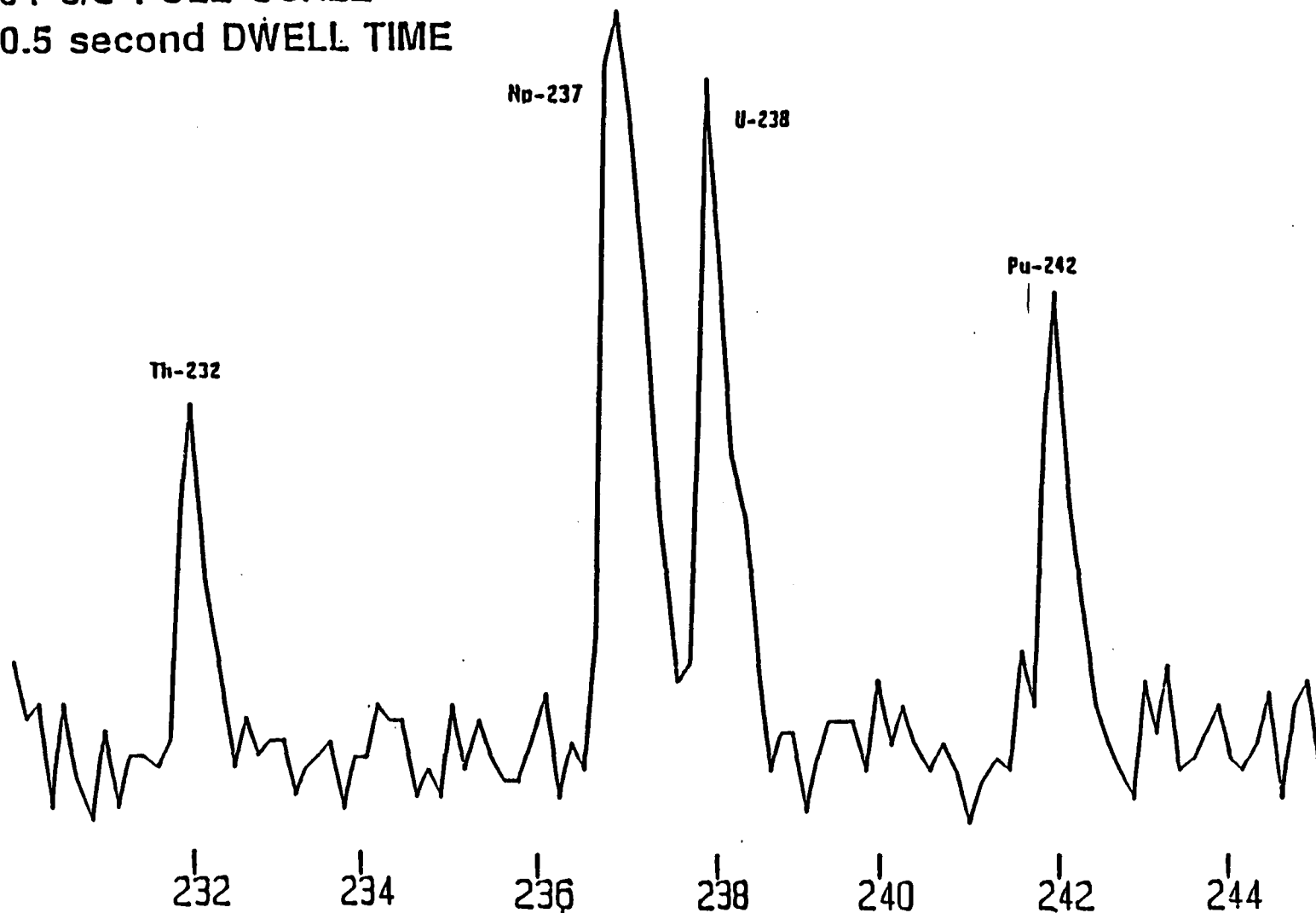
Long-lived radionuclide mass analysis using ICP-MS. Np, U, and Pu peaks represent
approximately 10 pg/ml; Th approximately 5 pg/ml.

DRUM ASSAYER

A waste drum assayer has been developed at our Laboratory which
should be useful for the measurement of radionuclides in bulk food
samples. The analyzer permits both the direct measurement of
transuranic radionuclides and gamma emitters. The sensitivity for
transuranic radionuclides is approximately 1 nci/g, while that for
gamma emitters is on the order of 0.1 to 1 pCi/g. Also, based on
bremsstrahlung radiation measurement, Sr-90 can be measured at
concentrations of 100 pCi/g. We therefore feel that this type of
instrument could be employed for the direct measurement of gamma
decay radionuclides in food.

TYPICAL SENSITIVITIES FOR THE ICP/MS

Fission/activation products = 0.1 to 1 pCi/g

Transuranics = 1 nCi/g

Sr-90 = 100 pCi/g

DRUM ASSAYER
FOR MEASURING RADIONUCLIDES IN FOODS

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This summary describes a completely portable, one-man-operable instrument capable of quantifying the radioactive content of 208-liter (55-gallon) drums. It could be calibrated for other sample configurations as well. All radioisotopes are measured simultaneously in just a few minutes. The assayer uses two measuring techniques: segmented gamma-ray spectrometry and neutron counting. A drum (or other container) to be assayed is placed on a rotating turntable by a self-contained electric hoist.

A collimated high-resolution germanium diode gamma-ray spectrometer vertically scans the rotating drum to measure the intensity of gamma rays as a function of energy emanating from the drum. Most fission and activation products and some transuranic radionuclides emit measurable quantities of monochromatic photons that serve as "fingerprints" of those radioisotopes. Comparison to the emission rate from known standards provides a quantitative measure of radioactivity from each gamma-ray emitter in the drum. This same germanium spectrometer is used to measure the bremsstrahlung radiation from Sr-90. By manipulating the software with the on-board computer, the intensity of the Sr-90 bremsstrahlung in the assayed drum is also compared to that of standards, and the Sr-90 concentration is quantified.

In the absence of large quantities of gamma-emitting fission or activation products, the isotopes U-235, U-238, Np-237, Pu-2349, Pu-241, Am-241, Cm-243, and Cm-244 are generally measurable at adequate sensitivity to separate TRU and non-TRU wastes based on their gamma-ray emissions. The computer utilizes these measured transuranics and the code ORIGEN[1] to predict the concentration of Pu-238, Pu-240, and Pu-242 expected to be present. The neutron yield for the assemblage of transuranic isotopes, assumed to be present as the oxide, is calculated and compared to the measured neutron emission rate obtained with the neutron sensitive proportional counters. The neutron counters have also been calibrated with standard drums containing known concentrations of appropriate transuranics in a variety of matrix materials. If the

presence of fission or activation products masks the detection of gamma rays from transuranic isotopes, a positive neutron count identifies the presence of transuranics. The net neutron count rate is used to quantity the total TRU concentration of the drum based on the expected neutron yield from a mixture of transuranic isotopes of the same composition as that in the drum.

All data acquired and all calculations performed by the software are stored on hard disc and backed up on floppy disc for archival or subsequent manipulation. An onboard printer provides immediate hard copy of as much or as little data as desired and can even be used to print a shipping manifest.

Typical sensitivities for the system are:

fission/activation products = 0.1 to 1 pCi/g,

transuranics - 1 nCi/g, and

Sr-90 = 100 pCi/g.

[1]   Radiation Shielding Information Center, RSIC Computer Code Collection, "Origen2," CCC-371, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

A RAPID PROCEDURE FOR THE MEASUREMENT OF TRANSURANIC ELEMENTS AND THORIUM

- Dissolve sample

- Add tracers Pu-242, Am-243 and Th-234

- Coprecipitate with iron hydroxide

- Coprecipitate as the oxalate

- Electrodeposit on a stainless steel disc

- Measure transuranic elements and thorium by alpha energy analysis

- Determine yield from tracers

A RAPID PROCEDURE FOR THE MEASUREMENT
OF THE TRANSURANIC ELEMENTS AND THORIUM

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Richland, Washington USA

The concept involved here is to quickly remove the transuranic elements from interfering materials (and radionuclides if this is a problem) sufficiently well so that they can be electrodeposited as a group and measured by alpha energy analysis. The procedure involves the following basic steps.

Step 1. The sample is first brought into solution.

Step 2. Radioisotope tracers, including Pu-242, Am-243, and Th-234 (if appropriate), are added.

Step 3. A small amount of Fe carrier ($\sim$10 mg) plus sodium sulfite is added to this solution and it is subsequently made basic by addition of ammonium hydroxide to allow formation of an iron hydroxide precipitate. This precipitate serves to carry the thorium and the transuranic elements.

Step 4. The mixture is centrifuged and the solution discarded while the precipitate is dissolve in dilute hydrochloric acid then diluted with water. The pH is made basic with ammonium hydroxide which results in a second iron hydroxide precipitate forming.

Step 5. Following centrifuging and discarding the solution, the precipitate is dissolved in dilute hydrochloric acid and diluted with water, and a small amount of sodium sulfite is added to maintain the transuranic elements in lower valence states.

Step 6. A small amount of Ca carrier (1 to 2 mg) is then added and the pH adjusted to approximately 3 to allow formation of an oxalate precipitate. The iron forms a very soluble oxalate, thus remaining in solution. This and two subsequent oxalate precipitates serve to remove any remaining iron.

Step 7. The final oxalate precipitate is then dissolved in a small amount of sulfuric acid (0.5 ml concentration H_2SO_4) and the pH is adjusted to the "gold end point" for thymol blue using dilute ammonium hydroxide (first 5 M and then 0.5 M).

Step 8. The solution is then placed in an electrodeposition cell where the transuranic elements are electrodeposited on a 1 cm^2 area of 2.5 cm diameter stainless steel disc.

Step 9. Electrodeposition is conducted for a one-hour period at a current of 1 amp.

Step 10. Immediately before turning off the current 1 ml of concentrated NH$_4$OH is added to the cell and electrodeposition continued for an additional minute. The current is then turned off, the solution is discarded, the electrode washed with water, then ethanol, and air dried. Following alpha energy analysis, the radiochemical yield as determined from the radioisotope tracer content and the concentrations of the radionuclides of interest are calculated.

Samples with a large amount of iron such as soil extracts or vegetation ash may require partial removal of iron prior to initiation of this procedure. In these cases, the tracers are added to the soil or vegetation ash prior to dissolution or leaching. The samples are then leached with HCl and HNO$_3$.* The solution is then diluted to about 3N acid. To this solution is added oxalic acid (about 200 grams^a), and following its dissolution NH$_4$OH is added while stirring until pH 2 to 3 is reached and oxalate precipitation is complete. The oxalate precipitate containing the transuranics and Th is filtered, washed with Ph 3 HCl and muffled to destroy the oxalate precipitate and produce CaO. The residue is then dissolved in HCl.

At this point it is possible to proceed with Step 3 of the stepwise procedure.

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*   Leach with hot 6 N Hcl for about 20 minutes with stirring. Leach residue residue similarly with 8 N HNO$_3$, then 6 N Hcl and then water and discard the residue.

a) Too much oxalic acid (saturated solution) tends to dissolve the Pu causing a low yield.

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DETERMINATION OF Sr-89/90

SAMPLE PREPARATION PRIOR TO THE ANALYSIS OF $^{89+90}Sr$

1. Sediments:

Dry in drying oven at 105^oC overnight and sieve through a 250 um sieve. 100-200 g of dried and sieved sediment is needed for analysis.

2. Fruit and vegetables:

Clean and chop 1-2 kg of samples, weigh and dry in an oven overnight at 105^oC. Weigh dried sample and calculate the % of dry matter. Ignite the sample in a muffle owen (see ignition of samples - procedures). The temperature should be raised carefully to 550^cC (the sample can burn at approximately $200-300^oC$ if the temperature is raised too rapidly). Weigh the ash.

3. Milk

Fresh milk could be used for analysis if a high activity of Sr-90 is expected. Otherwise freeze dry 2-3 l of milk. Calculate the % of dry weight. Ignite at 550^oC. Again, the temperature shoud be raised carefully. Weigh the ash.

4. Meat

Cut 1-2 kg fatless meat (reject sinews) into small pieces and dry it at 105^oC. Calculate the % of dry weight. Ignite the sample at 550^oC. The temperature should be raised carefully, particurally in the range from 200 to 350^oC in order not to loose sample due to spattering. Weigh the ash.

5. Fish:

a) Small fish:
Take 1-2 kg of sample, gutted and well washed, cut into pieces and dry at 105^oC in oven. Calculate the % of dry weight. Ignite at 550^oC. Raise the temperature successively, being extremely careful in the range from $150-350^oC$. Weigh the ash.

b) Large fish:
Analyse separately muscle and bone. Remove internal organs and skin. Wrap the sample in aluminium foil, heat at 105^oC in a drying oven for
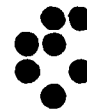
0,5 hour. Immediately separate the meat from the bones. At least 500 g of meat and 100 g of bones are needed. Weigh separately the muscle and the bones and dry them again at 105°C overnight. Calculate the % of dry weight. Ignite at 550°C in muffle furnace. The procedure is the same as with small fish.

IGNITION OF SAMPLES

Since strontium is not volatile, the majority of samples are prepared by dry ashing. Obtaining the required precision and accuracy in radiochemical analyses for natural or fallout radionuclides in materials such as food, vegetation, soils, sediments and water usually requires large samples. Sample identification, original weight and ash weight determination are the same operations as those performed for standard chemical analysis. It should be noted, however, that ash weights as taken are not considered as basic data, but are used as an intermediate step in calculating the activity in the original sample.

Ashing equipment

Muffle furnaces in several sizes should be used,, primarily because of the large variety of samples prepared. A large capacity (1m^3) muffle which may be operated at 550°C continuously is ideal since many different samples or very large samples may be accommodated. Porcelain ware is used in this laboratory. After ashing several samples, porcelain trays tend to became rough from loss of porcelain by fusion with materials with high alkali salt content such as milk or potatoes. Once these trays are etched, it becomes difficult to clean them completely. Therefore, some ash is lost and a possible source of contamination of future samples is produced. The loss of ash may be unimportant but the chance of cross-contamination cannot be passed off lightly. But porcelain trays will retain their smooth surface longer than silica trays, even though traces of metals fuse into the glaze. All large capacity furnaces used in ashing operations should be fitted with fire retardant screens and should exhaust to the outside, since during the early part of the ashing considerable quantities of volatile compounds with low flash points are evolved. These compounds tend to condense in the stack close to the furnace and present a serious fire hazard. Forced draft ovens will tend to disturb the ash with a cosequent loss of material and possible cross-contamination from one sample to another, and are therefore not recommended.

Procedures

Dry ashing is conducted as a two stage process. The first stage is

done at about 125°C to completely dry the sample. Subsequently the temperature is raised at intervals over an 8 hour period to 550° to produce an ash with the least possible amount of carbon. Bone is ashed at about 900°C. The length of time required for drying large samples is 16 to 24 hours. Table 1 lists critical temperatures where ignition could occur. The temperature of the furnace should be raised slowly over a period of 8 hours (or more if it is necessary) in this critical temperature range. When the upper limit has been reached without sample ignition the furnace temperature can be raised more rapidly to 550°C and the samples ashed for 16 hours.

TABLE 1

Preliminary ashing temperature

Material	Temperature
Eggs	150-250°C
Meat	150-250°C
Fish	150-250°C
Fruit(fresh)	175-325°C
Fruit(canned)	175-325°C
Milk(wet)	175-325°C
Vegetables(fresh)	175-225°C
Vegetables(canned)	175-250°C
Root vegetables	200-325°C
Grass	225-250°C
Flour	200-250°C
Dry beans	175-250°C
Fruit juices	175-225°C
Grains	225-325°C
Macaroni	225-325°C
Bread	225-325°C

DETERMINATION OF Sr-90 AND Sr-89 IN VARIOUS SAMPLES

1. Weigh out at least 100 g of ashed sample (or dried sediment) into a 1 liter beaker. Add 100 ml of conc. HCl and 10 ml of strontium carrier solution (20mg/ml). Leave to stand overnight to achieve isotopic equillibrium.

2. Filter under suction on a 9 cm or 11 cm black band filter paper supported by a glass frit. Wash the residue on the filter with distilled water. In the case of sediment, repeat the leaching of the

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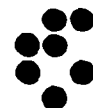
residue with 100 ml of conc. HCl and allow to stand overnight. Next day filter under suction and combine the filtrates.

3. Heat the filtrate at about $60^{\circ}C$. Add 75 ml of 65% glycollic acid and add conc. ammonia solution to obtain a pH=5.

4. Pass the warm solution down an ion exchange column (diameter 50 mm, height 100mm, exchanger Dowex 50x8, 50-100 mesh).Discard the eluate containing 3^+ metal ion complexes and part of the Ca. Wash the column with 800-1000 ml of 0,15M ammonium citrate solution to eluate Ca and Sr.

5. Heat the solution at $80^{\circ}C$, add 12 g of oxalic acid and NaOH to pH=5-6. Allow the oxalates to settle overnight.

6. Decant the clear solution from the precipitate, separate the remaining solution by centrifugation.

7. Add fuming HNO_3 to the oxalate precipitate and stir. Transfer the suspension to a beaker and heat. Add dist. water until the solution becomes clear. Repeat the dissolution and precipitation steps two or three times until a pure precipitate of $Sr(NO_3)_2$ is obtained.

8. Dissolve the precipitate of $Sr(NO_3)_2$ by adding 10 ml of dist. water and transfer quantitatively to a 150 ml beaker. Add 1 ml of Fe^{3+} solution (5 mg Fe^{3+}/ml), 1 ml of 1:1 NH_3 saturated with barium hydroxide, and then NH_3 to pH=8 ($Fe(OH)_3$ precipitates). Filter through a black band filter paper and reject the precipitate.

9. Add 1 ml of glacial acetic acid, 2 ml of 25% ammonium acetate and heat for 2-3 min. Afterwards add 1 ml of saturated ammonium chromate and heat for 3-5 min. Filter (black band filter paper) and reject the Ca-chromate precipitate.

10. Add conc. NH_3 to filtrate (the colour of the solution changes from orange to yellow) and approximately 0,2 g of ammonium carbonate in order to precipitate $SrCO_3$. Heat for 2 min. and cool in a beaker containing cold water. Record the time of separation.

11. Filter under suction on an A-2 porous crucible (Gooch crucible). Transfer the $SrCO_3$ precipitate to 35 ml specially designed centrifuge tube containing a pre-weighed counting planchette with small additions of alcohol. Centrifuge for 2 min. at 3000 rpm. Dry the precipitate, weigh and count the activity of radiostrontium on a beta counter.

12. Determine the chemical yield for Sr gravimetrically.

Isolation of Y-90

13.   After an appropriate waiting time to establish radioactive
      equilibrium between Sr-90 and Y-90 (about 20 days), dissolve the
      $SrCO_3$ precipitate in 25 ml 14M HNO_3 and add 2 ml of Y-carrier (20 mg
      Y-90).

14.   Equilibrate 40 ml of TBP with an equal volume of 14M HNO_3 by
      shaking for one minute.

15.   Transfer the sample to a 250 ml separatory funnel, add 15 ml 14M
      HNO_3, 20 ml of equilibrated TBP and shake for 5 minutes. Allow the
      phases to separate and transfer the aqueous (lower) phase to a clean
      250 ml separatory funnel. Record this time as the time of separation
      of yttrium from strontium. Add another 20 ml of equilibrated TBP and
      shake for 5-10 minutes.

16.   Allow the phases to separate and then combine the second TBP
      fraction with the original TBP fraction in the 250 ml separatory
      funnel.

17.   Shake the organic phase twice for two minutes with 50 ml 14M
      HNO_3 to wash the extracts. Discard the aqueous portions.

18.   Strip the yttrium from the TBP with two 30 ml portions of water.
      Transfer the aqueous solutions to a 150 ml beaker.

19.   Evaporate to 15 ml. Add 1 ml of saturated oxalic acid solution
      dropwise. Adjust the pH to 2-3 by adding drops of NH_4OH. Allow the
      yttrium oxalate precipitate to digest for about an hour.

20.   Filter under suction on an A-2 porous crucible (Gooch crucible).
      Transfer the crucible with the precipitate to a muffle furnace and
      heat for one hour at $800^\circ C$.

21.   Cool to room temperature and transfer the precipitate to a 35 ml
      specially designed centrifuge tube containing a pre-weighed counting
      planchette with small additions of alcohol. Centrifuge at 3000 rpm
      for two minutes.

22.   Dry the Y_2O_3 precipitate, weigh and count the activity of Y-90
      on a beta counter.

23.   Calculate the chemical yield for yttrium gravimetrically.

CALCULATIONS

$$A_{tot} = A_{89Sr} + A_{90Sr} + A_{90Y} \quad (T_1)$$

- - - - - - ^{90}Y activity

A_{89Sr}

A_{90Sr}

$A_Y^{①}$

$A_Y^{②}$

$A_Y^{③}$

T T_1 T_2 T_3 time

isolation of radiostrontium	measurement of the $^{90 \cdot 89}Sr$ activity	isolation of ^{90}Y	measurement of the ^{90}Y activity
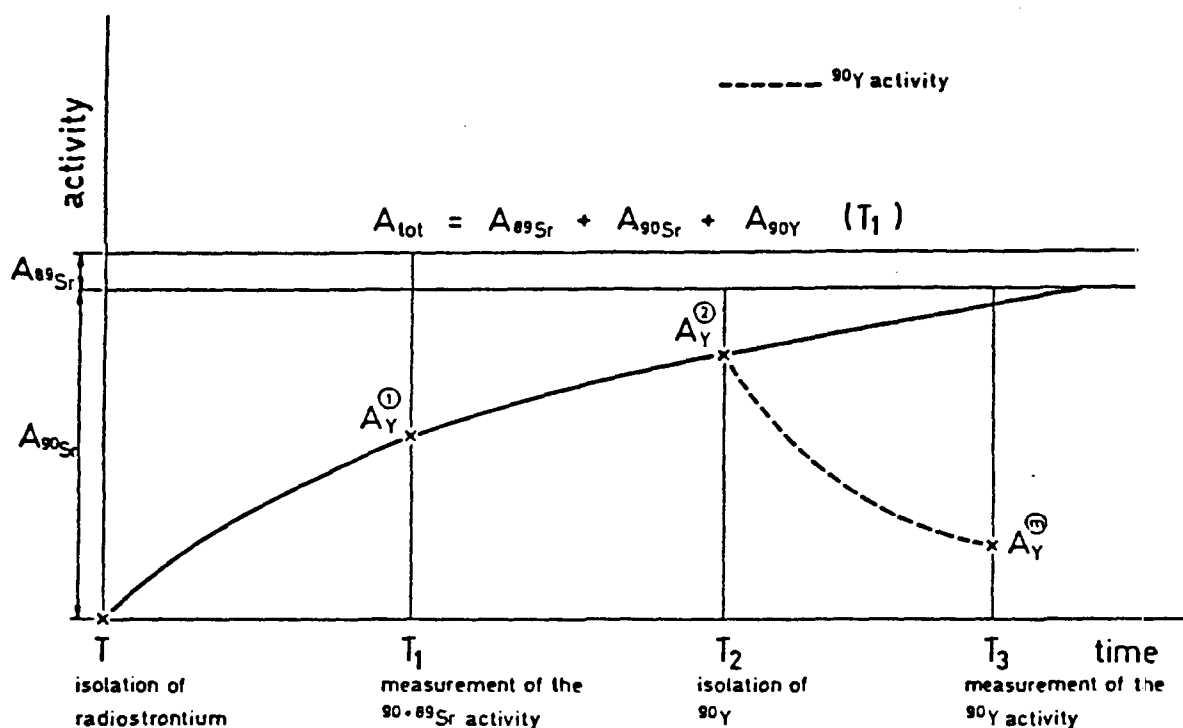
$$A_{tot} = \frac{R_N \, (T_1) \, (cps)}{I_{count} \cdot I_{chem, Sr} \cdot m \, (kg)} \quad (Bq/kg)$$

$$A_Y^{③} = \frac{R_N \, (T_3) \, (cps)}{I_{count} \cdot I_{chem, Y} \cdot m \, (kg)} \quad (Bq/kg)$$

$$A_{90Sr} = \frac{A_Y^{③}}{(1 - e^{-\lambda T_2})} \cdot e^{\lambda(T_3 - T_2)}$$

$$A_{89Sr} = A_{tot} \, (T_1) - A_{90Sr} (2 - e^{-\lambda T_1})$$

R_N = $R_T - R_B$

R_T = total count rate

R_B = background count rate

I_{count} = counting efficiency

I_{chem} = chemical yield

m = sample fresh weight

λ = ^{90}Y decay constant

REAGENTS

1. Concentrated HCl
2. Strontium carrier - 20 mg Sr/ml
   (48,4 g $Sr(NO_3)_2$/l 1:99 HNO_3)

3. Yttrium carrier - 20 mg Y/ml
4. 65% glycollic acid
5. Concentrated ammonium
6. 0,15M ammonium citrate solution
7. Oxalic acid
8. Sodium hydroxide
9. Fuming nitric acid
10. Iron carrier - 5 mg Fe/ml
    (36 g $Fe(NO_3)_2$x9H_2O/l HNO_3)

11. Ammonium hydroxide solution (1:1) saturated with Barium hydroxide
12. Glacial acetic acid
13. 25% ammonium acetate solution
14. Saturated ammonium chromate solution
15. Ammonium carbonate
16. Ethyl alcohol
17. Tributylphosphate(TBP) saturated with 14M HNO_3
18. 14M HNO_3

Contract No. 5454/R1/RB

A C T I V I T Y   R E P O R T

2nd RCM OF THE AGENCY'S CO-ORDINATED RESEARCH PROGRAMME ON "RAPID INSTRUMENTAL AND SEPARATION METHODS FOR MONITORING RADIONUCLIDES IN FOOD AND ENVIRONMENTAL SAMPLES", Vienna 12-16 August 1991

DEVELOPMENT OF RAPID ANALYTICAL METHODS FOR Am-241

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BACKGROUND

In the framework of the IAEA Co-ordinated Research Programme on Rapid Instrumental and Separation Methods for Monitoring Radionuclides in Food and Environmental Samples, the original programme of the Department of Nuclear Chemistry was modified at the first RCM in Warsaw, Poland, so that the part dealing with Sr-89,90 was to be omitted.

In the first phase of the work (reported in Warsaw) the limits of detection for ^{241}Am by gamma spectrometry of its 35.9% abundant 59.5 keV gamma ray were determined for two detectors, i.e. a low energy photon detector (LEPD) of the maximum size currently commercially available (disc 50 mm diameter, 20 mm deep), and an HP Ge well-type detector with a 5 ml hole.

It was intended that the major use of the well-type detector would be to measure ^{241}Am by gama spectroscopy in small concentrates separated by relatively simple and rapid radiochemical procedures from large bulk samples, thus taking advantage of the high efficiency of the detector combined with a large initial sample size.

WORK PERFORMED

(i) Non-destructive gamma spectrometry

Using the LEPD with a 100 ml sample (e.g. soil) or a 5 ml sample in the well-type HP Ge detector, detection limits for a 24 hour count of about 0.5 Bq/kg or 1 Bq/kg, respectively, could be achieved.

We have now shown that using ashed biological samples, the further reduction of mass enables a limit of detection on the LEPD of about 0.1 Bg/kg (dry weight basis) to be obtained. Correspondingly, for more active samples, a shorter counting time i.e. a more rapid result, can be obtained.

Using a 500 ml Marinelli beaker, further improvement is possible, to about 0.2 Bq/kg for soil samples for an "over the weekend" count. It was shown that in the 60 keV region the LEPD is about 2.5 to 3 times more efficient than a conventional Ge detector. An added bonus of gamma spectroscopy is that it allows measurement of interesting naturally-occurring radionuclides such as ^{210}Pb (47 keV) ^{238}U (via ^{234}Th at 63 keV) and ^{230}Th (67.7 keV). The sensitivity of the LEPD with a 500 g sample in a Marinelli beaker for ^{230}Th is such that levels in many soils can be quantified (detection limit about 30 Bq/kg).

It would seem worthwhile in pursuing non-destructive gamma spectrometry, to combine it with a method of rapid ashing of bulk food and/or vegetation samples.

(ii) Gamma spectrometry of Am-241 using preconcentration chemistry

a) The idea of using the high counting efficiency of the well-type detector for the 59.5 keV gammas of ^{241}Am (about 30% absolute for a small source) with a rapid and simple radiochemical separation of ^{241}Am from a bulk sample has been developed. The stage of development reached by autumn 1990 is described in a paper presented at the 6th International Symposium on Environmental Radiochemical Analysis in Manchester, U.K., 18 - 23 September 1990, entitled "Possibilities for determination of ^{241}Am in environmental samples by gamma counting, with and without radiochemistry". This paper has now been accepted for publication in Science of Total Environment[1].

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Since then, work has continued, mostly using soil samples which represent the most challenging matrix. At the same time, they are also of great interest since fall-out levels of ^{241}Am in topsoil in the northern hemisphere are quite similar to the detection limits currently obtained with this method.

For soil most radiochemical work has been done using calcium oxalate as a collector precipitate following acid leaching of dry ashed samples. Lately, the chemical yield determinations have been improved by using ^{243}Am tracer, which also has gamma rays (75 keV, and ^{239}Np gamma rays at 103, 106 keV, etc). Unfortunately, the 74.7 keV peak of ^{243}Am is overlapped by the 74.8 keV ^{212}Pb peak, so that sufficient ^{243}Am tracer must be added to avoid this error. However, use of large amounts of ^{243}Am is undesirable since this raises the background under the 59.6 keV ^{241}Am peak. Therefore it is desirable that the radiochemical scheme removes ^{212}Pb and its precursors.

Lately, efforts have been made to design and test a radiochemical scheme which will include plutonium as well as americium; after separation of the Am containing precipitate, this would be followed by separate determination of Pu by alpha spectrometry. Further radiochemical purification of the Am-containing precipitate then allows alpha spectroscopy of Am if desired.

b) Summary of procedures tested

I. FOODSTUFFS

Various kinds of vegetables (potatoes, cabbage, leak, apples) and milk powder spiked with ^{241}Am were dry ashed, leached with 1:1 nitric acid and Am collected on calcium oxalate or LaF$_3$, and the precipitate measured in the well-type Ge detector and gamma spectrometer.

The recoveries of added ^{241}Am were from 70 - 84% in the case LaF$_3$, or 90 - 99% for calcium oxalate.

II. SOILS

Most experiments were performed on large samples (100 - 200 g) where problems become acute, and differences between soils (clay

content, Fe, Mn concentrations) make the use of a standardized procedure difficult. With such soils, precipitation of calcium oxalate directly after acid leaching gave very variable yields; it was found that precipitation of hydroxides at high pH, redissolution in acid and then calcium oxalate precipitation gave better results.

A modified procedure based on that described by Livens et al[2] for Pu and Am determination (which is based on the scheme of Holm and Ballestra in the recent IAEA Technical Report No 295[3]) is also being tested. This is a little complicated and lengthy, but gives good clean gamma spectra for ^{243}Am (Figs 1 and 2).

By addition of ^{242}Pu and ^{243}Am tracers at the beginning of the procedure, the alpha spectroscopic determination of Pu is combined with the gamma spectroscopic determination of ^{241}Am, using ^{243}Am as a yield monitor. Further, the Am containing precipitates, $Fe(OH)_3$ or Ca oxalate, can then be dissolved and the conventional radiochemical separation steps of ion exchange (cation exchange in HCl, anion exchange in methyl alcohol-nitric acid medium to separate Am from rare earths) applied to prepare an alpha spectroscopy source after electrodeposition (see Fig 3). These radiochemical approaches are shown schematically in Figs 4a, b, and 5.

Five basic procedures were devised as follows:

A) - Dry ashing, addition of ^{243}Am, (around 0.1 cps) 20 mg La^{3+}
   - Leaching with 1:1 HNO_3, filtration
   - Co-precipitation on LaF_3
   - Measurement in well-type Ge detector

B) - Dry ashing, addition of ^{243}Am
   - Leaching with 1:1 HCl, filtration
   - Co-precipitation on Ca oxalate
   - Measurement in well-type Ge detector

C) - Dry ashing, addition of ^{243}Am
   - Leaching with 1:1 HCl, filtration
   - Co-precipitation on metal hydroxides
   - Dissolution in 1:1 HCl
   - Co-precipitation on Ca oxalate
   - Measurement in well-type Ge detector

D) - Dry ashing, addition of ^{243}Am and ^{242}Pu
   - Leaching with HNO_3 or HCl (1:1), filtration
   - Co-precipitation on metal hydroxides (then on Ca oxalate if necessary
   - Dissolution in 1:1 HNO_3
   - Separation of Pu on anion exchanger
   - Co-precipitation of Am from column eluate on calcium oxalate
   - Measurement of ^{241}Am in well-type Ge detector
   - Work-up of Pu fraction for alpha spectrometry

E) - as D to step 5, then
   - Co-precipitation on $Fe(OH)_3$
   - Dissolution in HCl, separation of Fe by anion exchange
   - Separation of Am from R.E.E by anion exchange in $MeOH-HNO_3$
   - electrodeposition, alpha-spectroscopy of ^{243,241}Am.

APPLICATIONS, RESULTS

(i) A large sample (about 10 kg) of dried surface soil (0 - 3 cm) from Lublin, Poland, was well ground and ball milled, and used as an in-house test soil material. Subsamples were also spiked with ^{241}Am as test samples.
As mentioned above when using ^{243}Am as a gamma tracer, the 74.8 keV line can also arise from ^{212}Pb. Therefore for samples with high ^{212}Pb contents, a sufficient excess of ^{243}Am should be added. The 103 and 106 keV peaks of ^{239}Np (daughter of ^{243}Am) can also be used, but their intensity is weaker. In the well-type detector, the 63.3 keV line of ^{234}Th (from ^{238}U) also deteriorates the precision with which the (small) 59.5 keV peak of ^{241}Am can be measured. (On the LEPD this is not a problem due to its much better resolution).
Result for ^{241}Am in the Lublin soil are shown in Table 1, using procedure C) above.

Gamma and alpha spectra of americium fractions from spiked and unspiked Lublin soil are shown in Figs 1-3.

Table 1: ^{241}Am in Lublin soil by radiochemistry and gamma spectrometry

Sample mass g	% yield of ^{243}Am		% yield of ^{241}Am spike	^{241}Am cont. found Bq/kg*
	74.8keV correct. for ^{212}Pb	103+106keV ^{239}Np		
82.3	55.6	60.1	64.4	
82.3	55.8	47.0	65.3	
82.3	87.8	75.8	77.9	
164.2	61.7	81.7	not spiked	0.24
149.5	57.5	-	not spiked	0.18

*using yield at 74.8 keV

(ii) Chernobyl area soils

Soil Bragin 7, 0 - 5 cm: the ^{241}Am content found by radiochemical concentration and gamma spectrometry was 15.7 ± 3.4 Bq/kg (around 1000 Bq/m^2) whereas by LEPD non-destructive gamma spectrometry the value was 12.4 Bq/kg (1 result).

Soil Bragin 7, 5 - 10 cm: the mean ^{241}Am content by radiochemical separation was 0.58 ± 0.27 (6 determinations) Bq/kg, and 0.89 Bq/kg by LEPD (without separation).

Soil Gdenj 6, 0 - 3 cm: The ^{241}Am content by LEPD gamma spectrometry was 65 Bq/kg.

Plutonium determination: In soil Bragin 7, 0 - 5 cm, the contents of ^{239,240}Pu and ^{238}Pu were also determined. The mean concentrations were 11.2 ± 2.2 (4) Bq/kg of ^{239,240}Pu, and 5.6 ± 1.7 (4) Bq/kg of ^{238}Pu.

Generally, in soil from the Chernobyl area, the ^{241}Am to total Pu ratio was around unity, suggesting that gamma spectrometry of ^{241}Am could be used as a rough but quick guide to plutonium levels.

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Rapid Determination of ^{90}Sr By TBP Extraction

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Abstract

An improved method for determination of ^{90}Sr in food and environmental samples was developed , based on a tributylphosphate (TBP) extraction of its daughter ^{90} Y . Results of ^{90}Sr activity in grass collected after the Chernobyl event and of ^{90}Sr in various IAEA reference materials are given .

I .Introduction

The ^{90}Sr encountered in biosphere mainly originated from nuclear explosions, reactor aceidents, etc. It is produced with a fission yield of about 5.7% , the tatal amount of ^{90}Sr deposited on the surface of the earth amounted to approximately 5 $\times 10^{17}$ Bq . After the Chernobyl nuclear power plant accident an increase of the ^{90}Sr deposition took place.

Most methods for determination of ^{90}Sr require a long in growth period , usually 10 days to 2 weeks after purirfication of strontium. Some methods to determine ^{90}Sr are listed in Table 9.

This paper presents a rapid method for the determination of ^{90}Y by tributylphosphate extraction of the ^{90}Y daughters which are usually known to be in equilibrium .The method is sensitive to 0.2 Bq per Kg of dry grass and milk powder and 2 Bq per Kg of soil.

II .Experiment

Figure 1 shows the flow of analysis.

```
┌─────────────┐   carriers
│ leached     │──────────────────────
│ sample ask  │←──────────────────────
│ 10N  HNO₃   │   Sr⁺², Ba⁺²,Y⁺³, Ce⁺³
└─────────────┘
       │
       ▼
┌─────────────┐
│ TBP         │
│ EXtractions │
└─────────────┘
       │
       │───→── HNO₃     Discard
       ▼
┌─────────────┐
│ washing     │
└─────────────┘
       │
       │──←──── alcohol anhydrous
       ▼
┌─────────────┐
│ NH₄ OH      │
│ stripping   │
└─────────────┘
       │
       │──←──── 6N HNO₃
       ▼
┌─────────────┐
│ oxalate     │
│ precipitate │
└─────────────┘
       │
       ▼
┌─────────────┐
│ ⁹⁰Y         │
│ count       │
└─────────────┘
       │
       ▼
```

Yield by EDTA titration

Fig 1.Flow of analysis

The ^{90}Y is separated directly from the ash solution and measured in a low background bata counter. Samples are prepared by dry asking techuiqmes. The ash for analysis is leached in conc. nitric acid. The ^{90}Y with Y^{+3} carrier is extracted into equilibrated tribatylphosphate. The separated ^{90}Y is further purified by precipitation backextracting from TBP by NH$_4$ OH. After dissolving the precipitate of Y(OH)$_3$,the ^{90}Y is precipitated as the oxalate and counted in a low background beta counter.

III .Experiment and results

1.Extraction parameters

Change the concentration of TBP ,acidity of the aqueous solution , time of extraction to determine the chemical recovery.The results are shown in Tab 1-3.

Tab. 1 Recovery -[TBP]
[HNO$_3$]=15N   Time of extraction =2 min.

	[TBP]-[Kerosen] vol/vol		
recovery %	30%-70%	60%-40%	100%-0%
	78.9	96.5	100

Tab.2 Recovery -Acidity of aqueous solution
[TBP]=100%   Time of extraction =2 min.

[HNO$_3$]	3N	6N	10N	15N
recovery %	35.2	54.6	83.3	100

Tab. 3 Recovery -Time of extraction
[TBP]=100% [HNO₃] =15N

Time(min)	0.5	1	2	3
recovery %	100	100	100	100

2.Backextraction condition

After extraction and phase separation, add alcohol-anhydrous to the organic phase and well mixed than add concentrate ammonia well mixed to backextract and heated in water bath for half hour. Centrifuge for 5 min. remove all organic and aqueous phase, add 1ml 6N HNO ₃ to dissolve the precipitate of the Y(OH) ₃ . Using staturated oxalic acid solution to produce Y₂ (C₂ O ₄) ₃ .
Table 4 shows the backextraction condition.

Table . 4 Backextraction condition
2ml 100% TBP 2ml 15N HNO₃ contains 20.24mg Y

Phase ratio ammonia: TBP	1:1	2:1	3:1
recovery %	82.6	96.7	93.1

3.Distribution ratio

Using radioactivity tracer and liquid scientillation counting system to determine the distribution ratio D.Table .5.shows D.

Table 5 Distribution ratio

Nuclide	Y-90	Sr-90	Cs-137	Ce-144	Co-60	Pm-147
D	46	$7*10^{-2}$	$1.35*10^{-3}$	0.15	$2.8*10^{-4}$	0.82

4.Sample pre-treatment procedure

4.1 Grass sample

Collect the grass which is above 5cm of groud surface and weight air-dry and cut into small piece and carbonated on a plate by electrical furnace, then put it into muffle furnace to ash at 450 ℃ for 12 hour until the ash become white. Using 15N HNO_3 to leach all soluble nuclide in boilling condition.

4.2 Milk powder

Put the milk powder in to crucible and be carbonated on electrical furnace until become black ash . Then put into muffle furnace at 450 ℃ for 12 hour to further ash, until it become white . Using 15N HNO_3 to leach .

4.3 Soil

Using 15N HNO_3 to leach all soluble nuclides.

5.Decontamintion coefficient

Using radioisotop trace and the whole procedure to determine the decontamination coefficient . The results of decontamintion coefficient are shown in Table 6.

Table 6 .Decontamination coefficient Dc. .

Nuclide	Sr-90	Cs-137	Co-60	Ce-144	Pm-147	Eu-152
Dc	$5.0*10^3$	$4.0*10^3$	$2.3*10^3$	$1.9*10^3$	$1.2*10^3$	10.4

6.Trace experiment

Using standard solution of $^{90}Sr - ^{90}Y$ to determine the difference between radioactivity recovery and chenical recovery and using liquid scintillation counting to determine the detection efficiency of low-level counting system which is used to measure the radioactivity of $Y_2 (C_2 O_4)_3$ in our experiment .Table 7 is the difference between radioactivity recovery and chemical recovery .

Table 7. Radioactivity and chemical recovery and the
detection efficiency.

Chemical recovery	Radioactivity recorery	Detection efficiency
73.7 %	72.8 %	33.7 %

Also we use standard solution of ^{90}Sr — ^{90}Y to see the purity of Y_2 $(C_2 O_4)_3$ and to calculate the half life of Y-90 . The resulf is shown in Fig .2

From Fig.2 that we find the half life of Y_2 $(C_2 O_4)_3$ is 65.0 hr that is very close to 64.1 hr which is given by Techical Reports Series No.295 of IAEA.
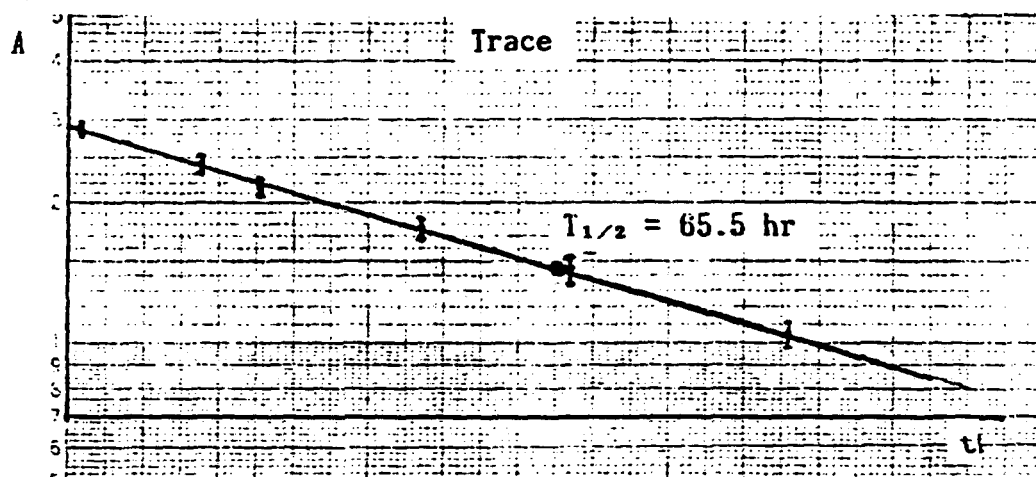
Fig.2 Half life of Y_2 $(C_2 O_4)_3$

7.Analytical procedure

7.1 Add 20mg Y ,50mg Sr, 20mg La, 20mg Ba, 20mg Ce, carriers to 5g ash of grass , milk powder or soil.

7.2 Add 50ml conc .HNO$_3$ to leach all soluble nuclides at biolling condition for one hour. After cooling, centrefuge for 5 min, separate the liquid and residue, using 10ml conc. HNO$_3$ to wash the residue twice. Collect the liquid together.

7.3 Using 10ml 100% TBP equilibrated with conc.HNO$_3$ to extract for

2 min. Repeat the extraction for three times, but 7ml 100% TBP for another two times .

7.4 Collect all organic phase and use 10ml 12N HNO$_3$ wash it and repeat washing 5 times.

7.5 Add 25ml alcohol-anhydrous to mix the organic phase then add 20ml conc. ammonia solution well mixed and heated for 0.5 hour in hot water bath to backextract.

7.6 Centrifuge for 5min, and remove all liquid, add 10ml staturated solution of oxalic acid to produce yttrium oxalate and heated in hot water bath for half hour to congulate the precipitate.
Filter the precipitate with dischargeable filter, and using 10ml 2% oxalic acid to wash. Air-dried then measure the radioactivity with low-background β counting system.

7.7 After radioactivity measuring dissolve the yttrium oxalate with 1ml 6N HNO$_3$. Then using EDTA to determine the recovery of yttrium.

8.Limit of detection
The limit of detetion is calculated according to the equation :

$$D = \frac{3\sqrt{B/T}}{W \cdot Y \cdot \eta}$$

here: B: blank count rate s^{-1}
      T: measuring time of sample   s
      W: weight of smple   g
      Y: chemical recorery of yttrium
      η : detect efficiency of counting system to Y-90

For grass   D =0.197 Bq/Kg dry grass
For milk powder   D =0.185 Bq/Kg milk powder
For soil   D =2.4   Bq/Kg soil

9.Analysis of reference material

Table 8. Comparison of analysis result and reference value

reference material	analysis result Bq/kg	reference value Bq/kg	error %
A -14	1.54±6%	1.7 (1.5-1.7)	9.4
IAEA-321	3.42±6%	3.3 (3.16-3.44)	3.6
IAEA-152	7.9 ±8%	7.7 (7.0-8.3)	2.5
IAEA-154	6.9 ±7%	6.9 (6.0-8.0)	0
SOIL-6	25.3±3%	30.34(24.2-31.67)	17

We use this procedure to analyse some reference materials such as milk powder and soil taken from IAEA . The comparison between the analysis results and refertnce value is shown in Table 8.
Fig. 3 shows the half life of Y-90 in some samples.

10.Analysis of test samaple

The unknown test sample IAEA-156 which is dry grass is analysed . The result is 20.0±10% Bq/ kg. According to AQCS 1991 publication the ^{90}Sr in IAEA-156 is 14.8 Bq/kg , the confidence interval is 13.4-16.3 Bq/ kg ,our result is higher. The half life of Y-90 in IAEA-156 is also shown in Fig 3.The γ spectrum of IAEA-156 befor and after analysis is shown in Fig.4 .

IV.Conclusion

TBP can be used as a extractant for analysis ^{90}Sr in food an environment sample. The procedure is easy and quick. Six samples can be analysed in one day for one person. The decontamination coefficient is high except En-152. In order to sweep En-152, further research should be taken .

The limit of detection for grass is D_L =0.2 Bq/kg(dry grass); for milk powder is D_L =0.19 Bq · kg^{-1}; for soil is D_L =2.4 Bq · kg^{-1}.
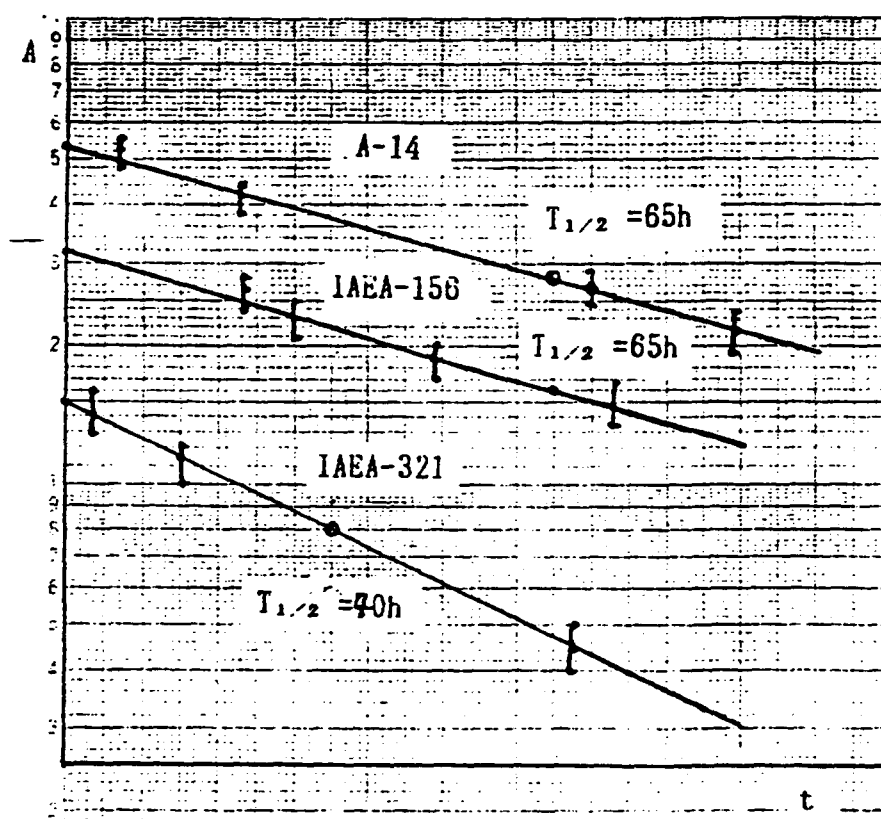
Fig.3 Half life of Y-90 in some samples
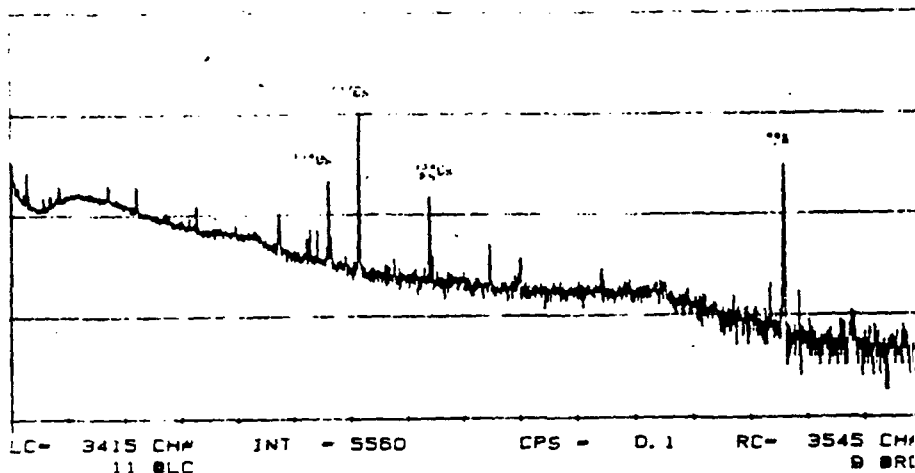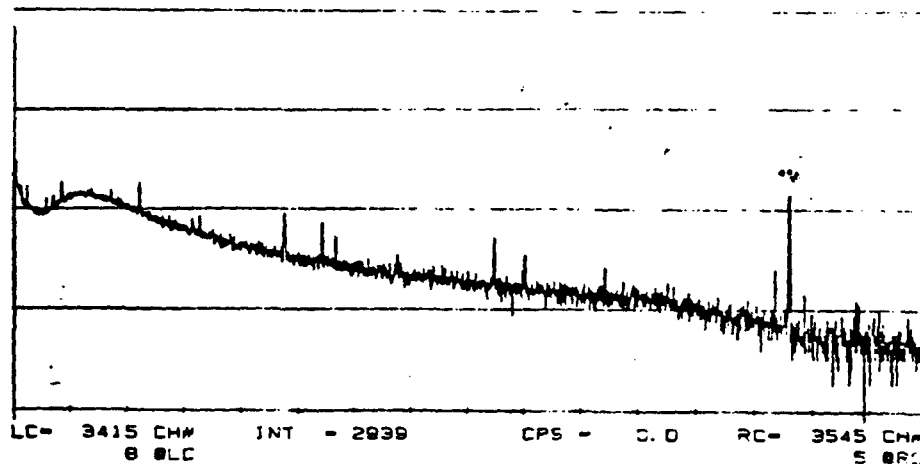
Fig.4   γ spectrum of IAEA-156

V. Reference

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Table 9. Listing of selected methods suitable for the determination of ^{90}Sr in various materials

Characteristics of the method	Reference	Material to be analysed
Ca-Sr-separation by fuming nitric acid, measurement of ^{90}Sr in a low-level beta counter	20 (1957)	Milk, bone, tissue, vegetation, soil
Extraction of Y with HDEHP[di(2-ethylhexyl)phosphoric acid] purification of Y by stripping and extraction processes. Beta counting of ^{90}Y	16 (1965)	Bone ash
Ion exchange separation of Ca from Sr. Beta counting of ^{90}Y	9 (1967)	Milk, vegetation, meat, fish, rainwater, oyster shells
Separation of ^{89}Sr, ^{90}Sr and ^{90}Y. LS and Cerenkov counting	6 (1975)	Not specified
Separation of ^{89}Sr, ^{90}Sr and ^{90}Y. LS and Cerenkov counting	17 (1975)	Not specified
Isolation of Sr-Ca without separation. Cerenkov counting	18 (1976)	Water
Extraction of Sr with dicyclohexyl-18-crown-6	13 (1977)	Rocks, minerals, living bodies
HDEHP extraction of ^{90}Y. LS counting	4 (1978)	Plant and animal samples
Preconcentration of ^{90}Sr with Sr carrier, isolation of Y oxalate. Cerenkov counting	11 (1979)	Water
Extraction of Sr with dicyclohexyl-18-crown-6, measurement of Sr with low-level GM counter	14 (1979)	Milk
Separation of Sr using standard methods. Cerenkov measurement of ^{89}Sr and ^{90}Y without interference from ^{89}Sr	7 (1979)	Not specified
Separation of Sr. Cerenkov counting of ingrowing ^{90}Y	8 (1982)	Biological material
TBP (tributylphosphate) extraction of Y, measurement with low level beta counter	10 (1983)	Milk
Cs and Sr extraction using various crown ethers in a mixture of dinonyl naphthalene sulfonic acid, TBP and kerosene	5 (1984)	Waste solution
Extraction of Sr with dicyclo-18-crown-6-hexane using ^{85}Sr tracer	2 (1985)	Waste solutions
Separation of Ca and Sr by ion exchange, separation of Ca from Sr by fuming nitric acid, measurement of ^{90}Y by beta counting	12 (1986)	Soil
Extraction of Y with HDEHP, removal of interfering ^{90}Th, beta counting of ^{90}Y	3 (1986)	Sea water
Extraction of Sr and Y with DBP (dibutylphosphate), stripping of ^{90}Y with 1 M HNO$_3$, Cerenkov counting	1 (1986)	Water
Extraction of K followed by Sr extraction as 18-crown-6 complex	15 (1987)	Milk, geological samples
Precipitation, ion chromatography	21 (1988)	Model substances of different composition

S. ZHU

Rapid determination of Plutonium by Extraction and grid ionization Chamber

I .Introduction

The method of highest sensitivity for Pu analysis is α-spectrometry. α-spectrometry is often used for the analysis of environmenal samples. To avoied errors, Pu samples are first purified using different techiques, that is ion exchange, extraction coprecipitation or chromatograghy. Because of the rather time-consuming ion exchange or chromatography processes, there is now an increasing tendency to extract Pu.

The use of parallel grid ionization chamber in cambination with selective extraction agent offers a new way for simple and rapid nuclide specific determination of σ-emitters.

II .Experiment

1.Apparatus

parallel grid ionization chamber:

measuremental area : 300 Cm ^{2}

flowing gas : 90% Ar + 10% CH $_4$

gas pressure : 1.8×10^5 Pa.　　gas flow : 20 ml/ min

Energy resvlution :36 Kev　(fore ϕ 10 mm ^{239}Pu electrodeposition
source)

Integrate background 13 Cph (4- 6 Mev)

detection limit : 3×10^{-4} Bq

detection efficiency :22 % (for 300 Cm ^{2})
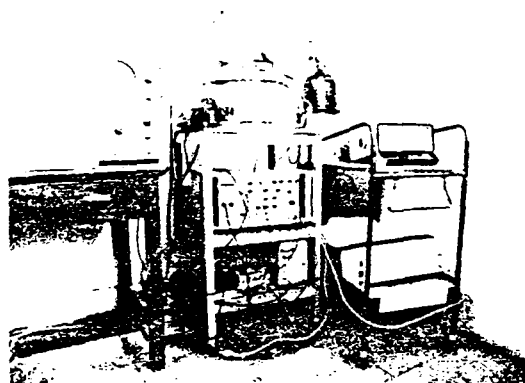
picture of parallel grid ionization chamber

Fig. 2 shows the structure of parallel grid ionization chamber
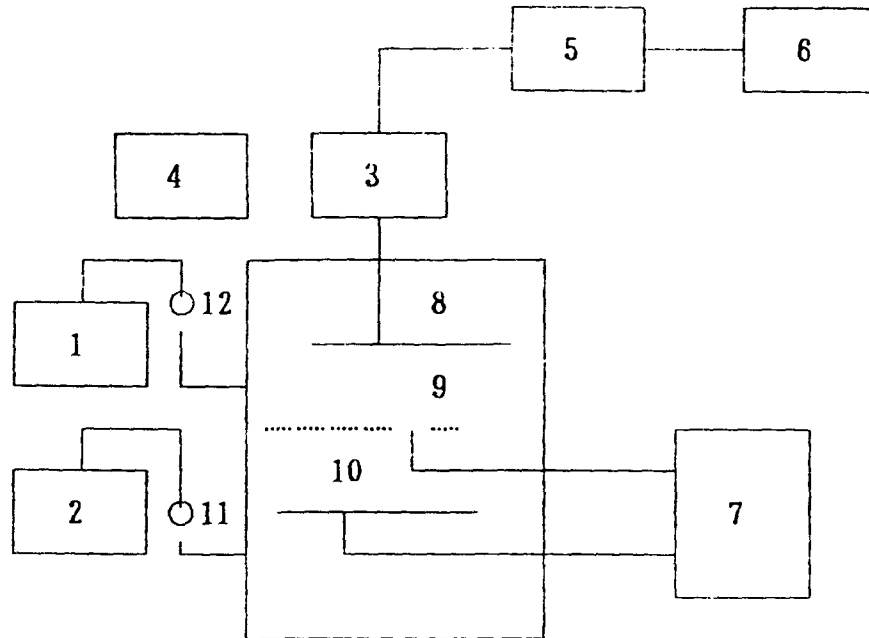
1. gas tank   2. pump   3. preamplifier   4. pulse generator

5. main amplifier   6. multichannel analyzer

7. high pressure power   8. anode   9. grid   10. cathode

11. pumb valve   12. stability valve

2.Source plate
   The source plate is made of aluminium with diameter 170 mm and thickness 0.1 mm

Fig. 3 shows the flow of analysis
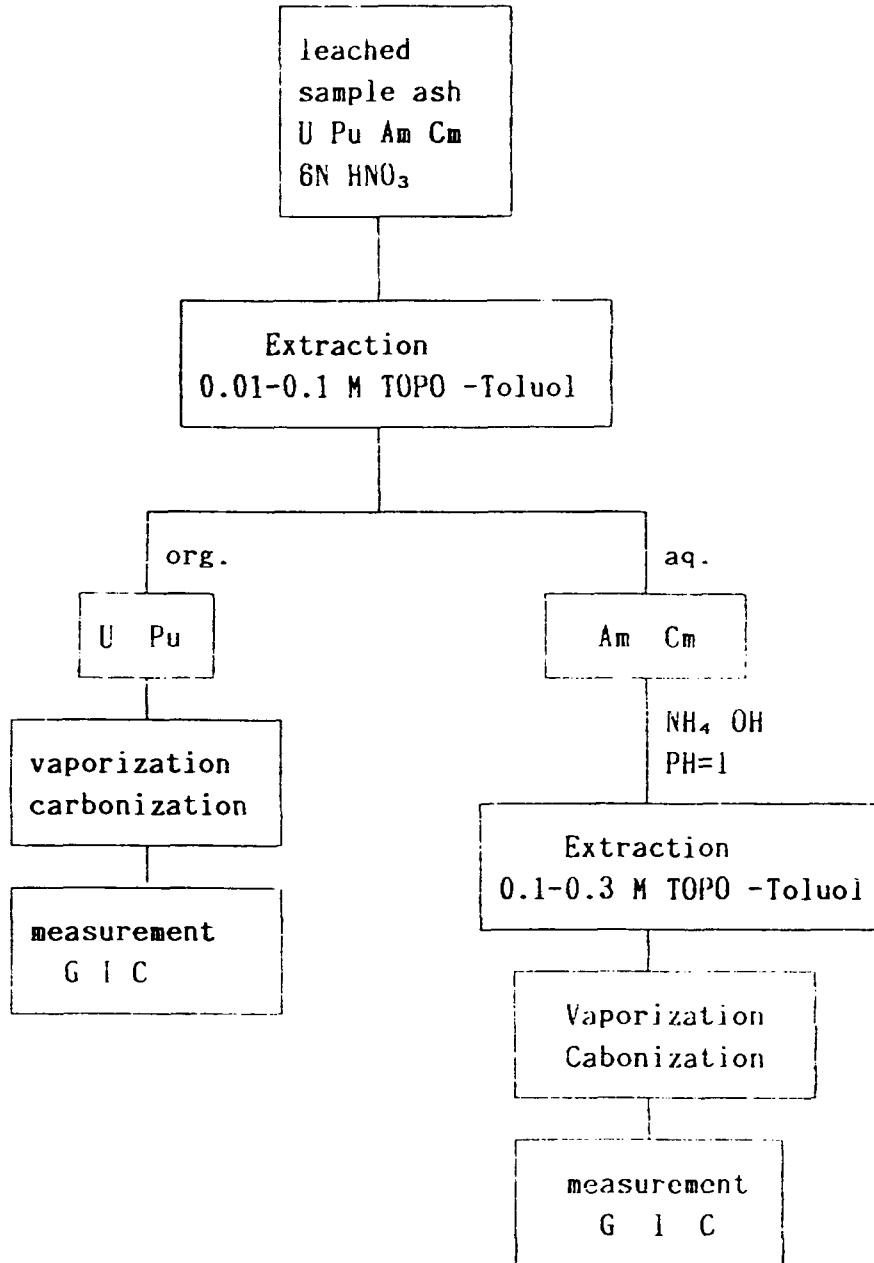
Fig.3 Flow of analysis

III .Some results
1.Pu(IV) distribution ratio

HNO$_3$ = 10 N

TOPO(M)	0.01	0.05	0.1
D	25	45	94

2.Resolution of organic source

TOPO(M)	0.01	0.05	0.1
resolution Kev	54	55	64
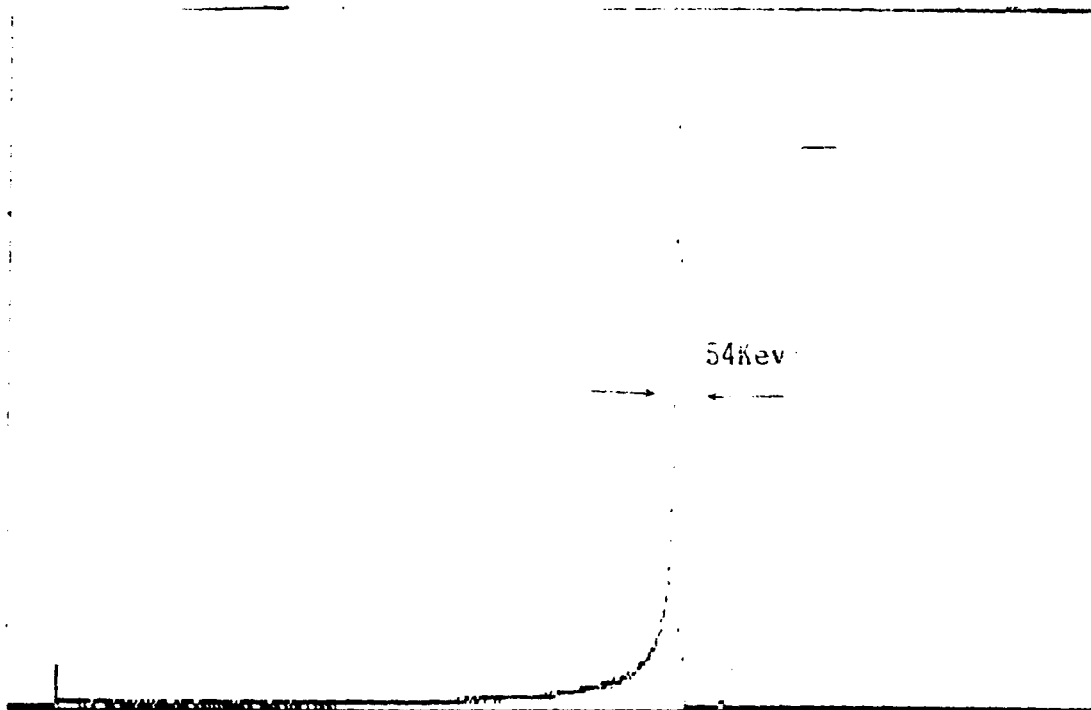
Fig. 4 spectrum

3.Grass ash sample spectrum

5g of grass ash is analysed by this prosedure. The spectrum is shown in Fig. 5.
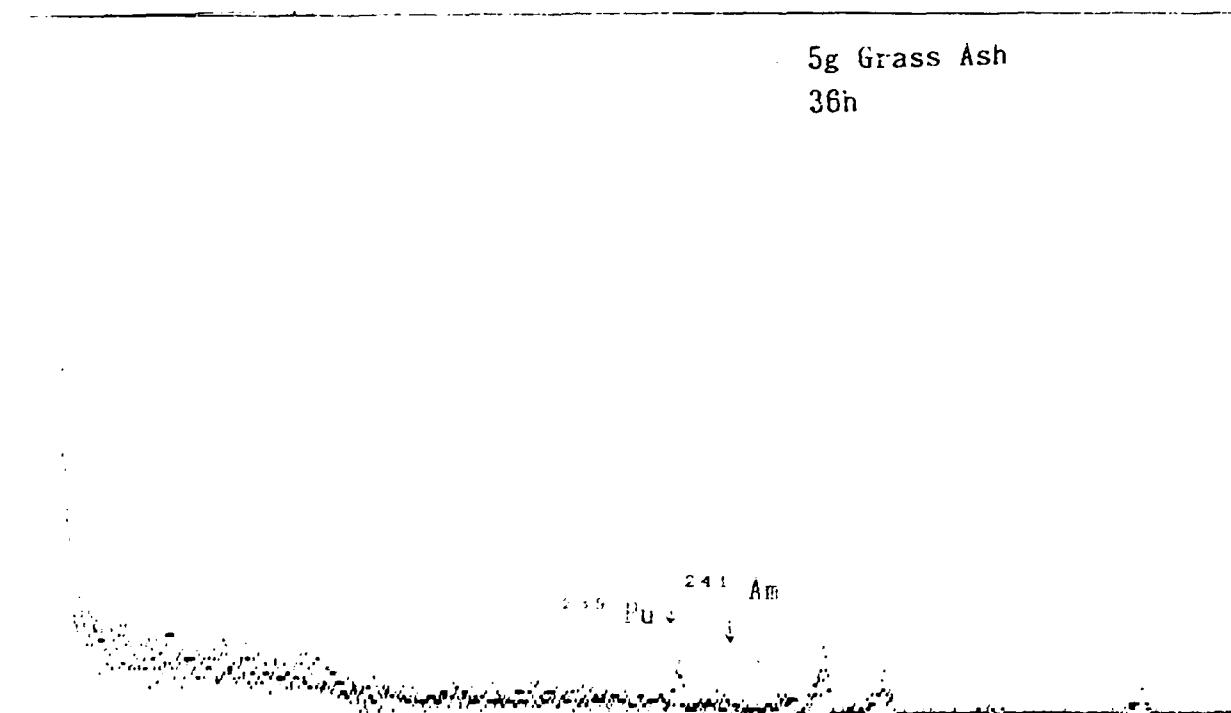
Fig.5 Spectrum of grass ash

IV.References

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An Instrument Based on an Insertion Probe for

Monitoring Radionuclides in Bulk Foodstuffs

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Introduction

Events following the Chernobyl reactor accident highlighted the need for rapid methods of monitoring fallout radionuclides in food. Even five years later, there is still a need to monitor radionuclides in certain types of foodstuffs produced in certain areas of the world. This project was initiated to study the feasibility of adapting a probe, which was developed earlier at Chalk River for measurements in boreholes, for the measurement of gamma-emitting radionuclides in bulk foodstuffs. This waterproof probe, which is about 2.5cm in diameter and 60cm long, contains a 0.5in x 2in NaI(Tl) detector, high voltage supply and preamplifier. It operates on 12V DC power. It could be inserted into loose bulk materials and liquids in order to measure the concentrations of radionuclides present. The probe could be coupled to a rather simple ratemeter for screening measurements or to a more sophisticated microprocessor-based instrument, which would allow quantitative measurements to be carried out by less skilled personnel. In the early stages after an accident the probe would probably be most useful for screening samples, because the spectra would be complicated due to the presence of short-lived gamma-emitters. After the short-lived activities had decayed away, the probe could be used for quantitative measurements of residual caesium isotopes.

Modelling the Response of the Probe

When a detector is inserted into a bulk material it will respond to gamma rays emitted by radionuclides present in the material. In addition, the detector will be shielded from radiation from the external environment by the material being measured. The count rate of photopeak events recorded by the detector will be a function of the concentration of measured radionuclides in the material and the geometry.

The response can be expressed as:

$$CR = E_p \cdot \phi \qquad\qquad 1.$$

where: CR is the photopeak count rate ($\sec^{-1}$)
E_p is the photopeak efficiency of the counter
counts$\cdot$photons$^{-1}\cdot$cm^2
ϕ is the uncollided flux (photons$\cdot$cm$^{-2}\cdot$sec^{-1})

Analytical expressions for ϕ are given in reference 1. In the case of a point at the centre of a sphere the uncollided flux is given by:

$$\phi = \frac{S_v}{\mu_s} (1-e^{-\mu_s R_o}) \qquad\qquad 2.$$

where S_v is the source strength photons$\cdot$cm$^{-3}\cdot$sec^{-1}
μ_s is the linear attenuation coefficient (cm^{-1})
R_o is the radius of the sphere(cm)

S_v is related to the radionuclide concentration C (Bq$\cdot$cm^{-3}) by:

$$S_v = C \cdot I \qquad\qquad 3.$$

where: I is the γ-ray intensify (photons$\cdot$decay^{-1})

Substituting 3 into 2 and the result into 1 gives:

$$CR = E_p \cdot \frac{C \cdot I}{\mu_s} \quad (1-e^{-\mu_s R_0}) \qquad\qquad 4.$$

It would be difficult to calculate the efficiency E_p theoretically because of the shape of the crystal and the complicated structure of the probe, so it was decided to measure it empirically. The variation of CR with radius is proportional to the variation of ϕ which is shown in Table 1 for an aqueous source of ^{137}Cs ($\rho=1$, $\mu_s=0.0863$) and for $S_v=1$ photon$\cdot$cm$^{-3}\cdot$sec^{-1}. It is evident from the table that the flux essentially reaches the limiting value for $R_0 = \infty$ when $R = 90$cm. Furthermore, the flux reaches 90 percent of the limiting value (ie. 10.43) when R_0 is between 20 and 30 cm. Hence, when the size of the source is larger than an equivalent sphere with $R_0 = 20-30$ cm the countrate of the detector can be considered to be independent of geometry, within an acceptable degree of error. After this point the countrate only depends on the radionuclide concentration. Containers that are larger than 20-30 cm in radius should be measured using a grid in order to get a better mean value.

Reference 1, also gives equations which can be used to derive the flux at the centre of a cylinder. In this case:

$$\phi = \frac{S_v}{\mu_s} \quad G(\mu_s\, h,\, \mu_s\, R_0) \qquad\qquad 5.$$

where: S_v and μ_s are as defined previously
h = height of the centre of the cylinder (cm)
R_0= radius of the cylinder (cm)
and values for the function, G are given in plots in reference 1.

Results for the fluxes from ^{137}Cs in water contained in cylinders with H = D (height = diameter) and H = 2D are given in Tables 2 and 3, respectively. The case for a cylinder with H = D is similar to that for a sphere with the flux reaching 90 percent of the maximum at H = 40-50 cm (roughly equivalent to a sphere with R_0 = 20-25cm). In the case of a cylinder with H = 2D the flux rises more slowly with H, which reflects the asymmetry between H and D (ie. the vertical paths reach the limiting length before the horizontal ones). Although this shape is less ideal from the point of view of counting efficiency, it is closer to the usual shapes of drums and barrels.

The figures given in Tables 1 to 3 would apply to a point detector surrounded by the material being measured. In fact, the actual situation is more complicated since the detector in the probe has a finite size and it is surrounded unevenly by shielding material (the stainless steel housing, photomultiplier tube etc.) and an air space. Although the data gives useful information on the expected variations in ϕ (and hence, count rate) with changes in shape, the approximations become poorer as the size of the source

decreases. In order to improve the analysis, a Monte Carlo simulation was run using the SANDYL[2] code. The results obtained for aqueous sources in cylindrical geometries with H = D and H = 2D are shown in Figures 1 and 2, respectively. The simulations were performed at a number of energies in the energy range of interest for monitoring food. The "counts" on the vertical axes in the Figures are uncollided photons which enter the detector volume. It is evident from Figures 1 and 2, that it takes longer for the response to higher energy gamma-rays to converge on a limiting value as H increases. This is because of the increase in range in the material with increasing photon energy. For a given photon energy the response is higher and it converges more slowly as the density decreases. This is illustrated by the curve for E = 0.6 MeV and density = 0.5g•cm^{-3} shown on Figure 2.

The responses calculated using equation 5 for E = 0.6 MeV in the cases of cylinders with H = D and H = 2D are compared with the Monte Carlo simulations in Figures 3a and 3b. The values from equation 5 were normalized to the simulations at 20cm and 150cm in Figures 3a and 3b, respectively. As suspected, equation 5 gives poorer results for smaller sizes, where the approximations are poorer. However, even in the 40cm size range the errors are not too bad (<20%). Since the Monte Carlo simulations are time consuming and require a larger computer, it would be advantageous to use equation 4 or 5 to generate the geometry corrections for actual instrumental measurements.

Sensitivity of the Probe to a Volume Source

The sensitivity of the probe was determined by empirical measurements in a cylindrical fibre-glass fish tank (61cm radius x 68cm height). The probe was clamped on a support so that the centre of the NaI(Tl) crystal was close to the centre point of the tank. Spectra were accumulated with a Canberra Series 10 analyser or a Canberra model 8100 analyser, when the Series 10 was out of service. The spectra either were stored on cassette tape and later transferred to a PC and stored on diskette or were transferred directly from the analyser to a PC. Peak areas and net counts in the ^{137}Cs window were determined using LOTUS 1-2-3.

The background (total counts in the region of the ^{137}Cs peak) was first determined in the empty tank (Background 1) and then re-determined with the tank filled with water (Background 2). The results are given in Table 4. It is evident that the water in the tank provides considerable self-shielding (a 7.6-fold reduction in countrate was measured). This reduction in background improves the sensitivity of the probe, but the changes in background with different materials would have to be measured by placing windows on the spectrum below and above the peak of interest (^{137}Cs in this case).

After the determination of Background 2, the water in the tank was spiked with [137]Cs (353Bq/L) and Cs carrier (13mg/L). The net response in the photopeak of ^{137}Cs, as measured with the probe, is given in the third column of Table 4. The sensitivity of the probe to ^{137}Cs was calculated using the equations of Currie[3] and the results are also given in Table 4.

The tank was then emptied and refilled with a solution of KCl (11.6 Bq of ^{40}K per L). There was no observable net response in the region corresponding to the ^{40}K photopeak (1.46 MeV) even after a counting time of 58,000 seconds. Consequently, it was not possible to estimate the efficiency of the probe for higher energy gamma-rays; however, given the lack of net response, the probe evidently is not sufficiently sensitive to measure higher energy gamma-emitters in food.

Conclusions

The probe, with a 0.5 in by 2 in NaI(Tl) detector, is sufficiently sensitive to measure ^{137}Cs and ^{134}Cs at levels in food which are below WHO limits, but it is not sufficiently sensitive to measure higher energy gamma-emitters. A larger detector would be needed to improve the high energy sensitivity, but a larger detector would require a larger probe, which would be more difficult to insert into bulk solid materials. The modelling of the changes in response with geometry indicates that it is possible to correct for this effect with a reasonable degree of accuracy. Thus, we can conclude that it is feasible to design an instrument to measure Cs isotopes in food based on the use of this insertion probe. The instrument would have to have additional windows in order to account for changes in background due to self-shielding. Ideally, for quantitative measurements the instrument should incorporate a microprocessor so that the geometry corrections can be made automatically.

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Table 1

Variation of Uncollided Flux at the Centre
of a Spherical Source with Radius

R_0 (cm)	$\phi*$(photons$\cdot$cm$^{-2}\cdot$sec^{-1})
10	6.70
20	9.53
30	10.72
40	11.22
50	11.43
60	11.52
70	11.56
80	11.58
90	11.59
100	11.59
∞	11.59

* for S_V = 1 photon$\cdot$cm$^{-3}\cdot$sec^{-1}

^{137}Cs: $E\gamma$ = 662 keV

Table 2

Variation of Uncollided Flux at the Centre of a Cylindrical Source (H = D) with Height

H (cm)	$\phi^*(\text{photons} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1})$
20	7.42
30	9.04
40	10.08
50	10.83
60	11.15
70	11.30
80	11.39
90	11.47
100	11.51
120	11.56
140	11.59
∞	11.59

*for S_V = 1 photon $\cdot \text{cm}^{-3} \cdot \text{sec}^{-1}$

^{137}Cs: E_γ = 662 keV

Table 3

Variation of Uncollided Flux at the Centre of a Cylinder (H = 2D) with Height

H (cm)	$\phi*$(photons$\cdot$cm$^{-2}\cdot$sec^{-1})
20	5.33
30	6.95
40	8.00
50	8.69
60	9.39
70	9.97
80	10.30
90	10.60
100	10.80
120	11.12
140	11.31
160	11.40
∞	11.59

*for S_v = 1 photon$\cdot$cm$^{-3}\cdot$sec^{-1}

^{137}Cs: $E\gamma$ = 662 keV

Table 4

Sensitivity of the Probe for ^{137}Cs

Background 1 (cps)	Background 2 (cps)	Response to ^{137}Cs* (counts•sec^{-1})
1.152	0.142	0.534
1.173	0.164	0.456
1.142	0.153	0.471
		0.498
		0.489
means:		
1.16	0.153	0.479

Efficiency = 1.36×10^{-3} cps.Bq^{-1}•L

*353 Bq•L^{-1}

Limit of Detection[3] for 100 and 400 Second Counting Times

	T = 100 s	T = 400 s
L_C	67 Bq/L	18 Bq/L
L_D	154 Bq/L	72 Bq/L
L_Q	919 Bq/L	316 Bq/L

Figure 1

Simulated Response for a Cylinder with H = D
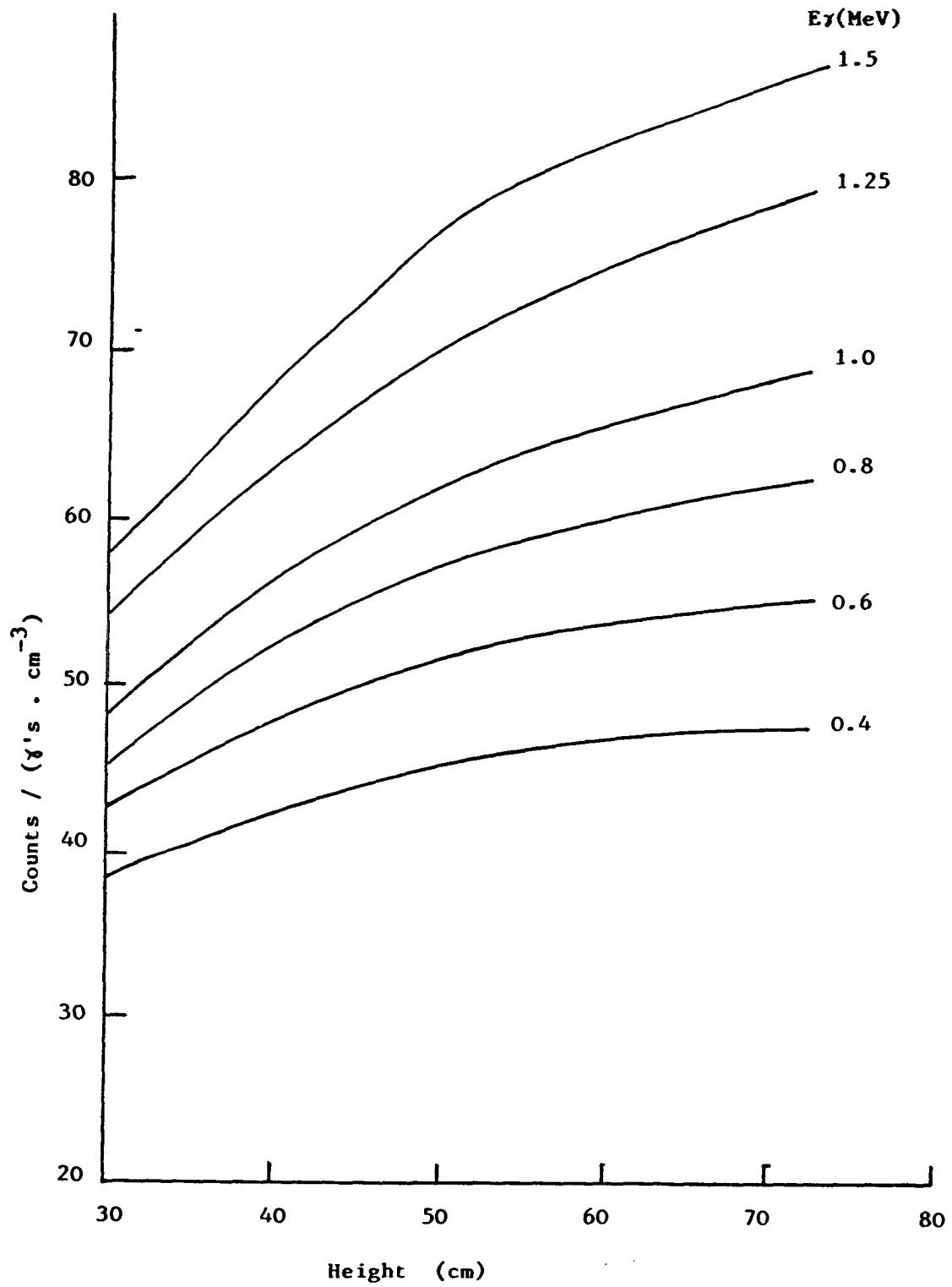
Figure 2

Simulated Response for a Cylinder with H=2D

E = 0.6 MeV
Density = 0.5g·cm^{-3}

E(MeV)
Density = 1.0g·cm^{-3}
0.6

0.4

Couhts/(γ's·cm^{-3})

Height (cm)
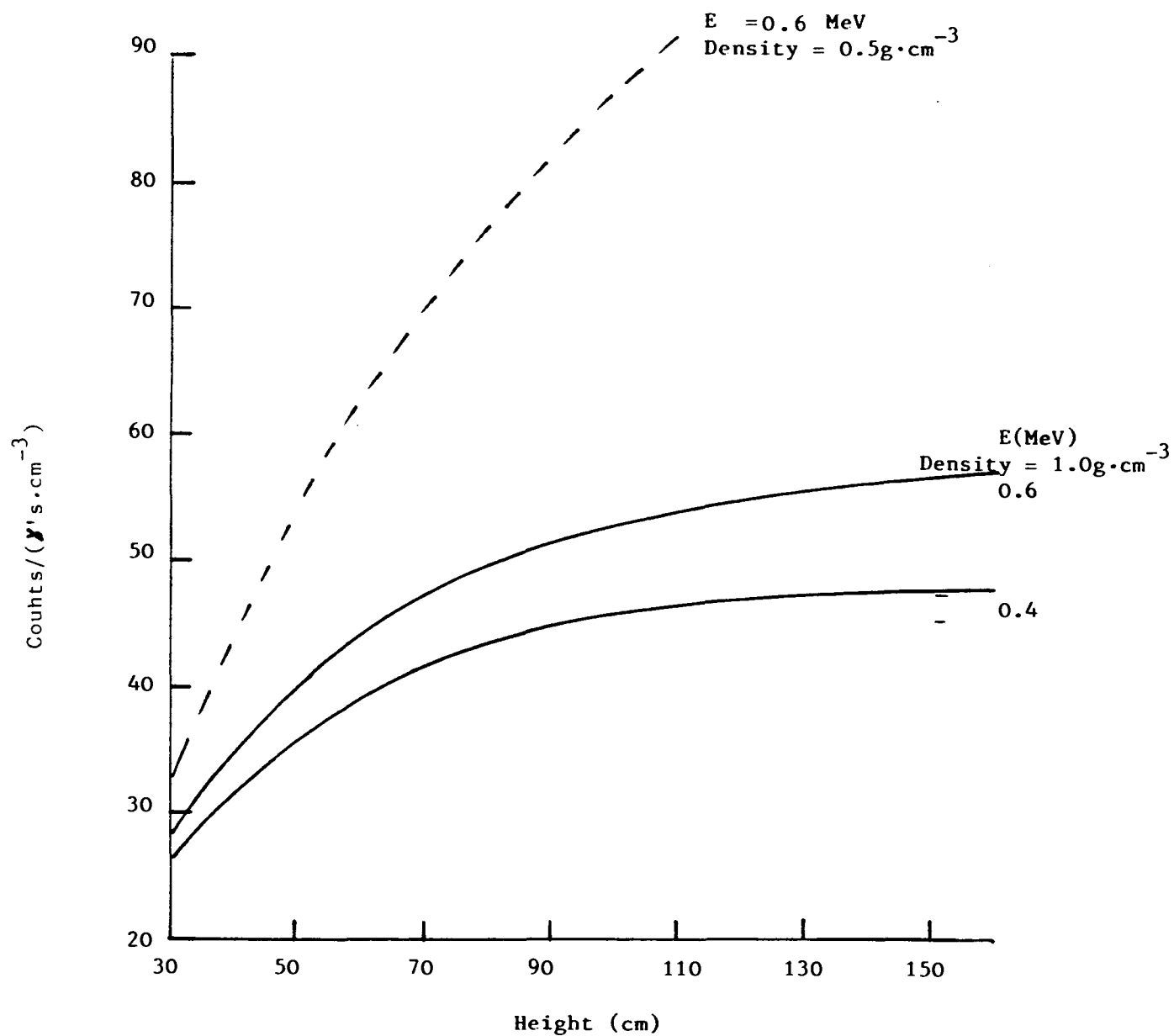
Figures 3a and 3b

Comparison of Responses Calculated from Equation 5 (———) with Results
of the Monte Carlo Simulation (———) for Density =1 and Eγ=0.6 Mev

3a
H = D

Height (cm)

3b
H = 2D

Height (cm)
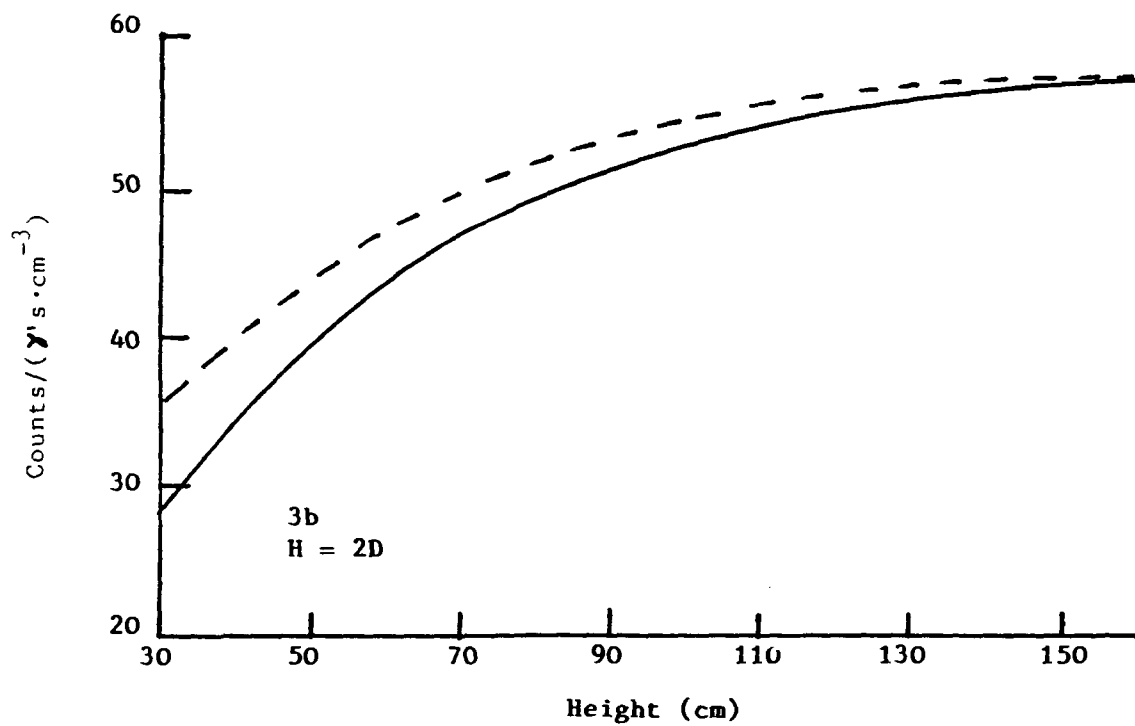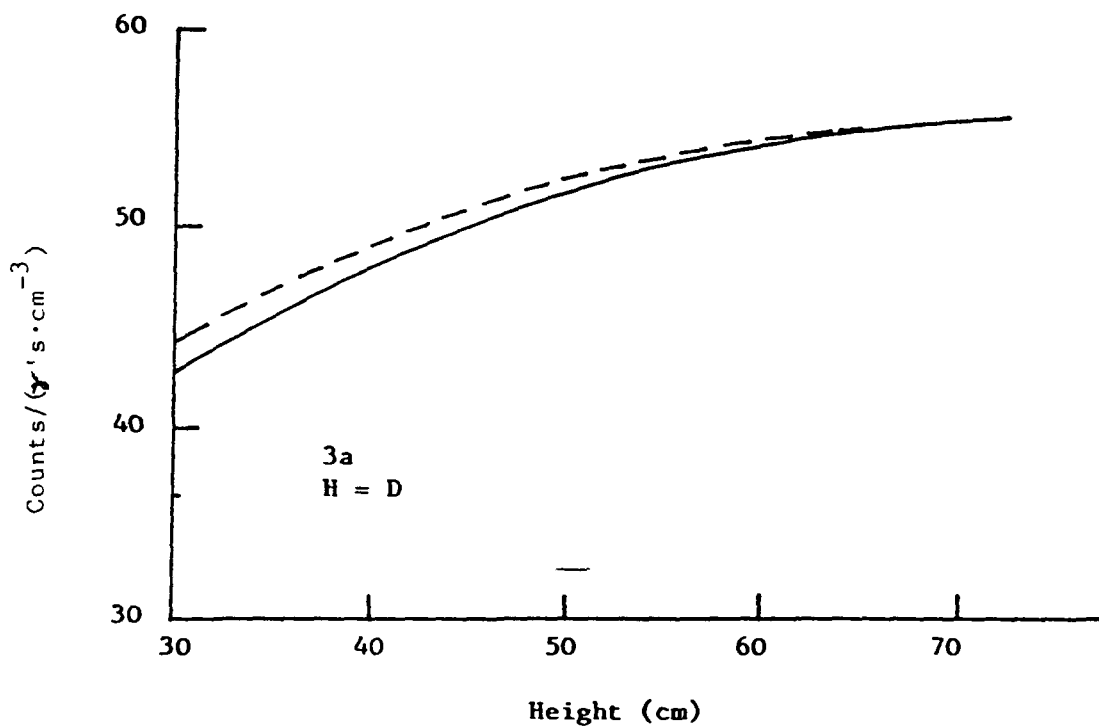
Guidelines for Planning and Design

of

Mobile Radiological Units

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INTRODUCTION

A significant number of mobile radiological units are in operation worldwide aiming at to provide reliable radiological data. They mainly have been designed and constructed on a national basis according to the particular needs and commitments of the specific laboratory or country. In most cases, these units are intended to be used in emergency situations for in-situ radiological measurements of accidentally released radioactivity, sometimes for monitoring environmental pollution. As the purpose of these units is very diversified in regard to the kind of vehicle and its in-built measuring equipment the varying outfit of these units cannot be adopted in general for other countries aiming at to improve their capability for in-situ radiological measurement.

In order to achieve harmonizaton of equipment and comparability of radiological data being obtained from field measurements it is necessary to have general guidelines available for designing mobile radiological units taking into account different scenerios and tasks to be achieved.

PURPOSE

In the very early stages of an accident most of the information available on the quantity of radioactive material being released, its radionuclide composition and the likely progression of the accident will come from the operator, and will be based on the conditions in the plant. Few environmental monitoring results from off-side can be expected within the first few hours. In this very early phase, decisions on the application of protective measures will therefore, be based largely on plant status and forecasts of changes in that status as well as on meteorological data. As time progresses, results will increasingly become available from the monitoring of radionuclides in the environment (e.g. dose rates and concentration of radionuclides in air and particular materials such as water, food etc). Monitoring results can be used to estimate potential doses to people and the need for further protective measures can thus be determined from a comparison with intervention level of dose. Decision making in an emergency will however be more rapid and effective if the intervention levels of dose are expressed in terms of level of radionuclides presented in an appropriate environmental materials. The latter are termed "derived intervention levels (DILs)" and are the practical expression of the intervention level of dose. Contamination of an environmental material at the derived level is predicted to result an exposure at the intervention level of dose. The need for, and extend of, protective measures can be determined by direct comparison of the monitoring results with the derived levels.

GOAL

GENERAL GUIDELINES

—

for designing a mobile radiological unit taking into account

different scenarios and tasks.

OPTIONS FOR MOBILE RADIOLOGICAL UNITS

- Sattelite

- Space shuttle

- Helicopter

- Ship, boat

- Train, waggon

- Truck, car

- Robots

- Portable devices

MOBILE RADIOLOGICAL UNIT

WHY ?

IMMEDIATE RESPONSE IN AN EMERGENCY RESULTING IN DOSE LIMITATION TO THE PUBLIC

PROBLEM:

Exposures resulting from controlled radiation sources under normal operating conditions.

GUIDANCE TO DOSE LIMITATION:

1. International Commission on Radiological Protection (ICRP) Recommendations of the International Commission on Radiological Protection No. 26, 1977

2. International Atomic Energy Agency, Basic Safety Standards for Radiation Protection, Safety Series No. 9, IAEA, Vienna, 1982.

PROBLEM:

Source of exposure not under control and potential exposure will disrupt normal living:

Accident situations

GUIDANCE TO DOSE LIMITATION:

1. International Atomic Energy Agency, Basic Safety

    Standards for Radiation Protection, Safety Series

    No. 81, IAEA, Vienna, 1986

Accident Situations

INTERVENTION

Application of appropriate protective measures to restrict the

exposure of individuals

INTERVENTION LEVELS OF DOSE

At which the introduction of appropriate measures for the protection

of the public should be considered.

Decision making in an emergency will be more rapid and effective if the

INTERVENTION LEVEL OF DOSE

is expressed in terms of levels of radionuclides present in appropriate environmental materials:

DERIVED INTERVENTION LEVELS (DILs)

contamination of an environmental material at the derived levels is predicted to result in exposure at the intervention level of dose.

GUIDANCE TO

DERIVED INTERVENTION LEVELS (DILs)

1. IAEA, Safety Series No. 9

2. IAEA, Safety Series No. 72

3. IAEA, Safety Series No. 81

4. ICRP No. 40

5. Codex Alimentarius

MONITORING

- NEED FOR

- EXTENT OF

protective measures can be determined by direct

comparison of the monitoring result with the

derived levels

Monitoring results can be used to estimate potential

doses to people

ACCIDENT PHASES

EARLY   a. before a release

b. majority of release occurs

INTERMEDIATE

LATE

ACCIDENT PHASES

EARLY   FIRST RELEASE TO FEW HOURS

INTERMEDIATE   FIRST FEW HOURS - SEVERAL DAYS

LATE   SOME WEEKS TO YEARS
                                                    (DAYS)

Concerned with return to normal

living conditions

PATHWAYS OF EXPOSURE

EXTERNAL from plume or facility deposition on ground or skin

INTERNAL **INHALATION**

in the plume or resuspended material

INGESTION

consumption of food and water

TABLE I. EXPOSURE PATHWAYS, ACCIDENT PHASES AND PROTECTIVE MEASURES FOR WHICH INTERVENTION LEVELS MAY BE ESTABLISHED [3]

Potential exposure pathway	Accident phase	Protective measure
1. External radiation from facility	*Early*	Sheltering Evacuation Control of access
2. External radiation from plume		Sheltering Evacuation Control of access
3. Inhalation of activity in plume		Sheltering Administration of stable iodine Evacuation Control of access
4. Contamination of skin and clothes		Sheltering Evacuation Decontamination of persons
5. External radiation from ground deposition of activity	*Intermediate*	Evacuation Relocation Decontamination of land and property
6. Inhalation of resuspended activity	*Late*	Relocation Decontamination of land and property
7. Ingestion of contaminated food and water		Food and water controls

Note: The use of stored animal feed to limit the uptake of radionuclides by domestic animals in the food-chain can be applicable in any of the phases.

Relevant Derived accident intervention phase level (DIL)

Exposure pathway

Processes to be modelled/data

Intervention level of dose

EARLY

Cloud gamma dose rate

External gamma dose from cloud

Release prognosis

Time integral of the nuclide concentration in air

Inhalation of cloud

Metabolism of inhaled nuclide

External beta dose to skin from cloud

External beta dose from deposits on skin and clothing

Deposition of airborne material onto skin and clothing

Dosimetric models for external radiation and for internally incorporated nuclides

Individual habits and characteristics, e.g.
— age
— breathing rate
— dietary intake
— time spent indoors
— shielding provided by buildings
— agricultural practices
— food preparation and processing

Intervention level of dose

INTERMEDIATE

Gamma dose rate above a contaminated surface

Deposition concentration of nuclide on the ground

External gamma dose from deposited nuclide

Migration of nuclide away from contaminated surface

Inhalation of resuspended material

Resuspension of deposited material

Deposition concentration of nuclide on pasture

Ingestion of animal produce

Transfer of deposited nuclides through food-chain

Metabolism of ingested nuclide

Concentration of nuclide in foodstuffs

Ingestion of foodstuffs

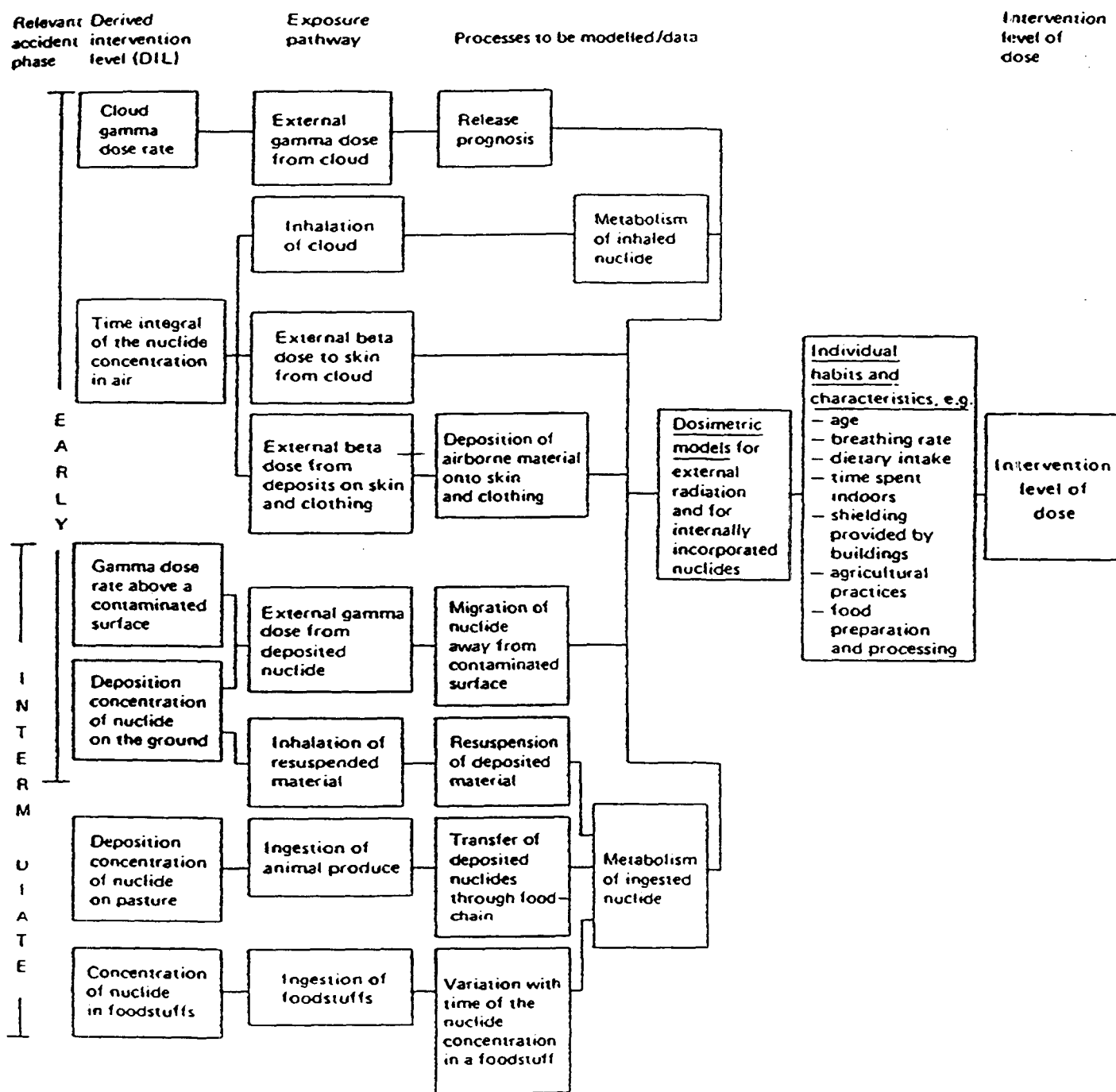Variation with time of the nuclide concentration in a foodstuff

FIG.1. *Processes that need to be modelled in establishing derived intervention levels for single nuclides:* DIL = IL/DCF, *where DIL is the derived intervention level; IL is the intervention level of dose; and DCF is a dose conversion factor which relates the two quantities via the processes/models shown.*

TABLE II. INTERVENTION LEVELS FOR PROTECTIVE MEASURES IN THE EARLY AND INTERMEDIATE PHASES OF AN ACCIDENT [3][a-e]

Early phase

Protective measure	Dose[a] (mSv or mGy)	
	Whole body[b]	Lung[c], thyroid and any single organ preferentially irradiated
Sheltering	5 - 50[d]	50 - 500
Administration of stable iodine		50 - 500[e]
Evacuation	50 - 500	500 - 5000

Intermediate phase

Protective measure	Dose equivalent committed in first year (mSv)	
	Whole body	Individual organs preferentially irradiated
Control of foodstuffs and water	5 - 50[d]	50 - 500
Relocation	50 - 500	Not expected

[a] Dose projected in the short term (see para.416).

[b] Where several organs or tissues are irradiated at low levels of dose the effective dose equivalent should also be calculated and compared with the whole body dose.

[c] In the event of high dose alpha irradiation of the lung, the numerical values apply to the product of the relative biological effectiveness (RBE) and the absorbed dose in milligrays. For planning purposes, an RBE of 10 is suggested.

[d] Or effective dose equivalent.

[e] Thyroid only.

Note: Special consideration should also be given to the implications of irradiation of pregnant women and other specially sensitive groups.

TABLE III. USEFUL QUANTITIES FOR DERIVED INTERVENTION LEVELS (DILs)

Derived quantity	Relevant exposure pathways	Relevant protective measure
External gamma dose rate $(Sv \cdot s^{-1})$	External gamma irradiation from plume and from deposited material	Evacuation, sheltering, relocation
Time integral of radionuclide concentration in air $(Bq \cdot s \cdot m^{-3})$	Inhalation of plume	Sheltering, evacuation, stable iodine
	External beta irradiation from plume	Sheltering, evacuation
	External beta irradiation from deposition on skin	Sheltering, evacuation
Ground deposits of radionuclides $(Bq \cdot m^{-2})$	External beta and gamma irradiation from deposited material	Evacuation, relocation
	Inhalation of resuspended material	Evacuation, relocation
Concentration of radionuclides in foodstuffs, pasture or drinking water $(Bq \cdot kg^{-1})$	Ingestion of foodstuffs or drinking water	Restrictions on production or consumption

COMPARTMENTS OF INTEREST

AIR

WATER

MILK

MEAT

OTHER FOODS

VEGETATION

SOIL

RADIONUCLIDES OF INTEREST

- FISSION PRODUCTS

- ACTIVATION PRODUCTS

- NATURAL RADIOACTIVITY

TABLE I. FISSION AND ACTIVATION PRODUCTS WHICH MAY BE OF CONCERN IN HUMAN EXPOSURE [4]

	Nuclide[a]	Half-life[b]	Fission yield %	Major decay
Fission products	Sr-89	50.5 d	4.77	β^-
	Sr-90*, Y-90	28.7 a, 64.1 h	5.76	β^-, β^-
	Zr-95, Nb-95	64.09 d, 35.0 d	6.51	$\beta^-\gamma$, $\beta^-\gamma$
	Mo-99*, Tc-99m*	2.747 d, 6.006 h	6.09	$\beta^-\gamma$, $\beta^-\gamma$
	Ru-103*, Rh-103m*	39.272 d, 56, 116 min	3.03	$\beta^-\gamma$, $\beta^-\gamma$
	Ru-106, Rh-106*	372.6 d, 29.92 s	0.4	β^-, $\beta^-\gamma$
	Te-129m	33.6 d	0.661	$\beta^-\gamma$
	I-131*	8.021 d	2.875	$\beta^-\gamma$
	Te-132*, I-132	76.856 h, 2.3 h	4.282	$\beta^-\gamma$, $\beta^-\gamma$
	Cs-137, Ba-137m	30.0 a, 2.55 min	6.136	β^-, γ
	Ba-140*, La-140*	12.751 d, 1.6779 d	6.134	$\beta^-\gamma$, $\beta^-\gamma$
	Ce-144*, Pr-144	284.45 d, 17.28 d	5.443	$\beta^-\gamma$, $\beta^-\gamma$

[a] An asterisk indicates that half-life has been revised according to Ref. [VII.2].

[b] Half-life is given in minutes (min), hours (h), days (d) and years (a). One year = 365.25 days.

TABLE I. FISSION AND ACTIVATION PRODUCTS WHICH MAY BE OF CONCERN IN HUMAN EXPOSURE [4]

Activation products	H-3*	12.35 a	β^-
	C-14	5730 a	β^-
	Fe-55*	2.75 a	EC
	Fe-59*	44.53 d	$\beta^-\gamma$
	Mn-54	__312.5 d	EC, γ
	Co-60	5.27 a	$\beta^-\gamma$
	Zn-65*	243.9 d	EC, γ
	Cs-134*	754.2 d	$\beta^-\gamma$
	Np-239*	2.355 d	$\beta^-\gamma$
	Pu-241, Am-241*	14.35 a, 432.0 a	β^-, $\alpha\gamma$
	Cm-242*	162.94 d	α
	Pu-238*	87.7 a	α
—	Pu-239*	2.411×10^4 a	α
	Pu-240*	6.563×10^3 a	α
	Pu-242*	3.735×10^5 a	α

[a] An asterisk indicates that half-life has been revised according to Ref. [VII.2].

[b] Half-life is given in minutes (min), hours (h), days (d) and years (a). One year = 365.25 days.

RADIONUCLIDES OF INTEREST

Focus on fission and activation products which

contribute significantly to human exposure.

Taking into account different accident

scenarios

Guidance: IAEA Technical Reports Series No. 295

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ACCIDENT SCENARIOS

(Source: IAEA Technical Reports Series No. 295)

Uranium-fuelled reactor

- Meltdown with failed containment

- Meltdown with particle containment

Nuclear fuel reprocessing plant release

Plutonium fuel fabrication plant release

VI-2. POTENTIAL RADIONUCLIDE RELEASES

Other nuclear accidents which may result in major atmospheric emissions but which are not specifically discussed here include the following:

— Plutonium fuelled reactor meltdown
— Breeder reactor meltdown
— High flux radionuclide production reactor meltdown
— Fast flux reactor meltdown
— Nuclear powered ship/submarine reactor meltdown
— Satellite re-entry and burnup of satellite nuclear power source
— Nuclear weapon destruction by chemical explosion
— Criticality at nuclear materials processing plant
— Fusion reactor fuel loss.

Each of these possible accidents may release a unique spectrum of radionuclides and this should be considered in developing radioanalytical capabilities.

Nuclear weapon detonation would be a major source of fission products. Some of the possible scenarios for atmospheric release are:

— Venting from underground tests
— Venting from underwater nuclear tests
— Above ground nuclear testing
— Nuclear war.

RADIONUCLIDES OF INTEREST

Although several hundred radionuclides are produced by nuclear explosions or are present in irradiated reactor fuel, only a limited number contributes significantly to human exposure. Radionuclide produced in fission and activation processes which may contribute significantly to human exposure in the event of an accident are listed in Table...

In regard to internal exposure from ingestion of food and water and to the contamination of environmental materials, which are part of the immediate path ways leading to contamination of food, the most important radionuclides to be assessed following a release of radionuclides from a uranium fuelled reactor to the environment are: Cs-134, Cs-137, I-131 and other gamma emitters, the beta emitters Sr-89, Sr-90, and tritium, and the alpha emitters Pu-238, Pu-239+240, Am-241 and Cm-242.

Many other radionuclides would be present in debris from a nuclear accident, and their potential contribution to human exposure depends on the type of accident and the circumstances at the time of the accident. Since there are several types of fuel, the spectra of radionuclides that would be present accidental releases could be somewhat different.

RADIONUCLIDES OF SPECIFIC INTEREST

The most important radionuclides to be assessed

following a release of radionuclides from a

uranium-fuelled reactor to the environment are:

Gamma emitters: Cs-134, Cs-137(Ba-137m), I-131, others

Beta emitters: Sr-89, Sr-90, H-3

Alpha emitters: Pu-238, Pu-239+240, Am-241, Cm-242

CONCLUSION

MEASURING CAPABILITY OF MOBILE RADIOLOGICAL UNIT

External gamma dose rate	$Sv \cdot s^{-1}$
Time intergral of radionuclide concentration in air	$-\ Bq \cdot m^{-3}$
Ground deposit of radionuclides	$Bq \cdot m^{-2}$
Concentration of radionuclides in food, pasture or water	$Bq \cdot kg^{-1}$

Meteorological data: temperature, humidity, wind speed and direction etc.

GUIDELINES

should include recommendations on

- kind of truck / car and its design for:

    - emergency situations

    - routine radiological monitoring

- equipment for

    - sampling

    - sample preparation

    - measuring radioactivity

    - measuring meteorological data

    - data acquisition and evaluation

    - data transmission

(FIRST APPROACH)

SUGGESTIONS FOR DESIGNING A MOBILE RADIOLOGICAL UNIT

Taking into account the underlying basics mentioned above a Mobile Radiological Unit for monitoring of food and environmental samples should include:

Truck

- preferably air-cooled engine, all-wheel driven,

  suitable for operating independently and

  self-sustaining even in a hot climate

  (e.g. air-condition, special tyres, generator)

Mobile Unit to house:

Radiological laboratory, working and sample storage area

Design may include a movable laboratory container.

BASIC EQUIPMENT

- gamma dose rate devices

- gamma dose rate probe connected to a telesonde or mounted on a meteorological mast.

- pen dosimeters

- contamination monitor

- gamma dose rate instrument: sensitivity $10^{-7} - 10^{-2}$ Sv/h.

- digital rate meter with external power supply

- gamma proportional counter

- hand monitor for surface contamination monitoring

- air pollution sampler and filters (glass fibre)

  Flow rate: 80m³/h. including iodine sampling, charcoal cartridges to be used with the air sampler.

INDOOR EQUIPMENT

- measuring device for iodine cartridges comprising of digital rate meter, NaI detector (3"x3") and lead shielding coupled to a PC, printer and software for evaluation of gamma spectra.

- measuring device for air_filter total beta and gamma measurements.

- NaI bench-top gamma spectrometric system comprising of NaI detector (8% resolution), lead shielding to house Marinelli beakers and polyethylene bottles (0.5 or 1 liter), amplifier, high voltage devices etc. PC aided system with printer, plotter and software for spectra and data evaluation.

* Optional:

HP Ge detector; rel. efficiency >20%, minimum resolution: 1,9 keV

Additional Equipment

- provision of meteorological mast comprising of devices for measurement of :

  - temperature

  - atmospheric pressure

  - humidity

  - wind direction

  - wind speed

  - data transmission to indoor recording stations

- acoustical and optical alarm system for in- and outdoor radioactive contamination

- protective clothings and masks

- refrigerator

- homogenizer (kitchen blender)

- grinder

- balance

DATA

- recording station for meteorological data.

- recording station for radiological data.

- transmission station: telefax (wireless) or modem.

DETERMINATION OF RADIOSTRONTIUM IN SOIL SAMPLES

USING A CROWN ETHER

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ABSTRACT

A simple and rapid method has been developed for the separation and successive determination of total radiostrontium in soil. The method consists of three basic steps: oxalate precipitation to remove bulk potassium, chromatographic separation of strontium from most inactive and radioactive interferences utilizing a crown ether (Sr. Spec, EIChroM Industries, IL USA), oxalate precipitation of strontium to evaluate the chemical yield. Radiostrontium is then determined by liquid scintillation counting of the dissolved precipitate. When 10 g samples of soil are used the sensitivity of the method is about 10 Bq/kg. The chemical yield is about 80%. The separation and determination of radiostrontium can be carried out in about 8 hours.

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INTRODUCTION

Radiostrontium is one of the most hazardous fission products because it is concentrated in bone. Relatively simple and rapid radioanalytical methods are available for its analysis when only Sr-90 is present in a sample. These methods are based on the selective separation and successive counting of Y-90[1] , the daughter of the long lived (half life = 28 years) Sr-90. Far more complicated and time consuming procedures are required when total radiostrontium has to be measured. Such a need may occur soon after the accidental release of fission products in the environment, when the contribution of Sr-89 (half life = 52 days) to the total radiostrontium activity is still significant.

All procedures for the total analysis of radiostrontium[2] are rather complicated and slow since they require the separation and purification of strontium from various inactive and radioactive elements present in complex sample matrices by chemical procedures exhibiting only limited selectivity. Exemplary is the standard method of analysis of radiostrontium[2] , based on the precipitation of strontium with fuming HNO_3 . This method, which consists of nine different precipitation steps, requires between 20 and 30 days. Hence the search for simpler and more rapid radioanalytical methods which should take advantage of more · selective separation agents. Rapid methods for radiostrontium analysis are particularly important in emergency cases, when many samples have to analyzed in order to enable the relevant authorities to make rapid decisions on the control of food consumption or implement other radiation protection measures based on the contamination level of the environment. In the case of radiostrontium in food the analytical determination should enable its identification

at a concentration level at least one order of magnitude below the Derived Intervention Level (DIL) recommended by WHO and IAEA[3], fixed at 100 Bq/kg, namely at 10 Bq/kg.

The search for selective separation agents for strontium. The synthesis of crown ethers having the ability to form strong complexes with alkali and alkaline earths was first reported by Pedersen[4] in 1967. Since then considerable efforts have been made by chemists to utilize these compounds for analytical chemistry applications. The attractiveness of crown ethers lies in their property to form very selective complexes with many metal ions by properly choosing the cavity size and the nature of the substituents present in the crown ring[5,6,7]. In 1986 McDowell et al.[8] demonstrated by solvent extraction studies that the cavity size and the flexible structure of dicyclohexano-18- crown-6 and its derivatives provide a very selective complexing environment for Sr ions. On these premises several attempts have been recently made at developing radioanalytical methods based on the use of this crown ether as a selective solvent extraction reagent of radiostrontium[9-14]. However all these methods are characterized by one or more of the following limitations: high pHs are required for the Sr separation, losses of crown ether occur due to its partial water solubilization, the selectivity is limited since the crown ether is used in a solvent extraction procedure. To be practically exploited for the analysis of Sr in environmental samples a crown ether must then be additionally characterized by high solubility in a non-water miscible environment, be practically insoluble in water, its complexing power must be high in strongly acidic media (to avoid troublesome neutralization procedures) and easily reversible, possibly by only increasing the pH of the water solution in which Sr has to be recovered after separation from other cations.

Horwitz et al. [15] have shown that such a situation holds when a 1M solution of bis-4,4'(5')[(t-butyl)cyclohexano]-18-crown-6 (from now on abbreviated as DCH18C6) (Figure 1) in 1-octanol is absorbed on an inert chromatographic support. Such a compound has recently become commercially available under the trade name Sr·Spec (EIChroM Industries, Inc.).

Although the possibility that Sr·Spec could be successfully applied also to environmental analysis of samples containing radiostrontium, such as soil samples, was mentioned in the title and conclusions of ref. [16], no such application has been so far demonstrated and reported. The reason resides in the difficulties which are bound to be encountered in obtaining very clean separations from K, an abundant constituent of all soils. The selectivity data for Sr over Ca and K (two major components of all types of soils) have been in fact obtained by Horwitz et al. [16] using relatively low concentrations of these two elements which were not representative of the conditions encountered in practical soil analysis. Since both K and Ca also show some degree of affinity for the crown ether, it has to be expected that they will tend to replace Sr when their concentration exceeds that of radiostrontium by several orders of magnitude. Such a situation occurs in soil samples. In terms of chemical equilibria such a situation can be described by stating that at high concentrations of K and Ca the equilibrium,

$$Sr^{2+} + 2NO_3^- + DCH18C6 = Sr(NO_3)_2 (DCH18C6) \qquad /1/$$
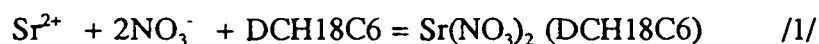
very much displaced to the right in absence of K and Ca, will be partially reversed due to presence of the other two equilibria

$$Ca^{2+} + 2NO_3^- + DCH18C6 = Ca(NO_3)_2 (DCH18C6) \qquad /2/$$

$$K^+ + NO_3^- + DCH18C6 = K (NO_3)(DCH18C6) \qquad /3/$$
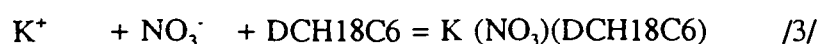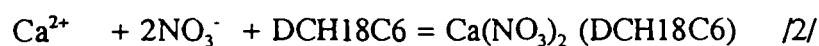
This paper demonstrates that, providing a suitable chemical procedure is followed, the ▪ application of Sr. Spec to soil analysis is possible. The advantages over traditional methods of separation and determination of total radiostrontium (Sr-89 and Sr-90) are the increased rapidity and simplicity. The new separation and determination method requires only one day against the 20-30 days of the standard method[2]. Moreover a sensitivity of 10 Bq/kg, sufficient for many purposes, is easily achievable.

EXPERIMENTAL

Materials. All reagents used were of analytical grade purity. For developing the procedure and testing the results the IAEA's standard reference material, Soil-6 was used. The composition of Soil-6 is:

Radionuclide composition	Content [Bq/kg]
Cesium-137	53.7
Plutonium-239, 240	1.04
Radium-226	79.9
Strontium-90	30.34

Chemical composition	Content [%]
Al_2O_3	8.9
CaO	22.9
Fe_2O_3	3.7
K_2O	2.9
MgO	1.9
Na_2O	0.6

SO$_3$	0.3
SiO$_2$	38.5
TiO$_2$	0.5

Material lost on ignition

at 900°C (water, organic)   19. 8

The tracers Sr-90(Y-90), Sr-85, U-232 + U-233, Pu-236 and Am-243 were obtained from the stocks of the IAEA's Laboratories at Seibersdorf. Other tracers were prepared either by neutron activation (K-42) or by chemical separation of the parent - daughter couples (Th-234 from U-238 and Ra-228 from Th-232).

Chromatographic separations. These were performed utilizing the Sr. Spec chromatographic material purchased from ElChroM, Industries, Inc. , Evanston, Il.USA. The material consists of bis-4,4'(5')[(t-butyl)cyclohexano]-18-crown-6 absorbed on an inert chromatographic support. This chromatographic material exhibits selectivity towards Sr ions[16] with respect to several other cations (Li, Na, Mg, Al, Mn, Fe, Co, Ni, Cu, Zn, Cd) from 3M HNO$_3$ solutions. According to the manufacturer the amounts of other elements eluted with 5 free column volumes (fcv) of 3M HNO$_3$ are: 65. 8% K, 98. 7% Ca, 15% Ag, <0. 4% Ba, . 6% Hg, 0. 8% Pb. It must be however taken into account that these selectivities were derived from experiments performed with the elements present at comparable, low concentration levels[15,16]. Sr can be easily removed by very dilute (0. 05 M) HNO$_3$ or simply water.

In most of the chromatographic separations the conditions specified in Table A were used. The load solution containing Sr and the other elements to be removed was always in

3 M in HNO_3. The beaker containing the sample solution was in each run washed with 2 fcv. of 3 M HNO_3 and the liquid added to the column. The non retained elements were in most cases eluted (scrubbing elution) with 22 fcv of 3 M HNO_3. Sr was then removed from the column (stripping elution) with 6 fcv of distilled water.

Glass or polyethylene columns with plastic fittings were used. The proper flow rate was assured only by gravity.

Radiation measurements. Beta radiation was measured by a low background liquid scintillation counter type 2250CA (Packard). To 1 ml of Sr solution in 1M HNO_3 15 ml of scintillation cocktail Instagel (Packard) were added. Blanks were prepared in the same way as the samples. Samples and blanks were measured immediately after each other. In the beta-spectrum "Sr-90" and "Y-90" gates were selected in the channel regions 15-250 and 250-1000, respectively. The first one contained the Sr-90 peak without its low energy contribution and the tailing of the high energy Y-90 peak. In this way the often intense fluorescence light was eliminated. The latter gate contained only part of the total Y-90 peak. The detection efficiency of Sr-90 in the "Sr-90" gate was 90%, that of Y-90 in the "Y-90" gate was about 50%. The time of measurement varied from some minutes up to 100 minutes for real soil samples.

The intensities of the gamma-radiations of the tracers used for the test experiments were determined by a 75x75 mm NaI(Tl) detector connected to a multi-channel analyser, type 7150 (EG&G Ortec). Intensities measured in the selected channel region and corrected for the background and the decay were related to the intensities of the load solution determined

in the same way. Tracer activities were selected so that the time of the measurement of the, given fractions was not more than 20 minutes. For checking the purity of the strontium strip solutions gamma-spectrometric measurements were carried out by a GMX HPGe detector of 30% relative efficiency (EG&G Ortec) and a multi-channel analyzer MCA Series 90 (Canberra).

For checking the purity of the strontium strip some alpha-spectrometric measurements were also carried out. To the strip solution containing about a few μg of strontium 100 mg of $Fe(NH_4)_2(SO_4)_2$. $6H_2O$ or 2ml of a 15% $TiCl_3$ solution were added to reduce the higher oxidation states of the actinides. Then 50 μg of neodimium as nitrate and 5 ml of 40% HF were added to coprecipitate the actinides (plutonium, americium, uranium). Samples, filtered through a 0.1 μm membrane filter, were analysed by a silicon detector, type PD-600-24-100--AM (Canberra) connected to a spectrometer Alpha-King 676 (EG&G Ortec) and an ADCAM System (EG&G Ortec).

The activities of the samples after the separation process were in all cases compared with the initial ones.

ICP-AES measurements. The strontium strip solutions were also analysed by ICP-AES for some components. A PLASMAKON S35 instrument (Kontron) was used. The concentration of the processed sample was related to the concentration of the soil, determined by the same method, using an aliquot of the unseparated dissolved soil.

Test experiments. For testing the ability of the Sr-Spec material to separate Sr from representative amounts of K and Ca, some synthetic load solutions containing 30 µg of Sr carrier, various amounts of (Sr-Y)-90 or Sr-85 tracers in 3 M HNO$_3$ and 3 mg (in one case) and 30 mg (in another case) of K and Ca, were prepared. The 3 mg case simulates the treatment of a soil sample weighing about 0.1 g. The 30 mg case simulates the treatment of a sample weighing about 1g. The chromatographic separations were carried out using the conditions I of Table A.

Separation and determination of strontium from soil samples. The separation and determination of radiostrontium was carried out following the procedure schematically shown in Table B. To a weighed quantity of soil ash, ranging between 5 and 10 g, 10 mg of Sr carrier was added. The samples were dissolved with the repeated addition of 40% HF and 14M HNO$_3$ (100-200 ml of each). Before evaporation to dryness 3 to 5 g of H$_3$BO$_3$ were added and the sample was dissolved in 200 ml of 1 M HNO$_3$. The sample was filtered and/or centrifuged and the residue checked for activity. To the boiling filtrate 5 to 10 g of oxalic acid were added. The pH was then adjusted to between 5 and 6 with a 25% solution of NH$_3$. After 10 minutes the solution was cooled, centrifuged and the precipitate washed twice with 70 ml of distilled water. The oxalate precipitate was dissolved with three 20 ml portions of concentrated HNO$_3$ and the residue collected with 10 to 20 ml of 3 M HNO$_3$. Column separations of Sr were then carried out according to the experimental conditions III of Table A. After the stripping elution of Sr with distilled water the Sr chemical yield was determined by gravimetry. To this aim the Sr strip solution was warmed, 200 mg of oxalic acid added to it, and the pH adjusted between 9 and 10 with a 25% solution of NH$_3$. The strontium oxalate precipitate was boiled for 10 minutes, cooled, filtered on a weighed filter paper, and

dried in an oven at 50°C for 30 minutes. By weighing the precipitate the chemical yield was calculated. After this step the precipitate was dissolved in 2 ml of 1 M HNO_3. The solution was mixed with 15 ml Instagel and counted, together with a blank, in the liquid scintillation counter.

The experiments performed for testing the influence of the various parameters on the chemical separation procedure were conducted by adding tracers to the soil samples (without addition of the carrier). The chromatographic separations were performed according to the experimental conditions II of Table A.

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RESULTS AND DISCUSSION

Preliminary experiments on simulated solutions. In order to test the ability of the chromatographic material to efficiently separate radiostrontium from yttrium-90 (i) and from relatively large quantities of K and Ca (ii), experiments with a 3 M HNO_3 solution traced with (Sr-Y)-90 (for i) and with 3 M HNO_3 solutions, also containing K and Ca, labelled with Sr-85 (for ii), were performed. The experiments were conducted using the conditions I of Table A.

The results of the experiment (i) are shown in Figure 2 in the form of measured intensity vs. number of free column volumes (#fcv). The separation of Y-90 from Sr-90 is quantitative. Small quantities of Sr-90 appear in the scrubbing elution only after having passed 20 fcv of 3 M HNO_3. Strontium is then easily stripped in a concentrated form with a few fcv of distilled water.

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The results of experiments (ii) are shown in Figure 3 in the form of % of strontium.

released from the column during the scrubbing elution, calculated with respect to the initial

Sr-85 tracer activity of the sample vs. number of free column volumes (#fcv). The data

indicate that when the quantity of K and Ca is 30 mg the strontium fractions not retained by

the column, after 20 fcv of 3 M HNO_3 have been passed through it, amount to 7% (30 mg

K) and 2. 5% (30 mg Ca). The fractions become negligible (<1%) when only 3 mg of K

or Ca are present. Since in practice soil samples ranging from a few grams up to several

tents of grams have to be analyzed (the actual sample size depends on the activity

concentration of radiostrontium), K and Ca quantities ranging from few milligrams up to

some grams have to be expected in actual soil analyses. This means that, due to the

competing role of K and Ca for the active material of the chromatographic column (the crown

ether), some losses of radiostrontium will occur during the scrubbing elution. This effect can

be however accounted for by carefully checking during each analysis the chemical yield of

the radiochemical procedure. A very large error on the successive determination of

radiostrontium will be on the other hand caused by the non negligible amounts of K which

will accompany the stripped radiostrontium. The error is caused by the natural radionuclide

K-40, emitting high energy beta particles which strongly interfere in the liquid scintillation

counting of radiostrontium. These experiments therefore lead to the conclusion that the ·

degree of selectivity of the Sr-Spec material, although good, is not high enough to permit a

sufficiently clean separation of Sr in a single chromatographic step.

Separation and analysis of radiostrontium from soil without previous removal of

the bulk K. The just mentioned conclusion has been further confirmed by an experiment

which data are shown in Figure 4. In this experiment a 5 g sample of Soil-6, ashed and

solubilized in 2 fcv of 3 M HNO$_3$, was labelled with Sr-85 and K-42 tracers and then passed .

through a Sr-Spec column using the conditions II of Table A. The elution chromatogram of

Figure 4 indicates that after a scrubbing elution with 18 fcv of 3 M HNO$_3$ 78% of the initial

Sr can be recovered by a stripping elution with 6 fcv of water. This recovered Sr is however

not sufficiently purified since it contains 0. 6% of the initial K. In practical soil samples,

weighing between 5 and 10 g, this would represent a K-40 activity of about 3 to 10 mBq, i.

e. an activity often comparable with that of the radiostrontium itself. It follows then that a

reliable radioanalytical procedure for radiostrontium requires the previous removal of the bulk

quantities of K present in the sample.

Separation and analysis of radiostrontium from soil with previous removal of the

bulk K. Optimal precipitation pH. The removal of the bulk K can be easily accomplished

by oxalate precipitation. In this way also other alkaline metals, such as cesium and rubidium,

also having interfering long-living radionuclides (Cs-137, Cs-134, Rb-87) can be eleminated.

In order to optimize the pH of the precipitation procedure 10 g of Soil-6, ashed and

solubilized in HNO$_3$, were brought to dryness and then dissolved in 200 ml of 1 M HNO$_3$.

After filtration Sr-85 and K-42 tracers were added to the solution. The solution was then,

divided into two equal 100 ml portions, one was further diluted to 200 ml with 1M HNO$_3$,

and 4 g of oxalic acid were added to precipitate the alkaline earth metals. The pH of the

solutions were adjusted to about 2 to 3, in one case, and to 5 to 6 in another (the one diluted

to 200 ml), using a 25% solution of NH$_3$. After 10 minutes the solutions were cooled,

centrifuged and the precipitate washed twice with 70 ml of distilled water. The supernates

and the precipitates washing solutions were then counted for Sr-85 and K-42. The results

indicated that when the precipitation is carried out at pH between 2 and 3, 63% of the initial Sr and 37% of the initial K are present in the liquids. When the precipitation is instead carried out at pH between 5 and 6 and at higher dilution, 2% of the Sr and 100% of the K go into the liquid. Therefore this pH range appears to yield optimal Sr -K separations. The use of higher pHs has to be avoided because of the precipitation of iron hydroxide.

Separation and analysis of radiostrontium from soil with previous removal of the bulk K. Optimization of the scrubbing elution. To evaluate the optimal number of fcv of 3 M HNO_3 to be used for the scrubbing elution of the column two different tests were performed, using 18 fcv and 26 fcv, respectively. Two 5 g samples of Soil-6, ashed and solubilized in 3 M HNO_3, were labelled with Sr-85 and K-42. After oxalate precipitation at pH between 5 and 6, the two residues were dissolved in 2 fcv of 3 M HNO_3 and passed through chromatographic columns, using the conditions II of Table A. After the scrubbing elution with 18 fcv and 26 fcv of 3 M HNO_3, Sr was eluted with 6 fcv of distilled water. The results of the two tests are summarized in Table C and in Figure 5. Although the scrubbing elution with 26 fcv of 3 M HNO_3 increases the loss of Sr from 6% to 17%, a more pure solution is obtained, especially in terms of Ba and Pb. In both cases the amount of K is below the detection limit (< 0. 1%), indicating the efficiency of the oxalate precipitation step in removing this interference.

ICP-AES measurements were also used to determine the degree of removal of various inactive elements from the initial Soil-6 dissolved sample. By adding selected tracers to the dissolved sample the purification obtainable from various actinides was investigated as well. The entire set of results obtained is shown in Table D.

Determination of the Sr chemical yield. The chemical yield of the radioanalytical • procedure cannot be determined by using Sr-85 as tracer because this radioisotope increases the background of the liquid scintillation counting, mainly through Compton electrons generated in the interaction of the gamma radiation with the scintillation cocktail. The yield must therefore be determined gravimetrically. To this aim about 1 mg of strontium per g of soil ash was added to the soil samples. This quantity is dictated by the need to reduce the error introduced in the gravimetric calculations by the non accounted presence in the sample of natural strontium. This amounts to about 20 µg per g of soil. The chemical yield of our radiochemical procedure has been determined by using the chromatographic conditions III of Table A. The need to use larger columns arises from the presence of larger quantities of Sr. The gravimetric determination of Sr was carried out by adding 200 mg of oxalic acid to the heated Sr strip solution and then adjusting the pH to between 9 and 10 by a 25% solution of NH_3. The chemical yield, determined by weighing the strontium oxalate precipitate, was always in the range 80% to 90% (average 85%±5%) for Soil-6. After the determination of the chemical yield the strontium oxalate was carefully dissolved in 2 ml of 1 M HNO_3 , mixed with 15 ml of the scintillation cocktail, and then counted.

Radiochemical purity of the radiostrontium in the stripping elution fraction. In • absence of Sr-89 the radiochemical purity of the separated radiostrontium can be checked by following as function of time the ingrowth of Y- 90, the daughter of Sr-90, in the stripping elution fraction. If by the time radiochemical equilibrium is reached the total activity is twice the one measured at the very end of the separation procedure, the radiochemical purity of the separated radiostrontium can be claimed.

In Figure 6 the total activity of the radiostrontium, purified by the scheme of Table B, is plotted as function of time. Also shown are the intensity of Sr-90 (Sr-90 gate) and of Y-90 (Y-90 gate). The time zero corresponds with the end of the radiochemical separation process. The data show that after about 600 hours the equilibrium between the Sr-90 parent and the Y-90 daughter is reached and that the total activity is twice the activity at time zero. These results therefore confirm that the developed radiochemical procedure yields a stripping elution fraction which can be defined as radiochemically pure.

Determination of radiostrontium in soil samples. Comparison with reference material. The reliability of the developed method has been checked by comparing the results of the radiostrontium analysis, performed on samples containing known values of radiostrontium with recommended (intercomparison material) or certified values (reference material). The analysis of the intercomparison material Soil-375 has lead to a value of 88. 2 Bq/kg±10% (recovery 62%), in reasonable agreement with the recommended value. The analysis of the reference material Soil-6 (certified value 30. 34 Bq/kg, confidence interval 24. 2 - 31. 67) has lead to the value 24. 2 Bq/kg ± 12% (recovery 84%).

Multiple use of the chromatographic columns. The possibility to reuse the same chromatographic column for multiple analyses is particularly attractive in order to reduce both the time and cost of analysis (in 1991 the cost of Sr. Spec is 22. 5 US$/g). To check this possibility known amounts of the Sr-85 tracer were added to 5 g samples of Soil-6 after these had been ashed and solubilized in 3 M HNO_3. The radiostrontium solutions were then successively analyzed by the same chromatographic column using the experimental conditions II of Table A. The strontium recoveries in the five consecutive runs were: 83%, 89%, 85%

and 90%. The results clearly indicate that a reuse of the column for at least five times is possible.

CONCLUSIONS

The method developed for the separation and successive analysis of radiostrontium in soil presents the following advantages:

- It can be successfully used for the determination of total radiostrontium (Sr-89 and Sr-90), a need arising in accidental conditions. If necessary, the separate content of the two radionuclides can be obtained utilizing the different energies of the Sr-89 and Sr-90 in of the beta spectrum[17].

- It is relatively simple as basically consists of only three steps, i. e. oxalate precipitation of alkaline earths (removal of bulk quantities of potassium), chromatographic separation of strontium (removal of most other inactive and radioactive elements), oxalate precipitation of strontium (determination of chemical yield).

- It is relatively fast since the separation and counting procedures require about 8 hours (to this time the time of leaching the sample - about 1 day - or for destroying it - about 3 days - has to be added.)

The main limitation of the method consist in its limited sensitivity, mostly due to the relatively high background of the liquid scintillation measurements. For soil samples weighing about 10 g the limit of detection of radiostrontium is about 10 Bq/kg. Soils with lower activity require larger samples and therefore larger columns.

Among the possible interfering radionuclides (see Table D), only those of Pb, Pu, and some other actinides, may cause problems in the determination. However this will only occur if their concentration in the soil is extremely high and that of radiostrontium is close to its limit of sensitivity.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Figure 1.   Crown ether used for the separation of radiostrontium.

Figure 2.   Chromatographic separation of Sr-90 from Y-90 from 3M HNO_3 (simulated

solution traced with (Sr-Y) 90).

Figure 3.   Influence of K and Ca on the release of Sr from the chromatographic column

during the scrubbing elution with 3M HNO_3 (simulated solutions traced with

Sr-85).

Figure 4.   Chromatographic behaviour of Sr and K when the bulk concentration of

potassium is not removed by precipitation (dissolved Soil-6 sample traced with

K-42 and Sr-85).

Figure 5.   (a and b) Chromatographic behaviour of Sr after removal of the bulk

concentration of potassium (dissolved Soil-6 samples traced with K-42 and

Sr-85). In both chromatograms no K-42 was detectable.

Figure 6.   Ingrowth of Y-90 in the Sr-90 separated from a Soil-6 sample.

Table A

Experimental conditions used in most of the chromatographic separations

	I	II	III
column packing [mg]	250	750	2500
column length [cm]	8	8	8
column diameter [mm]	3.6	6	11
flow rate [ml/min]	0.1 to 0.2	0.3 to 0.6	1 to 2
1 free column volume, fcv [ml]	0.8	2.5	8

The Sr load solution had a volume of 2 fcv. The Sr load was completed by adding 2 additional fcv of 3M HNO_3 used to rinse the beaker containing the dissolved sample in 3M HNO_3.

The Sr was separated from the non retained elements by
eluting them (scrubbing elution) with 3M HNO_3. In most experiments 22 fcv were used.

Sr was recovered from the column (stripping elution) with 6 fcv of distilled water.

Table B
Separation scheme of strontium from soil samples
5 to 10g soil ash

addition of 10 mg Sr carrier

SAMPLE DISSOLUTION	destruction of soil with mineral acids: conc.HNO$_3$, 40%HF, H$_3$BO$_3$

evaporation, dissolution
in 200ml of 0.5M HNO$_3$,
addition of 5 to 10g oxalic
acid, pH adjustment with NH$_3$

POTASSIUM REMOVAL	calcium-magnesium-strontium oxalate precipitation at pH 5-6

centrifuging,
washing with 2x70ml of water,
oxalate destruction with
conc. HNO$_3$, solubilization
in 2 fcv 3M HNO$_3$

REMOVAL OF OTHER ELEMENTS	strontium separation with Sr.Spec chromatographic column

scrubbing elution	stripping elution of
of non retained	Sr with 6 fcv of dis-
elements with 22	tilled water, boiling,
fcv of 3M HNO$_3$	addition of 200 mg oxalic acid

CHEMICAL YIELD DETERMINATION	strontium oxalate precipi- tation at pH 9 - 10

Sr determination
by gravimetry, dis-
solution with 2 ml of
1M HNO$_3$, addition of
15 ml Instagel

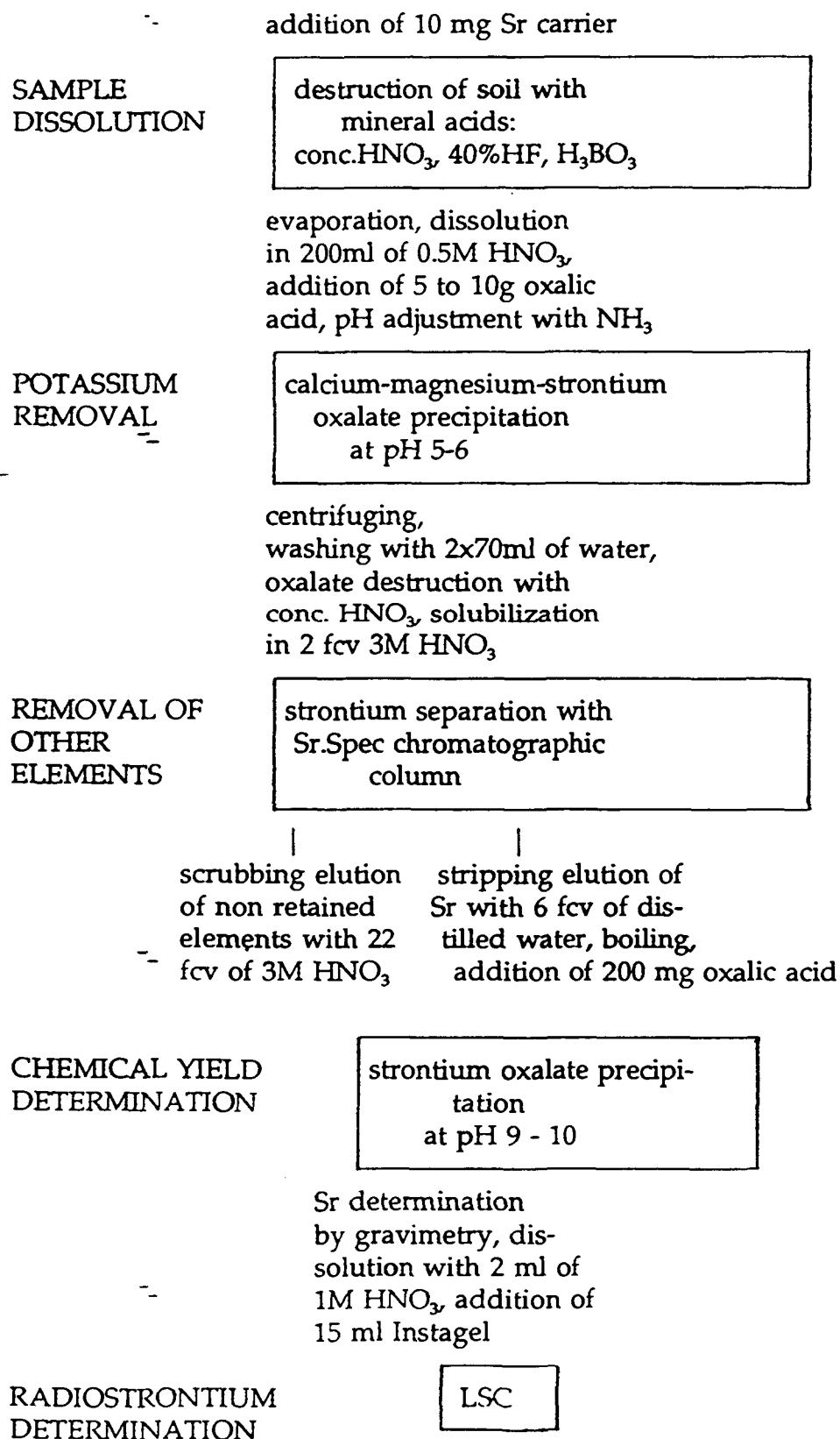| RADIOSTRONTIUM DETERMINATION	LSC

Table C

Optimization of the scrubbing elution conditions after

removal of bulk potassium by oxalate precipitation

Element	Concentration of the various elements in the Sr elution strip [%]	
	scrubbing elution with 18 fcv of 3M HNO₃	scrubbing elution with 26 fcv of 3M HNO₃
Sr	94	83
K	<0.1	<0.1
Ca	0.002	0.00015
Mg	0.0002	0.0003
Ba	2.6	0.04
Fe	0.0003	0.0003
Pb	2.1	1.1
Cd	not measured	<0.4
Al	not measured	0.13

The results are expressed as % of the element in the 6 fcv of the elution strip, calculated

with respect to initial activity in the dissolved Soil-6 sample.

Table D

Degree of removal of various inert and radioactive elements from a Soil-6 sample
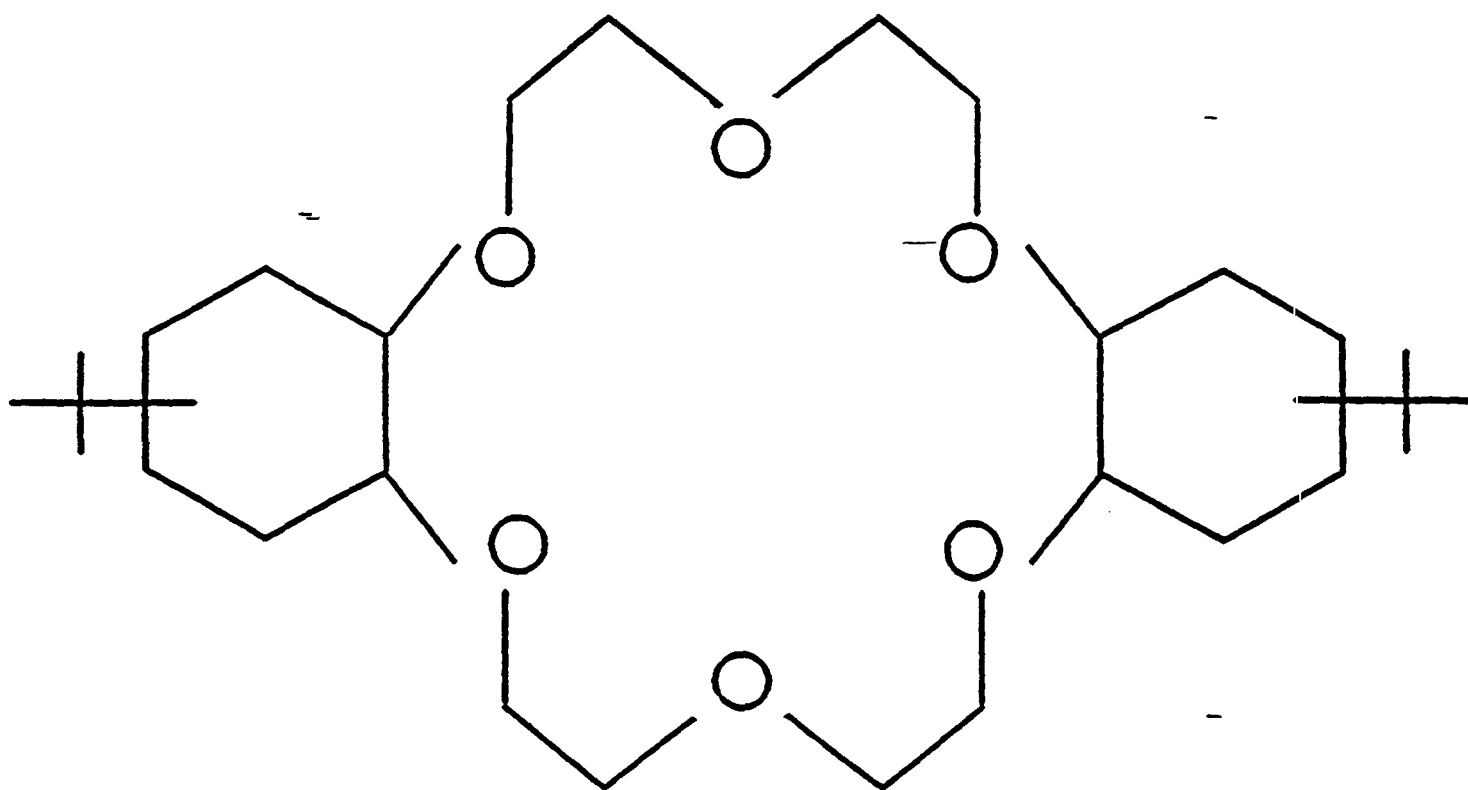(Elution scrubbing with 26 fcv of 3M HNO_3, elution stripping of Sr with 6 fcv of water)

Element or radionuclide	Initial amount or activity in the dissolved sample	Fraction of element in the 6 fcv of the Sr elution strip (%)	Method of analysis
K	60 mg	<0.1	tracer study, gamma counting
Cs-137	30 Bq	<0.3	gamma-spectrometry
Mg	55 mg	<2xE-3	ICP-AES
Ca	815 mg	<5xE-4	"
Ba	0.8 mg	1	"
Ra-228		<4	tracer study, gamma counting
Al	240 mg	<0.2	ICP-AES
Pb	0.3 mg	<15	"
Sb-125	0.6 Bq	<10	gamma-spectrometry
Y	0.1 mg	<0.1	tracer study, LSC
Mn	3.2 mg	<E-3	ICP-AES
Fe	130 mg	<5xE-4	"
Cu	0.06mg	<0.3	"
Cd	0.01mg	<0.4	"
Ac-228		<5	tracer study, gamma counting
Th-234		<10	"
U-232+ U-233		<2	tracer study, alpha spectrometry
Pu-236		<40	"
Am-243		<1	"

For tracer studies the initial amount of the carrier is usually not known/given.

The fraction [%] is calculated with respect to the initial quantity (or activity) in the dissolved Soil-6 sample.

Figure 1

4,4'(5')-bis(tert-butylcyclohexano)-18-Crown-6

Cavity Diameter 2.7-2.9 A
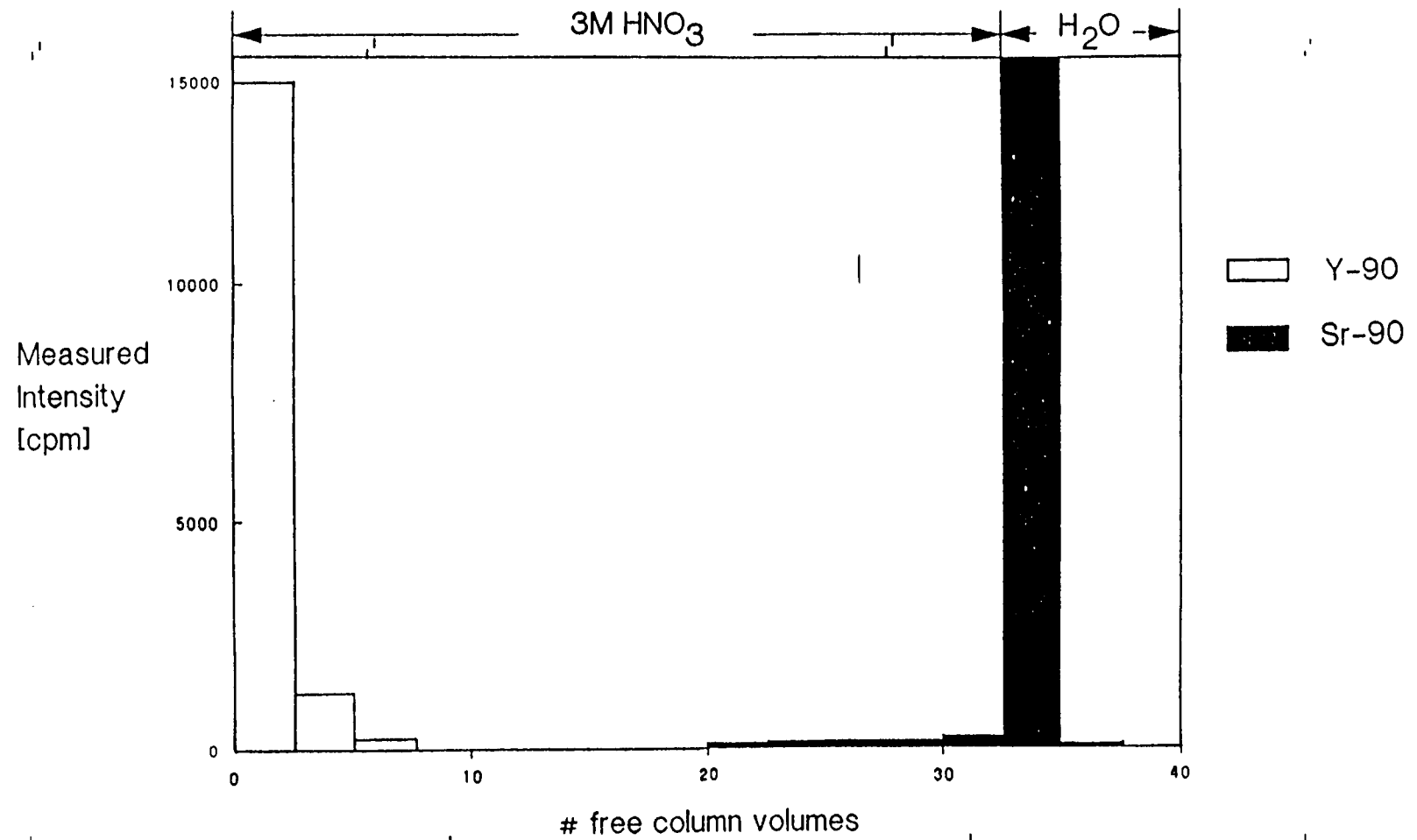
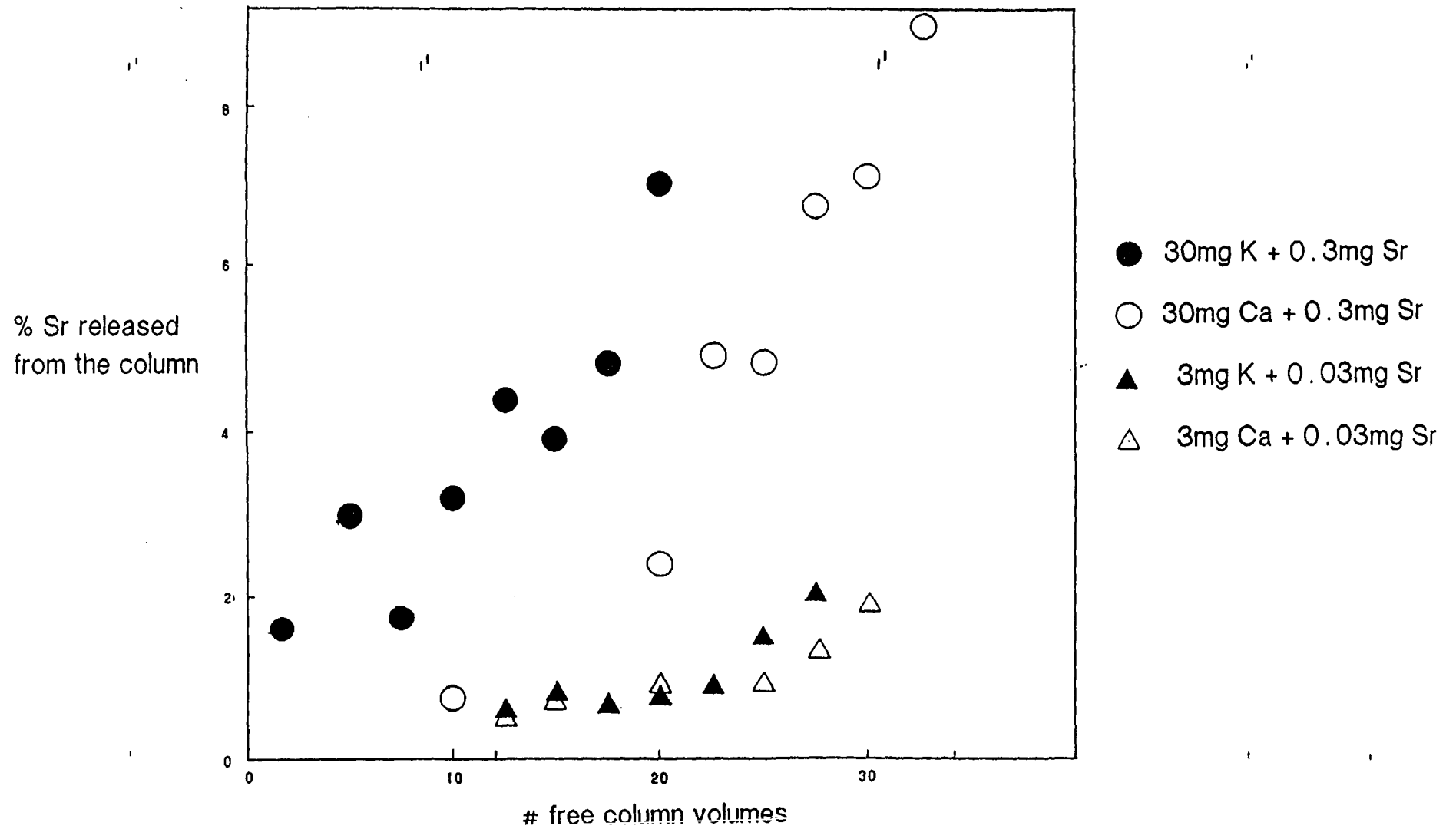Sr crystal ionic diameter 2.26 A

Figure 2

Figure 3

Legend:
- ● 30mg K + 0.3mg Sr
- ○ 30mg Ca + 0.3mg Sr
- ▲ 3mg K + 0.03mg Sr
- △ 3mg Ca + 0.03mg Sr

Y-axis: % Sr released from the column
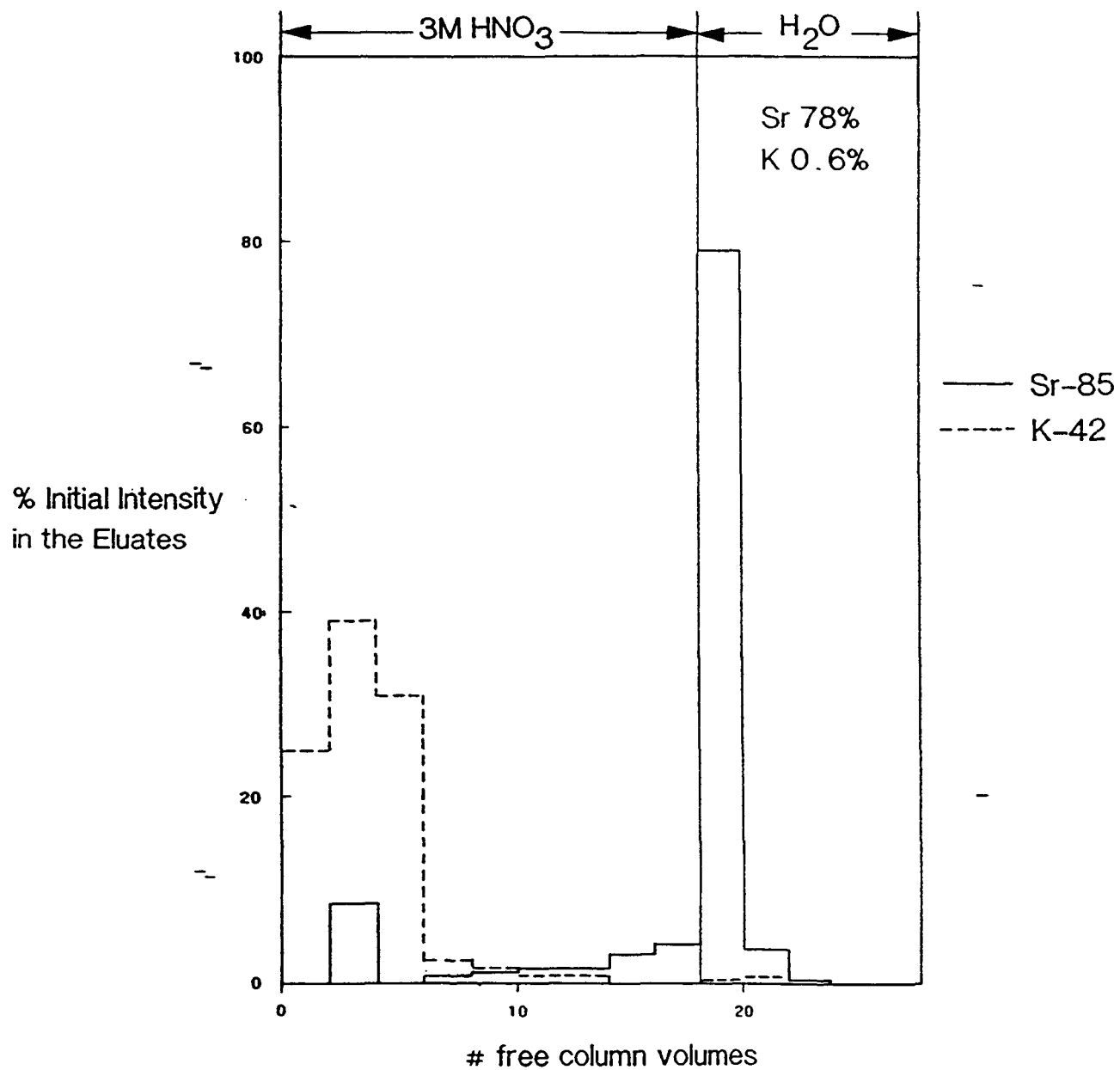
X-axis: # free column volumes

Figure 4

Figure 5

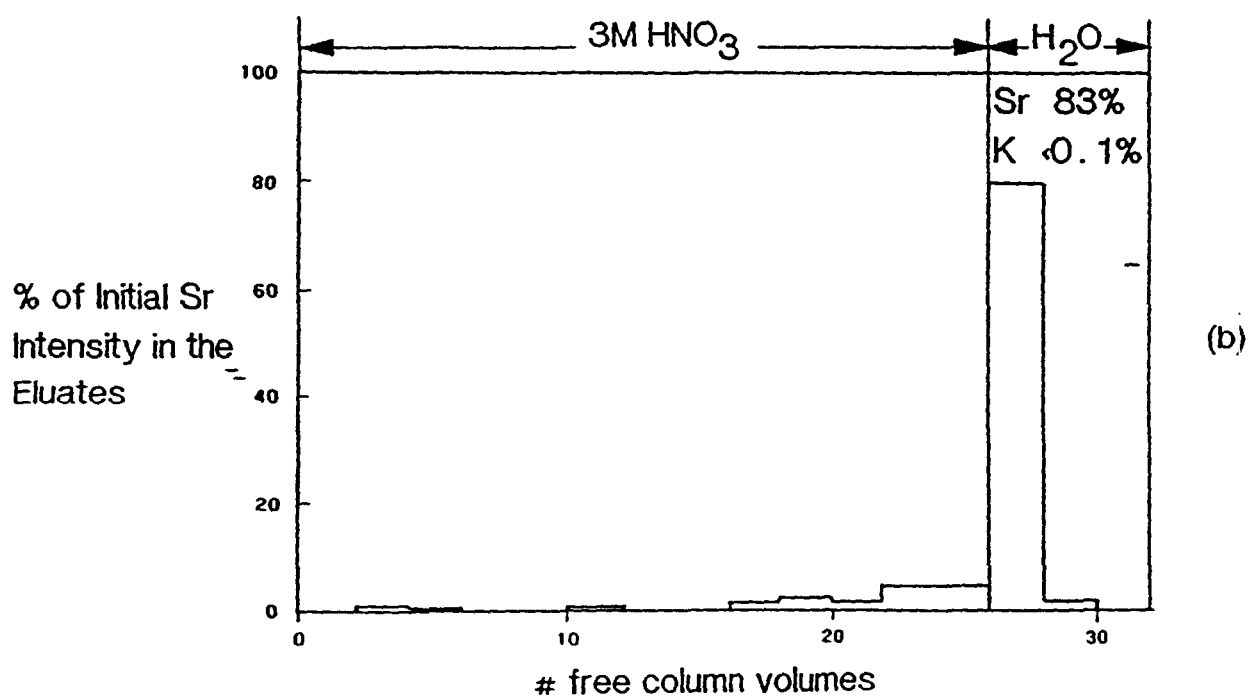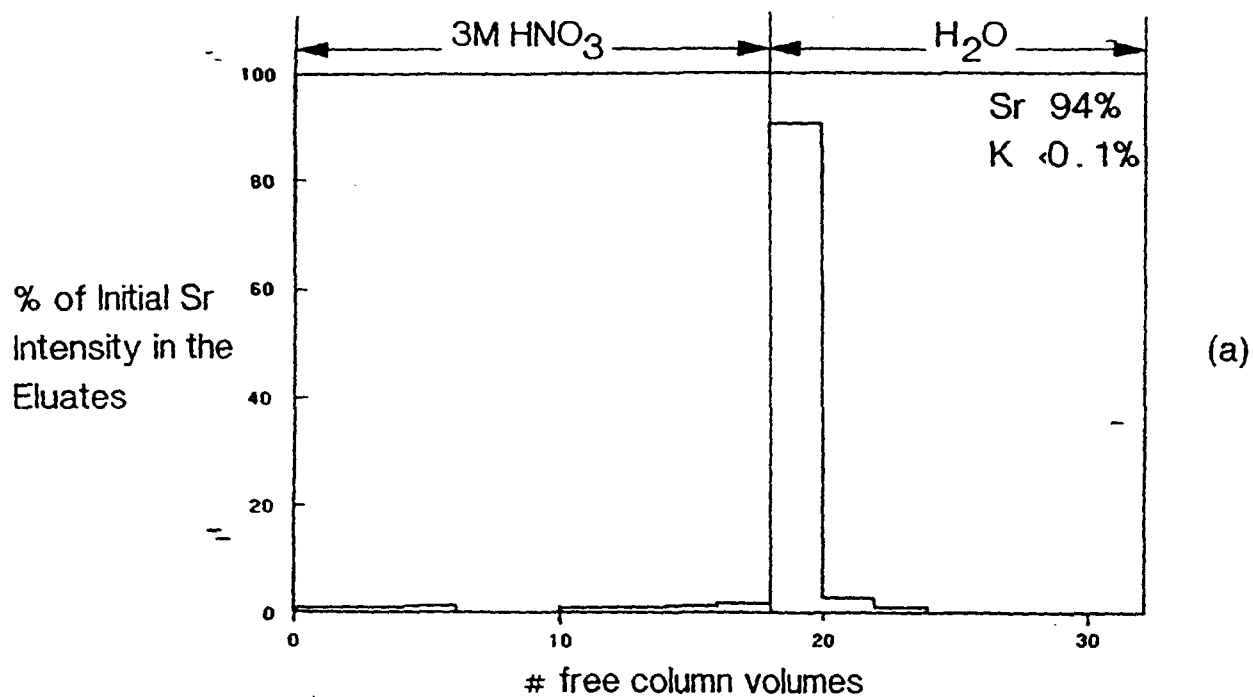# Figure 6
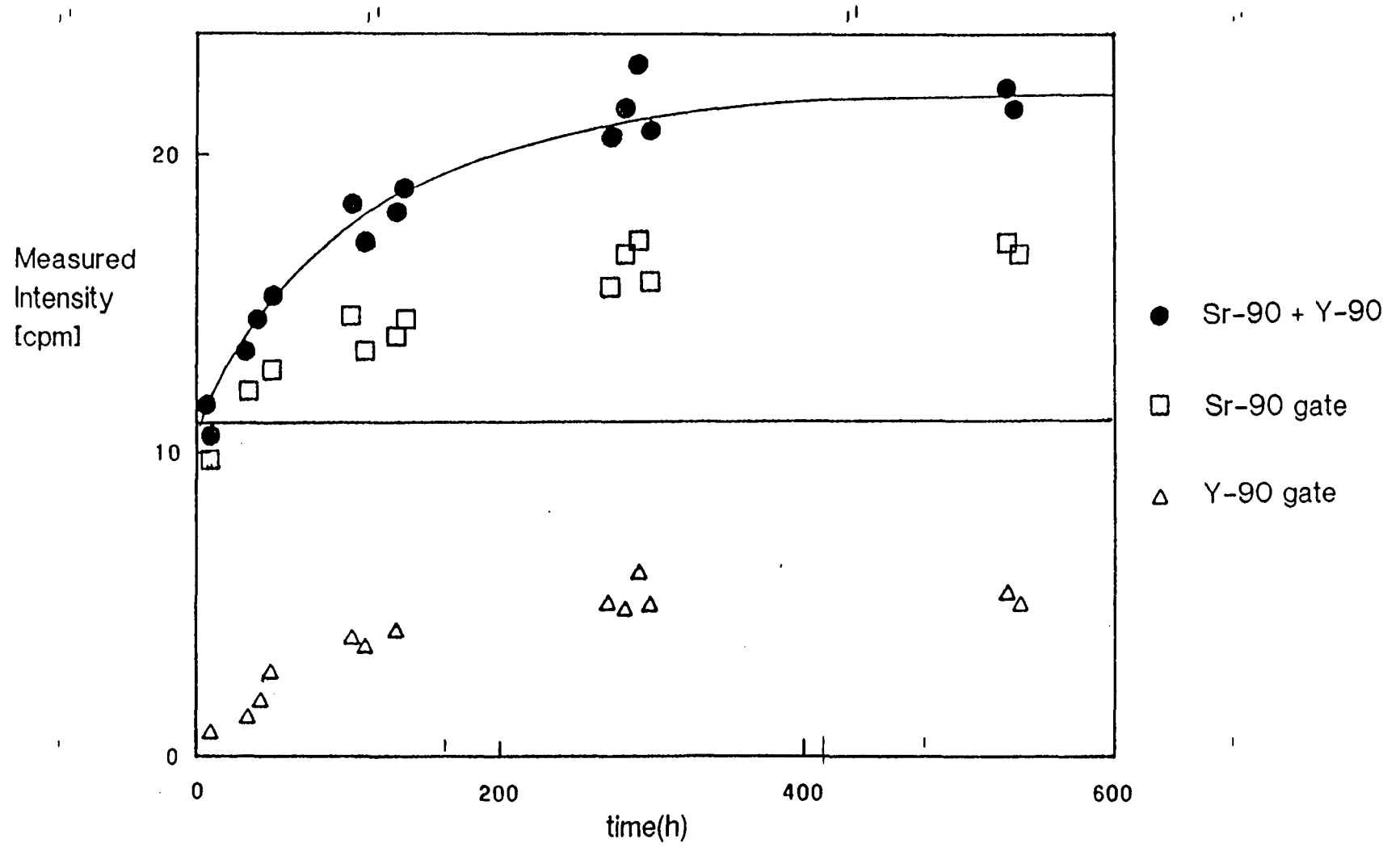
PROGRESS REPORT

IAEA/CRP Agreement No. 5744/CF

"RAPID INSTRUMENTAL AND SEPARATION METHODS
FOR MONITORING RADIONUCLIDES IN FOOD AND
ENVIRONMENTAL SAMPLES"

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HEALTH, SAFETY and ENVIRONMENTAL GROUP

BHABHA ATOMIC RESEARCH CENTRE

TROMBAY

RAPID INSTRUMENTAL AND SEPARATION METHODS FOR MONITORING RADIONUCLIDES IN FOOD AND ENVIRONMENTAL SAMPLES
(IAEA/CRP, Agreement No. 5744/CF)

A. RAPID INSTRUMENTAL METHODS

1. 4 channel Gamma Monitor for food materials :

This is an instrument with 4 single channel analysers connected in series with discriminators set to measure ^{137}Cs & ^{134}Cs, ^{40}K, ^{206}Ra and ^{228}Th simultaneously using 7.5 cm x 7.5 cm NaI(Tl) detector. ^{134}Cs and ^{137}Cs are estimated together, ^{226}Ra is estimated from ^{214}Bi gamma (1.76 MeV) peak and ^{228}Th determined from ^{208}Tl (2.62 MeV) gamma peak.

With sample size of 200 g and counting time of 1000 Sec the detection limits are :

^{137}Cs + ^{134}Cs	24 Bq/kg
^{40}K	550 Bq/kg
^{226}Ra	130 Bq/kg
^{228}Th	170 Bq/kg

Three equipments of this kind have been made and used in rapid monitoring of food items.

2. Development of moving filter type Environmental beta Monitor

A micro-processor controlled air particulate beta activity monitor has been developed. It incorporates two end-window GM counters for evaluating short lived and long lived radioactivity. The durations of sampling, extent of filter strip advancement, counting and data processing are regulated through the microprocessor. This monitor is capable of detecting as low as 0.02 Bq/m^3 of beta activity in air with 8 hr sampling at 80 1/min flow rate. The counting schedules can be programmed to detect short and long lived radionuclides associated with nuclear accident

releases. In normal operating conditions, the instrument can be used are continuous monitor for radon-thoron activity levels in air. One such instrument is already operating for the last six months at Bombay.

3. Development of a Beta counting system for rapid assessment of radioactivity in milk

Necessity of developing direct instrumental method to evaluate milk radioactivity rapidly without ashing and chemical separation has been felt. An instrument based on beta counting is under development. In this the detector consists of 15 cm x 15 cm solid state plastic scintillator having a large number of holes of dimension 0.2 cm dia and 14.5 cm deep for holding the sample. This scintillator is coupled to a P.M. tube. Each hole can hold 0.45 ml of milk and the complete detector can hold 250 ml of milk. The system is being designed to detect activities of 40 Bq/litre which is the activity limit for the milk.

4.(a) A portable in-situ Gamma Spectrometer

A portable 1 K multichannel gamma spectrometer using HPGe detector is being developed. This will be used for rapid in-situ determination of environmental natural and fallout deposited radioactivity. The spectral data will be processed by a microprocessor. The electronic instrumentation has been completed and is being used with NaI(Tl) detector. Portable HPGe detector is awaited.

4.(b) Vehicle mounted counting setup for gamma emitters in environmental samples

A 6 cm diameter NaI(Tl) detector system connected to a PSR-6 portable single channel analyser made by Nuclear Enterprise U.K. has been calibrated to count air filters, vegetables and grass for ^{131}I and ^{137}Cs. The details of the instrument setup are as follows :

i)   Detector   :   6 cm dia NaI(Tl)
ii) Single channel   :   PSR-6
     analyser
iii) High Voltage   :   975 V
iv) Wind width   :   1 V
v)   Discriminator   :   for ^{131}I = 1.6
     setup   for ^{137}Cs = 5.5

vi) Background of   :   for ^{131}I set up = 15 cps
     the system inside   for ^{137}Cs set up = 5.5 cps
     the vehicle
vii) Calibration factor for 10 cm dia charcoal filter
     with 1 m^3 sample volume :
              ^{131}I in air 1 cps above
                        —background   = 8.64 Bq/m^3
viii) For milk calibration factors for ^{131}I milk 1 l
     in Marinelli Beaker :
     for 1 litre sample 1 cps = 28   Bq
          ½ litre sample 1 cps = 18.5 Bq
ix) For ^{137}Cs in water in 1 l Marinelli Beaker :
        1 cps above Bkg = 60.5 Bq

    The counting work can be carriedout inside the vehicle
in the field and results can be ready within half an hour.

..(c) Laboratory Measurements System

    50 cc volume HPGe Detector system connected to 2 K MCA
(Canbera 35 Plus) has been calibrated to give immediate
measurement of gamma emitters in environmental samples.

    10 cm or 7.5 cm dia Petri Dish, 1 litre Marinelli
Beaker (completely filled or half filled) geometry are used
for counting. The system is having a 7.5 cm lead shielding
with Cu and Cd lining inside.   Calibration factors for
different samples, and for important radionuclides incase of
accidental release are given in the following Table-1.

Table-1

Calibration factors for the HPGe
gamma counting system - peak area counting

Radionuclide in the sample & counting geometry	Efficiency factor for 1 cps on the peak area

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i)   I-131 in Air 10 cm diameter
charcoal filter 1 m^3 volume   108.7 Bq/m^3
of air filtered, Petri dish
geometry

ii)   I-131 in Air, 2.5 cm dia.
charcoal paper with 0.15 m^3 311.0 Bq/m^3
vol of air filtered, Petri
dish geometry

iii)   I-131 in Milk
1 litre Marinelli Beaker
geometry
     a) 0.5 L Milk   330.0 Bq/l
     b) 1.0 L Milk   203.3 Bq/l

iv)   I-131 in Water
1 litre Marinelli Beaker   204.6 Bq/l
geometry

v)   Cs-137 in Water or Milk in   416.0 Bq/l
1 litre Marinelli Beaker

B. RAPID RADIOCHEMICAL SEPARATION METHODS

I. TBP Extraction method for rapid evaluation of Sr-90 in milk and food samples

A solvent extraction method for Sr-90 estimation by separating Y-90 using TBP extraction has been standardised recently. The nitrate separation using fuming nitric acid requires about 15 days to evaluate Sr-90 since Y-90 growth has to be allowed. In the new method, after the ash of milk and food samples is ready the analysis takes about 4 to 5 hrs. to give the SR-90 result.

In this method Y-90, from already equilibrated ash solution in conc. HNO_3 is directly extracted with TBP along with carrier back extracted with dilute acid. Finally Y is precipitated as oxalate and counted in a low background beta counter.

Results of Sr-90 activity determined by the conventional nitrate precipitation method and new solvent extraction method are compared in the following table.

Table-2

Comparison of results of Sr-90 activity
analysed by two different methods

Sample No. & Description	Method used and activity obtained.	
	Nitrate Precipitation Method (Bq/kg)	Solvent ext. Method (Bq/kg)
1. Milk Powder (S-28)	0.16	0.19
2. Milk Powder (S-S)	1.70	1.50
3. Milk Powder (M-C)	0.80	0.83

Ash of any sample brought to solution in concentrated HNO$_3$ can be directly used for Y-90 extraction. The decay of Y-90 can be followed for the purpose of verification of purity. The residue in the conc. HNO$_3$ dissolution of ash and fuming HNO$_3$ treatment can be used for Sr-89 determination.

II. Sr-90 estimation by Solvent Extraction with D2EHPA (HDEHP)

The method is based on the carrier free Y-90 extraction from 0.08 NHCl with 5% D2EHPA in tolunene-I and back extract with 3N HNO$_3$. Y-90 in the HNO$_3$ solution is evaporated and transferred to a S.S. planchet and counted in a low background counter. This method has been published by F.E. Butler in 1962. In case of milk sample, with initial separation of Ca, Sr & Y etc. with cation exchange resin the D2EHPA method takes about 2 hrs to complete the analysis.

The same method has been modified to have the Y-90 counting by directly taking the D2EHPA extract with liquid scintillation cocktail & count with a liq.scint spectrometer equipment. This method can be completed within 2 hrs. This solvent extraction of Y-90 can be utilised for any environmental and food sample which can be brought to solution in 0.08 N HCl. 20% D2EHPA extracts ^{90}Sr from 0.08 N HCl leaving behind Y-90. With Instagel as as liquid scintillator cocktail, this ^{90}Sr extraction gave 20% overall efficiency.

5% D2EHPA in ~~tolerance~~ extracts Y-90 from 0.04 NHCl. With Instagel cocktail, Y-90 extraction gave 57% overall efficiency.

^{90}Sr spiked sea water gave 80% recovery by this method of 20% D2EHPA extraction. Decontamination factor for Cs-137 and I-131 were more than a thousand.

This extraction method for Y-90 separation is very useful in case of soil and sea water samples.

III. Rapid Separation of ^{131}I and ^{137}Cs in milk and water sample

When activity levels are low, the direct gamma counting of milk and water samples take very long time, intial concentration step increases the sensitivity.

^{131}I in aqueous samples can be concentrated by absorption on AgCl in acidic condition. In case of milk, initial treatment with TCA, separation of precipitated casin and stirring the acidified (dil. HNO_3) clear solution with about 500 mg AgCl gives all the ^{131}I (more than 95%) picked up by AgCl which can be counted in a well crystal gamma spectrometer. In case of water samples acidification and direct stirring with AgCl all ^{131}I gets absorbed on to AgCl.

About half an hour stirring has been found sufficient to give reproducible result. The total time required will be about 3 hrs.

In case of ^{137}Cs, the aqueous solution should be stirred with ammonium phosphomolybdate (AMP) after acidification with HNO_3. After an hour of AMP settling time, decantation, filtration and centrifuging one can get the AMP ready for counting in a gamma spectrometer having a well type detector. The analysis can be completed within 2 hrs.

AgCl concentration of ^{131}I and AMP concentration of ^{137}Cs reduces the counting time significantly. These methods have been used for sea water and milk samples analysis.

IV. Rapid Separation method for transuranics (Pu, Am & Cm)

Methods are being standardised for solvent extraction separation of Pu, Am and Cm from preconcentrated environmental samples and direct counting of organic extract by liquid scintillation counting.

For Pu determination, solvent extraction by TTA, back exteaction and reextraction to 5% D2EHPA and direct liquid scintillation counting of Pu-alphas is planned. This will reduce the time required for Pu analysis to a significant extent. After bringing the sample to solution, this separation step can be carried out within 1½ to 2 hrs.

With Instagel scintillator cocktail in the packard 1550 LSS, Pu-239 counting had 70% efficiency with 5.3 cpm background Pu-239 estimated in a few sediment sample gave results by both LSS method & Si surface barrier detector, in close agreement.

Presently the liquid scintillation counter is used with discriminator settling adjusted to count Pu alpha pulses and also the output from the liquid scintillator is connected to a 2K MCA to see the alpha spectrum. The unit at present does not have the Pulse Shape Analyser (PSA) unit which is being planned to be incorporated in the system to improve the resolution.

The work is in progress for direct extraction to a liq. scintillation cocktail containing extracting reagents like high mol. amine (TIOA) and Di2 ethyl hexyl phosphoric acid and then count by liquid scintillation counting.

Solvent extraction using specific reagent and then direct liquid scintillation counting is being investigated as a general rapid method for beta and alpha emitters in environmental samples.