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Experiments for Training in Nuclear and Radiochemistry

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Abstract

An experimental training programm for education in Nuclear and Radiochemistry is outlined.
Didactical aspects are discussed, the installation of a suitable radiochemical laboratory is described and the precautions for radiation protection summarized.

Experiments including theoretical introduction, survey of apparatus and materials involved and experimental procedures are given for the topics of

- Radiation and their Measurement
- Radiochemical Methods
- Application of Radioisotopes

Technical Terms most often used during the course are explained and a comprehensive literature survey is finally compiled.

Zusammenfassung

Experimente zur Radioisotopentechnik
Ein experimentelles Ausbildungsprogramm in Kern- und Radiochemie wird beschrieben.
Didaktische Aspekte werden diskutiert, die Einrichtung eines dafür geeigneten radiochemischen Labors beschrieben und die erforderlichen Strahlenschutzmaßnahmen zusammengefaßt.
Experimente mit einer theoretischen Einführung, einem Überblick der notwendigen Geräte bzw. Materialien und der experimentellen Durchführung werden beschrieben für die Teilbereiche.

- Kernstrahlung und Meßtechnik
- Radiochemische Arbeitsmethoden
- Anwendung von Radionukliden

Häufig benutzte technische Begriffe im Verlaufe des Radioisotopenkurses werden erläutert. Ein umfassender Literaturüberlick ist zusammengestellt.

Content: page

Appendices

Experiments: page

1 Introduction

Basis of the courses performed and described in this paper is the experience and practice for more than 25 years of experimental training in the field of handling with Radioisotopes in our School of Nuclear Technology. These courses have regularly been taking place since 1957 on an annual average of five to ten times. They apply to students, natural scientists and engineers of all branches, but also to those technicans and laboratory assistants who work in the field of chemistry, physics, biology or medicine wishing to become familiar in handling and measuring sealed and especially open radioactive substances. The average course duration is three weeks with lectures and practical parts in an approximately equal ratio. Object of the course is to transfer basic knowledge being necessary for the handling of Radioisotopes. It concerns radiochemical methods, techniques of radiation detection measurement and radiation protection. Simultaneously the course serves its participants as reference for competence (Nachweis der Fachkunde) as health physicist in a scope of the Regulations of Radiological Protection in the Federal Repuplic of Germany.

In the eighties the training activities being supported and organized by the Nuclear Research Center of Karlsruhe, also increased in foreign countries. Especially in developing countries like Latin America or East Asia there is a great deficiency in practical education. So it might be well understood that the Brazilian Atomic Energy Agency CNEN (Communição Nacional de Energia Nuclear) asked the German institutions for help in facilities for more practical education both in equipment and know-how knowledge. In December 1979 within the Scientific Nuclear Technical Cooperation Programme PRONUCLEAR an experimental course in the field of Nuclear Chemistry and Nuclear Radiation Measuring took place for the first time in Brazil at the University of Recife (Departamento de Energia Nuclear).

A supplementary course concerning topics in Nuclear and Radiochemistry was attached in January 1982. The main object of these courses is to enable and qualify the lecturers and staff of the home departments in order to practice the education in experimental nuclear technology by their own managment.

The courses consisted most of all of practical experiments, only about one third of the time was adressed for lectures and seminars. About 40% of the participants were lecturers of the university, others being scientists from different Brazilian institutions, all engaged in the field of nuclear and reactor technology. The practical education in this field became now a fixed element of the master degree course in nuclear technology at the University of Recife. Similarly to the programme in Brazil experimental training courses were also performed at IPEN (Lima) (Instituto Peruano de Energia Nuclear) for the Peruvian Atomic Energy Commission, as well as for the Radioisotope Center in Colombo (Sri Lanka) and Chiang Mai (Thailand). Corresponding inquiries for similar education programmes have been made already for different countries, also under the auspices of the International Atomic Energy Agency (IAEA).

Proceeding to the courses mentioned above an isotopic laboratory was installed and partly equiped by the donation of apparatus and materials from KfK. Likewise in Peru and Thailand where the education is now hold by their own staff these two countries will finally be able to perform a continuous training on the field of nuclear chemistry, radiation measuring and protection, which is addressed not only to students but also to the local industry and hospitals.

The intension of the given report is to explain the experimental programme for the nuclear and radiochemistry education and to present rough didactical copies for the practical instruction. Furthermore we hope to enable studying participants to follow the lessons more easily and to carry out the given experiments by themselves.
Program and exercises in this report are proceedings of the seminars hold at DEN/Recife Brasil and IPEN/Lima Peru.

2 Training Programm, Didactical Aspects

Each training course has always been guided by two supervisors at minimum. Maximum number of participants is in the range of 15 to 24, depending on the possibilities of laboratory installation. Not more than 3 participants for each experimental and counting device should be allowed.

The programme of our course generally consists of three parts (Appendix 1)

(a) Radiation and its Measurement
(b) Radiochemical Methods
(c) Application of Radioisotopes

In the first part the participants should get familiar with the different types of radiation, their interaction with matter and the corresponding mode of detection. At the end of this training part the participants are expected to be able to determine the types of radiation qualitatively and quantitatively by the different measuring methods given in the experiment. Besides exercises and seminars the sucess is examined by an experimental test: different unkown mixture of radionuclides, specially composed, have to be analysed by means of the measuring equipment.

Theoretical and practical parts include the following subjects (S=seminar, P=practical part)

- Nuclear Radiation, Formation and Interaction	S
- Gas Counters	S
- Errors and their Correction	S
- Absorption of Decay Particles	S
- Scintillation and Solid State Counters	S
- α- and γ-Spectrometry	S
- Liquid Scintillation Counting Theory and Applications	S

- Detector Calibration	P
- Absorption of β-Particles	P
- Attenuation of γ-Radiation	P
- Backscattering of β-Particles, Selfabsorption	P
- Multi-Channel-Spectrometry by Scintillation and Solid State Counters	P
- Liquid Scintillation Counting	P
- Identification of Unknown Radionuclides	P

In the <u>second part</u> radiochemical methods are in topic. Basic knowledge in handling radioisotopes, radiation protection and absorption, carrier-techniques in radiochemical separations are presented. Following this part, the participant will be able to separate short-lived radionuclides from genetic systems and to identify them using their half-life and decay energy.

Experiments are always selected to cover actual topics like scavenging in decontamination and radionuclide enrichment, solvent extraction using tributylphosphate as a method for nuclear fuel reprocessing, ion exchange for the separation of fission products. The following subjects will be given:

- Basic Methods in Radiochemistry	S
-Separation of Radioisotopes	S
- Determination of Selected Fission Nuclides	S
- Radioactive Decay Genetical Relationships	S
- Radiation Protection Measurement	S

- Co-Precipitation and Adsorption (Scavenging)	P
- Precipitation with Carrier	P
- Solvent Extraction: Separation of U and Th from Fission Products	P
- Separation of Fission Products by Anion Exchange	P
- Separation and Analysis of Selected Fission Products (Sr, Cs, I)	P
- Cs-Ba-Separation by Chromatography	P
- Analysis of Radioactive Decay Curves	P
- Half-Life Determination of ^{238}U	P
- Measurement in Contaminated Areas	P
-Survey of Radioactivity in Air and Water	P

The final training part deals with the application of radiation measuring and radiotracer techniques in various fields of research and laboratory works. The experiments are chosen in consideration of the respective scope applicable in the home department, e.g. uses of the irradiation facilities of the zero power research reactor in Lima have been surveyed, whereas technical applications of radiotracers like isotope dilution technique in agricultural problems were topic in Brazil.

Subjects concern:

- Activation Analysis S
- Chemical and Physico-chemical Application of Radiotracers S
- Radioisotope Labelling S
- Activation Analysis: Determination of Ag and Tl in Technical Grade Lead P
- Tracer Technique: Solubility of PbI_2 P
- Isotope Dilution Analysis: I^- Determination in Presence of Large Quantities of Cl^- and Br^- P
- Insuline Labelling with ^{131}I P

The course ends always with a practical control for sucess. For final work, the topics 'Identification and Separation of an Unknown Mixture of Radionuclides' or ' Quantitative Analysis for Trace Elements in Samples by Neutron Activation (e.g. coconut, topas, natural uranium ores)' are performed by the chosen techniques and methods discussed during the course.

To guarantee the success meticulously care of the participants has to be taken in order to behave themselves absolutely correct in conducting an experiment. A practise has to be developed for use of essentially higher activities then applied during the course.

It is important to complete this training after a suitable time (about two years) with some topics in an advanced course (about two weeks). It likewise enables us to exchange experiences with the local staff and to give advises for further study and investigations in the subjects given in this course.

Some topics are shown below:

- α-Spectrometry S
- Neutrons, Interaction and Detection S
- Szilard-Chalmers-Effect S
- Scavenging, Theory and Application S
- Survey of Liquid and Gaseous Effluents of Nuclear Power Plants S
- Application of Radionuclides in Research and Industry S
- Application of Laboratory Neutron Sources for Activation Analysis S

- α-Spectrometry (Calibration, Sample Preparation, Identification of unknown α-Emitters P
- Moderation and Absorption of Neutrons P
- Change of the Chemical Bond of Ethyl Iodide by (n,γ)-Processes P
- Change of Oxidation State of Manganese by (n,γ)-Processes P
- Separation of the ^{80m}Br-Isomeric State P
- Examination of $^{32}PO_4^{3-}$-Adsorption on $Fe(OH)_3$ P
- Homogeneous Isotope Exchange Reaction of Ethyliodide P
- Measurement of Liquid Levels P
- Determination of Layer Thickness P
- On-Line Neutron Activation for Process Control P

For institutions of those countries either operating or constructing a research or power reactor, a supplementary course with the topic of ' Chemistry in Nuclear Power Plants' (with experiments e.g. 'Survey of α-Emitters in Nuclear Power Plants', 'Determination of ^{3}H and ^{14}C in Liquid and Gaseous Effluents of Nuclear Facilities', or 'Determination of Fission and Activation Products in Primary Cooling Circuits of Nuclear Power Plants', or 'Environmental Radioactivity in the Food Chain' is indicated. Similar courses also on an international level are presently running at the School of Nuclear Technology. Increasing importance especially in developing countries gain isotopic neutron sources or neutron generators. With ^{252}Cf a neutron flux ϕ up to $10^7 n/cm^2 s$ is easily available, while the costs are moderate and the maintenance negligible. Surch a source is applied in Karlsruhe for specific fields of research as well as for education.

The radionuclides produced are of short half life so that painful radiation protection might be avoided. It should be noticed that a similar radioisotope course can be performed without further standard nuclides using activation products like ^{128}I, ^{28}Al, ^{56}Mn or ^{36}Cl (see corresponding KfK-report).

3 Experimental Part

3.1 Installation of a Radiochemical Training Laboratory

A radiochemical training laboratory consists of the two main parts (Appendix 2):

(a) Laboratory Room
(b) Counting Room

Both of them should be mutually attached and easily acessible in order to permit a rapid measurement of samples. The floors, the walls, the cupboards and the surfaces of benches and fume-hoods in the laboratory must be made of non porous materials like glazed stoneware or polyethylene. The area has to be defined and signed. A protection against deportation of a possible contamination is to be installed at the exit (mónitor, change of protective chlothing).

A minimum of four fume hoods for radioisotope experiments (each for one group of a maximum of 3 participants) should be available. The following equipments for each laboratory device is recommended:

- Supply for water and gas
- Electric outlet
- Ceramic tray as support (minimum size 40 x 40 cm)
- Asbestos support
- Gas burner (either cartridge- or 'Bunsen'-)
- Tripod, asbestos wire gauze
- Infra-red lamp
- Sucking apparatus (pump, 'Wulff'-bottle)
- Support (stand), cramps
- Chemicals and reagents

Additional

- Filtering apparatus ('Büchner'-funnel)
- Beakers, Erlenmayer flasks, measuring cylinder
- Separatory funnel
- Racks

- Wash-bottle
- Rubber gloves, polyethylene gloves
- Tweezers, spatula, scissors, pH-paper, glass-rod, teat pipettes, pipetting assistants (e.g. rubberbulb), safety glasses

General Installations:

- Sink
- Reservoir for distilled or deionized water
- Storage tank for liquid effluents (radioactive and organic solvents)
- Bins for combustible and non combustible waste
- Centrifuge, balance, cabinet drier
- Contamination monitor, dose monitor

General Materials

- Ion exchange columns
- Pipettes (Volumetric- and Fortuna-type, Eppendorf-Pipettes with tips)
- Syrings
- Thermometers
- Centrifuge tubes
- Watch glasses
- Condenser
- Burette
- Gas ligther
- Stand with accessories
- Mortar
- Glass frit
- Al-planchettes
- Gloves (textile, rubber and one way-type)
- Supply bottles (Polyethylene)
- Plastic bags
- Test tubes

- Distillation apparatus
- Calcium chloride dry-tubes
- Stoppers
- Glue, adhesive tape
- Filter paper
- Vacuum grease
- Boiling chips
- Rubber tubes with fittings
- Evaporating dish
- Detergents

Equipment of the Counting-room

Each measuring device should be equiped with

- Scaler/timer
- GM-tube (thin end window type)
- Tube holder and castle
- Stop-watch
- Calculator or slide rule
- Set of aluminium and lead absorbers of known thickness ($1.4 - 1600$ mg/cm^2, $1 - 10$ g/cm^2)
- Slit-stop

Additional

- Ruler, pencil, carbon paper, rubber, table of isotopes, chart of nuclides

General Equipment

- Ordinary graph paper, semi-logarithmic graph paper, measuring minutes (Appendix 4)
- Liquid-scintillation-counting device
- NaI(Tl)-scintillation counter, well type (2 devices at minimum)
- Semiconductor counter
- Multi-channel-analyzer
- Printer, plotter

3.2. Aspects on Radiation Protection

The hazards involved in handling with radioisotopes are of two kinds: those due to external radiation and
those due to ingestion or inhalation.

The low activities used in the experiments described are not subject to danger from external radiation. The main hazard arises from ingestion, being avoided when proper techniques are used. A detailed instruction about radiation protection ('Strahlenschutzbelehrung') has to be given before starting any experimental work (Appendix 3). When handling with radioisotopes students should wear special laboratory coats. The operation with liquid radioactive solutions must be conducted inside a fume hood over a tray lined with absorbent paper. All surfaces of the laboratory benches being exposed to possible radioactive contamination should be covered with a suitable foil or tissue. The majority of the experiments described in this report does not require the use of gloves on the part of the student. Gloves constitute a hazard with inexperienced persons particularly when wet and may lead to spills. However, the students should get practice in their use so that in certain experiments a controlled use is recommended. At any time no gloves must be used in the counting room. No manipulation of radioactive material is allowed in the counting room, and it has to be assured as well that sources are not left in the room after each counting, To avoid unnecessary contamination books, calculators and similar materials should not be taken into the laboratory. In order to simulate a hot laboratory students should wear a simple pen-type dosimeter for control. To avoid any carrying contamination off the laboratory, a hand-feet-cloth-type contamination monitor has to be installed at the exit. In case of monitor alarm the contaminated parts have to be rinsed with warm (not hot!) water followed by a mild alkaline soap. The use of scouring and severe complexing agents increases the danger of incorporation through the injured skin.

The laboratory in any way should be monitored regularly for contamination by the staff, at least once a week. All radioisotope supplies have to be kept in a locked safe being shielded against possible radiation. For the personal responsible of handling stock solutions, sealed sources and neutron sources, the hazard due to external radiation can be considerable and film badges (or personal dosimeters) should be worn. Never handle radioactive sources without tangs.

For most of the countries special regulations for handling with radioactive sources (e.g. ICRP recommendations, International Council of Radiological Protection) are in law and the free handling of radioactivity is limited. To avoid special permissions and impositions these limits should not be exceeded for each experiment. Most of the given experiments use natural uranium and its daughter nuclides with high free handling rates (up to 300 g in the FRG). If necessary the use of artificial radioactive sources is indicated, isotopes with relatively short half-lives are recommended in general. Use of any α-active sample will create more dangerous contamination. For a considerable amount of experiments, isotopic neutron source activated radioisotopes (e.g. from ^{252}Cf, Am-Be, Pu-Be) substitute the commercially available standard nuclides (see separate KfK-Report).
Solid or liquid waste should be gathered separately. The controlled disposition of liquid waste to the refuse or drainage system is allowed upto the given limit of regulation but better, if stored in a separate tank. It can be drained off after checking for radioactivity has been performed. Special regulations of each country should be observed. Solutions with higher specific activity are gathered in a bottle to be stored until the short lived nuclides have been decayed sufficiently. Waste solutions of natural uranium or thorium are matter for reprocessing from time to time.

3.3. Experiments and Evaluation

The following radiochemical experiments should give a look into the manifold areas, in which the use of radiochemical materials is advantageous. From the plurality of experiments used during the courses at the "School of Nuclear Technology" those examples have been selected, where

- the amount of activity introduced in the experiment is small enough (beyond the limited value)

- the radionuclides are easy to obtain (mostly from the natural decay series)

- the didactical value of the experiment is high

Experiments are classified into the subjects

- radiation and its measurement

- radiochemical methods

- application of radioisotopes

Finally two experiments are given, suitable as final practical work. Experiments concerning the topics of chemistry in nuclear power plants are summarized at the end of the chapter. A detailed description will be available. If possible each experiment is set-up according to the following uniform scheme

- theoretical introduction

- apparatus and material

- experimental details

In order to make sure the success of each experiment, basic questions and problems are given at the end of each part.

A detailed discussion of the chemical and radiochemical basic principals for each experiment in detail is not given in order to limit the extent of the report. Technical terms used in the experimental part are explained in chapter 4. Otherwise, the reader is referred to the given literature survey in chapter 5 for further theoretical information. Literature data for the experiments are only given if detailed information is available.

3.3.1. Radiation and its Measurement

Experiments:

1. Preparation of Uranium Standard Sources

Objective: Using easily available chemicals the students should be enabled to prepare standard sources for detector calibration.

2. Characteristics of Gas Counters

Objective: Charateristics of different gas counters have to be recorded. The student has to fix the appropriate working voltage.

3. Calibration of a GM-Counter

Objective: Using various standard sources, the student should be able to calibrate a given counting device for quantitative determination.

4. Backscattering of β-Particles

Objective: The student should be able to estimate the influence of backscattering on the measurement. The dependence of backscattering on thickness and material of the support should be understood.

5. Absorption of β-Particles

Objective: Correlations between Maximum Range, Half-Thickness in Al and maximum β-energy have to be known. The student should be able to determine unknown β-emitters from simple and complex absorption curves.

6. Attenuation of γ-Radiation

Objective: The student will get familiar with the interaction of γ-radiation with matter. Using lead absorbers of known thickness, γ-energies have to be estimated.

7. γ-Spectrometry

Objective: A γ-ray spectrometer has to be calibrated and unknown γ-emitters identified.

8. Liquid Scintillation Counting

Objective: The student has to understand energy transfer and interferences in Liquid Scintillation Counting. He should be able to determine unknown low energetic β-emitters in quenched and dual labelled samples.

9. α-Spectrometry

Objective: The student will learn to prepare thin α-samples by electrolysis and to identify the radionuclides by α-spectrometry.

10. Moderation and Absorption of Neutrons

Objective: A suitable shielding for a laboratory neutron source has to be evaluated.

11. Computer-Aided Evaluation and Education in Radiation Measuring

Objective: The experiment will point out the possibilities to involve personal computers in data evaluation, counter simulation and spetrum display.

12. Instrumental Identifikation of Unknown Radionuclides

Objective: The student has to be able to identify an unknown mixture of radionuclides by instrumental radiation measuring techniques.

Experiment 1: Preparation of Uranium Standard Sources

Theoretical Introduction

To solve different problems of the radiation detection technique like adjustment and maintainance of detectors, determination of efficiency etc., the use of a suitable standard is necessary. The pre-conditions required from such a substance depend in particular on the intended purpose.

General considerations concern:

a) The half-live of the radionuclide used should be long enough to avoid frequent decay corrections.

b) The emitted radiation adequate to the intended measuring problem should be composed only of few compounds and the decay scheme must be known.

c) The radionuclide used should be available in high radiochemical purity and should satisfy radiation detection.

In the present case natural uranium is used. According to

$$^{238}\mathrm{U} \xrightarrow[4.5\mathrm{x}10^{9}\mathrm{a}]{\alpha} {}^{234}\mathrm{Th} \xrightarrow[24.1\mathrm{d}]{\beta^{-}(0.5\mathrm{MeV})} {}^{234\mathrm{m}}\mathrm{Pa} \xrightarrow[1.2\mathrm{min}]{\beta^{-}(2.3\mathrm{MeV})}$$

^{238}U in commercially available U-compounds is in radioactive equilibrium with ^{234}Th and ^{234m}Pa. While the α- and low energetic β-particles are easily absorbed, ^{234m}Pa with the same activity like its precursers is measured.
Sources of known activity can be produced by placing definite amounts of U_3O_8 in proper sample holders (planchette).
For adjustment, and calibration of proportional counters a pure α-source is necessary. α-emitters have a high radiotoxicity and are hardly available in small amounts.
In our case natural uranium isolated from its β-emitting daughters by a chemical separation shall be taken for the α-standard source.

Apparatus and Materials

- GM tube (end-window type) with a suitable tube holder
- Scaler / timer
- Al-planchette (Ø=30mm, height=2-3mm)
- Washer
- Al-foil ($50 mg/cm^2 = 0.15 mm$ thick)
- Double side adhesive tape
- U_3O_8 (A.R.)
- Glue
- Acetone

- Uranium-nitrate (A.R.) $UO_2(NO_3)_2 \cdot 6H_2O$
- HCL (1 M and conc.)
- NH_4OH (6 M)
- $(NH_4)_2CO_3$-solution (0.5 M)
- Filtering apparatus
- Beakers (100 and 250 ml)
- Bunsen burner
- Porcelain crucible with lid

Experimental Details

(a) Standard source for a GM-detector

(1) Fix the washer in the sample holder by means of some glue.

(2) Weight exactly 80 to 100 mg U_3O_8 in a planchette, distribute it homogeneously by shaking, and wet it with a few drops of acetone, mixed with some glue.

(3) After drying fix a sheet of Al-foil (o.15 mm thick) carefully onto the washer, in order to prevent from dusting and possible contamination.

(4) Self-absorption of the sample and density of the Al-foil cause both the α-radiation of ^{238}U and the low energetic β-radiation of ^{234}Th to be absorbed. The high energetic β-radiation of ^{234m}Pa (19% diminished by the Al-foil) will be measured.

(5) The activity of this sample can be calculated from the known amount of ^{238}U and its specific activity (1 mg ^{238}U = 12.28 Bq).

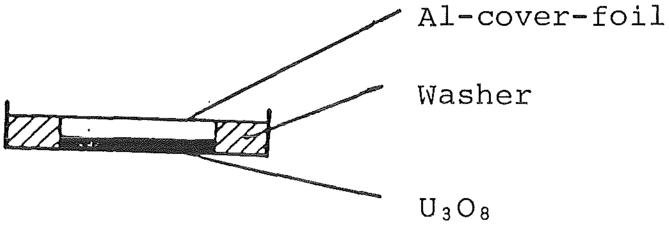


Figure 1: U-standard-source

(b) Preparation of a pure α-emitter for calibration of a proportional counter

(1) Dissolve about 1 mg uranium nitrate in 25 ml H_2O, add 3 ml HCl (1 M) and 3 ml $FeCl_3$-solution. NH_4OH is added until $Fe(OH)_3$ precipitate is observed.

(2) It is removed with 1-2 drops of HCl. Heat the solution until boiling and add 25 ml $(NH_4)_2CO_3$-solution.

(3) While uranium remains in solution as carbonate-complex, the carrier-free ^{234}Th and ^{234m}Th is adsorbed by the $Fe(OH)_3$-precipitate. The precipitate containing the whole β-activity compounds is filtrated or centrifuged and rejected.

(4) The carbonate-containing solution is heated and acidified by careful addition of HCl (conc.) to remove CO_2. NH_4OH is added dropwise until the light-yellow, β-inactive ammoniumdiuranate precipitates completely.

(5) The precipitate is filtrated and transferred into a beaker. By careful heating with increasing intensity ammoniumdiuranate is dried and finally changed into U_3O_8 by emission of NH_3. **(Caution: tends to dust by brisk NH_3-extrication).**

(6) The β-inactive U_3O_8 is used in definite amounts as α-emitter of known specific activity for the calibration of the α-plateau of a proportional counter. The increase of the β-activity occures with the half-life of the ^{234}Th (24.1 d). One hour after the $Fe(OH)_3$-precipitation the β-activity has reached 0.12 % of the present α-activity.

Experiment 2: Characteristic of Gas Counters

Theoretical Introduction

The detection and determination of nuclear radiation are based on the qualitative and quantitative measurement of the products affected by the interaction of the emitted particles with matter.
Two main methods are used today. The first depends on the ionization produced in matter by the passage of a charged particle, and the second one on light emission (called scintillation) produced by interaction of the radiation with a suitable phosphor. The scintillation method is most suitable for counting γ-photons and low energetic β-particles due to its feeble ionization.

Ionization detectors can be subdivided into two types, those which measure the ionization produced in a gas, called gas counters, and solid state counters (semiconductor counter) (table 1).

Table 1: Qualification of Different Detectors for α-, β- or γ-radiation

Detector	Type of Radiation		
	α	β	γ
Ionization chamber	+	(+)	-
Proportional counter	+	+	-
GM counter	+	+	+
Cloud chamber	+	+	(+)
Scintillation-crystal	(+)	+	+
Liquid-scintillation counter	+	+	+
Semiconductor counter	+	(+)	+

Gas counters consist in principle of an isolated central electrode in a suitable gas-filled chamber.
Between the outer wall and the central electrode a high potential is maintained (Figure 2).

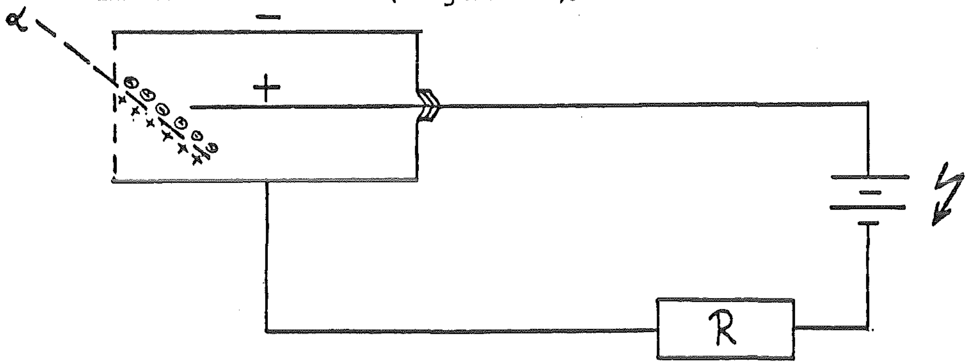


Figure 2: Circuit Diagram of a Gas Counter

At low voltage many electrons produced when an ionizing particle enters the chamber will recombine, before they reach the anode.
As the voltage increases all the ions are collected and a small current will flow which can be observed with a suitable detector. This is the region of the ionization chamber (region AB resp. A'B', Figure 3). The number of electrons produced depends on the nature of the particle (α- and β-plateau), the length of the track (particle energy) and the nature of the gas.
When the primary electrons have been accelerated to energies high enough to ionize gas molecules 'gas amplification' occurs which produces more and more secondary electrons.

Over this region between B and C (B'C') the distance of the curves for α- and β-particles is considerable. By use of discrimination of the pulse height the proportional counter is useful to distinguish between different types of radiation.

With still further increases in voltage the electrons have become an avalanche, the discarge spreading along the entire length of the tube.

The pulses produced are of fixed amplitude, independant of the energy and nature of the primary ionizing particle.

The positive ions which move much more slowly than the electrons are finally left as a protection around the anode. They reduce the electrode field intensity until no more electrons can be produced. The counter is thus rendered inoperative for a finite time, called 'dead time'.

Positive ions and electrons in striking the electrodes produce photons which by interacting with the walls of the counter, release photoelectrons that can start a fresh avalanche.

Therefore, counters working in this region (GM plateau DE), known as 'Geiger-Müller counter' mostly are filled with a quenching agent (ethanol, bromine) to absorb these photoelectrons.

At higher voltage beyound E a state of continous discharge occurs which may permanently damage the tube.

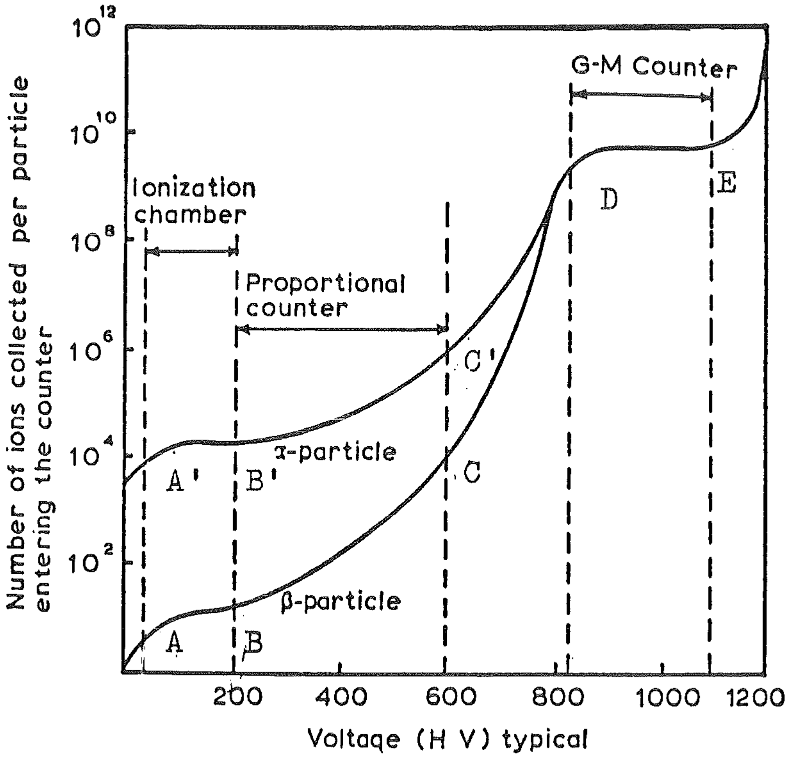


Figure 3: Ionization Curves against Applied Voltage

Introduction to the Experiment

If the count rate obtained from a given source of long half-life is plotted against the voltage V applied, a curve similar to that of figures 4 or 5 is obtained (not to be confounded with the ionization curve in figure 3!).

The plateau is reached when gas amplification is high enough that each particle entering the tube may be detected.

Before starting a gas counter operating voltage, background, and length and slope of the plateau have to be determined.

In the following practical course you have to record the characteristics of a proportional and a GM counter.

Apparatus and Materials

- Proportional counter
- GM counter
- Scaler / Timer
- α-source (^{210}Po)
- β-source (^{204}Tl)

Experimental Details

(1) The α-source is placed on the uppest shelf in the tube holder.

(2) The high voltage is slowly increased from zero until counting begins at the starting voltage V_s.

(3) Record a series of counts (1min) at V_s, V_s+40, V_s+80 volts, etc. until the count rate increases marcedly from the plateau.

(4) Repeat the measurements using the β-source.

(5) Plot a graph of log counting rate R_c against high voltage V (Figure 4 and 5).

(6) The operating voltage V_w of the counter is chosen about 1/3-way along the plateau. Note that in case of the proportional counter the applied working voltage for α-particles has to be lower than the starting voltage for β-particles.

(7) Determine the length of the plateau and the slope S at operating voltage.

$$\boxed{S = \frac{R_c(V_w+50V) - R_c(V_w-50V)}{R_c(V_w)} \cdot 100\ \%}$$

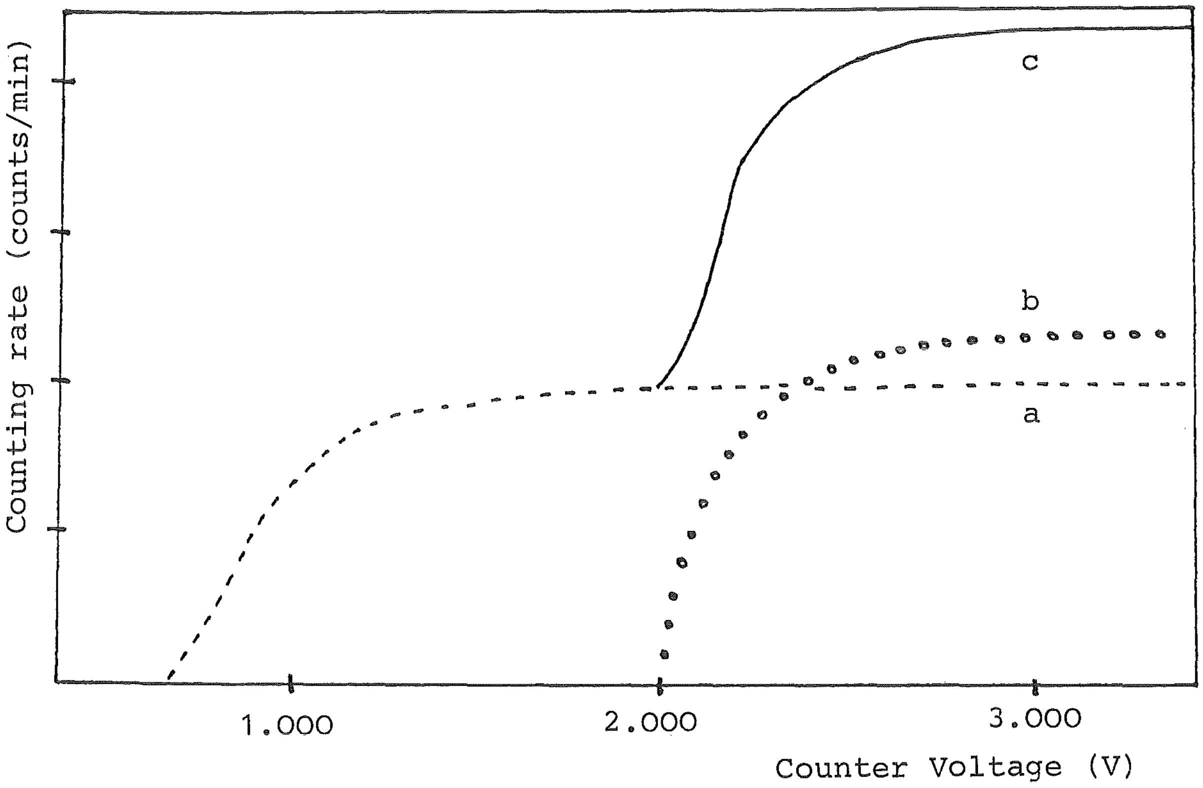


Figure 4: Characteristics of a Proportional Counter
a: for α-radiation
b: for β-radiation
c: for α- and β-radiation

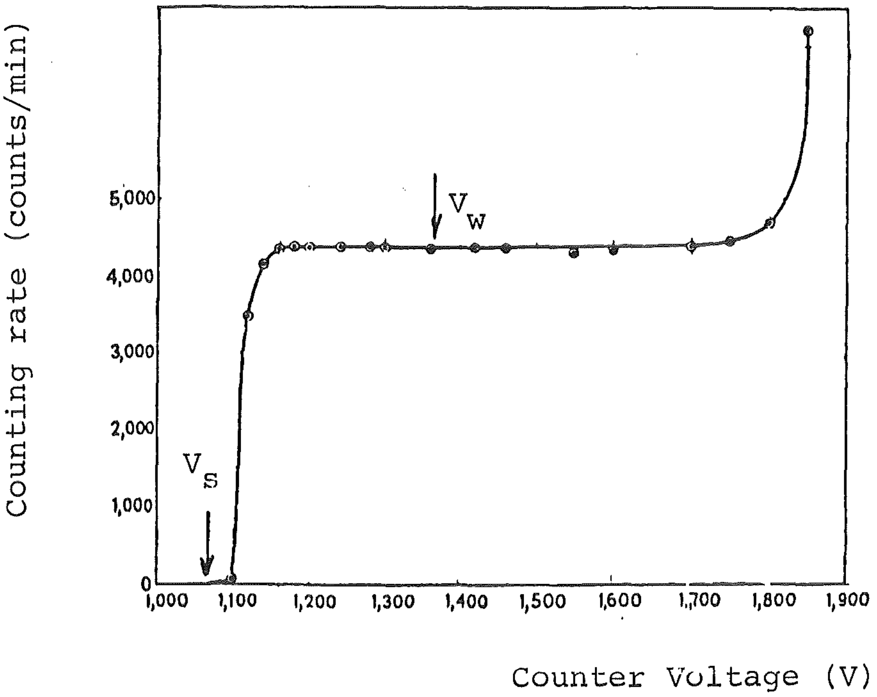


Figure 5: Characteristic of a Geiger-Müller Tube

Experiment 3: Calibration of a GM-Counter

Theoretical Introduction

The activity of a radioactive source (decays/s=Bq) cannot be determined directly by the usual measuring devices. In order to calculate the activity from a given measuring result (counts/s) you have to consider different factors, depending on the given nuclide, source, and apparatus.

Provided that the measuring technique is kept constant and only one nuclide is counted, you can take the 'efficiency' to correlate measuring result and activity.

By measuring a calibrated standard source of known emission rate R_E, the efficiency η is the per cent part of emitted particles or quants, registrated by the measuring apparatus. By considering the constant background part R_O of the counting rate R_M, the net rate R_N is calculated to $R_N = R_M - R_O$ and the efficiency η to

$$\boxed{\eta\ (\%) = \frac{R_N}{R_E} \cdot 100} \qquad (1)$$

It depends on nature and energy of the registrated radiation at constant measuring factors. In the following experiment the efficiencies of some radionuclides are to be determined and compared with regard to the nature of the radiation and to the β-maximum energy of the emitted β-radiation resp.

For the low activities of the sources used, no special protections are necessary. However never handle radioactive sources especially open ones without pincette or tangs.

Apparatus and Materials

- GM detector (end-window type)
- Al-planchette (∅ 30 mm)
- Calibrated radionuclide solutions with known activity (^{32}P, ^{204}Tl, ^{14}C, ^{54}Mn)
- Uranium standard
- Pipettes
- Heat lamp

Experimental Details

(1) Drop definite volumes of calibrated radionuclide solutions into Al-planchettes and dry.

(2) The activities of the different sources should be for:
^{32}P and ^{204}Tl: about 500 Bq
^{14}C and ^{54}Mn: about 2500 Bq

(3) Under identical measuring conditions the uranium standard and the 4 other radionuclides should be measured (R_M) and the net rates (R_N) calculated after subtraction of the background.

(4) The efficiencies are calculated from the known emission rates R_E of equation (1). They should be compared in respect to the different natures and energies.

(5) Make another experiment by varying the geometry (distance: source - detector).

Table 1a: Efficiency of the GM Counter for Different Radionuclides

Nuclide	(MeV)		Efficiency η (%)	
	E_βMax	E_γ	1st Position	4th Position
U-standard	2.3			
^{32}P	1.7			
^{204}Tl	0.76			
^{14}C	0.17			
^{54}Mn		0.84		

Experiment 4: Backscattering of β-Particles

Theoretical Introduction

In general only the part of radiation emitted in the direction of the counter will be measured (Figure 6). If a support is placed below the source, β-particles travelling away from the GM tube can be reflected to the detector and will increase the counting rate (Figure 7).

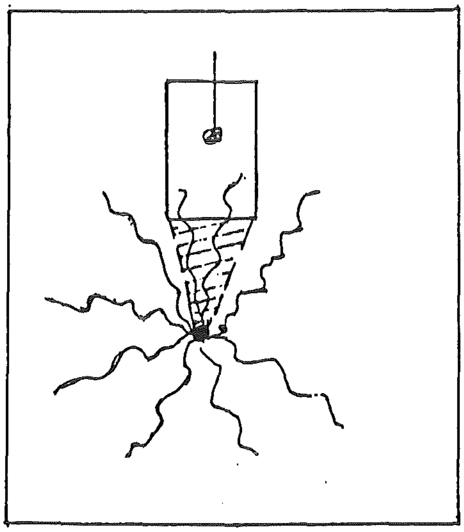


Figure 6: Part of Radiation detected by the Counter

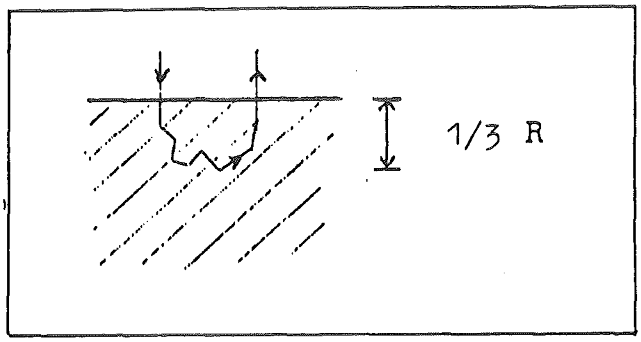


Figure 7: Backscattering Occuring in a Sample Support

The reflection is called 'backscattering'. The degree of backscattering is influenced by the following three factors

- (a) thickness of the support,
- (b) atomic number of the support,
- (c) energy of the radiation.

With either increasing atomic number and thickness of the support the degree of backscattering increases. It reaches a maximum at a thickness of about 1/3 if the maximum range of β-particles in the support ('saturation thickness'). Thus the efficiency of an end-window GM counter will vary considerably with the nature and thickness if the support of the source and will be affected also by the type of material used for the housing. To obtain reproduceable results it is essential therefore to use the same conditions throughout an experiment.

Matter of the following experiment is to find out the relation between backscattering expressed by the factor

$$\boxed{f_b = \frac{\text{counts/min (with reflector)}}{\text{counts/min (without reflector)}}} \qquad (1)$$

and nature and thickness of the support.

Apparatus and Materials

- Beta source (< 37 kBq, i.e. ^{204}Tl)
- Scaler/Timer
- GM tube (end-window type) with a suitable tube holder
- Set of alumium absorbers of known thickness (6-200mg/cm^2)
- Supports of different materials (i.e. plexiglass, graphite, aluminium, silver, tantalum, lead; all of saturation thickness (> 500 mg/cm^2).

Experimental Details

(1) Determine the background for at least 5 min.

(2) Place the β-source on a shelf in the tube holder at such a distance from the GM tube that it gives as much as possible but not more than 5.000 counts/min.

(3) Record the counting rate for 1 minute.

(4) Place the aluminium absorbers direct below the β-source and repeat the count.

(5) Do a series of counts using increasing thickness of aluminium until the counting rate becomes reasonably constant.

(6) Repeat the count by using different materials of saturation thickness each as support.

(7) Plot the calculated backscattering factors (1) on the y-axis against thickness of absorber in mg/cm^2 (Figure 8) respectively atomic number of the material (on graph paper, Figure 9).

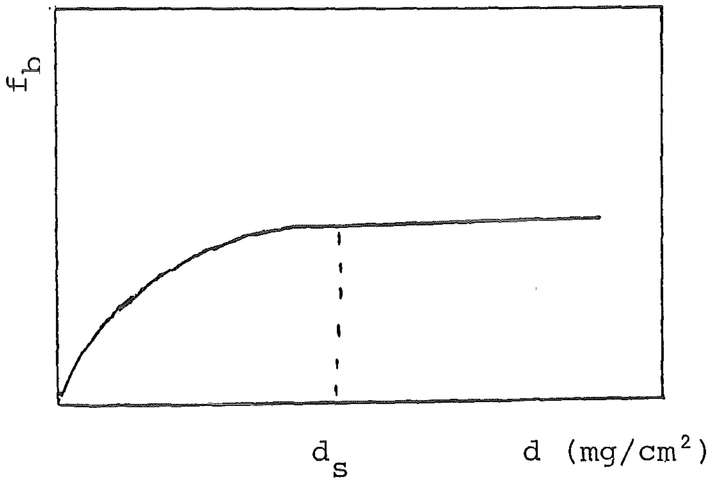


Figure 8: Backscattering Factor F_b Plotted Against the the Thickness of the Support (d_s = saturation thickness)

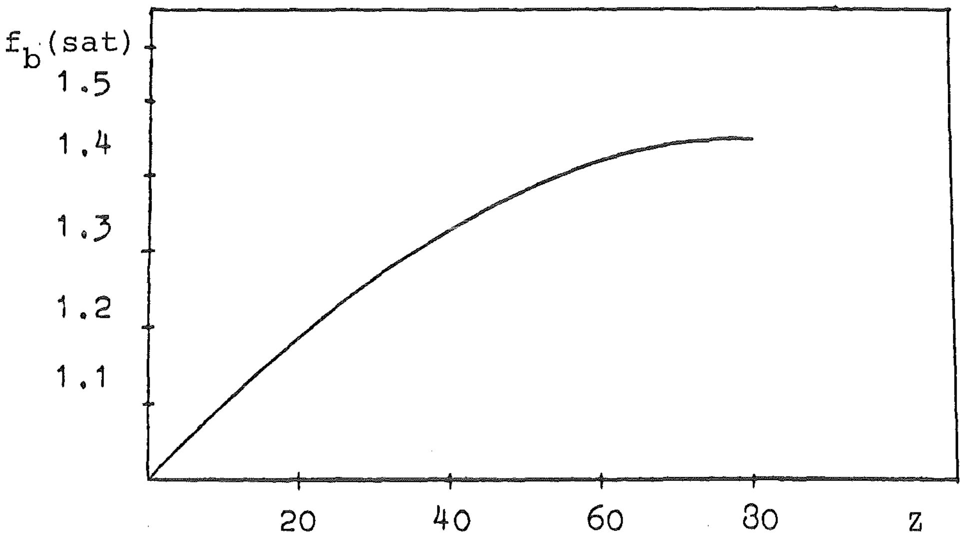


Figure 9: Backscattering Factor at Saturation Thickness f_b(sat) Plotted Against the Atomic Number Z of the Scattering Material

Experiment 5: Absorption of β-Particles

Theoretical Introduction

The analysis of the absorption of β-particles in matter is a simple method to determine the energy of β-radiation. It enables the identification of unknown radioisotopes.

β-radiation exists of electrons with a continuous energy distribution (Figure 10).

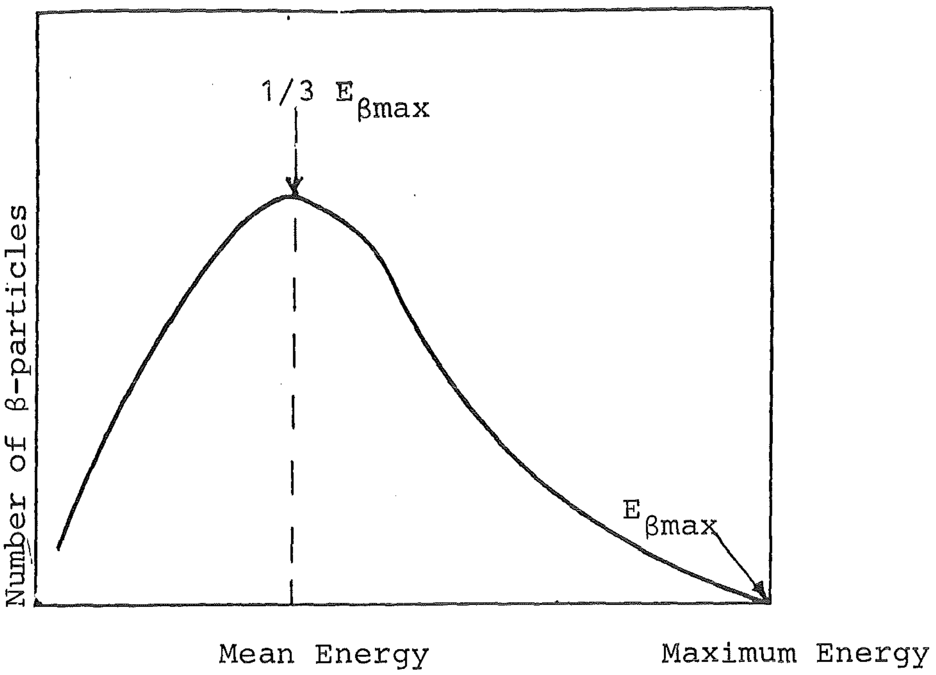


Figure 10: Energy Distribution of β-radiation

By interaction with matter they transfer their energy mainly by:

a) excitation or ionization of the absorbing atoms
b) inelastic nuclear scattering by emission of Bremsstrahlung

The ratio between excitation or ionization and the emission of Bremsstrahlung depends in the atomic number of the absorber. Bremsstrahlung is proportional to Z^2, hence the use of aluminium is preferred rather than lead.

In Figure 2 the log of the intensity of β-radiation is plotted against the thickness of the absorber (β- absorption Curve).

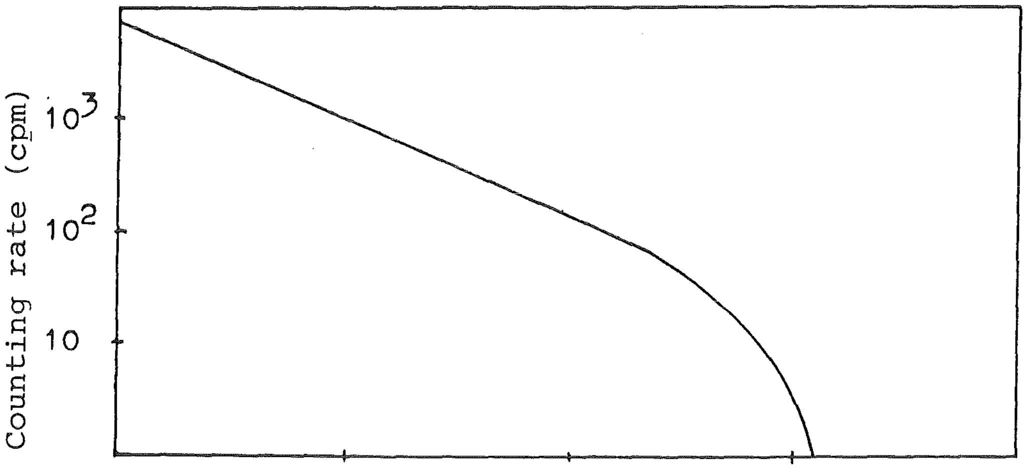


Figure 11: β-absorption Curve

The resulting graph is nearly linear. The exponential absorption of β-radiation from a simple β-emitter is a fortuitous result of the continous β-spectrum and the effects of scattering.

The absorption curves of different β-emitters should be measured in the following experiment and the maximum β-energies determinated.

Apparatus and Materials

- Beta sources, 4-40 kBq activity (e.g. ^{204}Tl, ^{90}Sr/^{90}Y)
- Scaler/Timer
- GM tube (end-window type) with a suitable tube holder (Figure 12)
- Set of aluminium absorbers of known thickness (0.005 - 6.0 mm ≙ 1.36 - 1620 mg/cm²)

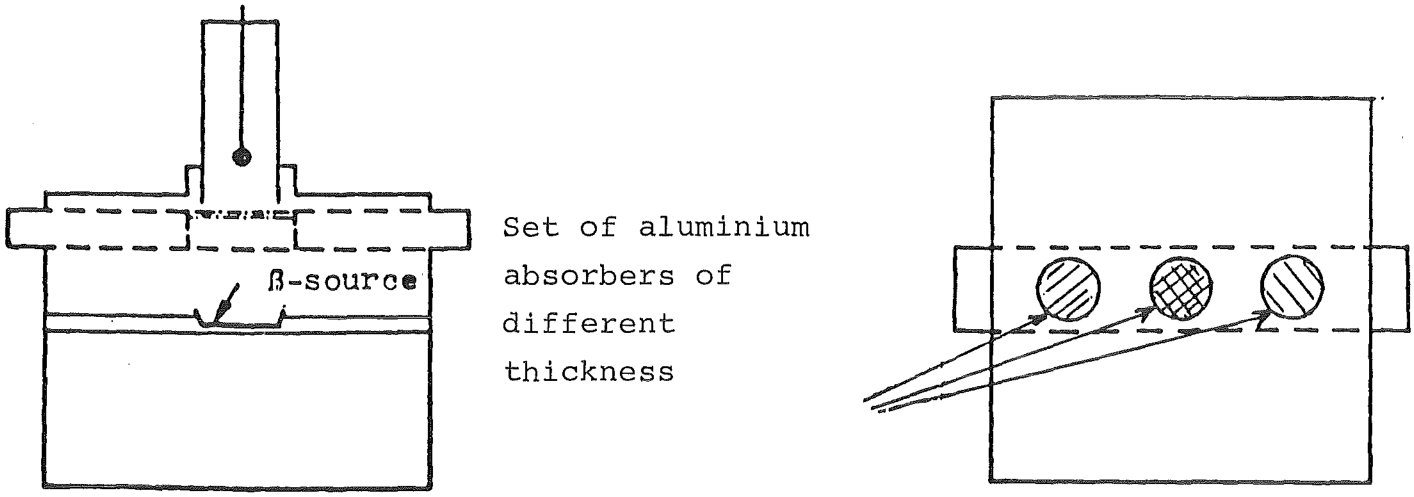


Figure 12: Measuring Apparatus (schematic)

Experimental Details

(1) Determine the background for at least 5 min.

(2) Place the β-source on a shelf in the tube holder at such a distance from the GM tube so that it gives not more than 10.000 counts/minute.

(3) Record for 1 min the counting rate.

(4) Insert an aluminium absorber of about 0.005 mm (1.36 mg/cm^2) thickness between tube and β-source and repeat the count (Figure 12).

(5) Do a series of counts using increasing thickness of aluminium until the counting rate becomes reasonably constant (slightly above the background).

(6) Plot a graph of log counting rate on the y-axis against thickness of absorber in mg/cm^2 on the x-axis. By substraction of the background (includes Bremsstrahlung and possible γ-radiation) you get the β-absorption curve.

(7) Determine the half-thickness from the graph and the maximum range of the β-particles from the point where the graph flattens out (Figure 13).

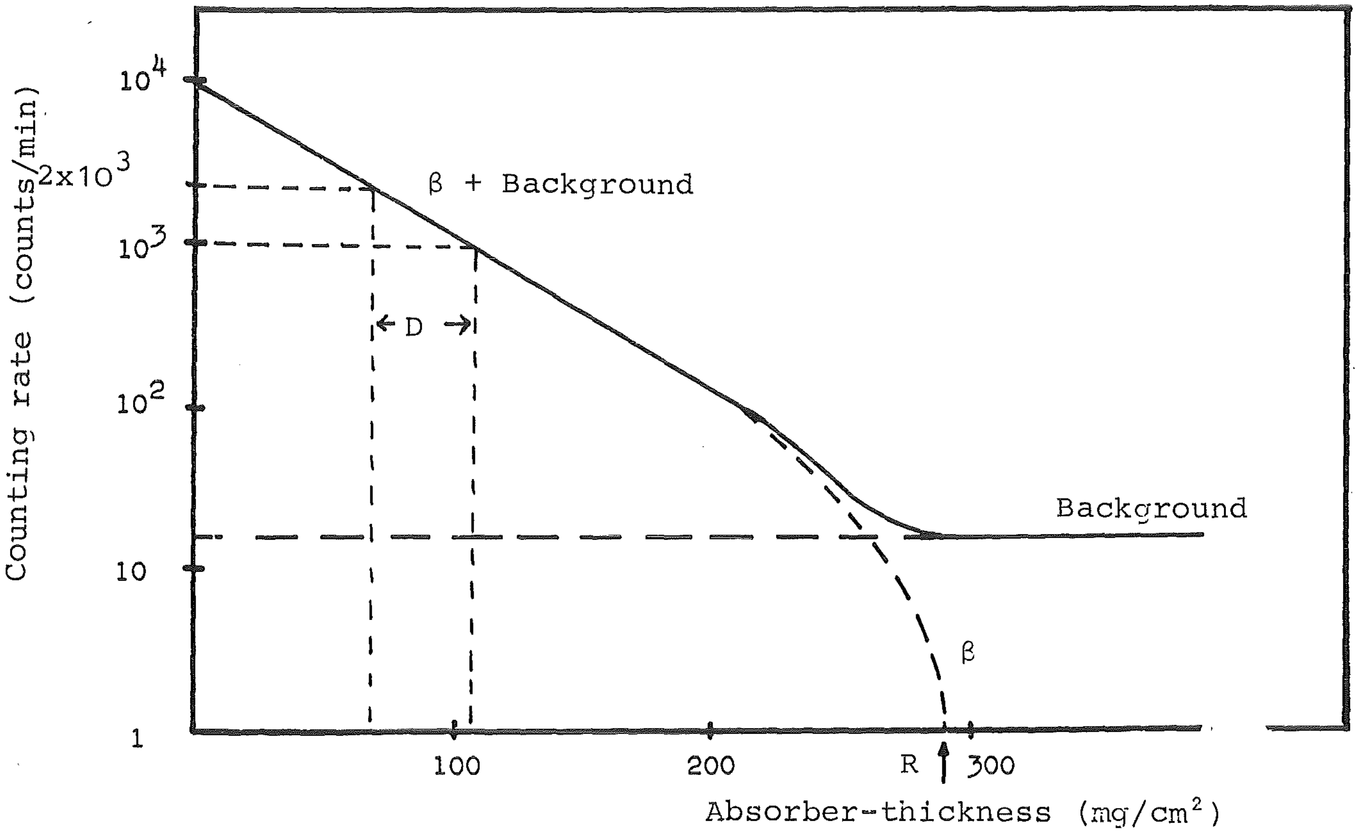


Figure 13: Determination of Half-thickness D and Maximum Range R

(8) Find out the maximum β-energy of the particle using the determined half-thickness and maximum range by use of Figures 15 and 16.

Absorption curves show frequently points of inflection caused by the presence of different components (two β-emitters, β- and γ-emitter, etc.). For the identification of the radioisotopes from their maximum β-energy it is necessary to resolve these curves (Figure 14). Such an analysis would be practicable only if the slopes differ by a factor of at least 2.

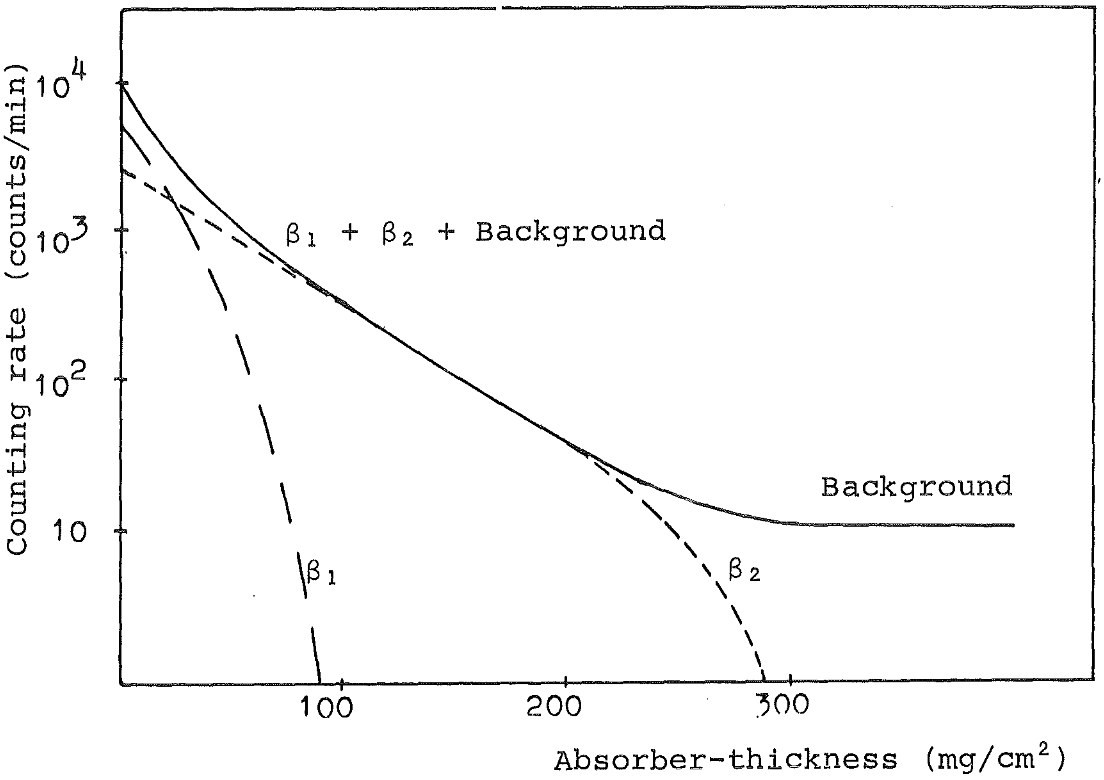


Figure 14: Analysis of the Absorption Curve of a Complex β-Spectrum (2 components):

-Substraction of the background

-Extrapolation of the linear part of the higher energetic component of the obtained graph to the y-axis

⟶ absorption curve of the higher energetic component (β_2)

-Substraction of the determined β_2-curve from the complex absorption curve

⟶ absorption curve of the lower energetic component (β_1)

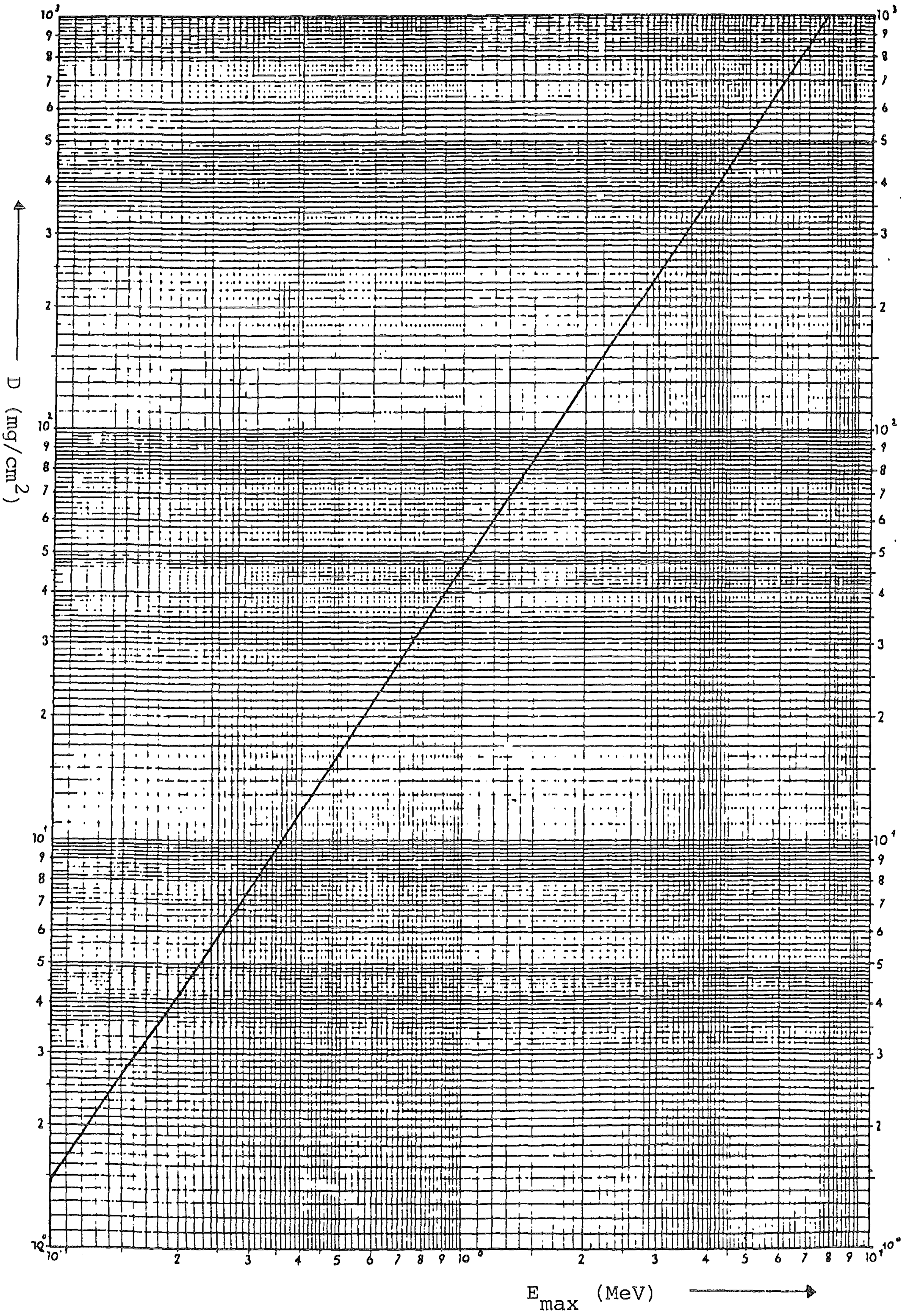


Figure 15: Half-thickness D of Al as a Function of Maximum Energy E_{max} of the ß-spectrum

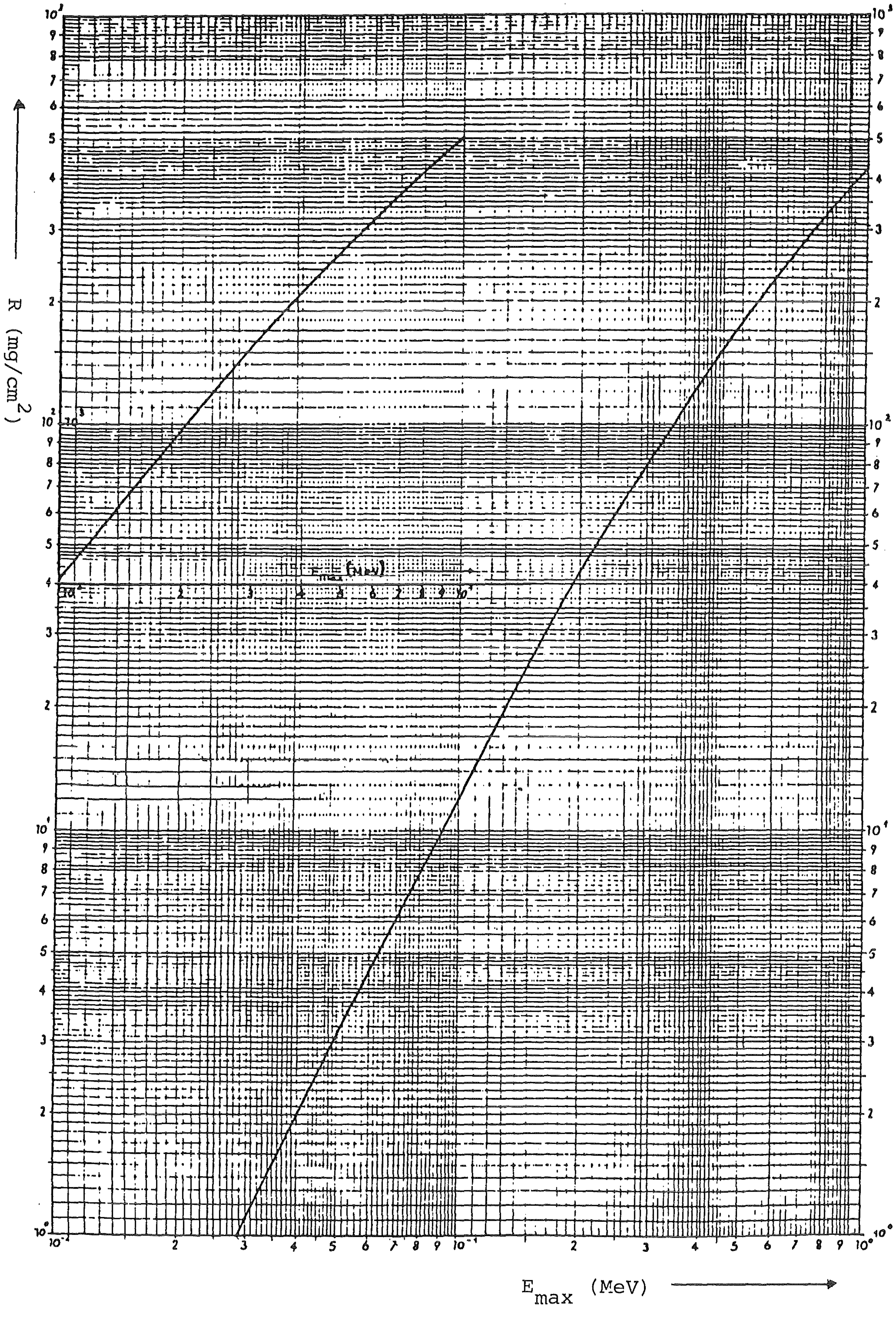


Figure 16: Maximum Range in Al as a Function of Maximum Energy E_{max} of the ß-spectrum

Experiment 6: Attenuation of γ-Radiation

Theoretical Introduction

Gamma radiation is an electromagnetic radiation similar to x-rays and light, but of high energy (short wavelength) and originating from the nucleus. Gamma radiations are associated with transitions between nuclear energy levels frequently accompanying alpha or beta decays. The energy of an excited state is generally lost in a succession of very rapid steps by the emission of several γ-rays. This produces a γ-spectrum which is discontinous unlike the β-spectrum. Due to the absence of charge γ-rays produce very little ionization (about 1.5 ion pairs per cm of path in air), and consequently the penetration is very considerable. The processes causing energy losses in gamma radiation differ essentially from those involved in corpuscular radiation. Gamma radiations produce ionization entirely by transferring their energies totally or partially to electrons; thus ionization is secondary in nature.
Three principle effects are important for the absorption of of γ-radiation: the photoelectric effect, Compton scattering and pair production.

(a) Photoeffect

The photoelectric effect is due to the γ-photon giving up the whole of its energy to an electron, which is ejected from the atom or molecule. Thus the electron aquires a kinetic energy of

$$\boxed{E_{kin} = h\nu - E_b}$$

where E_b is the binding energy of the electron, while the γ-quantum completely disappears (Figure 17).
Following the ejection of an electron, the electronic level is incomplete and has to be restored. In consequence characteristic x-rays can be observed. This effect predominates with γ-rays of low energy and in materials of high atomic number.

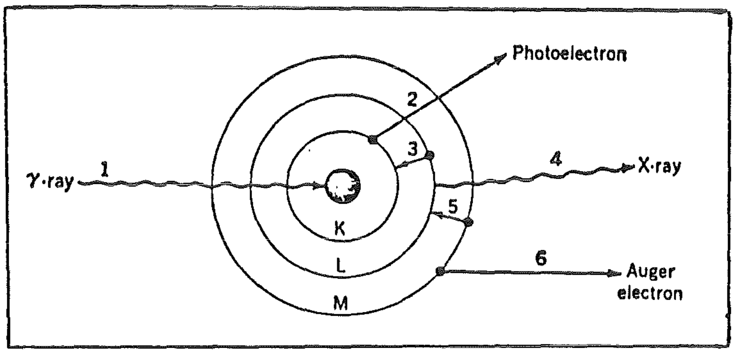


Figure 17: Photoeffect and its Consequences

(b) Compton Scattering

Compton Scattering is due to an elastic collision between a γ-photon and an electron. The incident gamma quantum transfers a part of its energy to an electron which is ejected at an angle in relation to the original path of the photon (Figure 18). Several collisions of this sort may occur until ultimately the photon is photoelectrically absorbed. The energy of the recoil electrons is continuous to a maximum which corresponds to a head-on collision, the photon being reflected through 180°. The Compton effect decreases with increasing energy.

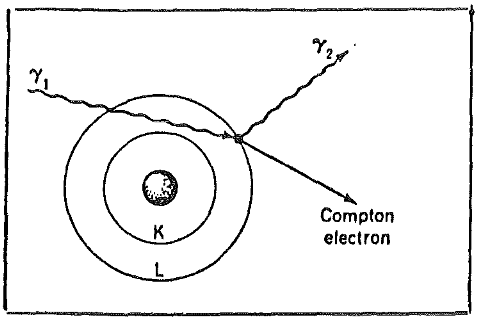


Figure 18: Compton Scattering

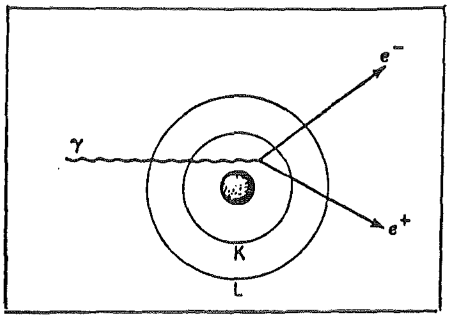


Figure 19: Pair Production

(c) Pair Production

Pair production is a process which involves the creation of a positron-electron pair in the coulomb field of an atomic nucleus by a gamma quant of at least 1.02 MeV (Figure 18). This is the minimum energy of the incident photon for pair production. The photon disappears and its energy is distributed between the energy of the two electrons and their mass equivalent.
The ultimate fate of positrons is annihilation. After they are slowed down by ionization in the same way as electrons, they eventually combine with an atomic electron. Their rest energy is dissipated in the form of two gamma quants each of energy 0.51 MeV, travelling in opposite directions.
Pair production increases with increasing energy.

The energy of a gamma ray can be determined by measurement of the

energy of the photoelectrons,

total energy of pairs,

or maximum energy of Compton electrons.

The first two methods are the most accurate.

A gamma quantum is detected by a GM counter if it is absorbed in the tube wall and ejects an electron or a positron into the sensitive volume of the counter. The absorption of the gamma ray in the counter gas generally can be neglected. The efficiency for γ-rays in GM counters (0.1 %) is much less than for beta rays (up to 8 %). Higher counting efficiencies and more precise energy determination are obtainable by use of solid crystal scintillation and semiconductor counters (see Experiment 7).

During the passage of gamma quanta through a substance, their intensity gradually decreases because of the absorption processes and approaches asymptotically to zero. In contrast to beta radiation, there is no maximum range value here. The absorption of γ-radiation by matter follows an exponential law. If the original intensity is I_0, the intensity I after passing through a thickness d is given by

$$\boxed{I = I_0 \cdot e^{-\mu \cdot d}}$$

where μ is the absorption coefficient. μ is a function of the density of the material. It may be considered as the sum of three separate coefficients characteristic for the photoeffect τ, Compton scattering δ, and pair production κ.

$$\boxed{\mu = \tau + \delta + \kappa}$$

The correlation between these partial absorption coefficients and the gamma radiation energy is given for lead in Figure 20.

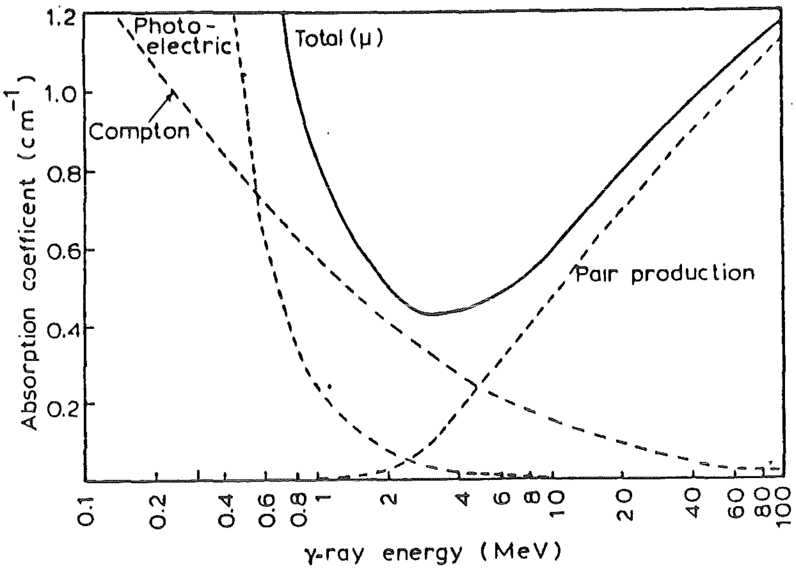


Figure 20: Total and Partial Absorption Coefficients for γ-rays in Lead

At low energies the absorption by photoeffect is predominant, falling off rapidly with increasing energy. At intermediate energies the absorption is mainly due to the Compton effect, whereas at high energies pair production with increasing cross section is most important.

In the following experiment the absorption curve for lead has to be measured and the half thickness D determined. D is given by the thickness of the absorber that diminishes the initial intensity to the half.

The γ-photon energy may then be found from the graph of energy against half-thickness (Figure 20).

Apparatus and Materials

- GM tube (end-window type) with a suitable tube holder
- Scaler/timer
- γ-sources (e.g. ^{137}Cs, ^{60}Co)
- Set of lead absorbers of known thickness (1.09 - 11 g/cm^2)

Experimental Details

(1) Determine the background for at least 5 min.

(2) Place the γ-source on a shelf in the tube holder at such a distance from the GM tube so that it gives not more than 10,000 counts/min.

(3) Record 1 min for each the counting rate with different thickness of lead.

(4) Plot the log of the net activity against the absorber thickness (in mg/cm^2).

(5) If a straight line is not obtained, resolve it into its components and determine the half-thickness D, the absorption coefficient μ, and the mass absorption coefficient μ_m given by

$$\boxed{\ln\frac{I_0}{I_{1/2}} = \ln 2 = \mu \cdot D}$$

or

$$\boxed{\mu_m = \frac{\mu}{\varrho}}$$

where ϱ is the density of the absorber.

(6) Determine the gamma energies from the half-thickness using Figure 21.

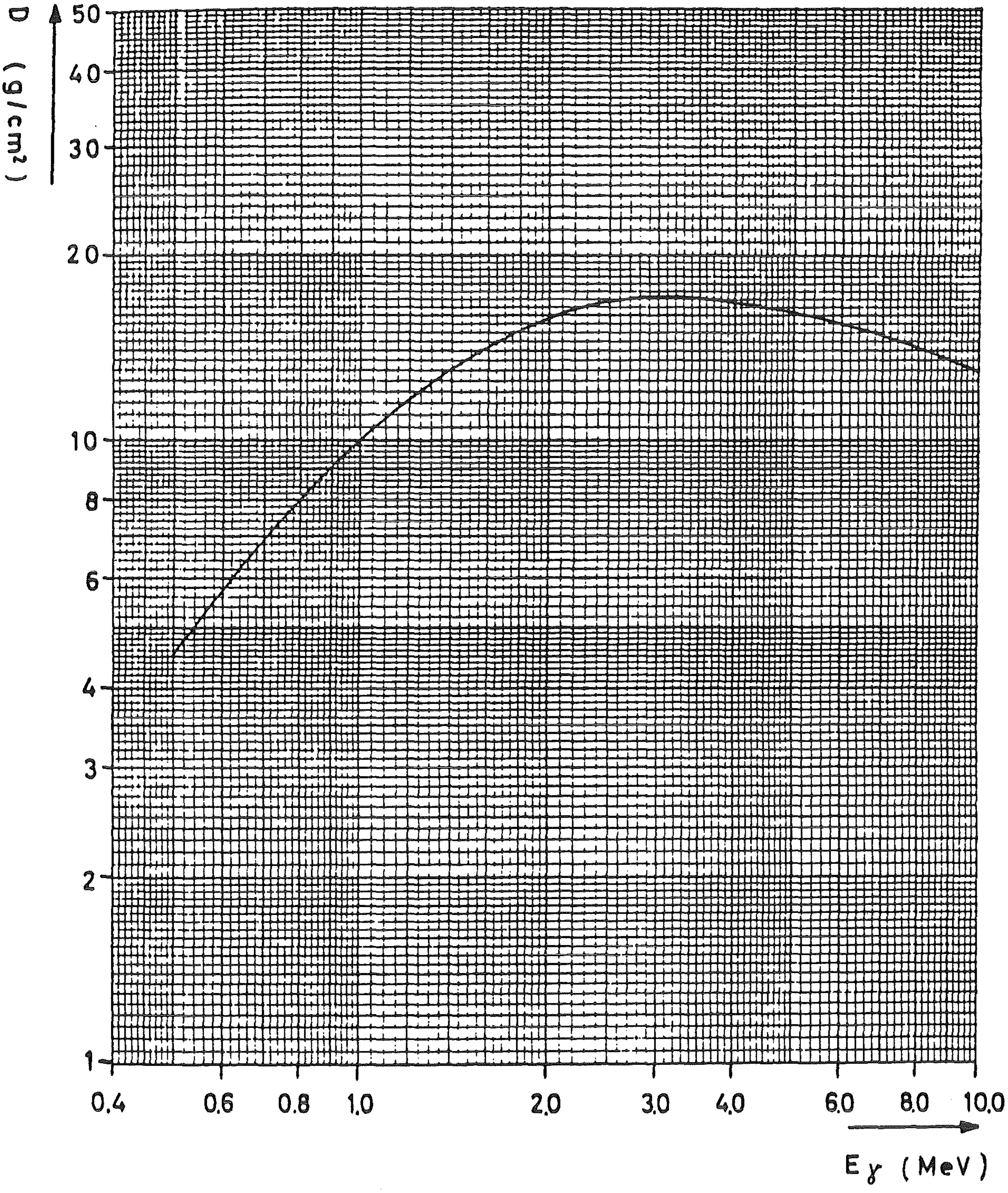


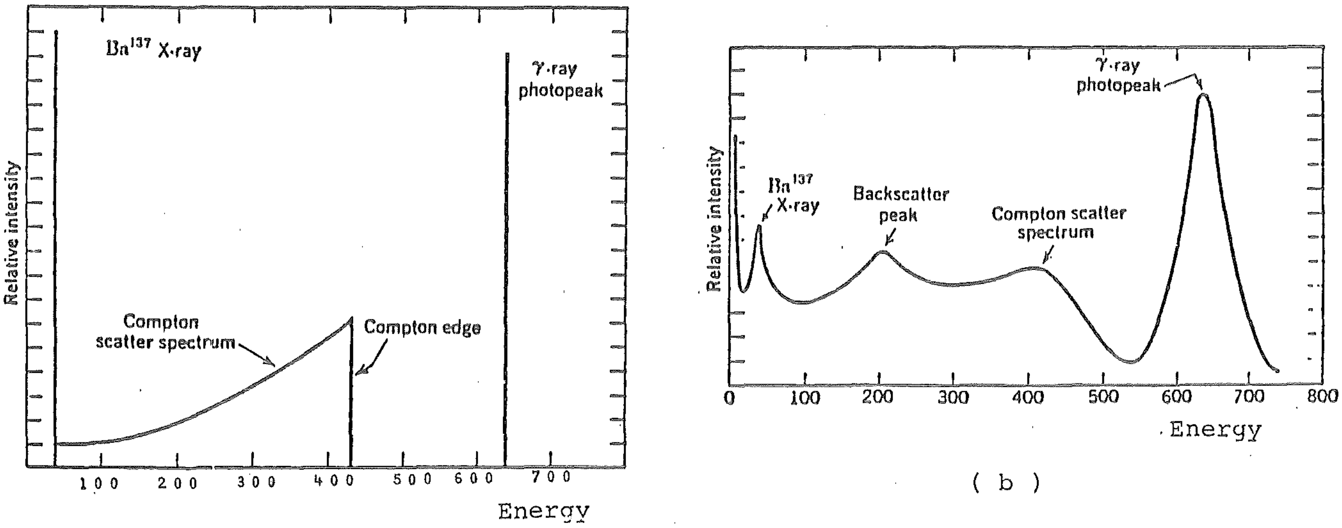
Figure 21: Half-thickness D for γ-photons in Lead Plotted Against the Energy E_γ

Experiment 7: γ-Spectrometry

Theoretical Introduction

Though absorption measurements are useful to determine the thickness required to reduce the γ-radiation from a particular nuclide to special amounts (see experiment 6:'Attenuation of γ-radiation'), it is necessary to use a γ-ray spectrometer to determine the energy precisely. For this purpose a NaI(Tl)-scintillation detector or better a Ge(Li)-semi-conducting detector is connected with a multi-channel pulse hight analyser and scaler. For theory of interaction of γ-quants with matter see Experiment 6.

Every γ-ray belonging to a particular energy group emitted by a given nuclide has exactly the same energy. In consequence the spectrum should exist of sharp lines. In practise however, a γ-spectrometer does not produce a line spectrum but a series of peaks, the centre of the peak corresponding to the energy of the γ-ray, and the base of varying width according to the quality of the scintillation or semi-conducting detector (Fig. 22/24)



(a)

(b)

Figure 22: γ-spectrum from an Ideal Detector (a)
γ-spectrum from an Real Detector (b)

In addition to the peak, which corresponds to the total energy of the γ-ray, lower energy components are also found. These are caused by the various interactions occuring in the crystal.

1: Photoelectric Effect

The result if this type of interaction is the production of photoelectrons with essentially the same energy as of the γ-ray. The great majority of these electrons are completely stopped within the crystal so that the net process is complete deposition of the γ-energy in the crystal. This gives rise to a photo- or full-energy-peak in the spectrum which is proproportional to E_γ.

2: Compton Effect

In this case, only part of the energy of the γ-ray is transferred to the electron. The Compton electrons are stopped in the crystal and the scattered γ-ray may be absorbed by a photoelectric interaction or may escape the crystal. If the former occurs, the total energy deposited is again E_γ and the pulse falls under photopeak.

However, if the γ-quant escapes without further interaction, only the energy of the Compton electron is deposited. It varies from zero to maximum value ('Compton Edge') given by

$$\boxed{E_C \simeq \frac{4E_\gamma^2}{4E_\gamma + 1}} \qquad (1)$$

As a result a very broad Compton peak is present in a γ-spectrum lower than the energy of the photopeak.

The better the chance that photoelectric absorption will occur, the larger will be the photoelectric peak in comparison to the lower energy components, The ratio is dependant on the ionization energy of the photoelectron (NaI ≃ 3oeV, Ge(Li) ≃ 3eV) and the size of the applied crystal (Figure 23).

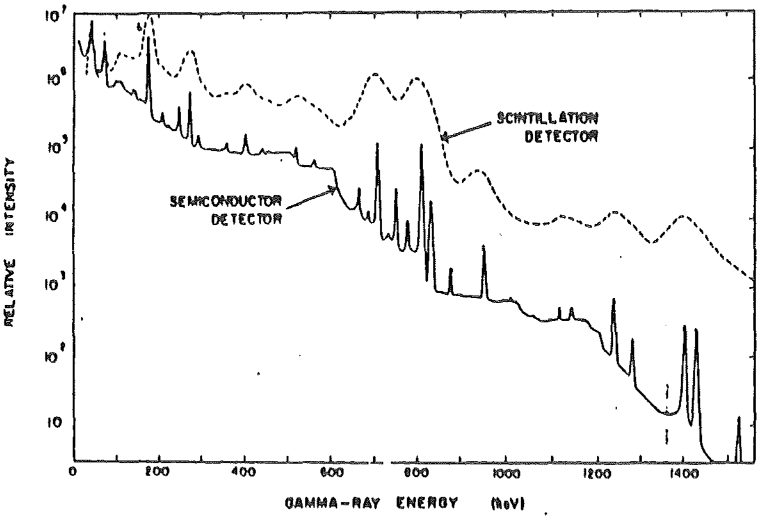


Figure 23: Comparison of Pulse-height Analyser Results for γ-rays from ^{166m}Ho Using Scintillation and Lithium-drifted Germanium Detector.

3: Pair Production

With γ-rays of high energy (>1.02 MeV), pair production also may result. The created negatron is stopped in the crystal; the positron loses energy until it is annihilated by conversion into two photons of 0.51 MeV each. This annihilation radiation (present in the spectrum of any positron emitter) may escape the crystal, or one or both photons may be captured.

Consequently, pair production results in peaks in the spectrum corresponding to

a) the energy of the negatron (double escape peak)
b) this energy plus 0.51 MeV resulting from the capture of one photon (single escape peak)
c) the negatron energy plus 1.02 MeV resulting from the capture of both photons of the annihilation radiation (full-energy-peak).

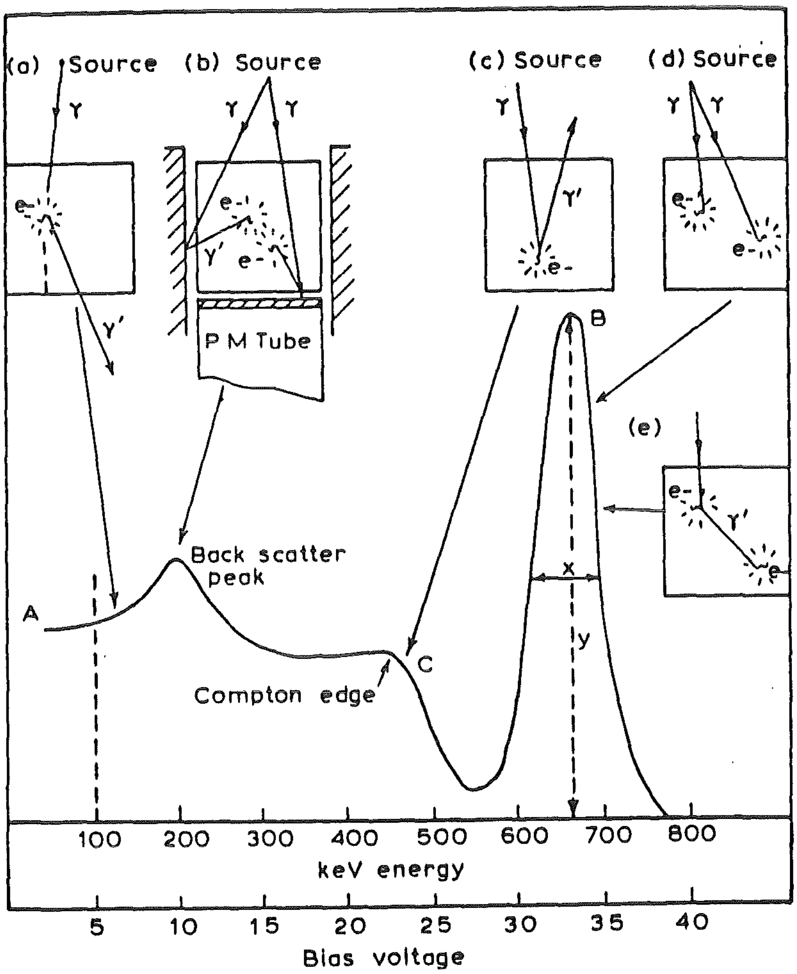


Figure 24: Interaction of γ-rays with a sodium iodide detector and their contribution to the γ-spectrum of ^{137}Cs. e^- shows an electron ejected by a γ-ray. The electron interacts with the phosphor to produce a light photon, the energy of the photon being proportional to the energy given to the electron by the γ-ray. (a), (b) and (c) show various types of scatter which all contribute to the spectrum from A to C. (d) and (e) show photoelectric absorption events, (e) showing scatter followed by photoelectric absorption. Both such events contribute to the photopeak B. γ' indicates a scattered γ-ray.

Apparatus and Materials

- Scaler/timer with multi channel pulse height analyser
- NaI(Tl)-scintillation counter
- Ge(Li)-semi-conducting counter
- ^{137}Cs-source (about 4 kBq)
- ^{22}Na-source (about 4 kBq)
- Unknown γ-emitters

Experimental Details

(1) Place the ^{137}Cs-source near the NaI detector. Set the amplifier gain and polarity so that the peak appears a little below the middle of the display.

(2) Collect the data and identify the photopeak. The mass of data to the left of the photopeak is the Compton distribution with a maximum value at the Compton edge. (A strong peak at low energy is the Ba X-ray at 37 keV, which follows internal conversion.)

(3) Read out the spectrum and make a graph of it (Fig.25)

(4) Place a ^{22}Na-source near the detector. Clear the memory and collect a spectrum again. Read out the spectrum and plot a graph of it (Fig.26).

(5) From the decay scheme (Fig.27) one could expect a similar spectrum. Discuss the dinstinct result compared to ^{137}Cs.

(6) Determine the central channel of each photopeak from the graphs of the ^{137}Cs and ^{22}Na spectrum and plot the gamma ray energy of the peak vs. the corresponding channel. A straight line through the data gives the energy corresponding to each channel of the multichannel analyser (Fig.28)

(7) The calibration curve can now be used to determine the energies of any different γ-ray source. Collect a spectrum of an unknown γ-emitter and determine the energies of the photopeaks.

(8) Calculate the energy of the Compton edge (equation 1) for the ^{137}Cs- and ^{22}Na-γ-rays and compare to the value obtained from the spectrum.

(9) Repeat the measurements (1.-8.) with the Ge(Li)-semiconductor detector and compare the results.

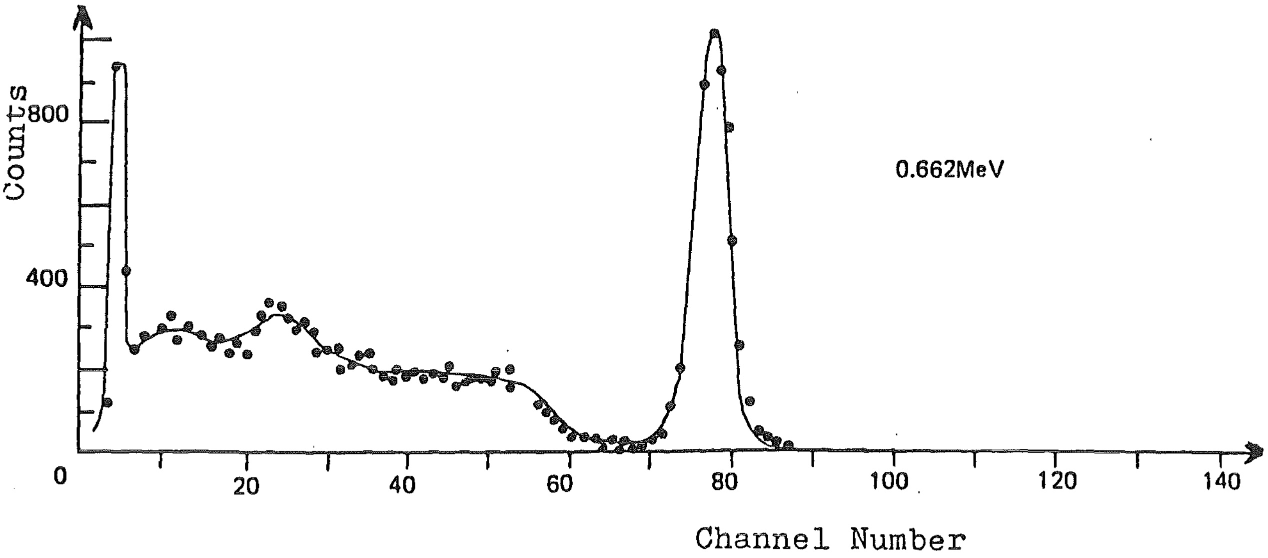


Figure 25: γ-ray Spectrum of ^{137}Cs

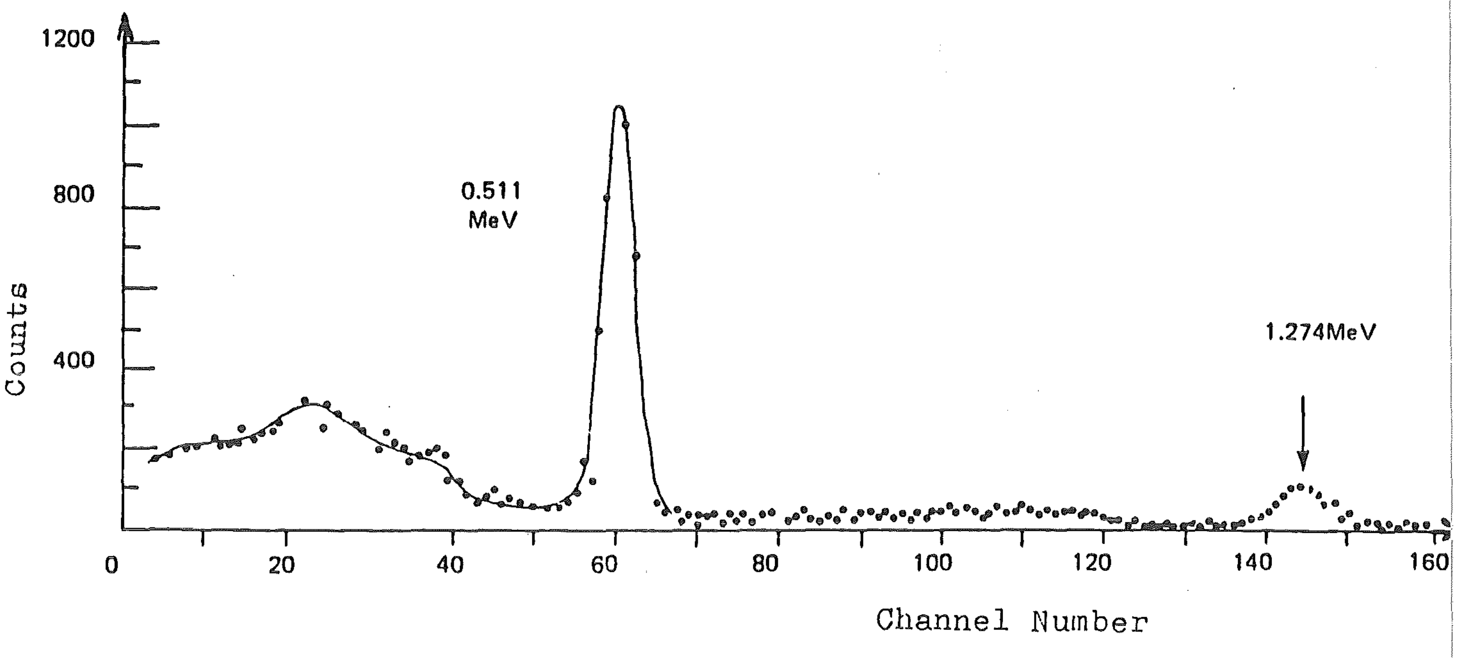


Figure 26: γ-ray Spectrum of ^{22}Na

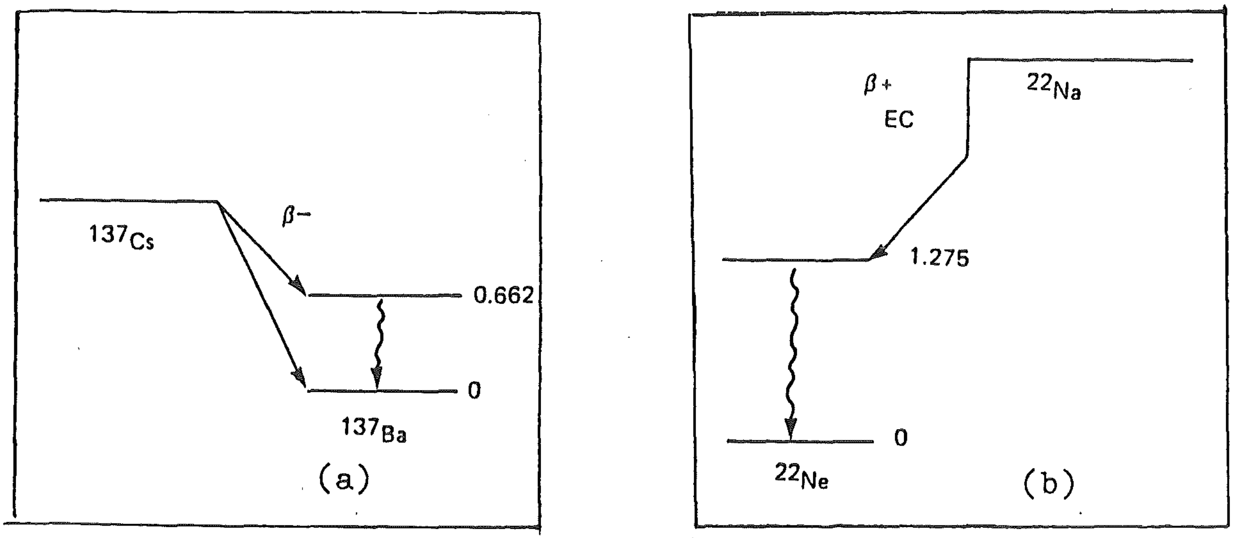


Figure 27: Decay scheme of ^{137}Cs (a) and ^{22}Na (b)

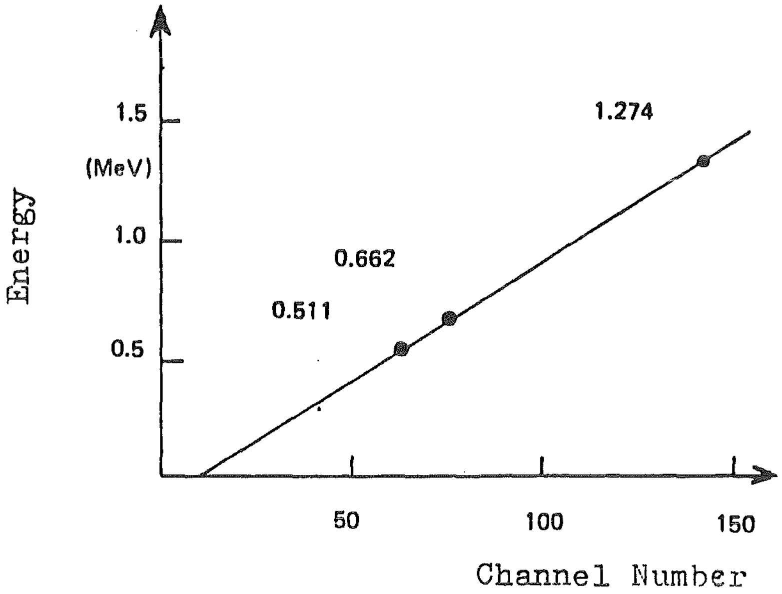


Figure 28: Energy Calibration Curve

Experiment 8: Liquid Scintillation Counting

Theoretical Introduction

The method of Liquid Scintillation Counting enables us to measure samples of low energetic β-emitters (like ^{3}H and ^{14}C) almost without absorption and self-absorption. The advantage over GM-tubes are considerable due to essentially high counting efficienies of the order 90% for ^{14}C and over 60% for ^{3}H. (^{3}H cannot be measured with a GM-tube.). The counter consits of a photomultiplier tube with a glass or plastic vial in optical contact. The vial contains the organic liquid scintillator (e.g. 2,5-diphenyloxazole, PPO) and the sample to be measured dissolved in a suitable solvent (dioxane, toluene). The whole apparatus is completely enclosed to protect it from light photons.

The main problem of Liquid Scintillation Counting consits of 'quenching', a process which interferes with either theproduction of light in the liquid scintillant (chemical quenching), or its transmission to the photomultiplier tube (colour quenching). Colour quneching is due to absorption of some of the light by coloured substances and results in a lowering of the energy of the radiation transmitted to the photocathode. Chemical quenching is caused by interference of dissolved substances (mostly molecules with polar groups like $-NH_2$, $-SH$, $CHCl_3$) involving the transfer of energy from the emitted radiation to the phosphor. It consequently degrades the energy by processes which do not produce emission of light. In consequence, quenching causes a fall in efficiency by shifting the observed β-spectrum into the direction of lower energy (Figure 29). Suitable corrections must therefore be applied.

The main methods used for quench correction involve the use of an internal standard, the sample channel ratio (SCR), and automatic external standardization with different variations.

The principle of the channel ratio method is based on the fact that quenching causes a shift of the whole β-spectrum towards lower energies. If different sections of the spectrum are counted (Figure 30), the ratio of the two counts will vary according to the degree of quenching. This process is carried out by setting an upper and lower discrimination level to each scaler. Using a series of samples with constant known activity but various amounts of a suitable quenching agent (e.g. chloroform), a calibration curve is plotted, appointing to each channel ratio the corresponding efficiency (Figure 31). The determination of the quenching parameter either can be made from the activity of the sample (Sample Channel Ratio SCR), or more conveniently using an external γ-source (External Standard Channel Ratio ESCR). This external standard interacts with the solvent and forms a continuous spectrum of Compton electrons, thus simulating a high activity in the sample and better statistic. Compton electrons undergo a similar energy shift due to quenching and are used as a measure of the reduced efficiency.

Another problem arises from dual-labelled samples (e.g. ^{3}H and ^{14}C). Since both isotopes decay by emission of a beta continuum from zero to the maximum, there will be a partly overlap in the pulse spectrum. A suitable technique for the determination of both isotopes involves setting two channels for counting. While in the upper channel (set with its lower discriminator above the ^{3}H maximum pulse height) only ^{14}C pulses are counted, in the lower window the sum of both nuclides (Screening Method) (Figure 32). The corresponding activities might be calculated by substraction.

Although the usefulness of liquid scintillation is outstanding for the determination of low energetic β-emitters, of course it enables us to follow all processes with direct or indirect emission of light photons.

Due to the intimate contact between the sample and scintillant in form of a homogenious liquid solution, α-particles are counted nearly up to 100%, in contrast to most traditional counters.

High energetic β-particles ($E_{\beta max}$ > 1 MeV) when travelling through a transparent medium at a speed exceeding the velocity of light in the same medium, create Cerenkov-light. This process provides their measurement without scintillator and chemical quenching. Liquid Scintillation as well might be the method of choice for γ-counting (preferably by using a special arrangement, Figure 33), n-detection (in heptane as solvent for fast neutrons or in a boron containing solvent for thermal neutrons), or chemo- and bioluminescence.

Using Liquid Scintillation as counting method the following investigations have to be performed:

(1) Efficiency determination for different types of radiation
(2) Quench correction using the Channel Ratio method
(3) Quantitative determination of unknown ^{3}H- and ^{14}C-samples
(4) Determination of dual-labelled compounds

Apparatus and Materials

- Liquid Scintillation Counter
- Counting vials
- Scintillation cocktail (dioxane, naphtalene, PPO, POPOP)
- Standard solutions: (^{3}H, ^{14}C, ^{32}P, ^{210}Po, ^{60}Co)
- Chloroform (quenching agent)
- Pipettes (50, 100 μl)

Experimental Details

Determination of Unquenched Samples

(1) Preparation of standard samples

Counting vial + 10 ml D-Szint + 100 µl ^{210}Po-standard solution
-"- + -"- + 100 µl ^{3}H -"-
-"- + -"- + 100 µl ^{14}C -"-
-"- + -"- + 100 µl ^{32}P -"-
-"- + 10 ml H_2O(dist)+100 µl ^{32}P -"-
γ-vial + 100 µ ^{60}Co -"-

(2) The prepared samples are measured and the coresponding efficiency calculated from the count rate of the known activity.

(3) The activity of different unknown ^{3}H and ^{14}C samples (unquenched) has to be determined.

Determination of Quenched Samples

(4) The standard sample (^{3}H or ^{14}C) is counted in two adjusted channels (Figure 30) and the corresponding channel ratio calculated.

(5) The measurement is repeated with the same sample after successive addition of increasing amounts of $CHCl_3$

(0.05 - 0.05 - 0.1 - 0.1 - 0.2 ml).

(6) For both isotopes the efficiency η(calculated from the count rates in channel A and the constant, known activity) is plotted against the corresponding channel ratio.

(7) Using the calibration curve the efficiency of the unknown quenched sample is determined and the activity calculated.

Determination of Dual-Labelled Samples (^{3}H and ^{14}C)

(8) With the channel setting from figure 4 the following efficiencies are determined by means of an ^{3}H and ^{14}C standard:

efficiency for ^{3}H in channel A $\longrightarrow$ $\eta_A(^3H)$
efficiency for ^{14}C in channel A $\longrightarrow$ $\eta_A(^{14}C)$
efficiency for ^{14}C in channel B $\longrightarrow$ $\eta_B(^{14}C)$

(9) The count rates of the unknown samples are determined in channel A (R_A) and channel B (R_B), and the corresponding activities calculated by the following formula

$$\boxed{A(^{14}C) = \frac{R_B\ (^{14}C)}{\eta_B\ (^{14}C)}} \quad \text{and} \quad \boxed{A(^3H) = \frac{R_A - A(^{14}C)\cdot\eta_A(^{14}C)}{\eta_A(^3H)}}$$

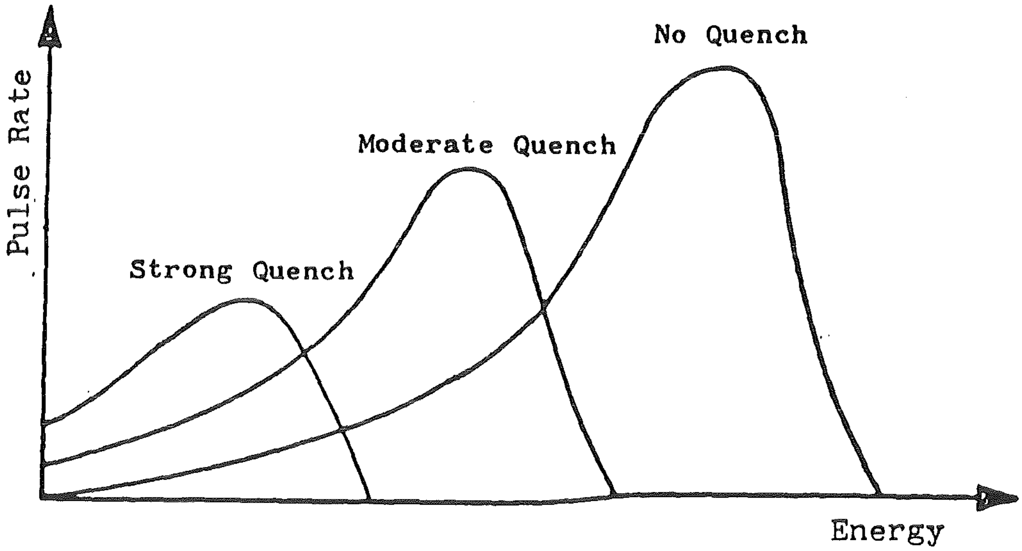
For the dual-labelled quenched samples the efficiencies are dependent on the amount of quenching and have to be corrected before from suitable calibration curves.

Literature

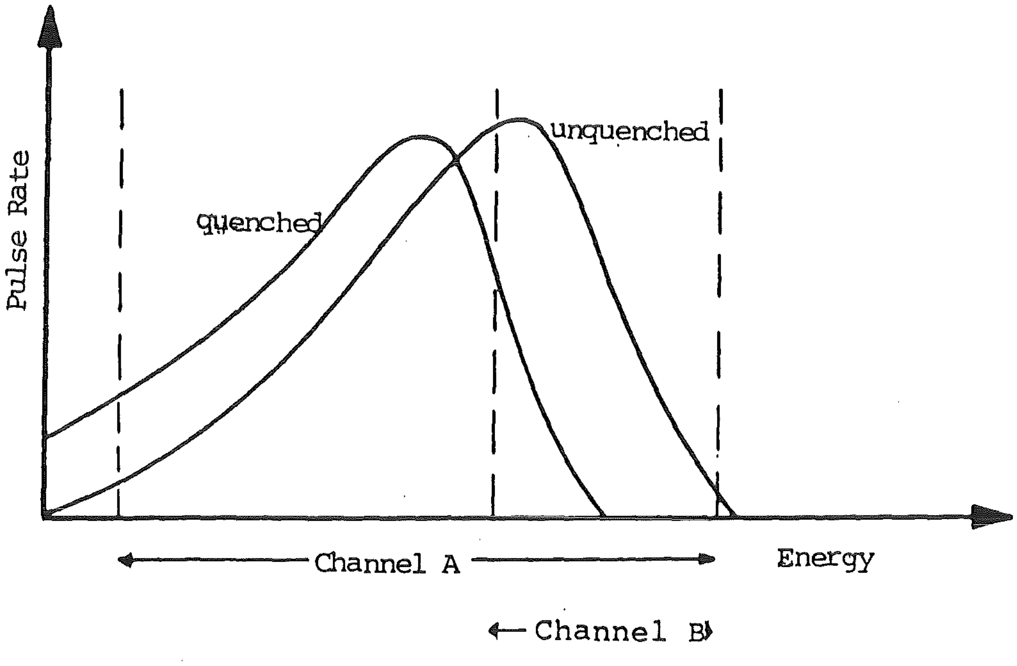
- C.-T. Peng, D.L. Horrocks, E.L. Alpen (Eds.) "Liquid Scintillation Counting, Recent Applications and Development", Volume 1+2, Academic Press, 1980

- P.E. Stanley, B.A. Scaggins (Eds.) "Liquid Scintillation Counting, Recent Developments" Academic Press, 1974

- D.L. Horrocks "Applications of Liquid Scintillation Counting" Academic Press, 1974



<u>Figure 29:</u> Spectra of Different Quenched ^{14}C-samples



<u>Figure 30:</u> Channel Setting for Quench Correction by Channel Ratio

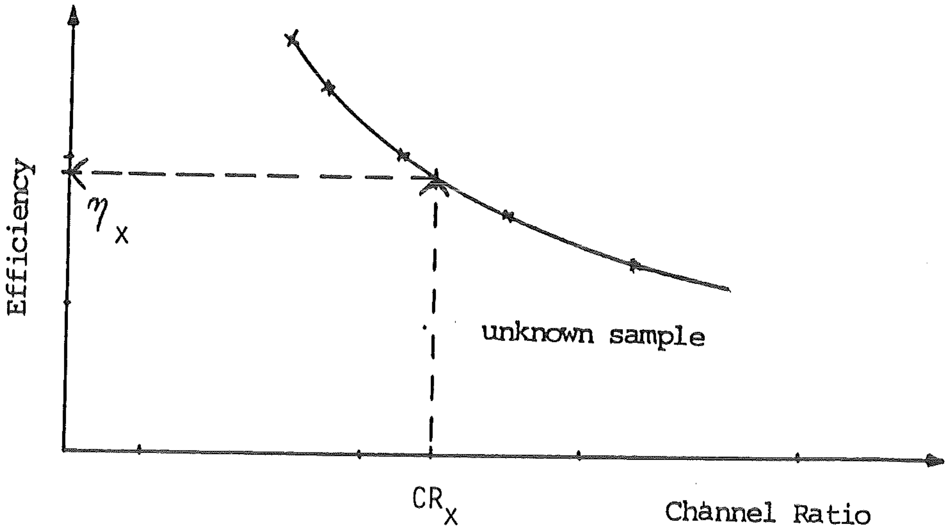


Figure 31: Calibration Curve

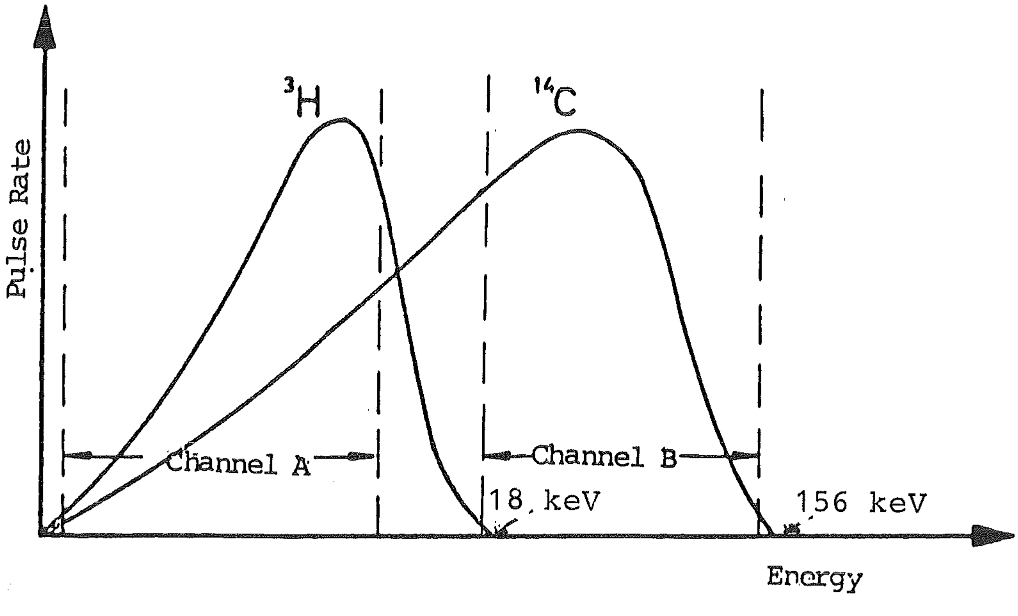


Figure 32: Channel Setting for Measurement of Dual-Labelled Samples

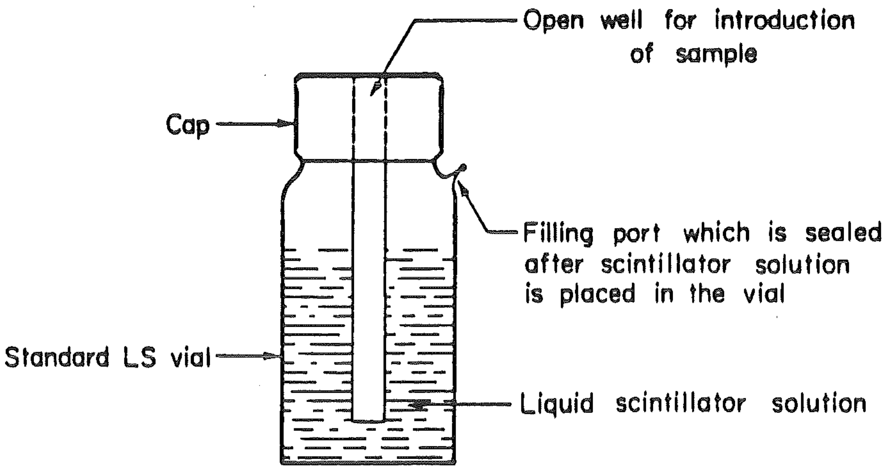


Figure 33: Vial for Counting Gamma Emitters (γ-vial)

Experiment 9: α-Spectrometry

Theoretical Introduction

α-particles (mass 4 a.m.u., charge +2) are characterized by intense ionization and consequently low range. The ionization produced increases as the α-particle slows down, rising to a maximum and then falling abruptly (Bragg curve, Figure 34). To ionize a molecule of oxygen or nitrogen an energy transfer of about 32.5 eV is required. In consequence a 4 MeV α-particle produces some 130,000 ion pairs in air before being stopped, corresponding to about 3 cm of air at S.T.P. or equivalent 0,01 mm of aluminium. α-particles are characterized by a precise energy and therefore show a line spectrum. When decaying from the ground state to an excited state of the daughter, α-active nuclides may emit several different groups of α-particles, each group having a definite energy (Figure 35).

Measuring of α-Particles

α-radiation is absorbed totally already by tiny layer thicknesses. It is important therefore to prevent either self-absorption in the sample by special preparation techniques (i.e. electroplating) and absorption between sample and detector by applying vacuum or intimate contact between radiation and sensitive counting volume (i.e. flow counter, liquid scintillation counter).
Energy determination measurements are practicable, if the α-particles loose their total energy in the sensitive volume of the detector. Despite their low efficiency which is limited by the sensitive surface diameter of $\leq$ 10 mm, solid state crystals in the form of surface barrier detectors for this purpose are applicable (Figure 36). These detectors are of p-n type silicon and are characterized by a narrow depletion layer. They are made of n-type silicon of which one surface has been exposed to air prior to coating with a thin layer of gold, resulting in a gold p-layer ($\leq$0.1 μm). The thickness of radiation sensitive depleted layer is $\leq$ 2 mm, enough to stop α-particles of about 80 MeV

(and electrons of $\leq$ 1.5 MeV, or protons of $\leq$ 20 MeV). To prevent failures due to absorption a vacuum is applied between the detector and the radiation source.

Separation and Sample Preparation

An important method in radiation protection is the determination of actinide elements like plutonium, neptunium and uranium in personal and environmental samples after previous separation (Lit.).

For this purpose the original sample is mineralized, the actinides transfered into anionic chloride complexes and extracted afterwards with the liquid ion exchanger tri-isooctylamine (TIOA).

By back-extraction under definite conditions (8 M HCl/ 0.05 M NH_4I for Pu, 4 M HCl/0.02 M HF for Np, and 0.1 M HCl for U) the actinides are separated. For the measurement on a low-background solid-state counter (surface barrier) the liquid extraction solutions either are evaporated to dryness and flamed, or more accurately electroplated on stainless steel plates. For quantitative spectrometric measurements the detector has to be calibrated by standard α-samples of known energy and activity.

In the following experiment different actinide solutions have to be mounted by electroplating and analysed afterwards by α-spectrometry using semi-conductor-surface-barrier detector. In plotting a calibration curve unknown α-emitters have to be identified.

Apparatus and Materials

- Surface barrier detector
- Multi-channel-analyser
- Liquid scintillation counter (LSC)
- Scintillation cocktail
- Analyte solution
- Standard solutions (^{237}Np, ^{239}Pu, ^{241}Am)
- Electrolytic cell
- Stainless steel plates
- H_2SO_4 (4 M , 1 M)
- NH_4OH (6 M)
- Methyl-red indicator

Experimental Details

Sample Preparation:

(1) For the determination of the absolute activity an aliquot of the analyte solution is mixed with 1o ml scintillation cocktail and measured by liquid scintillation counting in a suitable vial(efficiency for α-particles ≈100%).

(2) The 4 M H_2SO_4-standard and sample solutions are transfered into the electrolytic cell. After addition of methyl-red indicator the solution is titrated dropwise with 6 M NH_4OH until the colour of the indicator changes. With some further drops of H_2SO_4(1 M) the initial colour has to be restored.

(3) After placing the Pt-electrode (positive pole) in the electrolytic cell the solution is electrolyzed at about 200 mA for 90 min (Figure 37). Care should be taken that the stainless steel plates are absolutely clean and free of fat (metal polish, acetone).

(4) To determine the efficiency of electrolysis an aliquot of the solution (100 µl) is measured for activity (liquid scintillation counter) after 30, 60 and 90 minutes of electrolysis time.

Measurement:

(5) After drying (110 ^{0}C) the plates containing the carrier have to be analysed under vacuum with the surface barrier detector.

(6) From the net rates under each peak and the corresponding electrolysis efficiency, the counting efficiency has to be calculated.

(7) Using a calibration curve obtained by plotting the energy of the known α-particles (table 2) against the corresponding channel number the unknown nuclides should be determined.

Literature

- F.E. Butler, S.C. Aiken
  in "Quick Methods for Radiochemical Analysis"
  IAEA-Technical-Report-Series No.95, Vienna 1969

Table 2: Decay Energies of Different α-nuclides

Nuclide	Decay Energy (MeV)
Po-210	5.3045 ...
Ra-226	4.78450; 4.6019 ...
U-233	4.824; 4.783 ...
Np-237	4.788; 4.770 ...
Pu-239	5.155; 5.143 ...
Am-241	5.486; 5.443

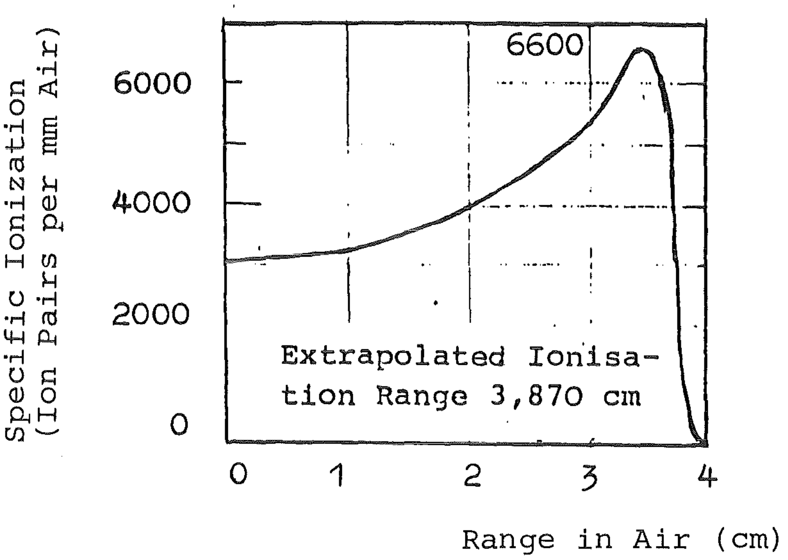


Figure 34: Specific Ionisation of α-radiation of ^{210}Po in Air as a Function of Way (Bragg Curce)

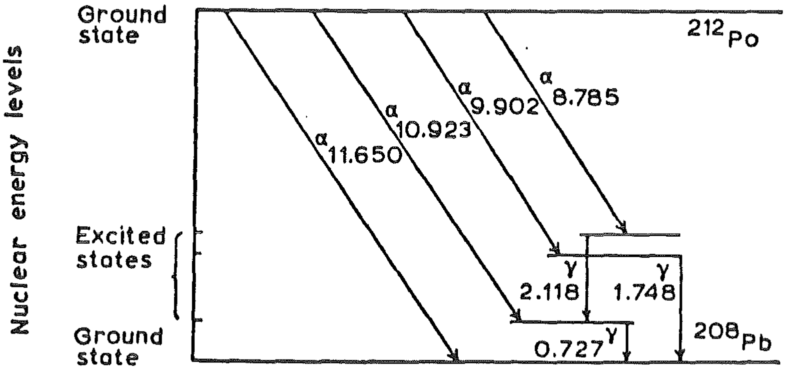


Figure 35: α-decay of ^{212}Po (the units are in MeV). The figure shows why α-emission is frequently accompanied by γ-emission since the product nucleus, in this case ^{208}Pb, may be in an excited state. The excess energy must be emitted as a γ-ray.

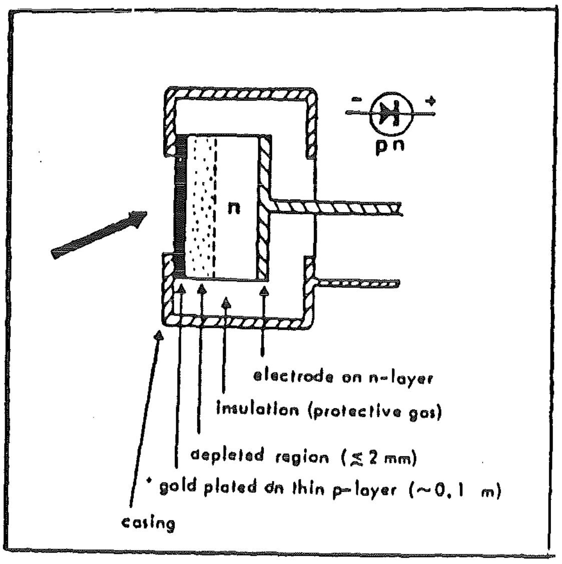


Figure 36: Surface Barrier Detector; the Thickness of the Gold and the p-layer is exaggerated.

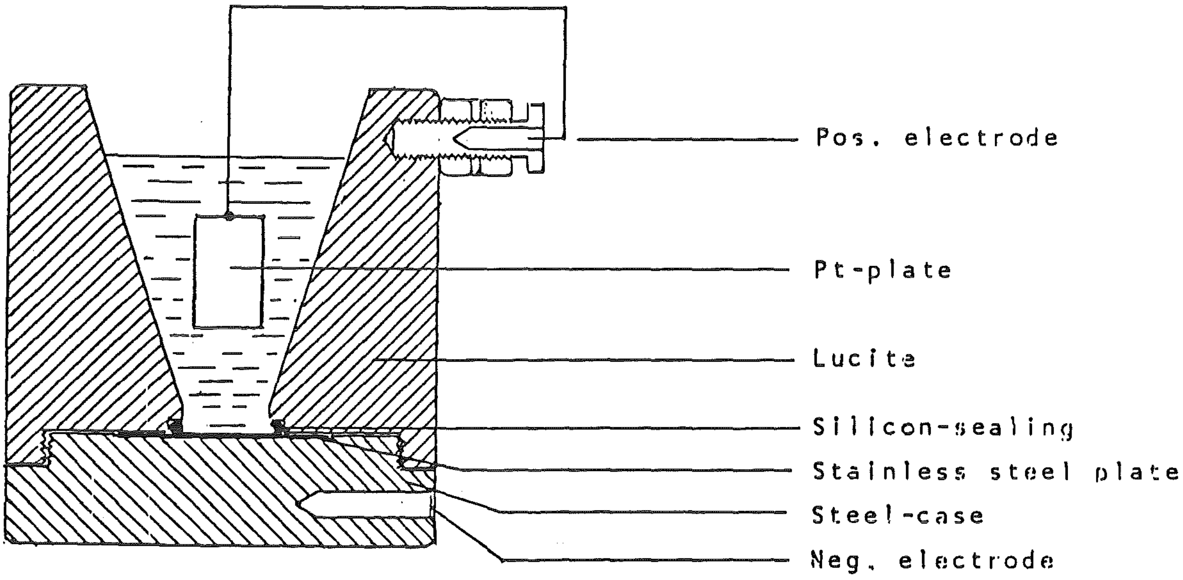


Figure 37: Electrolytic Cell

Experiment 10: Moderation and Absorption of Neutrons

Theoretical Introduction

Neutrons, discovered in 1932 by Chadwick, have a mass of 1 and charge of 0. As free particles they are unstable and decay by β^- ($T_{1/2} \simeq 10$ min) to a proton, an electron and an antineutrino. As they are easily captured by nulei when reduced to thermal energy, this process is rarely.
Free neutron arise essentially by induced nuclear fission e.g.

$$\begin{tikzcd} & & \text{2 fission products} \\ {}^{235}\text{U} + \text{n(thermal)} \arrow[r] & \left[{}^{236}\text{U}\right]^{*} \arrow[ur] \arrow[dr] & \\ & & \text{2-3 neutrons(fast)} \end{tikzcd}$$

spontaneous nuclear fission (^{252}Cf, 2.3×10^{12} n/s·g), in accelerating units by (p,n)- or (d,n)-reactions and in laboratory scale by radioactive neutron sources. The most common sources used are made of Ra-Be or Am-Be

^{9}Be ($\underset{\uparrow}{\alpha}$,n) ${}^{12}_{6}$C (1.5×10^{7} n/s per g Radium and 8×10^{6} n/s per g
Ra Americium)
Am

Neutron sources making use of the (γ,n)-reaction have a low efficiency but produce monoenergetic neutrons.
Being uncharged, neutrons produce no direct ionization in air and their penetration of matter is considerable, particularly in materials of high atomic number. They are slowed down ('moderated') by elastic collisions, preferably of nuclei of low atomic number (hydrogen, deuterium, carbon, etc.). Due to the high capture cross section of hydrogen, ($\sigma_{n,\gamma} = 0.3$b), deuterium is used as a moderator in nuclear reactors working with non enriched fuel.
Fast neutron cause a considerable biological hazard due to ionization produced in the body by collision with protons (backscattering). Shielding is commonly performed by water, paraffin, or carbon for neutron moderation, cadmium for the absorption of the moderated 'thermal' neutrons ($\simeq 0.05$ eV), and lead for the absorption of accompanying γ-radiation.

The detection of neutrons proceeds either by recoil protons or indirectly throughout a nuclear reaction. The counter tube most often used, consists of a boron (BF_3) gas containing counter working either in the GM, proportional or ionization region. Thermal neutrons, when entering the tube react with ^{10}B according to $^{10}B(n,\alpha)^7Li$, thus forming α-species that are detected by their ionization (Figure 38). The use of suitable metal foils instead is based on the determination of the induced activity.

In the following experiment a suitable shielding for a Am-Be neutron source has to be evaluated.

Apparatus and Materials

- n - source (e.g. Am-Be)
- NaI(Tl)-scintillation detector
- Boron counter tube
- Absorber materials (Pb, paraffin, B, Cd)

Experimental Details

The experimental detail is given in Figure 40.

The count rate of the following arrangments have to be determined (Figure 39).

(1) BF_3 / NaI (background)
(2) source - BF_3 / NaI
(3) source - paraffin - BF_3 / NaI
(4) source - lead - paraffin - BF_3 / NaI
(5) source - lead - paraffin - boron - BF_3 / NaI
(6) source - lead - paraffin - cadmium - BF_3 / NaI
(7) source - paraffin - cadmium - lead - BF_3 / NaI

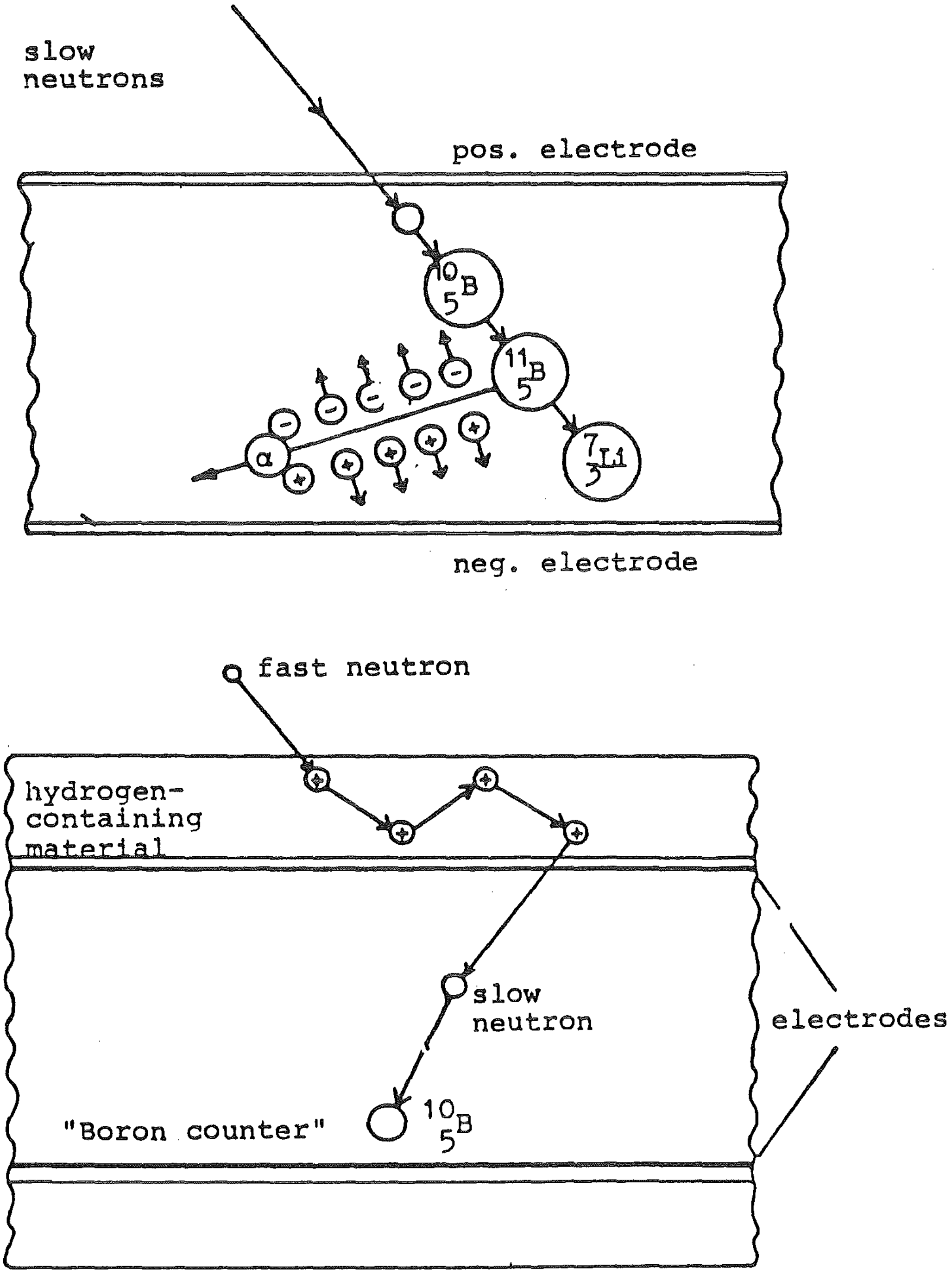


Figure 38: Detection of Neutrons: Boron Counter

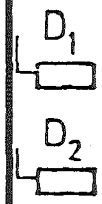
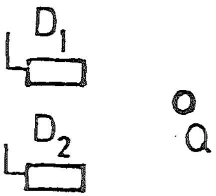
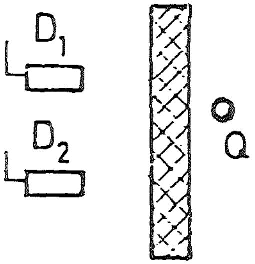
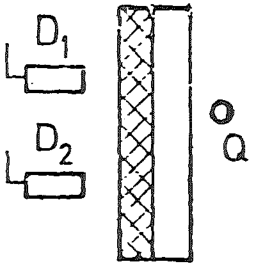
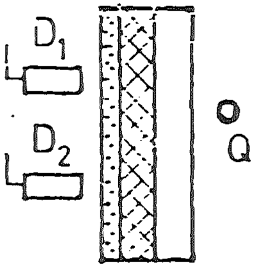
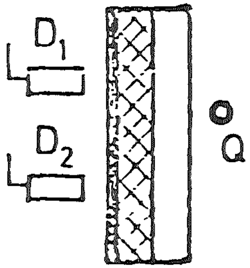
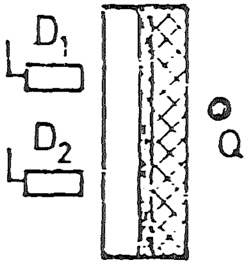
Q: SOURCE D: DETECTOR ☐ Pb ▨ Paraffin ░ B ▓ Cd	(1)  	(2)  	(3)  	(4)  	(5)  	(6)  	(7) 
D_1 SCINTILLATION COUNTER (cpm)							
D_2 BF_3-COUNTER (cpm)							

Figure 39: Shielding of a Neutron Source

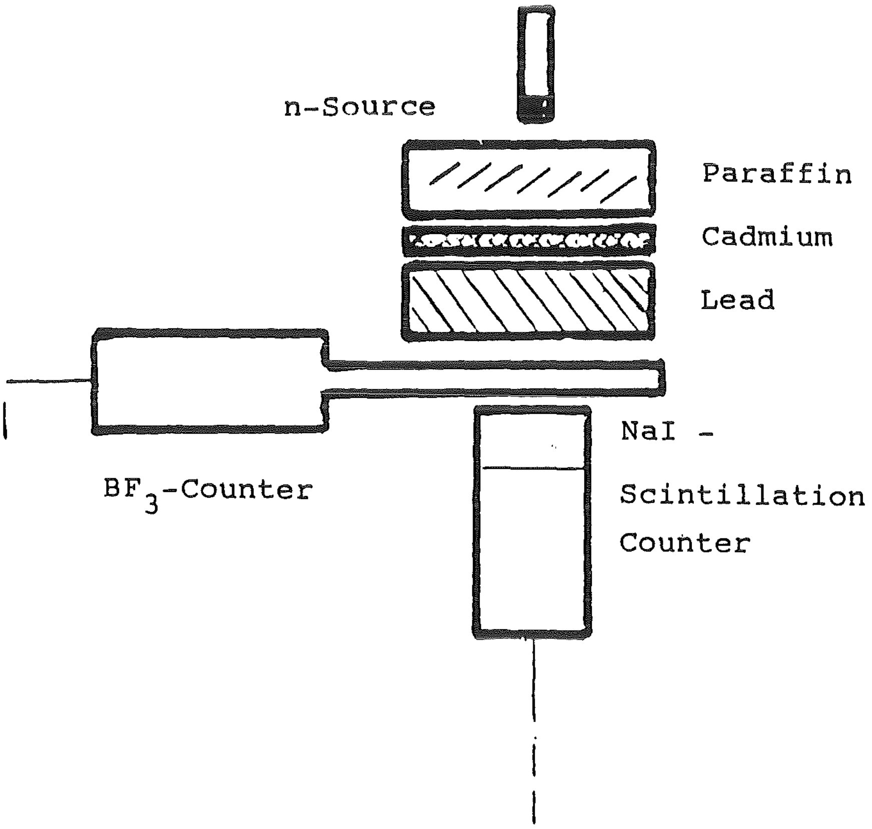


Figure 40: Experimental Arrangement for Moderation and Absorption of Neutrons

Experiment 11: Computer-Aided Evaluation and Education in Radiation Measuring

Theoretical Introduction

The following outline includes a summary of useful programs within a nuclear and radiochemistry training running on any IBM (e.g. XT) or IBM compatible personal computer. They include the following fields

a) Simulation of Costly Equipment (e.g. spectrometer)
b) Data Evaluation
c) Drawing Graphics
d) Educational Training Programs.

In the simpliest way the computer system consists of a personal computer for each group, having a double floppy system, a monitor, a keyboard, and a printer (for two groups each). A compilation of useful functions and commands (in DOS) is given at the end of this chapter. All programs will be running from MS-DOS with the appropriate command in quotation marks.

a) Simulation of Costly Equipment

- Program "V" simulates a γ-spectrometer with the general possibilities for display manipulation. Included are spectrum-display, energy calibration, qualitative and quantitative peak evaluation.

- Program "ALPS" enables the display of various α-spectra and its evaluation similar to "V".

- Program "SUPPORT" enables the graphical display of spectra from various emitters, especially low energy β-emitters measured with a Liquid Scintillation Counter. The superposition, substraction or addition of different spectra indicates the problem of quenching and dual labelling in Liquid Scintillation Counting.

b) Data Evaluation

- The commercially available program "SPEKTRAN F" provides a qualitative and quantitative high resolution γ-spectrum evaluation if the efficiency of the selected geometry is known.

c) Drawing Graphics

- "P71" provides a graphical display of the β-absorption curve measured in experiment 5. The statistical deviation (σ, 2σ etc.) as well as an instruction for curve evaluation is shown.

- "P207" provides the display of the evaluation diagram from experiment 21 in linear and semilog mode.

d) Educational Training Programs

- The training programs "P208" and "P67" summarize the characteristic features of radiochemical methods. The results of experiment 17 and 18 are discussed.

- "P219" provides a graph of the time function in activation analysis (see experiment 28). The influences of measuring time and cooling time on any given practical problem are discussed and displayed.

Function	Command or Key
display of content of disk	DIR
output on printer	PRINT
copy of disk	DISKCOPY
printout of display	Shift - PrtSc
reinicialization of DOS	Ctrl - Alt - Del

Experiment 12: Instrumental Identification of Unknown Radionuclides

Theoretical Introduction

To identify the radionuclides in a mixture of radioactive material, informations must be obtained either on

- the atomic number (from chemical reactions that characterize the nuclide as isotope of a known chemical element)
- the half life (directly measured or from analysis of a complex decay curve)
- type and energy of the emitted radiation (α-, γ-spectrometry, determination of β-maximum energies by absorption curves).

In the present experiment type and energy of an unknown radionuclide solution should be determined.

The following considerations should be kept in mind:

1. Several radionuclides genetically related may be present.
2. There may be some type of radiation with several energy groups in a special relation.

Apparatus and Materials

- GM counter (end-window type) with a suitable tube holder
- NaI(Tl)-scintillation counter or Ge(Li)-semiconductor counter with multi-channel pulse height analyser
- Unknown radionuclide solution
- Set of aluminium absorber of known thickness (1.36-1620 mg/cm^2)

Experimental Details

(1) Put a definite volume of the unknown radionulcide solution into an Al-planchette and dry it carefully (not too long, for some radionuclides could be volatile).

(2) γ-ray energies may be determined by means of a scintillation or semiconductor counter (see experiment experiment 7).

(3) β-radiation may be determined from their maximum energy applying absorption measurements with the GM counter (see experiment 5).
The sample has to placed in a suitable distance to the detector, so that loss of counts due to coincidences may be excluded ($\leq$ 10,000 cpm).

(4) The presence of α-emitters may be identified by absorption onto a thin foil or use of a proportional counter.

(5) From the resulting informations above, the present radionuclide may be selected refering to the following tables 3 and 4.

Table 3 : β-maximum Energies of Some Nuclides

E_β [MeV]	Nuclide	Half-life	Daughter Nucl.	Other β-ray Energies [MeV]	E_γ [MeV]
3.55 (67,2%)	Rh-106	30 s	Pd-106(stab.)	3,05(12,5%); 2.39(17%)	0.51;0.62,...
2.99 (97.7%)	Pr-144	17.3 m	Nd-144	2,30(1.2%);0,81(1,0%)	0.697, ...
2.27 (100%)	Y-90	64.8 h	Zr-90 (stab.)	0,52(0.02%)	...
1.71 (100%)	P-32	14.3 d	S-32 (stab.)	---	---
1.16 (~100%)	Bi-210	5.0 d	Po-210	---	...
0.766 (98%)	Tl-204	3,8 a	Pb-204(stab.)	---	---
0.61 (87%)	I-131	8.05d	Xe-131(stab.)	0,33(9.3%),...	0.36,...
0.546 (100%)	Sr-90	28 a	Y-90	---	---
0.53 (36.9%)	Ag-110m	253 d	Cd-110(stab.)	0.085(62.5%!),...	0.66;0.89,...
0.51 (93.5%)	Cs-137	30 a	Ba-137m	1.18 (6.5%)	---
0.31 (~100%)	Co-60	5.26a	Ni-60 (stab.)	1.48 (0,1%)	1.17;1.33
0.31 (76%)	Ce-144	284 d	Pr-144	0.18 (24%)	0.134,...
0.167 (100%)	S-35	88 d	Cl-35 (stab.)	---	---
0.156 (100%)	C-14	5730 a	N-14 (stab.)	---	---
0.085 (62.5%)	Ag-110m	253 d	Cd-110(stab.)	0.53 (36.9%), ...	0.66;0.89,...
0.039 (100%)	Ru-106	1.0a	Rh-106	---	---
0.015 (80%)	Pb-210	~22 a	Bi-210	0,061(20%)	0.047

Table 4 : γ-ray Energies of Some Nuclides

E_γ [MeV]	Nuclide	Half-life	Other γ-ray Lines [MeV]	$E_{\beta max}$ [MeV]
1.33 (100 +) [1] 1.17 (100 +)	Co-60	5.26 a	...	0.31 (~100%) [2], ...
0.89 (73 +) 0.66 (100 +)	Ag-110m	253 d	0.94 (33 +) 1.38 (25 +)	0.085 (62.5%) 0.53 (36.9%)
0.697(100 +)	Pr-144	17.4 m	....	2.99 (97.7%),...
0.66	Ba-137m	2.6 m	---	---
0.62 (44 +) 0.51 (100 +)	Rh-106	30 s	1.06 (6 +), ...	3.55 (67.2%), ...
0.36 (100 +)	I-131	8.05 d	0.64 (9 +), ...	0.61 (87%), ...
0.134(100 +)	Ce-144	284 d	0.08 (18 +),...	0.31 (76%), ...
0.047	Pb-210	22 a	---	0.015 (80%), ...

1) Relative intensity (most intense γ-ray line = 100 +)

2) Intensity of the mentioned decay in per cent of the decays

Exercises to 3.3.1

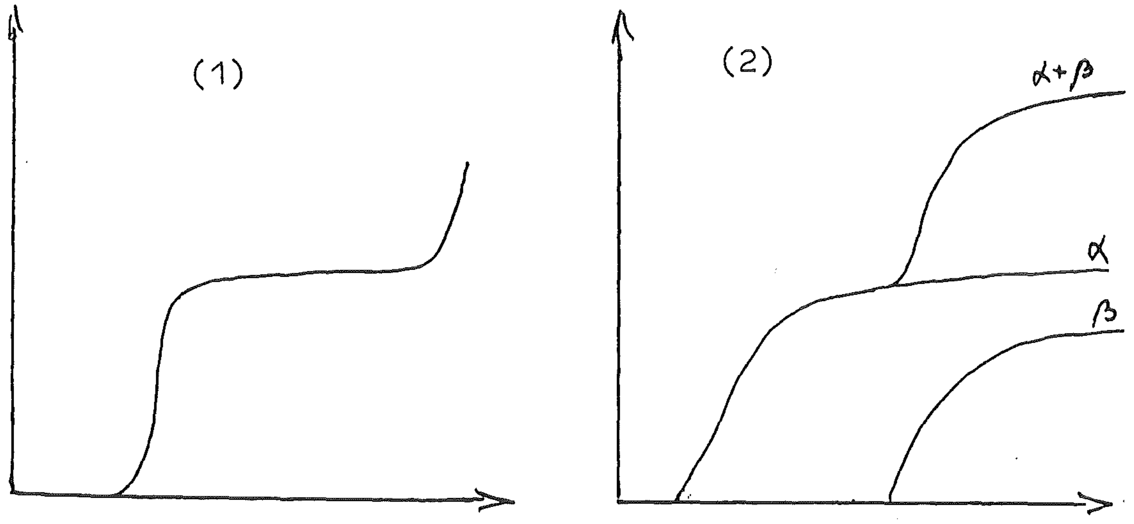
1. Explain the difference between
   (a) Activity
   (b) Emission rate
   (c) Count rate (or measuring rate)
   (d) Net rate

(Experiment 3)

2. Give the legend of abscissa and ordinate for a
   (a) calibration curve
   (b) Pulse height spectrum (Experiment 7)

3. The following figures show the characteristics of a GM (1) and a proportional counter (2).
   (a) Give the correct legends for x- and y-axis!
   (b) Mark the working voltage for α- and β-counting in each characteristic!

(Experiment 2)



4. Which is the correct sequence for an optimum Am/Be-source shielding (Pb, Cd, paraffin) ?

5. Describe the three principle effects responsible for the absorption of γ-rays.

(Experiment 6)

6. Explain the formation and practical value of the following characteristics in γ-spectrometry

   1: photopeak

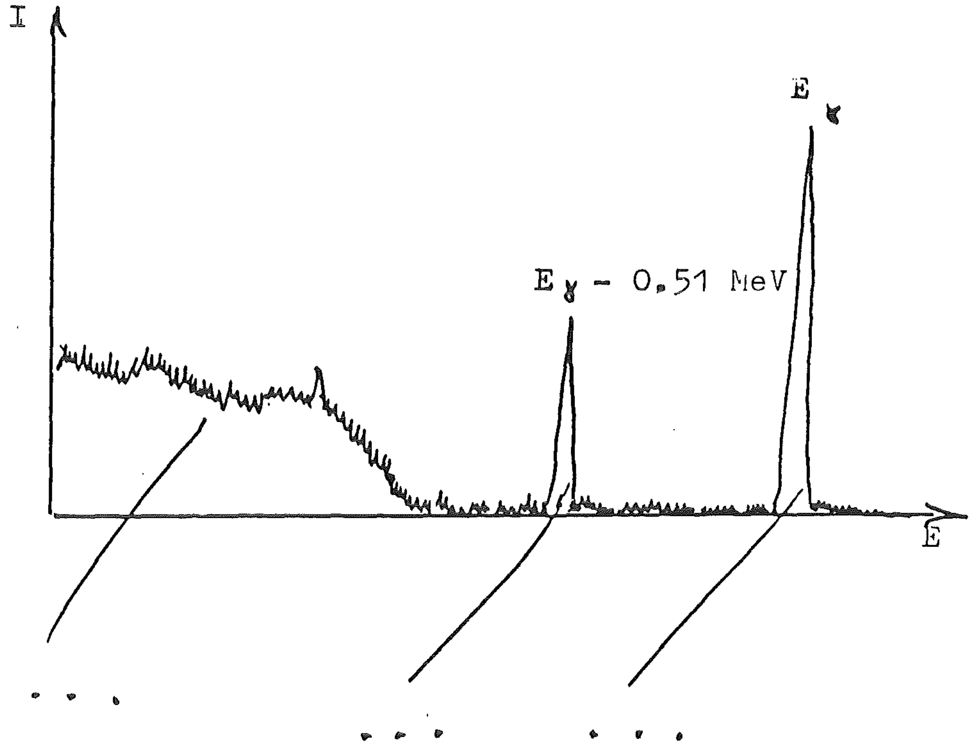
   2: 'Compton' spectrum

   3: single escape peak

   4: double escape peak

   Characterize the spectrum below!

(Experiment 7)



7. What does 'Quenching' mean in Liquid Scintillation Counting? Describe a method for its correction!

(Experiment 8)

3.3.2 Radiochemical Methods (Experiments)

Experiments:

13. Growth and Decay Rates in the System $^{137}Cs/^{137m}Ba$

Objective: The student should get familiar with the laws of radioactive decay. The half-life has to be determined by taking a decay curve.

14. Half-Life determination of ^{238}U

Objective: The half-life of a long-lived radionuclide has to be found out by determination of the absolute activity of a weighed amount.

15. Radionuclide Separation by α-Recoil

Objective: α-Recoil as a nuclear-physical separation method has to be learnt and applied.

16. Examination of $^{32}PO_4^{3-}$-Adsorption on $Fe(OH)_3$

Objective: The dependence of adsorption on the amount of carrier present has to be examined.

17. Scavenger-Precipitation

Objective: The student should be able to apply scavenging as method for decontamination and preconcentration of radionuclides.

18. Precipitation With Nonisotopic Carrier

Objective: Carrier precipitation as radiochemical separation method has to be applied in the U-decay-series.

19. Separation of ^{106}Rh from ^{106}Ru by Precipitaion

Objective: Isotopic carriers for radiochemical separation of the short-lived ^{106}Rh from ^{106}Ru have to be employed.

20. Solvent Extraction With Tri-n-Butyl-Phosphate

Objective: The PUREX-process in reprocessing of spent nuclear fuel has to be learnt and applied to a simulated feed solution.

21. Separation of Fission Products by Anion Exchange

Objective: Ion exchange as distribution method is reviewed. The students should be able to separate a fission nuclide mixture by anion exchange.

22. Preparation of a Carrier-Free ^{234}Th-Standard Solution

Objective: The method of solvent extraction and ion exchange has to be applied for preparation of a carrier-free ^{234}Th-standard solution.

23. Distribution Methods in the Uranium Series

Objective: The principles of solvent extraction and ion exchange are reviewed by simple experiments within the Uranium-series.

24. Survey of Radioactivity in Air and Water

Objective: Different methods for gross α- and β-determination in air and water have to be applied.

25. ^{3}H- and ^{14}C- Determination in Gaseous Effluents

Objective: The student has to be able to apply different methods for ^{3}H- and ^{14}C-determination in offgas streams of nuclear power plants.

26. Separation and Analysis of Selected Fission Products (Sr, Cs, I)

Objective: Quick methods for determination of the important fission nuclides of iodine, cesium and strontium are presented.

27. Measurement in Contaminated Areas

Objective: The student has to learn the basic methods and units in radiation protection. Dose monitoring and contamination control with monitor and smear test have to be applied.

Experiment 13: Growth and Decay Rates in the System $^{137}Cs/^{137m}Ba$

Theoretical Introduction

Radioactive decay is a statistical process. The rate of disintegration -dN/dt depends on the stability of the decaying nuclei and is proportional to the number N of active atoms present in the sample:

$$-\frac{dN}{dt} \sim N \qquad (1)$$

or $$\boxed{-\frac{dN}{dt} = A = \lambda \cdot N} \qquad (2)$$

where λ is the proportionality constant, known as the decay constant, and A the activity.
Integration of equation (2) results to

$$\ln N = -\lambda \cdot t + C \qquad (3)$$

To evaluate the integration constant C, let N_0 represent the number of atoms at time t = 0; then

$$\ln N_0 = C \qquad (4)$$

$$\ln N = -\lambda \cdot t + \ln N_0 \qquad (5)$$

and $$N = N_0 \cdot e^{-\lambda \cdot t} \qquad (6)$$

or $$\boxed{A = A_0 \cdot e^{-\lambda \cdot t}} \qquad (7)$$

λ may be expressed by means of the half-life $T_{1/2}$ as the time, when the disintegration rate decreases to one half of the original value.

$$\frac{A}{A_0} = 0.5 = e^{-\lambda \cdot T_{1/2}} \qquad (8)$$

$$T_{1/2} = \frac{\ln 2}{\lambda} \qquad (9)$$

The half-life is a definitive characteristic of a radioactive species and is completely unaffected by the previous history or present chemical or physical state of the sample (except for a few cases of electron capture decay.)

If significant decay of radionuclides occur in a reasonable working period, the half-life may be determined by direct observation with any suitable instrument. Starting with a suitable activity (about 5,000 cpm for GM counters) one could make observation of the decreasing activity at frequent intervals. The duration of each measurement should be short compared with the half-life. Note the starting time of each measurement and continue at least until the activity is less than 1/10 of its original value.

Transformation of equation (7)

$$\lg A = \lg A_0 - \lambda \cdot t \cdot \lg e \qquad (10)$$

$$\text{or} \quad \lg A = C_1 - 0.301 \cdot \frac{t}{T_{1/2}} \qquad (11)$$

From the equation above it can be seen that in plotting the logarithm of the observed activity (corrected for resolving time, background, etc.) against the time of observation, a straight line of slope $- 0.301/T_{1/2}$ is obtained. Thus the half-life may be calculated from the slope of this plot or read off as the time interval corresponding to a decrease in ordinate from any value of A to A/2 Fig. 41).

When a radioactive nuclide forms a daughter product which itself is radioactive, the rate of growth of the daughter actvity is determined by the difference between the rate of decay of the parent and the rate of decay of the daughter.
For the system

$$A \xrightarrow{\lambda_A} B \xrightarrow{\lambda_B} C \qquad (12)$$

the rate of formation of the daughter is given by

$$\frac{dN_B}{dt} = - \frac{dN_A}{dt} - \lambda_B N_B = \lambda_A N_A - \lambda_B N_B \qquad (13)$$

The final result is a differential equation of second order with the solution

$$\boxed{N_B = \frac{\lambda_A}{\lambda_B - \lambda_A} \cdot N_{A(O)} \cdot \exp(-\lambda_A \cdot t) - \exp(-\lambda_B \cdot t)} \qquad (14)$$

There are three cases of special interest:

a) <u>Secular Equilibrium</u> ($T_{1/2}$ parent >> $T_{1/2}$ daughter)

The parent activity shows no apparent decrease in intensity during the period of observation.
The daughter activity reaches a constant value after the rates of decay and formation are equal (Fig. 42).
Equation (14) may be simplified and becomes

$$\boxed{\lambda_A \cdot N_A = \lambda_B \cdot N_B = \ldots\ldots} \qquad (15)$$

or in activities A

$$A_A = A_B = \ldots\ldots \qquad (16)$$

Secular equilibrium means equality of disintegration rate between parent and daughter, but not equality in the number of atoms of each species!

b) <u>Transient Equilibrium</u> ($T_{1/2}$ parent > $T_{1/2}$ daughter)

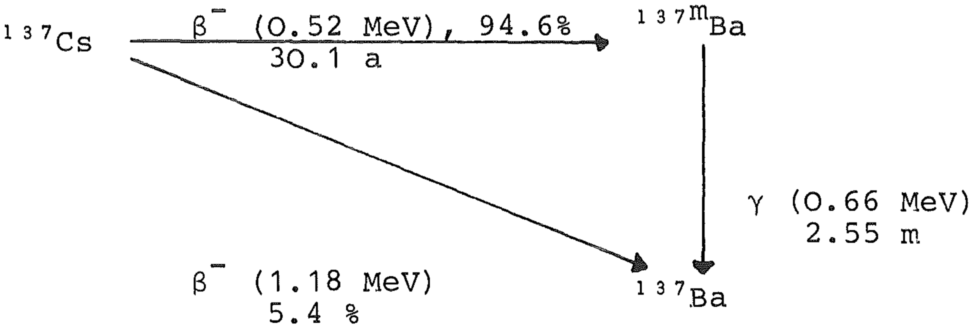
In this case the half-life of the parent is greater than that of the daughter, but sufficiently small for decay to be appreciable within the time of observation.
The daughter activity rises to a maximum and decays with the half-life of the parent nucleus (Fig. 43).
Simplification of equation (14) results in

$$\boxed{N_B = \frac{\lambda_A}{\lambda_B - \lambda_A} \cdot N_A} \qquad (17)$$

Since $\lambda_A/(\lambda_B - \lambda_A)$ is a constant, there will be a constant proportionality between N_A (the number of the parent atoms) and N_B (the number of the daughter atoms).

c) <u>No Equilibrium</u> ($T_{1/2}$ parent < $T_{1/2}$ daughter)
Assuming that there is initially no daughter activity present, the contribution of the parent activity to the total activity quickly becomes negligible. The amount of daughter activity passes through a maximum and after parent has decayed and the daughter therefore is no longer formed, it decays with its own half-life (Fig. 44)

In the present experiment the isotope ^{137}Cs is chosen as an example for study the phenomenon of secular equilibrium; its decay scheme is:



The parent (Cs) and daughter (Ba) species may be separated by a selective absorption of Cs^+-ions on ammonium-molybdato-phosphate, precipitated on chromatographic paper. When developing the chromatogram with HNO_3 (6M), Ba^{2+}-ions will migrate with the front of the solvent whereas Cs^+ remains at the starting point. The short lived daughter ^{137m}Ba decays at the front but will grow at the start from ^{137}Cs until secular equilibrium (Fig. 45).

Apparatus and Materials

- GM tube (end-window type) with a suitable tube holder
- Scaler/timer
- ^{137}Cs-source (about 1 MBq/ml)
- Filter-paper strip (coated with ammonium-molybdato-phosphate)
- Glass culture tube
- Scissors
- Al-planchette
- HNO_3 (6M)

Experimental Details

(1) Place about 2 ml of HNO_3 (6M) in a labelled culture tube, and then insert the filter-paper strip with the spot of radioactive material at the bottom (Fig. 46).

(2) Develop the chromatogram for about 3 min, remove the paper and mark the position of the solvent front. (The solvent will migrate about 2-3 cm.)

(3) Cut the front (0.5 cm above and 1 cm below, see Fig. 46) and fix it in the Al-planchette.

(4) Determine the count rates for about 30 min (measuring time: 1 min, pause time: 1 min), plot the logarithm of the corrected count rates against measuring time and determine the half-life of decay/growth (Fig. 41).

(5) Repeat procedure 1 to 4 with the bottom cut (^{137m}Ba) of the developed chromatogram (Fig. 46).

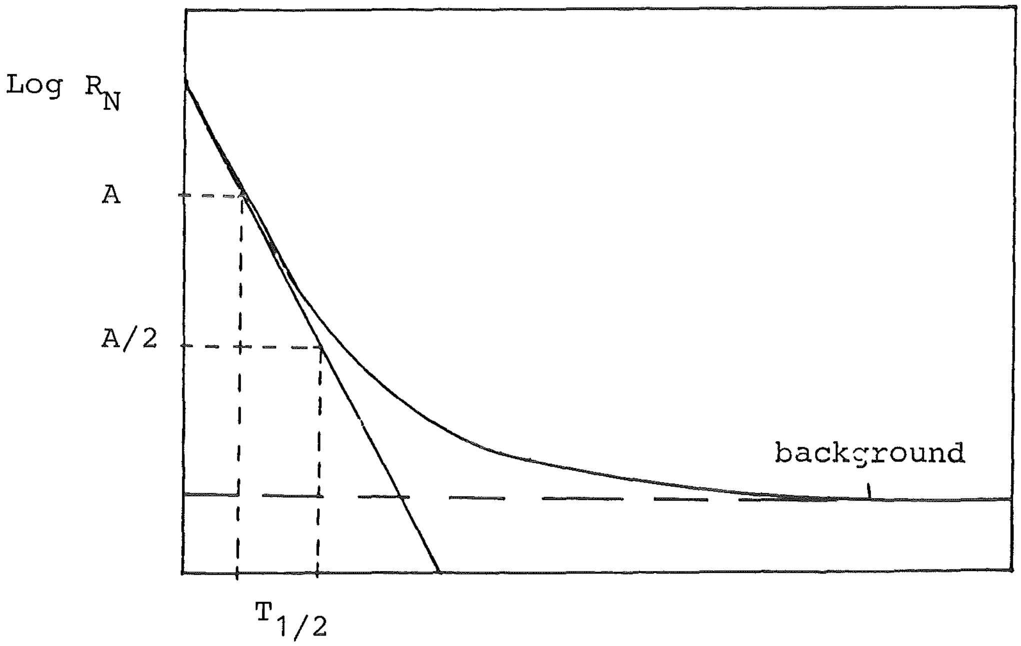
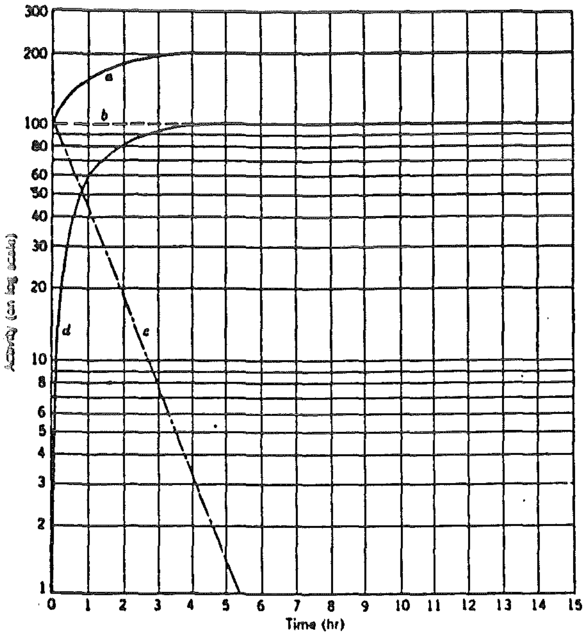
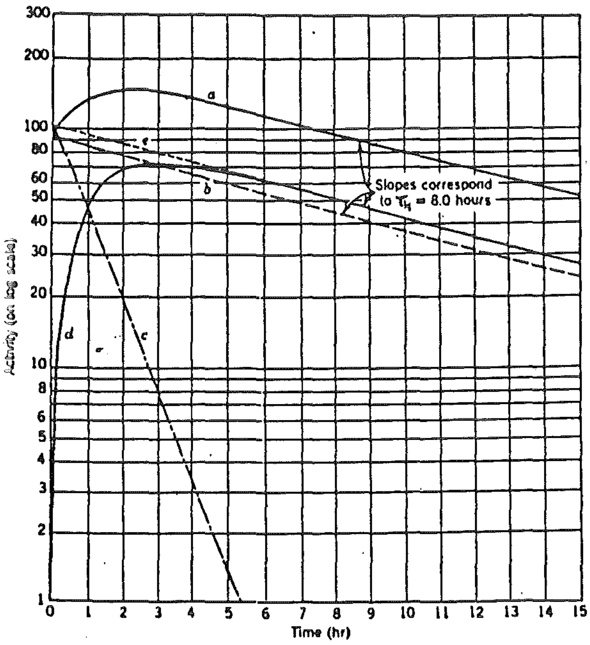


Figure 41: Determination of the Half-life from the Decay Curve



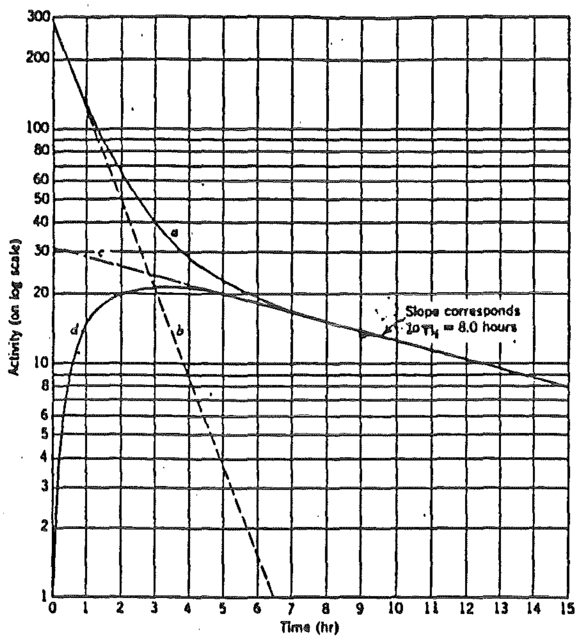
a: total activity of an initially pure parent fraction;
b: activity due to parent ($T_{1/2}$=8a); this is also the total daughter activity in parent-plus-daughter fractions;
c: decay of freshly isolated daughter fraction ($T_{1/2}$=0.80h);
d: daughter activity growing in freshly purified fraction.

Figure 42: Secular Equilibrium



a: total activity of an initially pure parent fraction;
b: activity due to parent ($T_{1/2}$=8.0h);
c: decay of freshly isolated daughter fraction ($T_{1/2}$= 0.80hr);
d: daughter activity growing in freshly purified parent fraction;
e: total daughter activity in parent-plus-daughter fractions.

Figure 43: Transient Equilibrium



a: total activity;
b: activity due to parent ($T_{1/2}$=0.80hr);
c: extrapolation of final decay curve to time zero;
d: daughter activity in initially pure parent.

Figure 44: No Equilibrium

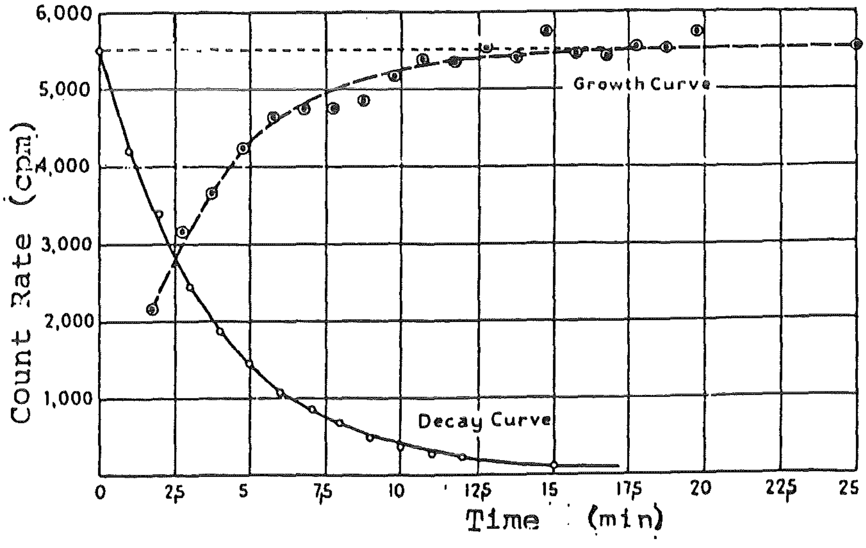


Figure 45: Secular Equilibrium for ^{137}Cs/^{137m}Ba

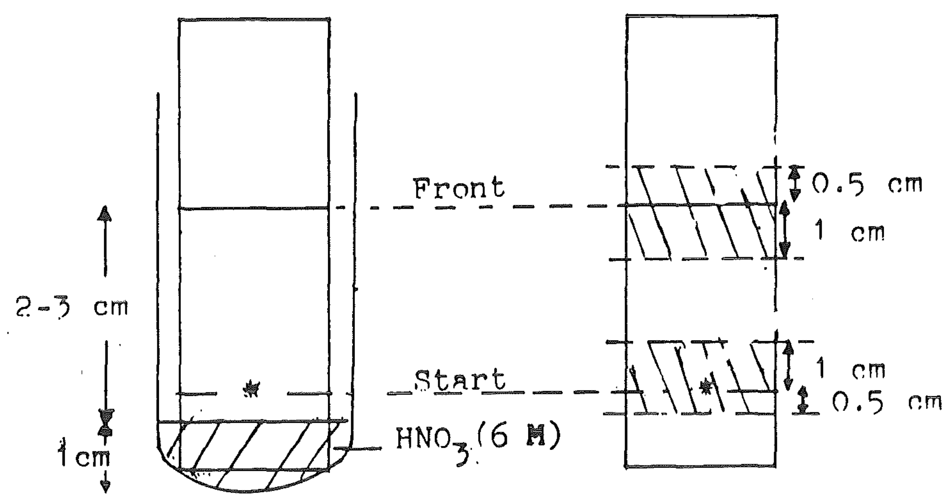


Figure 46: Chromatographic Separation of $^{137}Cs/^{137m}Ba$

Experiment 14: Half-Life Determination of ^{238}U

Theoretical Introduction

It is obviously impossible to measure the half-life of ^{238}U by following its decay. Such long half-lives may be calculated from the absolute activity of a defined amount of ^{238}U.
The activity of a radionuclude may be calculated according to the relation

$$A = N \cdot \lambda = \frac{m \cdot H \cdot N_L}{M} \cdot \frac{\ln 2}{A} \qquad (1)$$

$$\boxed{T_{1/2} = \frac{m \cdot H \cdot N_L}{M} \cdot \frac{\ln 2}{A}} \qquad (2)$$

A = Activity
N = Number of present atoms
λ = Decay constant
m = Mass of the radionuclide
H = Isotopic abundance
N_L = Avogadro´s number ($6.023 \cdot 10^{23}$)
M = Atomic weight
$T_{1/2}$ = Half-life

Uranium decays by α-emission, but it is in radioactive equilibrium with ^{234}Th and ^{234m}Pa

$$A(^{238}U) = A(^{234}Th) = A(^{234m}Pa) \qquad (3)$$

The latter decays by emission of high-energetic β-particles with a maximum energy of 2.33 MeV.
In this experiment ^{234}Th and ^{234m}Pa from
a) an uranium solution of known uranium contents and
b) from a carrier-free ^{234}Th-standard solution of known activity $A_{(Th)}$, will be coprecipitated using ZrP_2O_6 as absorber.

The two samples are covered with an Al-foil in order to absorb the α-particles from ^{238}U and the weak β-particles from ^{234}Th and are measured with a GM counter. The resulting rates $R_{(U)}$ and $R_{(Th)}$ in minutes thus are caused by the high-energetic β-particles of ^{234m}Pa.

From the known Th-standard activity, the efficiency of the GM counter is calculated to

$$\boxed{\eta = \frac{R_{(Th)}}{A_{(Th)}} \cdot 100 \ (\%)} \qquad (4)$$

The absolute activity of ^{238}U is thus obtained by

$$A(^{238}U) = A(^{234m}) = \frac{R_{(U)}}{\eta} \cdot 100 = \frac{R_{(U)}}{R_{(Th)}} \cdot A_{(Th)} \qquad (5)$$

Subsitution in equation (2)

$$\boxed{T_{1/2}(^{238}U) = \frac{m \cdot H \cdot N_L}{M} \cdot \frac{(\ln 2) \cdot R_{(Th)}}{R_{(U)} \cdot A_{(Th)}} \ [m]} \qquad (6)$$

or adequat

$$T_{1/2}(^{238}U) = \frac{m \cdot 0.993 \cdot 6.023 \cdot 10^{23}}{238} \cdot \frac{0.693 \cdot R_{(Th)}}{R_{(U)} \cdot A_{(Th)}} \cdot 1.9 \cdot 10^{-6} \ [a]$$

Apparatus and Materials

- $UO_2(NO_3)_2$ - solution with known amount of ^{238}U
- ^{234}Th-standard solution (carrier-free)
- HCl (2 M)
- $ZrOCl_2$-solution (4mg Zr/ml in 1 M HCl)
- $Na_2H_2P_2O_6$-solution (saturated)
- Filtering apparatus (27 mm Ø)
- 2 Beakers
- Al- planchettes
- Al-foil (50 mg/cm^2)

- Glue
- Fine filters (27 mm Ø)
- Heat lamp
- GM tube (end-window type) with a suitable tube holder
- Scaler/timer

Experimental Details

(1) Pour 5 ml HCl (2M) and 1 ml uranium solution (about 50 mg U) in a beaker, add 5 drops of $ZrOCl_2$-carrier solution and heat until boiling. Add 10 drops of a $Na_2H_2P_2O_6$-solution.

(2) Filter the ZrP_2O_6-precipitate while it is hot through a fine filter and wash twice with HCl (1M). The filter is fixed with some glue into an Al-planchette and carefully dried. (filter tends to shrink)

(3) After covering with Al-foil (50 mg/cm^2) the sample is measured with a GM tube ($\longrightarrow R_{(U)}$).

(4) Separation, preparation and measuring of ^{234}Th and ^{234m}Pa from 0.1 ml of the Th-standard solution has to be carried out under exactly the same conditions ($\longrightarrow R_{(Th)}$).

Experiment 15: Radionuclide Separation by α-Recoil

Theoretical Introduction

Carrier free radionuclides can be collected onto a metal plate by electrodeposition of the decay products of radon, resulting from a long lived mother nuclide. Such an arrangment allowing a continuous separation of a radionuclide from its parent substance is called a radionuclide generator or easily "radioactive cow" (Fig. 47).

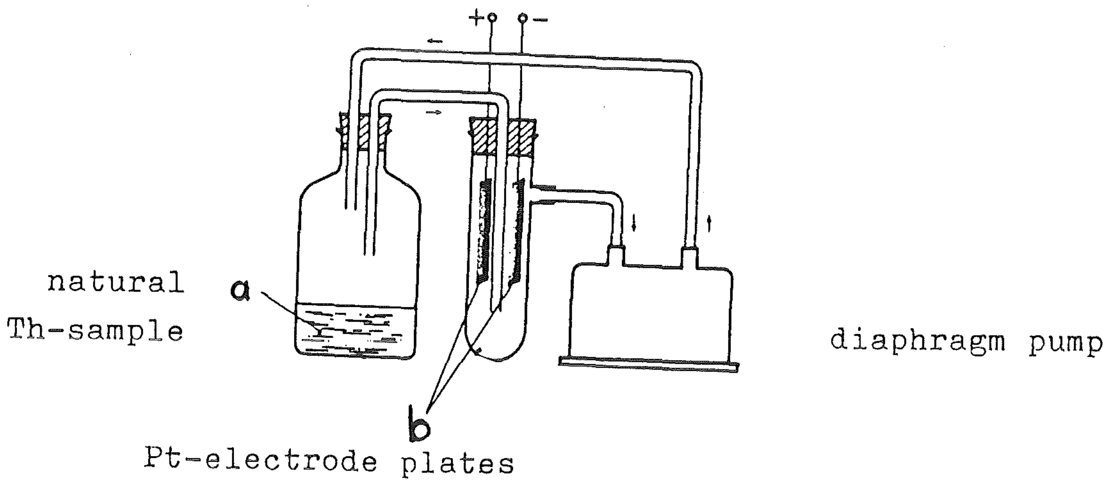
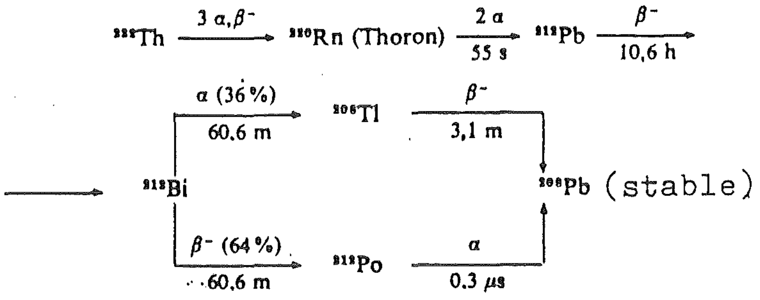


Figure 47: Arrangment for Electrodeposition of Carrier-free ^{212}Pb From Natural Thorium ("Thorium Cow")

a) Emanating Sample

b) Electrodeposition Cell

Aged natural thorium in the form of $Th(OH)_4$ (still better, ^{228}Th or ^{227}Ac in higher specific activity is used as emanating source in dust-proof package being permeable for gas. The gaseous radon-isotopes formed by the radioactive decay escape (emanate) out of the sample and form decay products with positive charge due to recoil effects:



These decay products might be deposited on a negatively charged metal plate (Pt).

The recoil energy E_R of a nucleus with the mass A after emission of an α-particle, calculated by

$$E_R = \frac{m_\alpha}{A} \cdot E_\alpha$$

is high enough to catapult the residual nucleus out of the sample surface (range in air about 0.1 to 0.2 mm). The method of α-recoil allows a simple possibility for the separation of carrier-free radionuclides, but otherwise gives rise to a continuous contamination of laboratory benches and instrumentation in case of careless handling. In the following experiment the daughter nuclide ^{208}Tl resulting from the parent ^{212}Bi is collected on a plane surface. ^{208}Tl has to be identified from its decay curve (Fig. 48). The radionuclide purity P at the time of separation t_o is calculated by

$$\boxed{P\% = \frac{R_N\ (^{208}Tl)}{R_N\ (total)} \times 100 = \frac{R_N\ (total) - R_N\ (impurity)}{R_N\ (total)} \times 100}$$

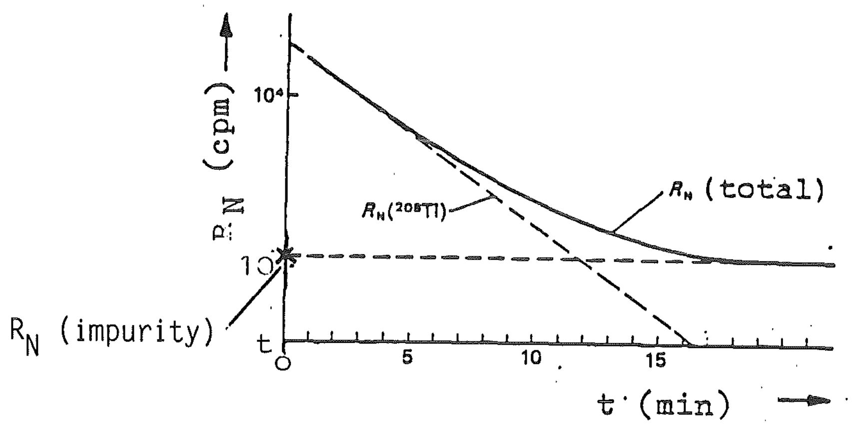


Figure48: Decay Curve of ^{208}Tl

Apparatus and Materials

- "Thorium-cow" (10 g natural thorium at least, better if available and safe for handling ^{228}Th)
- Metal electrode (Pt, 5 x 10 mm)
- Tweezers
- Source holder
- Stop watch
- GM-tube with suitable tube holder

Experimental Details

▷ Be careful when taking out the metal plates from the active "Th-cow" (fume hood)

(1) The plane platinum electrode is carefully placed onto the source holder after being loaded for some hours in the "Th-cow" with active deposit (^{212}Pb, ^{212}Bi, ^{208}Tl).

(2) Some minutes later the metal plate is removed (separation time) and the activity decay on the source holder measured in the GM-counting-box (1 minute measuring time - 1 minute pause).

(3) The background is determined after 30 minutes (10 half-lives) for a longer period (5 minutes).

Experiment 16:

Examination of $^{32}PO_4^{3-}$-Adsorption on $Fe(OH)_3$

Theoretical Introduction

Amorphous or microcrystalline precipitates with large surfaces like $Fe(OH)_3$ give rise to adsorption for different substances from the solution. Using $^{32}PO_4^{3-}$ as tracer the adsorption power of freshly precipitated $Fe(OH)_3$ has to be investigated. Therefore ^{32}P - labelled phosphate solutions of increasing concentration are contacted with a constant amount of $Fe(OH)_3$. The distribution of phosphate between adsorbent and solution is determined by measuring the respective activity.

The part adsorbed by the precipitate P_N and the part remaining in the solution P_L are calculated by

$$\boxed{P_N = \frac{R_{N1}}{R_{N1} + R_{N2}}} \quad \text{and} \quad \boxed{P_L = \frac{R_{N2}}{R_{N1} + R_{N2}}}$$

where

$R_{N1} + R_{N2}$ = total activity

R_{N1} = activity adsorbed by the precipitate

With C_P as phosphate concentration and M_P as total amount of phosphate, the amount phosphate X adsorbed by $Fe(OH)_3$ at the corresponding equilibrium concentration C_G is given by

$X = M_P \times P_N$ and $C_G = C_P \times P_L$ (s. table 5)

Table 5: Evaluation for PO_4^{3-}-adsorption

No.	R_{N1} [cpm]	R_{N2}	$R_{N1} + R_{N2}$	P_N	P_L	C_P (mmol/mol) M_P (mmol)	X (mmol)	C_G (mmol/ml)
1						–		
2						2×10^{-5}		
3						10^{-4}		
4						2×10^{-4}		
5						10^{-3}		
6						2×10^{-3}		
7						5×10^{-3}		
8						10^{-2}		
9						$1{,}5 \times 10^{-2}$		
10						2×10^{-2}		

An adsorption curve similar to the well known Langmuir-isothermal curve is obtained when the calculated values X (ordinate) and C_G (absicissa) are plotted in a double logarithmic scale.

If the PO_4^{3-}-concentrations differ considerably the adsorbed amount PO_4^{3-} is proportional to the equilibrium concentration in the solution C_G. Finally the region of saturation is reached, being partly superposed by iron-phosphate formation at higher PO_4^{3-}-concentrations (figure 49).

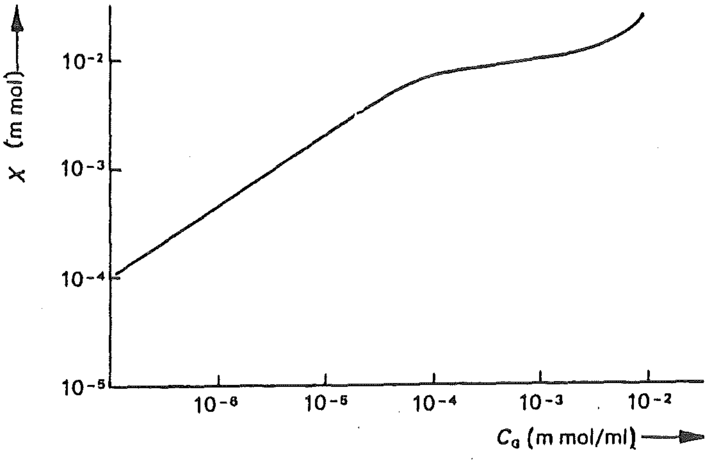


Figure 49: Adsorbed Amount of Phosphate X vs. Equilibrium concentration of Phosphate C_G

Apparatus and Materials

- NaI(Tl)-scintillation counter (well type)
- 10 centrifuge tubes (10 ml)
- $^{32}PO_4^{3-}$-solution (4 x 10^5 Bq/ml; carrier-free)
- KH_2PO_4-solutions (0.002 M, 0.02M, 0.2 M)
- Fe Cl_3-solution (25 mg Fe/ml)
- NH_4OH (1M)
- HCl (2M)
- Centrifuge

Experimental Details

(1) The ^{32}P -labelled phosphate solutions are prepared according to the following scheme (units in ml)

No.	KH_2PO_4 0.002 M	KH_2PO_4 0.02 M	KH_2PO_4 0.2 M	$^{32}PO_4^{3-}$	H_2O
1	–	–	–	1	4
2	0.1	–	–	1	3.9
3	0.5	–	–	1	3.5
4	1.0	–	–	1	3.0
5	–	0.5	–	1	3.5
6	–	1.0	–	1	3.0
7	–	2.5	–	1	1.5
8	–	–	0.5	1	3.5
9	–	–	0.75	1	3.25
10	–	–	1.0	1	3.0

(2) A constant amount of $Fe(OH)_3$ is precipitated by adding 0.1 ml $FeCl_3$ solution and 0.4 ml NH_4OH (1M) into each of the prepared centrifuge tubes.

(3) 0.5 ml of the corresponding phosphate solutions (1 to 10) is added and the suspensions left standing for 30 minutes (shake occasionally).

(4) Afterwards the suspension is counted for its total ^{32}P-activity using the NaI-detector. (The measuring device should be adjusted for the high-energetic β-radiation of ^{32}P). From the count rate the total activity $R_{N1} + R_{N2}$ (solution + precipitate) is calculated.

(5) Finally the suspension is centrifuged and the supernate carefully decanted (the last drop is absorbed by filter paper). The precipitates are dissolved in 1 ml HCl (2M) each and remeasured (R_{N1}).

Experiment 17 : Scavenger-Precipitation

Theoretical Introduction

Adsorption processes depend on external influences, such as temperature and surface charge, and are therefore unsuitable for specific separations. Nevertheless they have a considerable application in decontamination of radioactive waste water. Carrier-free radionuclides may be separated from a solution by adsorption on micro-crystallic or amorpheous precipitations with large surfaces ($Fe(OH)_3$, $Al(OH)_3$, $MnO(OH)_2$, etc.), called "Scavenger" - precipitation.

In the following experiment the effect of purification for $^{144}Ce^{3+}$ and $^{32}PO_4^{3-}$ should be examined for a $Fe(OH)_3$-precipitation.

The factor of decontamination DF is to be calculated.

$$DF = \frac{Rn\ (1)}{Rn\ (2)}$$

Rn(1) : net rate before purification

Rn(2) : Net rate after purification

Apparatus and Materials

- Na (Tl)-scintillation detector (well-type)
- Scaler/timer
- Radionuclide solution ($^{144}Ce^{3+}$, $^{32}PO^{3-}{}_4$)
- NH_4OH (6M)
- Fe Cl_3-solution (5mg ml)
- Filtering apparatus
- Fine filters
- Measuring vessel (10ml)
- Beaker (50ml)
- Test tubes

Experimental Details

(1) 2 ml of the aqueous contaminated solution should be measured (R_N1) and transferred into a beaker.

(2) After adding 1 ml of $FeCl_3$-solution (5 mg/ml) the mixture is heated.

(3) When boiling iron is precipitated as hydroxide with about 1 ml NH_4OH (6M).

(4) The precipitate is filtered and the solution diluted to 10 ml.

(5) An aliquot of 2 ml should be measured for activity (1/5 R_N2).

Experiment 18: Precipitation with Nonisotopic Carrier

Theoretical Introduction

Radiochemical separation methods do not basically differ from conventional classical chemistry. However, some special facts when handling radioactive species have to be taken into account and the methods have to be modified in consequence.
The following points of view should be considered:

- Separation factor respected to radionuclidic purity (not to be confused with radiochemical purity!)

- Time duration, especially when short-lived radionuclides have to be handled

- Radioresistance; most organic materials are easily decomposed by irradiation (radiolysis)

- Expense, and finally

- Possibilities for continuous process operation.

A comprehensive report on radiochemical separation methods for inorganic species is given by Coomber (in Coomber: Radiochemical Methods in Analysis, Plenum Press, N.Y., London 1975, pp. 175).

Besides its radioactivity the most characteristic feature of work with radioactive materials is that they widely have to be prepared and applied in amounts and concentrations far below the limits permissable by standard physical and chemical methods (table 6). The mass equivalent m for a radionuclide of a given activity A can be calculated by

$$A = \lambda N = \frac{\ln 2}{T_{1/2}} \times \frac{m\, N_L\, H}{M}$$

where

λ = decay constant

N = number of atoms

$T_{1/2}$ = half-life

N_L = Loschmidt's (Avogadro's) number

H = abundance

M = atomic weight

Table 6: Amounts Present in 3.7×10^4 Bq (1µCi) Carrier-free Radionuclides

RADIONUCLIDE	HALF-LIFE	AMOUNT
^{238}U	4.5×10^9a	3g
^{14}C	5×10^3a	10^{-7}g
^{3}H	12a	10^{-10}g
^{32}P	14d	4×10^{-12}g
^{234m}Pa	1.2m	1.5×10^{-15}g

Uranium ions may be detected by classical precipitation methods (e.g. as hexa-cyano-ferrate) but the amounts of shorter-lived radionuclides can be neither weighed nor detected by other analytical means. Usual chemical reactions do not occur due to its low material amounts.

Moreover there might be some surface effects giving contribution considerably to their behavior in extremely dilute solutions. Adsorption phenomena e.g. by contacting with vessel wall, beakers or filter paper, often lead to unexpected results (see experiment 17).

In very dilute solutions of radionuclides, formation of tracer colloids has been observed already below the solubility product, thus disturbing its regular distribution. They may be separated by dialysis, colloidal filtration, centrifugation, but could be avoided by acidification of radionuclide solutions. The formation of radiocolloids is in contradiction to the theory of a total dissociation for high dissolutions. Its presence is not limited to radionuclides, but otherwise not detectable.

In order to avoid losses or falsification of the results by adsorption, the tracer activity is commonly diluted with a non-radioactive macroscopic amount of substance called "carrier" or "hold-back carrier". In a chemical sense, the carrier substance takes on the function of the radioactive nuclides and carries them in the course of the chemical operation. By diluting the radioactive sample, adsorption effects remain restricted to the nonactive carrier atoms present largely in excess. Thus we can handle a larger amount of substance which follows the well-known laws of physical chemistry. It is essential for carrier and radioactive species to be in the same chemical form in order to avoid fractionation in the separations. Isotopic carriers (e.g. natural phosphorus for ^{32}P) behave chemically absolute identical to its radioactive isotopes. However they reduce the specific activity, irreversibly. Non-isotopic carrying, makes use of elements with a similar chemical behavior (e.g. Ba for Ra). This method is inevitable for unstable elements like Po, Pa or the actinides.

The effect of carrying and holdback-carrying sould be examined for the example of natural uranium

$$^{238}U \xrightarrow[4.5\times10^{9}a]{\alpha} {}^{234}Th \xrightarrow[24.1d]{\beta^-} {}^{234m}Pa \xrightarrow[1.17m]{\beta^-} \cdots \longrightarrow {}^{206}Pb \text{ (stable)}$$

^{238}U decays by α-emission resulting ^{234}Th which is unstable equally, forming ^{234m}Pa.

Purpose of the experiment is to separate ^{234m}Pa from its mother nuclides U and Th by precipitation.
Therefore Zr-ions (nonisotopic carrier for ^{234m}Pa) and natural thorium (holdback-carrier for ^{234}Th) are used. In adding PO_4^{3-} a precipitate of $Zr_3(PO_4)_4$ is formed, containing Pa.
The purity of the separation, expressed by the radionuclide purity P, may be determined from the decay curve of ^{234m}Pa (Fig. 50).

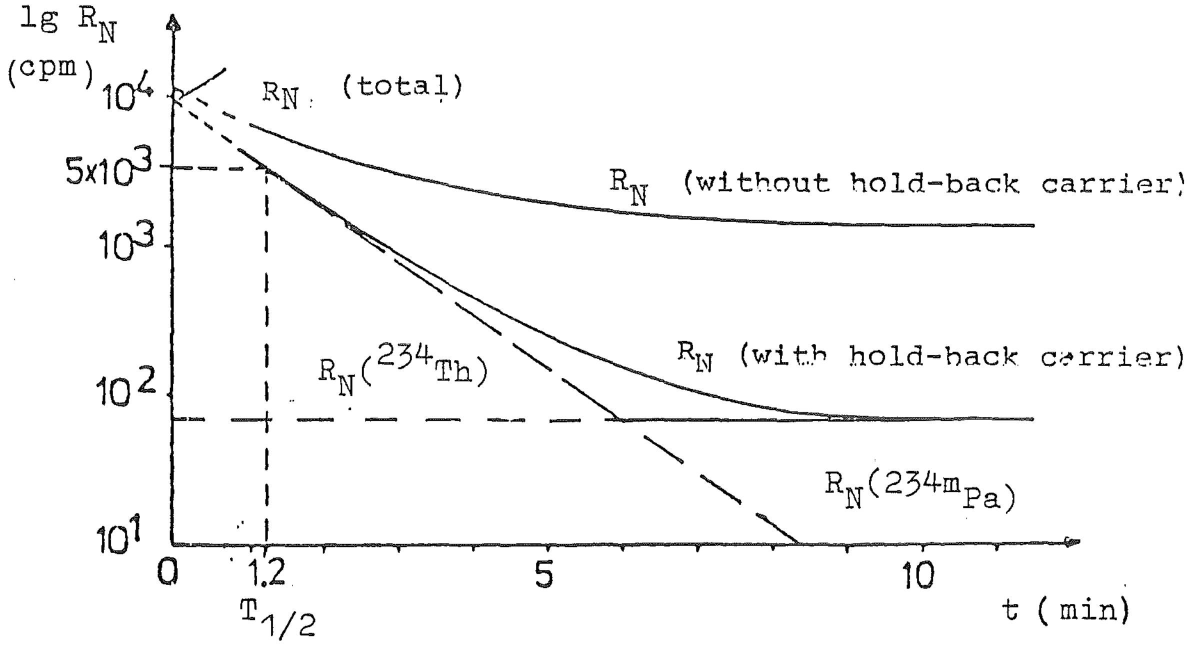


Figure 50: Decay Curve of ^{234m}Pa with ^{234}Th as Contamination

$$\boxed{P\% = \frac{R_N(^{234m}Pa)}{R_N(\text{total})} \times 100}$$

Apparatus and Materials

- Uranium nitrate solution (10ml, 50mg U/ml) ⟶ solution (1)
- Uranium nitrate solution (10ml, 50mg U/ml), containing $Th(NO_3)_4$ as holdback-carrier 20mg/ml) ⟶ solution (2)
- G-M tube (end-window type) with a suitable tube holder
- Scaler/timer
- $Na_2\,HPO_4$-solution (saturated)
- HCl (2M)
- Filtering apparatus
- Fine filters
- 2 Beakers (50ml)
- Stop watch
- Adhesive tape
- Sample support
- $ZrOCl_2$-solution in 1 M HCl (4mg/ml)

Experimental Details

▷ Due to the short half-life of ^{234m}Pa (1.17m) all details should be prepared before starting the procedure (filtering apparatus, stop watch, timer/scaler, etc).

(1) 10ml of the uranium solution (solution1) is placed in a beaker. After adding 3 drops of the Zr-solution (carrier), the mixture is heated together with a second beaker containing diluted HCl for washing.

(2) When boiling, Zr is precipitated with 2ml of a phosphate solution. The separation time is fixed with the stop watch when half of the solution has been filtered.

(3) After washing with about 1ml of the warm diluted HCl the filter is fixed on a support with an adhesive tape.

(4) The decay curve should be determined for 15 minutes on the uppest shelf of the G-M counting-box (measuring time: 30s, Pause time : 30s).

(5) The procedure is repeated with natural thorium (^{232}Th) as holdback-carrier for ^{234}Th (solution 2).

Experiment 19:

Separation of ^{106}Rh from ^{106}Ru by Precipitation

Theoretical Introduction

Isotopes of ruthen are formed by nuclear fission of uranium (integral fission yield > 15%). They might be separated as "fission-ruthen" from a solution of irradiated uranium, e.g. by distillation of the volatile ruthen-tetroxide, RuO_4, after oxidation with strong oxidizing agents. However, only the relatively long-lived isotopes ^{103}Ru ($T_{1/2}$ = 39.35d) and ^{106}Ru ($T_{1/2}$ = 368d) are found in the ruthen-solution one day after irradiation. When ^{103}Ru has decayed nearly completely (after about 1 year) a solution of pure ^{106}Ru in secular equilibrium with its daughter ^{106}Rh results.

$$^{106}\mathrm{Ru} \xrightarrow[368\mathrm{d}]{\beta^-;\ 0.04\ \mathrm{MeV}} {}^{106}\mathrm{Rh} \xrightarrow[30\mathrm{s}]{\beta^-;\ 3.6\ \mathrm{MeV}} \underline{^{106}\mathrm{Pd}}\ \text{(stable)}$$

In the following experiment ^{106}Rh is separated by carrier precipitation. Coprecipitation of ruthen is prevented by addition of Ru hold-back carrier. The radionuclide purity of the Rh-sample has to be determined (see exp. 18). ^{106}Rh is identified by means of its half-life.

Apparatus and Materials

- ^{106}Ru-solution (about 5 kBq/ml)
- $RuCl_3$-solution (10mg Ru/ml)
- KNO_2-solution (2M)
- $Na_3[Co(NO_2)_6]$-solution (20mg/ml, freshly prepared)
- Glacial acetic acid
- Acetic acid (10%)

- Beaker (50ml)
- Measuring cylinder (5ml)
- Filtering apparatus (4 cm ϕ)
- Fine filters
- Adhesive tape
- Stop watch
- GM-tube (end-window type) with a suitable tube holder
- Scaler/timer

Experimental Details

▻ ^{106}Rh has a half-life of 30 seconds. As well as in the preceding experiment all details should be prepared before starting the procedure. Measurement of the sample should start at least 30 seconds after chemical separation.

(1) Into a beaker (100ml) 3 to 5 drops glacial acetic acid, 5ml KNO_2-solution (2M) and 1 drop $RuCl_3$-solution as hold-back carrier are placed successively.

(2) 1ml of the ^{106}Ru-solution is added. The solution is warmed to 50° C and potassiumhexanitrocobaltate precipitated with 1 ml of a freshly prepared $Na_3[Co(NO_2)_6]$-solution.

(3) The precipitate is filtered and the stop watch started for separation time (reference time).

(4) After washing with some drops of acetic acid (10%) the filter membrane is fixed on the support with adhesive tape and immediately transfered into the counting-box.

(5) The overall counts are recorded at intervals of 15 seconds (no reset of the display).

▻ If a multichannel analyzer is available the activity more easily is recorded by multi-scaling.

Experiment 20 : Solvent Extraction with Tri-n-Butyl-Phosphate

Theoretical Introduction

Solvent Extraction holds a privileged position among radiochemical separation methods. With high separation factors, sufficient material throughput and the possibility of on-line process flow, it is applied in industry for chemical reprocessing of spent nuclear fuel.

Separation by solvent extraction is based on the different affinity of radionuclides between two unmixable liquid phases. The distribution of the element X is described according to Nernst as

$$[X]_{\text{aqueous}} \overset{D_X}{\rightleftarrows} [X]_{\text{organic}} \quad , \quad D_X = \frac{[X]_{\text{org.}}}{[X]_{\text{aq.}}}$$

The distribution coefficient D_X is a property of matter and has a constant value for a given organic phase and aqueous acidity. The selectivity of a solvent extraction process is described by the separation factor α, expressed by the quotient of the distribution coefficients of the species X and Y

$$\alpha = \frac{D_X}{D_Y}$$

Difficulties will arise for ions with similar chemical properties ($D_X \simeq D_Y$ or $\alpha \simeq 1$) like radionuclides, mostly being positively charged metal ions. They are highly hydrated and do not show any lipophilic tendency.

In most cases, these radionuclides are separated after previous chemical reaction steps like coordination-, association- or chelate-complexes.

The separation step of the PUREX-process (plutonium-uranium-refining by extraction) concerns the capability of tri-n-butyl-phosphate (TBP) as organic solvent to extract 4- and 6-valent metal nitrates from nitric acid medium (fig. 52).

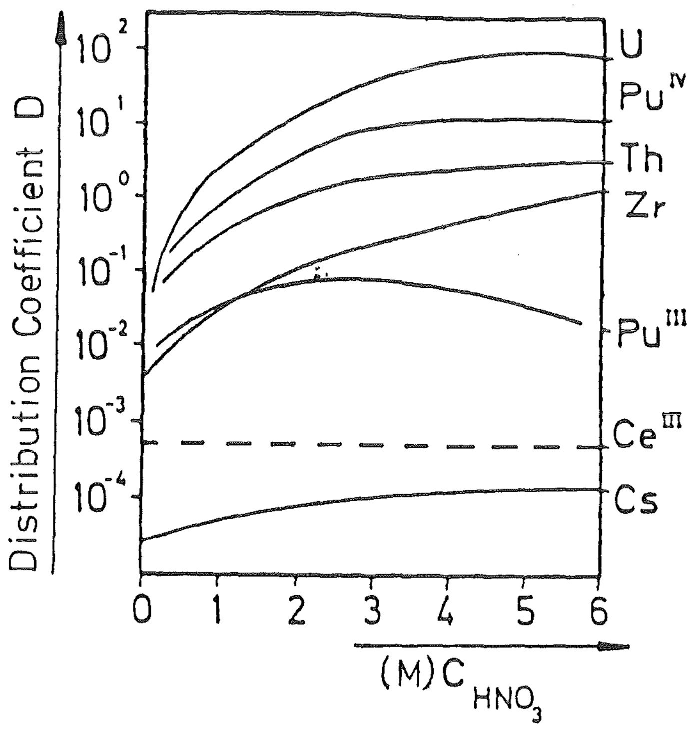


Figure 52: Distribution Coefficients for Fissionable Nuclides and Fission Products vs. HNO_3-concentration (metal concentration >> 0.1 Mol/l, 30% TBP in kerosene)

The aqueous feed solution (3 M HNO_3), containing U, Pu and the fission products is extracted in a counter current column with the organic TBP-solution (30% in kerosene). While 6-valent uranium and 4-valent plutonium (ev. 4-valent thorium) form complexes with TBP, the 1-, 2-, or 3-valent fission products remain in the the aqueous phase and may be stripped off as High Active Waste (HAW).

The separation of uranium and plutonium is effected on a second column by extracting the organic TBP-phase with aqueous HNO_3 containing a reducing agent like Fe $(SO_3NH_2)_2$, or most recently by electrolytic reduction without further solid waste.

While uranium as U^{4+} still remains in the organic phase, plutonium is reduced to Pu^{3+} thus highly decreasing the distribution factor (fig. 52).
Uranium is finally stripped into the aqueous phase with decreasing HNO_3-concentration (fig.53).

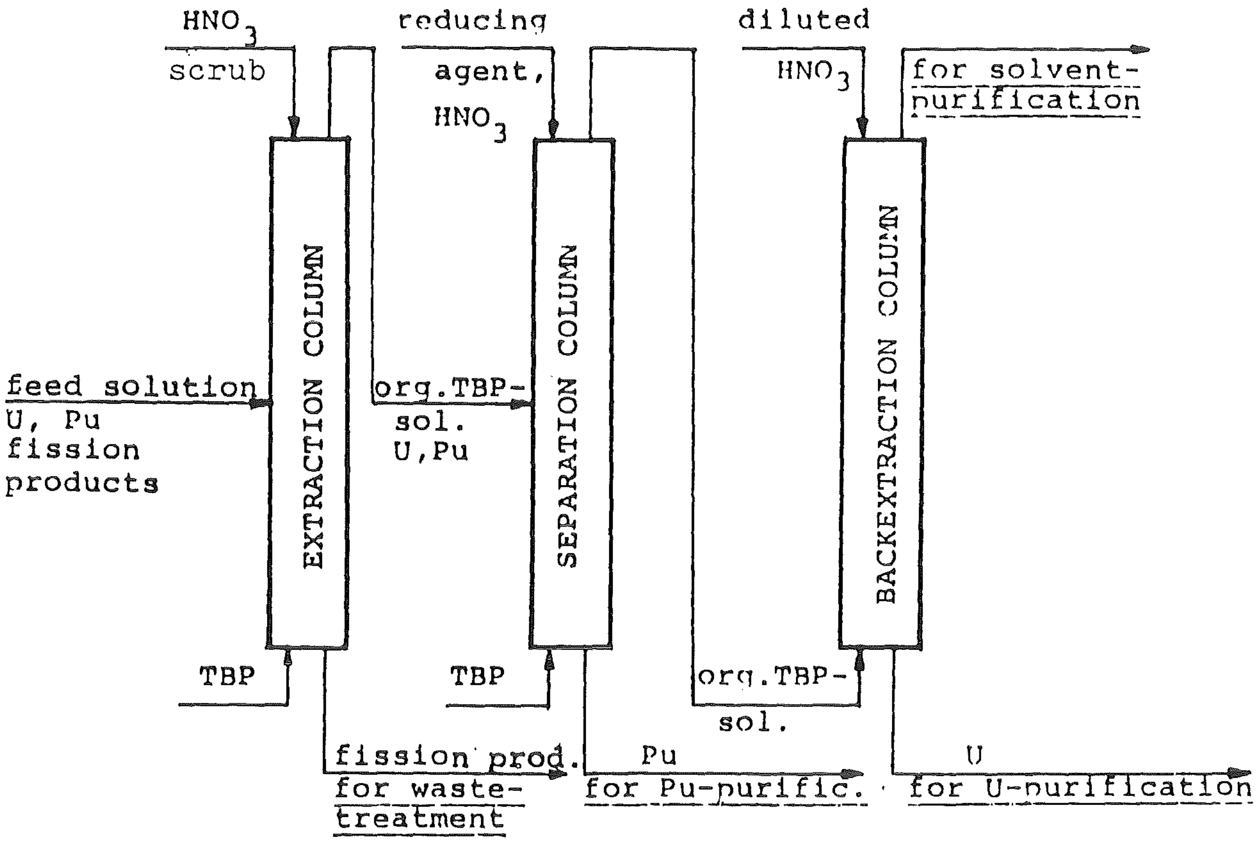


Figure 53: Scheme of PUREX-extraction Process

The extraction of 4- and 6-valent metal ions in faint acid medium may be described as

$$Me^{4+}_{aq} + 4NO_3^- \, aq + 2TBP_{org} \rightleftharpoons Me(NO_3)_4 \times (TBP)_{2\,org} \qquad (1)$$

and

$$MeO_2{}^{2+}{}_{aq} + 2NO_3{}^-{}_{aq} + 2\ TBP_{org} \rightleftarrows MeO_2(NO_3)_2 \times (TBP)_{2\ org} \qquad (2)$$

respectively.

Due to the large alkyl groups of TBP the complex compounds are organophil and consequently well soluble in organic solvents (kerosene). The distribution coefficient D as characteristic size for the extent of extraction is defined as

$$\boxed{D = \frac{[Me]_{org}}{[Me]_{aq}}} \qquad (3)$$

where $[Me]$ is the total metal concentration in the corresponding phase. The distribution coefficient for the TBP-extraction is given to

$$D = \frac{[complex]_{org}}{[Me]_{aq}} \qquad (4)$$

with application of the law of mass action to equ. (1)

$$K = \frac{[complex]}{[Me^{4+}] \times [NO_3^-]^4 \times [TBP]^2} \qquad (5)$$

the distribution coefficient finally becomes

$$\boxed{D = K \times [NO_3^-]^4_{aq} \times [TBP]^2_{org}} \qquad (6)$$

From equ. (6) one can see that the distribution coefficient increases with increasing nitrate content (in diluted solutions) (see fig.52).

To obtain a good separation the distribution coefficient of fissionable elements and fission products should highly differ. Depending on the nuclear fuel and amount of burn up this may be achieved in changing the acid concentration of the feed solution or by scrubbing the uranium and plutonium containing organic phase with different HNO_3-concentrations (4 M HNO_3 for ruthenium, 1.5 M HNO_3 for zirconium).

In the following experiment the elements of a simulated feed solution should be separated for fissionable nuclides and fission products by TBP-solution.
The distribution coefficients of Co, Zr, and Cs between TBP (30% in kerosene) and 3 M HNO_3, for Th as fissionable nuclide, with respect to the HNO_3 -concentration have to be determined by γ-spectrometry.

Apparatus and Materials

- "Feed"-solution (containing ^{234}Th, ^{238}U, ^{60}Co, $^{95}Zr/^{95}Nb$, $^{137}Cs/^{137m}Ba$, ^{144}Ce)
- TBP(30 % in kerosene)
- HNO_3 (3 M, 1.5 M, 0.01 M)
- Measuring cylinder
- Separating funnel
- Test tubes
- NaI(Tl)-scintillation detector
- Ge(Li)-detector with multi-channel analyser

Experimental Details

(1) 3 ml of the acidic feed-solution (3 M HNO_3) is extracted with 3 ml of TBP (30 %) for about 1 min.

(2) After phase separation, each of the both phases is collected in test tubes each and analysed by the Ge(Li)-semi-conductor counter.

(3) From the count rates of the γ-lines (see table 7) the distribution coefficients for Co, Zr and Cs have to be calculated (eq. (3)).

(4) The organic phase (containing most of the Th-activity) is washed with further 3 ml 3 M HNO_3.

(5) The purified organic (upper) phase is transfered to a measuring glass (10 ml), filled up to 9 ml with TBP-solution, and mixed.

(6) The solution is distributed into three portions and finally extracted a: 3 ml org. phase + 3 ml 3 M HNO_3

b: 3 ml org. phase + 3 ml 1.5 M HNO_3

c: 3 ml org. phase + 3 ml 0.01 M HNO_3

Each phase is separated and collected into a test tube and measured for its activity using the scintillation detector.

(7) From the ratio of activities for organic and corresponding aqueous phase the distribution coefficients are calculated and plotted in a diagram against acid concentration.

Table 7: γ-Energies and Abundance of the Employed Fission Nuclides

Nuclide	γ-Energies [keV] and Abundance [%]
^{234}Th	63 (5.7); 92 (6.8)
^{144}Ce	134 (10.8)
^{137}Cs	662 (84.6)
^{95}Zr	724 (43) ; 757 (54.6)
^{95}Nb	766 (99)
^{60}Co	1173 (99.88) ; 1333 (100)

Discussion

From the results of the experiment it may be seen that the required decontamination factor of 10^7 for safe handling is not obtainable in a single reaction step. Using counter-current extraction, sieve-plate columns and different acid concentrations for the scrubs, decontamination factors up to 10^3 per separation step are achieved. The purification of the fissionable nuclides is affected by two further extraction-reextraction cycles with subsequent ion exchange.

Zirconium as 4-valent element has the greatest distribution coefficient and thus the highest activity for the organic phase of all fission porducts. Due to its high specific activity and high fission yield (cummulative fission yield for Zr =46.4 %) the extractant may be decomposed thus hindering the reprocessing process (especially in mixer-settler plants).

The essentially smaller distribution coefficient enables thorium (uranium) to be reextracted from diluted nitric acid.

Literature

G. Koch in : C. Keller, H. Möllinger (Eds.)
Kernbrennstoffkreislauf Band II, Hüthig, Heidelberg 1978, pp. 9/56

Experiment 21: Separation of Fission Products by Anion Exchange

Theoretical Introduction

Ion exchange on synthetic resin exchangers is very widely used in radiochemical analysis. The scope of these materials has greatly been extended over the past 30 years with the use of complexing agents in cation exchange, eluents of high ionic strength in anion exchange and the use of mixed solvent systems. The mostly used synthetic organic ion exchanger consists of a three dimensional polymeric matrix onto which either cationic or anionic functional groups are affixed. If a pre-treated exchange resin of anionic functional groups is contacted with a solution containing cationic loaded radionuclides, an exchange process will occur according to

$$R{-}SO_3^{\ominus}H^{\oplus} + Me^{\oplus} \underset{\text{Elution}}{\overset{\text{Exchange}}{\rightleftarrows}} RSO_3^{\ominus}Me^{\oplus} + H^{\oplus}$$

The ion exchange equilibrium process is reversible, so that the cationic ions may specifically be eluted with increasing acid ($H^{\oplus}$) concentrations in order of their different adhesion strength. For its effective separation, the positively charged radionuclides have to be chemically treated before its ion exchange separation, e.g. by complexation with suitable anions.

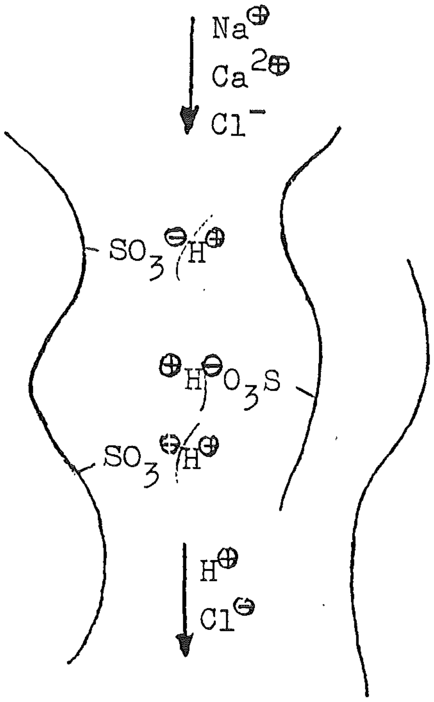


Figure 54: Structure of an Organic Ion Exchange Resin

Separation of radionuclides is caused by the different adhesion strength of the ions. The higher the electrochemical valency m and the lower the radius of the solvated (!) ions, the higher will be the strength of adsorption. Therefore

$$Me^{3+} > Me^{2+} > M^{\oplus}$$

and $$Cs^{\oplus} > Na^{\oplus} \gtrsim Li^{\oplus}$$

The separation factor, defined as quotient of the exchange constants of two ions to be separated, may be increased greatly when using complexing agents.

A great number of cations form anionic "Ansolvo"-acids with strong acid residues like $Cl^{\ominus}$,

$$Me^{m+} + n\ Cl^{\ominus} \rightleftarrows MeCl_n^{(n-m)^-} \qquad (2)$$

Kraus and co-workers[+)] have demonstrated the applicability of anion exchange resins in metal ion separation in the system of Dowex-1 and hydrochloric acid (Fig. 55).

Many metals form strong anionic complexes with chloride ions, while others form weaker anionic complexes or other form no complexes or only cationic ones.

By choosing the proper concentration of hydrochloric acid, non- or poorly adsorbed ions may be eluted while more strongly adsorbed ions remain in the resin bed.

The concentration of eluant may then be changed to cause elution of the latter ions.

Thus a separation of a considerable amount of elements may be affected.

The ion exchange properties of certain inorganic substances

+) Kraus and Nelson, Paper 837, Geneva Conference Vol. 7 (1956) including the hydrous oxides of zirconium and tin, acid salts such as zirconium phosphate, and salts of heteropoly acids, e.g. ammonium molybdatophosphate, have been described. Inorganic exchangers are much more resistant to high temperature and to radiation than organic exchangers and are not subject to swelling and shrinking with change in the ionic strength of the medium. They show high selectivities for certain ions. Especially the high affinity for caesium has been of great importance in the nuclear energy field.

High pressure ion exchange chromatography offers the advantage of high flow rates, reduced radiation damage to the resin, while gases formed by radiolysis remain dissolved.

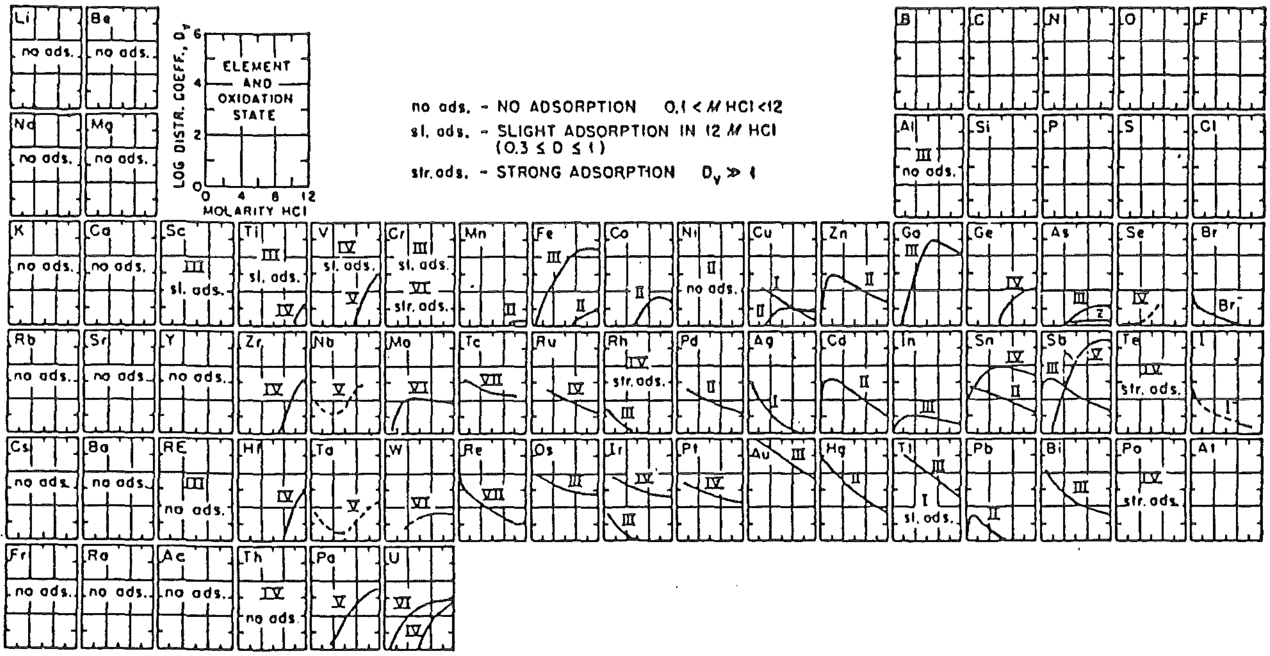


Figure 55: Adsorption of the Elements from Hydrochloric Acid

Purpose of the following experiment is to separate some elements, present in fission products. The radionuclides (^{60}Co, ^{95}Zr/^{95}Nb ^{125}Sb, ^{137}Cs/^{137m}Ba, ^{144}Ce) are chosen in regard to enable easy determination by scintillation (NaI) or semi-conducting counter. They should be separated by use of an anion exchange resin with solutions of different concentrations as eluent.

Apparatus and Materials

- Solution of fission products (3 M HNO_3)
- 12 M HCl
- 9 M HCl + 0.025 M HF
- 4 M HCl + 0.5 M HF
- 2 m NaOH
- Test tubes
- DOWEX - 1 exchange resin (50 - 100 mesh in 12 M HCl
- Glass column
- NaI (Tl) -scintillation counter (well type)
- Ge (Li) - semi-conducter counter with multi-channel analyser

Experimental Details

a) Preparation of the exchange column (Fig. 56):

(1) A thin wad of glass wool is inserted onto the bottom of a glass column (Fig. 56).

(2) The resin (Dowex-1, 50 - 100 mesh) in form of an acidic (12M HCl) aqueous slurry is poured into the column to about 2/3 of its length.

▷ Take care that the resin will not run dry or will have air bubbles!
At any time the liquid level should not drop below the top of resin!

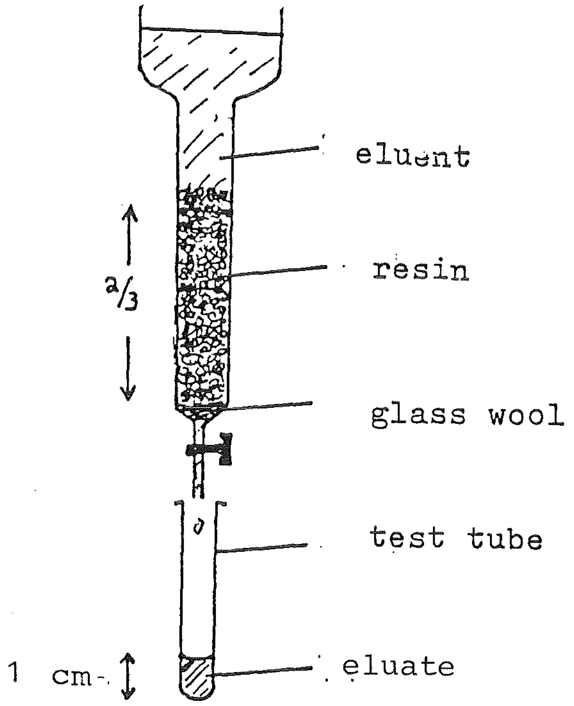


Figure 56: Ion Exchange Column

b) Separation:

(1) To the loaded column the sample is cautiously placed onto the top of the resin.

(2) To separate the non-complexable ions ($^{137}Cs/^{137m}Ba$, ^{144}Ce) the column is eluted dropwise with 6 ml of 12 M HCl, collected in 6 test tubes (1 ml each).

(3) Zr is eluted subsequently with 6 ml of 9 M HCl (+ 0,025 M HF) (tube number 7 - 12).

(4) With 6 ml of 4 M HCl (+ 0,5 M HF) the Nb- and Co-complexes dissociate and may be trapped in further 6 test tubes (13 - 18).

(5) Finally Sb is eluted with 6 ml of 2 M NaOH (19 - 24).

(6) The count rate of each test tube should be determined with the NaI (Tl)-scintillation detector.

(7) In plotting the count rate of each fraction against the number of test tube an elution diagram will be obtained.

(8) Examine the main fraction of each peak for purity by using the Ge (Li)-semi-conducting counter.

Experiment 22: Preparation of a Carrier-Free ^{234}Th-Standard Solution

Theoretical Introduction

The ^{238}U-isotope decays according to the following scheme:

$$\begin{tikzcd}
{}^{238}\mathrm{U} \arrow[r, "\alpha", "4.5\times10^{9}\,a"'] & {}^{234}\mathrm{Th} \arrow[r, "\beta^-(99.89\%)", "24\ d"'] \arrow[dr, "\beta^-(0.11\%)", "24\ d"'] & {}^{234m}\mathrm{Pa} \arrow[r, "\beta^-", "1.2\ m"'] & {}^{234}\mathrm{U} \arrow[r, "\alpha"] & \text{etc.} \\
 & & {}^{234}\mathrm{Pa} \arrow[ur, "\beta^-", "6.7\ h"'] & &
\end{tikzcd}$$

This experiment illustrates the separation of the daughter products produced in the decay of ^{238}U, using the techniques of solvent extraction and ion exchange.

Uranyl nitrate is extracted by ethyl ether while the nitrates of ^{234}Th and ^{234m}Pa remain in aqueous solution. The separation is continued on an anion exchange resin. Thus the carrier-free ^{234}Th obtained can be used in different radiochemical experiments.

Apparatus and Materials

- $UO_2(NO_3)_2 \times 6H_2O$
- Ethyl ether, saturated with water
- Separatory-funnel (200 ml, 500 ml)
- HCl (12 M)
- Anion exchange resin DOWEX I, 50-100 mesh (Hydrogen form)
- Glass-column (φ 1.5 cm; length 30 mm) with funnel and stopcock
- $K_4[Fe(CN)_6]$ (10mg/ml)
- Quartz crucible (8 cm φ)
- HCl (2 M)
- Beakers
- Hostaphane-foil

- Micropipettes
- Volumetric flask (10ml)
- Flow-counter (2 π-geometry)

Experimental Details

(1) Preparation of the exchange column: Insert a thin wad of glass wool onto the bottom of the column. The resin then is poured into it as slurry containing a rather large amount of HCl (12 M). Then wash with 50 ml HCl (12 M), the liquid adjusted to flow to about 2 ml/min. At any time the liquid level should not drop below the top of the resin.

(2) Dissolve 30 g $UO_2(NO_3)_2$ with 200 ml ethyl ether (saturated with water) in a separatory funnel and shake a few minutes, taking care to release the pressure frequently.

(3) The aqueous layer is poured into a second funnel and extracted once more with 100 ml ethyl ether. In case the ether layer is still couloured, repeat the procedure.

(4) Acidify the aqueous layer with 10 ml HCl (12 M).

(5) Pour the liquid, containing ^{234}Th and ^{234m}Pa, onto the prepared column and wash with 20 ml HCl (12 M).

(6) 1 ml of the eluent should be neutralized and examined for uranium with $K_4[Fe(CN)_6]$.

(7) If there is no more uranium in the solution place it into

a quartz crucible and evaporate to dryness on a hot plate. Dissolve with 5 - 8 ml HCl (2 M) and fill it up to a volume of exact 10 ml.

(8) Drop exactly 0.02 ml of the carrier-free ^{234}Th-solution on the hostaphane-foil stretched in the ring of the gas-counter and dry it with a heat lamp.

(9) Finally record the β-plateau of the flow-counter with the prepared sample, fix the operating-voltage analog to experiment 2 ("Characteristic of Gas Counters") and determine the count rate.

This counter is operated in the proportional region and may be used to measure α-activity in the presence of much higher β-and γ-activities with 2 π-geometry (Fig. 51). In the present case the β-rays of ^{234}Th together with those of ^{234m}Pa, with a total efficiency of 100% ($R_N = 0.5\ A\cdot(^{234}\text{Th}) + 0.5\ A\ (^{234m}\text{Pa})$) will be counted.

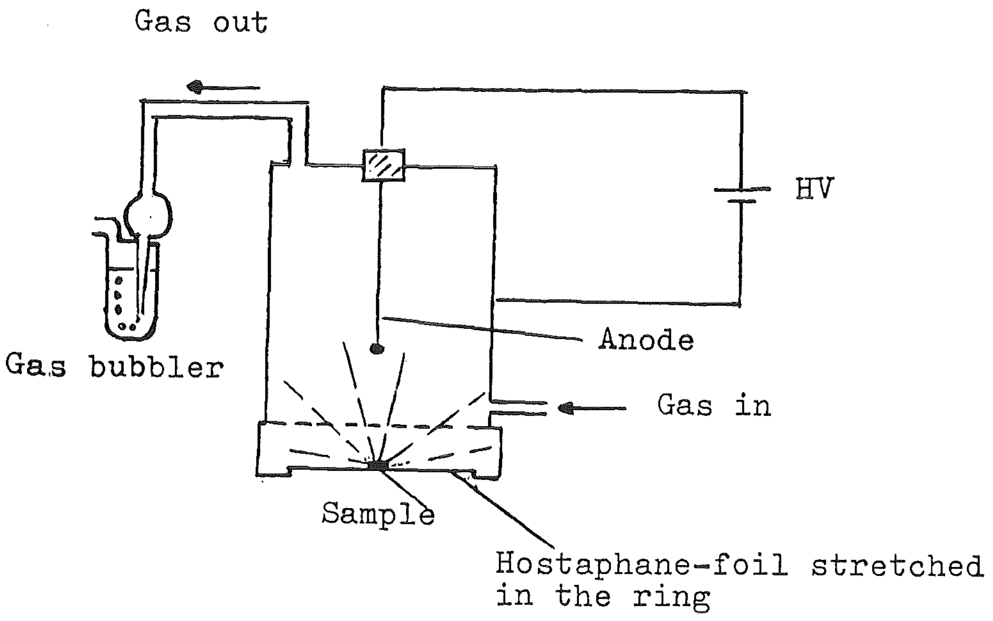


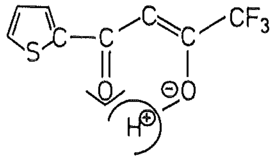
Figure 51: Flow-counter

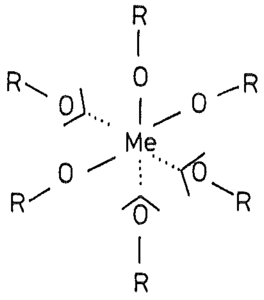
Experiment 23: Distribution Methods in the Uranium Series

Theoretical Introduction

Due to the easy availability of uranyl-nitrate, the state of secular equilibrium with its daugher nuclides ^{234}Th and ^{234m}Pa, and the short half-life of the latter the system enables an instructive demonstration of the application of distribution methods in radiochemistry.

The principles of solvent extraction and ion exchange have been reviewed in experiment 20 and 21. Because of the similar hydrophilic behaviour of metal cations, complexing and chelating agents are usually introduced. Thenoyl-trifluoroacetone (TTA) holds a privileged position in solvent extraction. It forms chelates with positively charged metal ions, their stability being dependant on the charge (the higher, the more stable) and the acidity of the system (competition between H^+ and Me^+).





As neutral complex with a great organic residue structure the chelate formed is highly organophil and easily to be extracted into the organic phase. From the ions involved, UO^{+}, Th^{4+}, Pa^{5+} the highly positive charged Pa forms the most stable chelate and thus is extracted even in 4M acidic HCl-solution.

In the second part of the experiment ^{234m}Pa has to be separated by ion exchange. Although all three cations will be fixed on a cation exchange column, the double valentic UO_2^{2+} is easily washed by dilute HCl (2M). In order to improve the selectivity of the separation between Th and Pa, the latter is complexed with citrate buffer, thus leaving Th finally on the column.

From the decay curve of the separated ^{234m}Pa sections, its half-life and radionuclidic purity has to be determined (see experiment 18).

Apparatus and Materials

- $UO_2(NO_3)_2 \times 6H_2O$
- HCl (4M, 2M)
- Thenoyltrifluoroacetone (0.5 M in toluene)
- NH_4^{+}-Citrate (5 %, pH = 2.5)
- $K_4[Fe(CN)_6]$-solution (5 %)
- Na-acetate
- Amberlite 120 R (X8, 50-100 mesh)

- Separation funnel (25 ml)
- Ion exchange column (15 cm x 1 cm)
- Stop-watch
- GM-counter (preferably liquid type)
- Scaler/timer

Experimental Details

A) Solvent Extraction

1. 500 mg $UO_2(NO_3)_2 \times 6H_2O$ are dissolved in a separation funnel in 10 ml HCl(4M). After addition of 10 ml TTA-solution, the phases are mixed vigorously for about 1 min.
2. After phase separation (separation time has to be fixed with the stop-watch!) the organic ^{234m}Pa - containing phase is transfered into the GM-counter and measured according to experiment 18.

B) Cation Exchange

1. Onto a cation exchange column a solution of 300 mg $UO_2(NO_3)_2 \times 6H_2O$ in 5ml H_2O is added.
2. Uranium is eluted slowly (1 ml/min) with 30 to 50 ml 2M HCl, until no more uranium is detectable in the eluent. (1 ml is neutralized with Na-acetate and 1 ml $K_4[Fe(CN)_6]$-solution added.)

3. ^{234m}Pa afterwards is complexed with 5 % citrate-solution (separation time!) and determined in the eluent by its decay.

If a liquid type GM-counter is not available, the final ^{234m}Pa-containing solutions are collected in a PE-counting vial (see experiment 8) and measured with the GM-end window counter.

Experiment 24: Survey of Radioactivity in Air and Water

Theoretical Introduction

Handling with open, radioactive sources causes an additional danger due to contamination and successive incorporation by inhalation or ingestion. Besides the direct contamination in the laboratory air and water may act as medium to transfer the activity outside of nuclear facilities and hence have to be surveyed continiously. The specific activity for free discharge of liquid and gaseous effluents is limited (e.g. in FRG by the regulations of KTA 1503/1504). It depends on the type of radiation, and chemical and biological properties of the concerning radionuclides.

In the following experiment, different methods for gross α- and β-determination in air and water as well are demonstrated.

Apparatus and Materials

- Large-area flow counter
- Suitable planchettes
- Filtering apparatus
- Evaporator
- Cabinet-oven
- Vacuum cleaner
- Stop-watch
- Water sample (^{204}Tl- contaminated)
- $CaCl_2$-solution
- $FeCl_3$-solution (21 g/l)
- HCl
- NaOH
- Na_2HPO_4-solution (36 g/l)
- Absorbent carbon

Experimental Details

Determination of radioactivity in water by evaporation:

(1) 250 ml of the water sample is evaporated in a large area planchette (don`t overheat!).

(2) The planchette is measured with a flow counter for one minute (R_M) and the specific activity A_{sp} calculated by the formula

$$\boxed{A_{sp} = \frac{(R_M - R_o) \times 10^3}{\eta \times f_{sa} \times 60 \times 0.25}} \quad [\mathrm{Bq/m^3}]$$

for water samples of low or medium content of solid a correction for self-absorption may be neglected ($f_{sa} \approx 1$)

Determination of radioactivity in water by precipitation:

(3) The specific activity of a 3 l water sample is enriched by successive addition of the following substances into a 5 l beaker:

- 10 ml saturated $CaCl_2$-solutions
- 3 l water sample
- 10 ml $FeCl_3$-solution
- HCl (diluted) to adjust the solution to ph 3
- NaOH unto ph 10.5 to 11
- 20 ml Na_2HPO_4-solution
- 0.5 g absorbent carbon

(4) After weighing the empty filter paper, a filter bed of 1 g absorbent carbon and 1 g filtering gel is deposited.

(5) The suspension is filtrated and the filter cake dried in a cabinet until constant weight.

(6) From the count rate of the dry sample the specific activity A_{sp} is calculated to

$$\boxed{A_{sp} = \frac{(R_M - R_o) \times 10^3}{\eta \times f_{sa} \times 60 \times 3}} \quad [\mathrm{Bq/m^3}]$$

The self-absorption factor is obtained from figure 57 according to the weight of filter paper and residue.

Determination of radioactivity in air:

(7) The aerosol activity is enriched by sucking about 50 m^3 air through a filter. The air input X in m^3 is calculated from the flow rate and time of suction.

(8) The filter is measured with the flow counter for one minute each by use of alternating the α- and β-operating point (total measuring time one hour).

(9) From the decay curve the cummulative half-life is determined and the activity for the time of separation extrapolated. The corresponding specific activity is calculated from

$$\boxed{A_{sp}\ (\alpha) = \frac{R_N(\alpha)}{\eta(\alpha_1)\ x\ 60}\quad x\ \frac{1}{x}}\quad \left[Bq/m^3\right]$$

and

$$\boxed{A_{sp} = \frac{R_N(\alpha+\beta)\ -\ R_N(\alpha)\ x\ \eta(\alpha_2)/\eta(\alpha_1))}{\eta(\beta)\ x\ 60}\quad x\ \frac{1}{x}}\quad \left[Bq/m^3\right]$$

$\eta(\alpha_1 7)$ and n (α_2), $\eta(\beta)$ relate to the efficiencies in the α- and β-operating point.

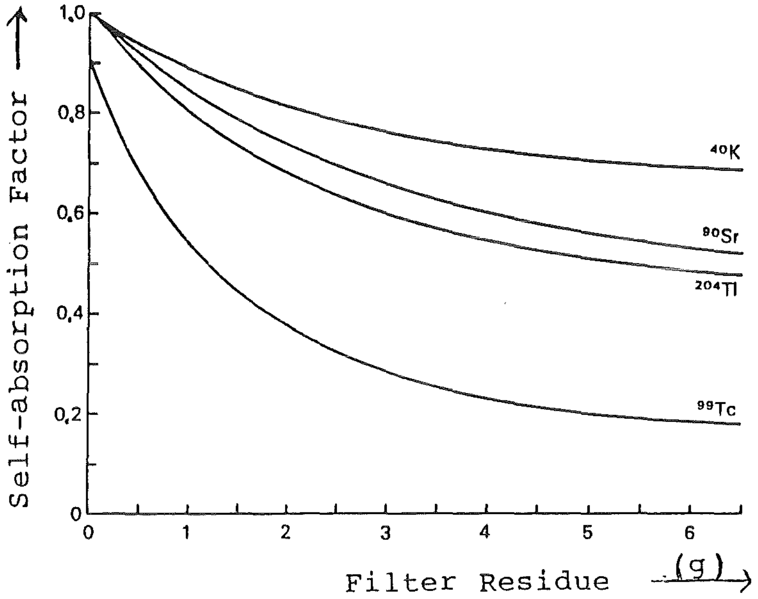


Figure 57: Correction Curve for Self-absorption

Experiment 25: ^{3}H- and ^{14}C-Determination in Gaseous Effluents

Theoretical Introduction

The legislation for radiation protection foresees maximum limits for radionuclides in gaseous effluents of nuclear plants and requires their continuous survey. Because of their unspecific low ß-energy a pre-concentration and chemical separation is necessary for ^{3}H and ^{14}C.

The determination of ^{3}H as tritiated water is based on the steps

- condensation (freezing) of air humidity
- separation from accompanying radionuclides by destillation
- measurement by use of liquid scintillation counting.

^{14}C as $^{14}CO_2$-compound is absorbed in a NaOH -scrub at a flow of <0.5 l/min. After chemical separation as $BaCO_3$ it is measured as gel by liquid scintillation counting.

A recent variation applies the adsorption of both nuclides on molecular sieves. Using a catalyst column ^{3}HH- and $^{14}CH_4$-gas might also be combusted and trapped by two further sieves (figure 57a) ^{3}H is afterwards exchanged from the sieve by mixing with inactive water. The amount of ^{3}H emitted per year A_E by a nuclear plant is calculated by

$$\boxed{A_E = A_C \times \frac{D_K}{D_B} \times \frac{1}{t}} \qquad [\mathrm{Bq/a}]$$

and

$$A_C = \frac{R_N \; (G + \Delta G_C)}{G_S \times \eta_D \times 60} \qquad [\mathrm{Bq}]$$

and for the corresponding ^{14}C-emissions by

$$\boxed{A_E = A_K \times D_K \times 8.74 \times 10^3} \qquad [\mathrm{Bq/a}]$$

and

$$A_K = \frac{R_N \times G}{\eta_D \times V \times G_S \times 60} \qquad [\mathrm{Bq/m^3}]$$

with

A_C = Activity of the cartridge in Bq
A_K = Activity concentration in Bq/m^3
D_K = Chimney throughput in m^3/h
D_B = Throughput of the bypass in m^3/h
R_N = Net rate in min^{-1}
η_D = Detector efficiency
G_S = Weight of subproduct for measurement
G = Weight of inactive H_2O or total precipitated $BaCO_3$ corresp.
ΔG_C = Weight gain of the cartridge
t = collecting time in years
V = Volume of air in m^3

Apparatus and Materials

- Molecular sieve in cartridge (e.g. Union Carbide type 3 Å, Fluka)
- Scintillation cocktail (D-Scint)
- Erlenmeyer-flask (500 ml)
- Distillation apparatus
- NaOH (5 M)
- NH_4Cl (1 M)
- $BaCl_2$ (1 M)
- Cab-O-Sil (Gel-former)
- Scintillation cocktail (5 g PPO, 0.5 g POPOP, 1 l toluene)
- Thielert-Scrubber
- Suction flask
- Glass frit (2D4, 50 ml)
- Liquid Scintillation Counter

Experimental Details

A) ^3H-Determination

(1) The loaded molecular sieve is weighed and poured into a flask containing 250 ml distilled H_2O.

(2) The suspension is stirred for 30 min, and transferred into a distillation apparatus.

(3) Two milliliters of the destillate (G_S) are pipetted into a PE-counting vial, mixed with 20 ml D-Scint and measured for 5 min.

B) ^{14}C-Determination

(1) The NaOH-scrub solution (50 ml) is poured into a beaker and 1 ml I^- and Cs^+-carrier each is added. After further addition of 10 ml hydrazinehydrate (24 %) and 120 ml 1 M NH_4Cl the solution is heated.

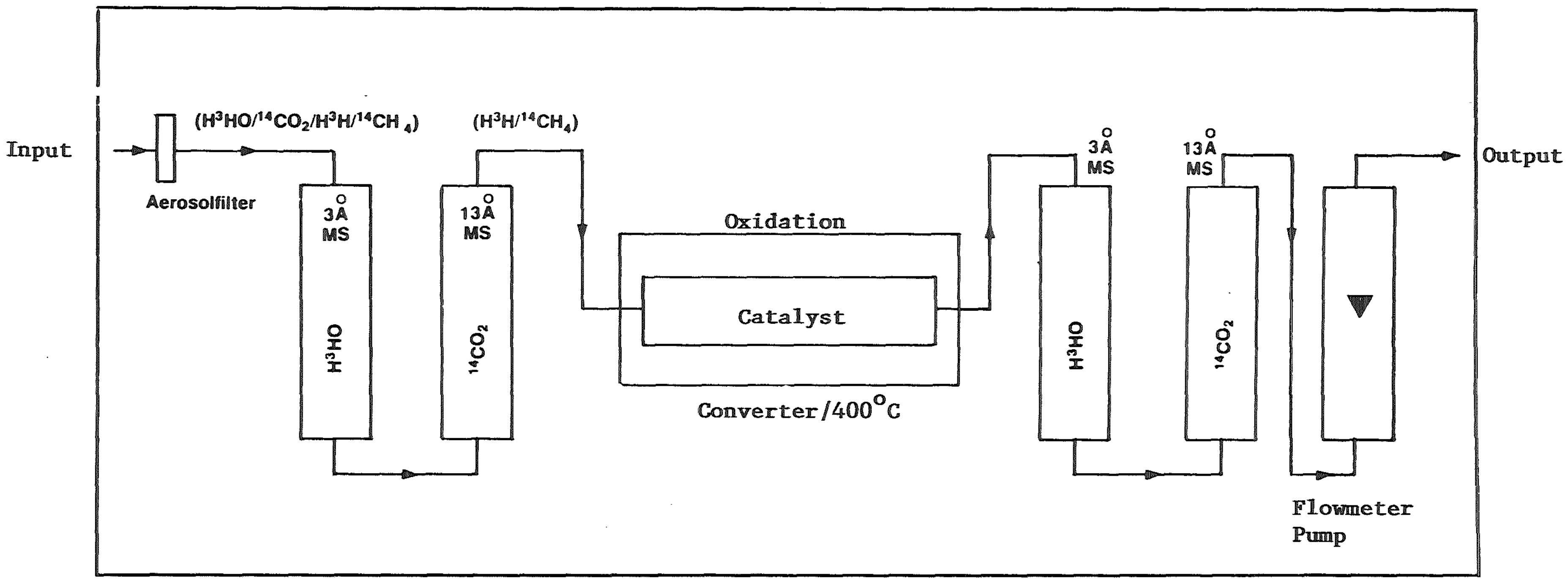
(2) $BaCO_3$ is precipitated with 20 ml 1 M $BaCl_2$ and the hot suspension filtered through a glass frit (weigh before!). The filter cake is washed with hot dist. water, alcohol and acetone.

(3) After drying at 120 °C (about 1 to 2 hours) the total $BaCO_3$-amount is determined (G).

(4) 1 g of the pulverized precipitate (G_S) is intimately mixed with 20 ml toluene-scintillator and 1 g Cab-O-Sil unto homogeneity and finally measured for 5 min.

Figure 57a

Principle



Experiment 26:

Separation and Analysis of Selected Fission Products (Sr, Cs, I)

Theorectical Introduction

Gross α- and β-counts from a water sample are available by evaporation or precipitation(see experiment 24).

If the activity exceeds the permitted value, a chemical separation is necessary in order to determine the radionuclides in question.

The experiment describes rapid procedures used for environmental activity survey. In applying characteristic radiochemical separation methods (ion exchange, heterogeneous isotopic exchange, solvent extraction, etc.) some representative radionuclides (fission products) are separated from water samples (or mineralized inorganic and organic environmental samples) and analyzed.

Apparatus and Materials

- NaI (Tl)-scintillation detector (well type)
- Beakers
- Filtering apparatus
- Separation funnel
- Filter paper (ϕ 9 cm)
- Centrifuge tubes
- Test tubes
- NH_4NO_3-solution (71.4 g NH_4NO_3 dissolved in 95.6 ml conc. HNO_3 and filled up to 1000 ml with H_2O)
- $NH_4H_2PO_4$-solution(3.62 g $NH_4H_2PO_4$ dissolved in 500 ml H_2O
- NH_4-molybdate solution(26.5 g $(NH_4)_6Mo_7O_{24}$ x $4H_2O$ dissolved in 250 ml H_2O)

- Gooch-asbestos
- HNO_3 (conc, and fuming)
- NH_4OH
- NaOH
- NaI
- $AgNO_3$
- $NaNO_2$
- $CHCl_3$
- Fe^{3+}-carrier
- Sr^{2+}-carrier
- Saturated $(NH_4)_2CO_3$-solution
- Saturated Na_2CO_3-solution

Experimental Details

a) Determination of ^{137}Cs

The separation is based on selective absorption on the synthetic organic ion exchanger ammonium-molybdato-phosphate (AMP). It is applied either as preformed filter layer or as a modified batch method.

(1) Into a 250 ml beaker the following materials are successively added: 90 ml NH_4NO_3-solution, 38.7 ml NH_4-molybdate-solution, after heating up to 80°C and continous stirring 0.5 g Gooch-asbestos and 12.9 ml $NH_4H_2PO_4$-solution. When the bright yellow precipitate appears stirring is continued for further 10 minutes at 80°C.

(2) The precipitate is carefully filtered, sucked and after covering the filter layer with a second filter paper, washed with about 50 ml H_2O.

(3) 1000 ml of the water sample is acidified with 100 ml conc. HNO_3, and after addition of 250 mg NaI slowly sucked (about 50 ml/min) through the preformed filter layer.

(4) The precipitate is finally transferred into a test tube and counted in the NaI-scintillation detector being calibrated previously for the energy of the ^{137m}Ba-daughter nuclide.

Modification:

(1') Into the acidified (100 ml conc. HNO_3) water sample (1000 ml) 0.5 g Gooch-asbestos and a solution of 6 g ammonium molybdato phosphate in conc. NH_4OH is added.

(2') The precipitate formed is filtered, sucked to dryness and measured as described above.

b) Determination of ^{131}I

The fission nuclide iodine-131 is separated either using heterogeneous isotopic exchange or by solvent extraction with $CHCl_3$ (CCl_4)

Heterogeneous Isotopic Exchange:

(1) The exchange layer is prepared by acidifying 1500 ml H_2O with 5 ml conc. H_2SO_4. Under stirring a solution of 1.86 g NaI x $2H_2O$ in 25 ml H_2SO_4 (1 M), 30 g Gooch-asbestos and 3.75 g $AgNO_3$ in 5 ml H_2O is successively added. The AgI-suspension is sufficient for about 15 determinations.

(2) The filter layer is formed by careful sucking 100 ml of the suspension through a hard filter. The layer is washed twice with 25 ml H_2SO_4 (0.1 M).

(3) The water sample (1000 ml) is acidified with 3 ml H_2SO_4 (conc.) and sucked through the exchange layer with a rate of about 100 ml/min.

(4) The layer is washed with 25 ml H_2SO_4 (0.1 M), sucked to dryness and transferred into a test tube.

(5) Using the NaI-scintillation detector calibrated for the corresponding γ-energy, the ^{131}I-activity is determined.

Solvent Extraction:

(1') In a separatory funnel 500 ml of the water sample is mixed with 10 mg NaI-carrier and acidified with 6 ml conc. H_2SO_4.

(2') After addition of 6 g $NaNO_2$ as oxidant, iodine is extracted into 350 ml chloroform and the organic phase separated. For complete iodine separation a second extraction with 100 ml $CHCl_3$ is recommended. The organic layers are combined and filled up to a volume of 500 ml.

(3') The measurement is carried out with a NaI-scintillation detector either using the total volume in a special counting cup or after reduction of iodine and precipitation as AgI in a test tube.

c) Determination of ^{89}Sr/^{90}Sr

^{90}Sr is a fission nuclide of high radiotoxity. For high sensitivity and precision in the determination, a quantitative Ca-Sr-separation with high technical effort is necessary. In the following experiment a simplified procedure is used for a rapid survey for radiostrontium.

(1) A water sample of 100 ml is transferred into a centrifuge tube and after addition of 20 mg Fe^{3+}- and Sr^{2+}-carrier each, adjusted to pH12 with NH_4OH (12 M).

(2) The $Fe(OH)_3$-precipitate is centrifuged and the supernate transferred into a second centrifuge tube.

(3) Saturated aqueous $(NH_4)_2CO_3$ is added to the solution until complete precipitation of the alkaline earth carbonate (check for completeness after centrifugation!).

(4) The $Sr(Ca)CO_3$-precipitate is centrifuged and washed with a few ml H_2O. 16 ml fuming nitric acid are added and the solution is cooled with ice bath for 15 minutes.

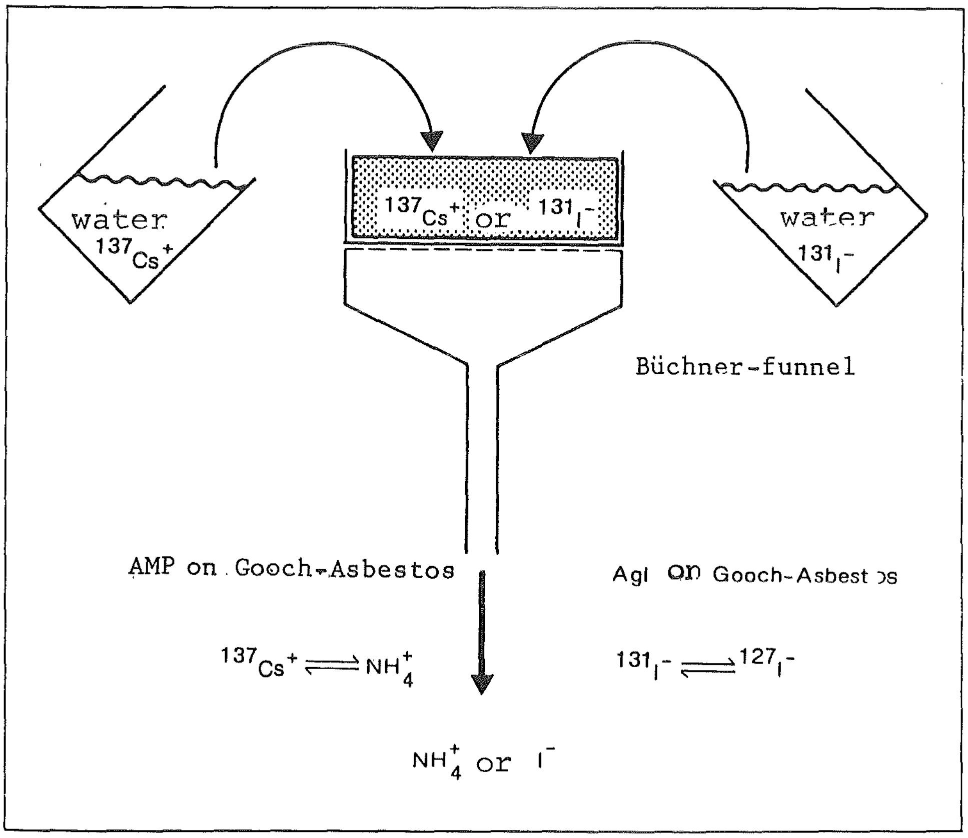
(5) In contrast to calcium, which is soluble in cold fuming nitric acid, $Sr(NO_3)_2$ being precipitated is separated by centrifugation and decantation.

(6) The precipitate is dissolved in about 10 ml H_2O and Sr^{2+} finally reprecipitated as $SrCO_3$ by addition of 1 ml NaOH (12 M) and 25 ml saturated Na_2CO_3-solution.

(7) The precipitate is centrifuged, washed and filtered through a glass-frit. After drying and weighing, the chemical yield of the separation process is calculated (20 mg Sr^{2+}-carrier $\approx$ 33.7 mg $SrCO_3$ = 100 %).

(8) The total β-activity determined with a GM-counter, refers to both strontium isotopes ^{89}Sr and ^{90}Sr. At the same time the daughter nuclide ^{90}Y, previously separated (point 1), gradually

grows in the sample and might be used as indicator for the ^{90}Sr-activity. Provided that the activity ratio of ^{89}Sr/^{90}Sr and total activity is high enough, both activities can be determined from a β-absorption curve right after ^{90}Y-separation.



Experiment 27: Measurements in Contaminated Areas

Theory, Units in Radiation Protection

Because of the nature of radioactivity it is of great importance that particular attention is paid to the measurements to assure adequate protection of the health of the workers in this field.

In order to accomplish this successfully, it is imperative to fix suitable units to define radiation sources and its effects. Competent for radiological units and measurements on the international level is the ICRU (= International Commission on Radiological Units and Measurements).

1. Activity

   Activity is the number of disintegrations per unit of time in a radioactive material

$$\boxed{\text{Activity} = \text{Decay Rate} = \frac{\text{Number of Disintegrations}}{\text{Unit of Time}}}$$

Recommended unit: The derived SI-unit for the activity of a radioactive material is Becquerel (symbol: Bq)

☞ Still admitted: The use of the "Curie" (Ci) as familiar unit is conditioned by history. One Curie is the amount of activity of 1 g natural Radium.

$1 \text{ Ci} = 3.7 \times 10^{10}$ Bq

$= 3.7 \times 10^{10}$ disintegrations/sec

$= 2.22 \times 10^{12}$ " /min

A derived unit used often is

$$\boxed{\text{Specific Activity} = \frac{\text{Activity}}{\text{Sample}}}$$

where the sample may be described by mass, volume or surface (e.g. Bq/kg, Bq/m^3, Bq/cm^2).

2. Dose

The effect of radiation on matter (air, solid matter, human body, etc.) is expressed by the term "dose".

a) Absorbed Dose

When ionizing radiation interacts with matter its loss of energy by different actions is described as

$$\boxed{\text{Absorbed Dose AD} = \frac{\Delta E}{\Delta m} = \frac{\text{Absorbed Energy}}{\text{Mass}}}$$

Recommended unit: The derived SI-unit of the energy dose is "Gray" (symbol: Gy).

1 Gray is equivalent to 1 Joule/kg.

Derived units of the energy dose are also all other quotients, formed with recommended units of energy and mass.

▷ Still admitted: "Rad", abbreviation for radiation absorbed dose (symbol: rd).

$$1 \text{ rd} = \frac{1}{100} \text{ Gy}$$

$$= \frac{100 \text{ erg}}{\text{g}} = \frac{6.2 \times 10^7 \text{MeV}}{\text{g}}$$

b) Ionisation Dose

The accepted unit of dose has been derived from a unit of energy dissipation, defined as the quantity of X-radiation (or γ-radiation) which produces an amount of electrical charge in a unit of matter.

$$\boxed{\text{Ionisation Dose ID} = \frac{\Delta Q}{\Delta m} = \frac{\text{Electric Charge}}{\text{Mass}}}$$

Recommended unit: The derived SI-unit of the ionisation dose is "Coulomb per kilogram" (symbol: C/kg).

▷ Still admitted: "Röntgen" (symbol: R).

$$1\ \text{R} = \frac{258}{1{,}000{,}000}\ \text{C/kg} = \frac{1\ \text{Electrostatic Unit}}{1.293\ \text{mg Air}}$$

$$= \frac{2.08 \times 10^9\ \text{Ion Pairs}}{1\text{cm}^3\ \text{Air}}$$

In contrast to the absorbed dose the ionisation dose may be measured directly.

c) Dose Equivalent

Various types and distributions of radiation do not produce the same biological effect. It has been proposed therefore that a derived unit should be applied taking into account the ionisation density in human tissue. It is described by the amount of energy lost per unit of length called "Linear Energy Transfer" (LET). From this measurable LET-value you obtain the "Quality Factor" (= QF).

$$\boxed{\text{Dose Equivalent DE} = \text{Absorbed Dose} \times \text{QF} \times \ldots}$$

Some other factors may be considered.

Recommended unit: The SI-unit for dose equivalent is "Sievert"
1 Sievert is equivalent to 1 Joule/kg
"Sievert" (symbol: Sv).

▷ Still admitted: "Rem", abbreviation for rad equivalent men
(symbol: rem).
1 rem = 1/100 Sv

d) Quality Factor

The quality factor described above as relative biological effect of radiation is determined by the specific ionisation (LET-value). QF = 1 is defined for quantum radiation effecting 100 ion pairs per μm water.

Type of Radiation	X ß γ	ß <0.03 MeV	n	α	Recoil Nuclei
QF	1	1.7	1 - 10	10	20

The determination of the dose equivalent consequently is based on

a) measuring resp. calculation of the energy dose and

b) determination of the type and energy of the radiation.

'In praxi' the following simplification can be used for γ-radiation of medium energy (0.2 to 2 MeV) and tissue absorber (human body):

$$1 \text{ R} \simeq 1 \text{ rd} \simeq 1 \text{ rem.}$$

3. Dose Rate

Dose rate is defined as the change (increase) of dose per unit of time

$$\boxed{\text{Dose Rate} = \Delta D/\text{Unit of Time}}$$

Recommended unit:	Absorbed dose rate	1 Gray/sec
	Ionisation dose rate	$1\ \frac{\text{Coulomb}}{\text{kg x sec}} = 1\ \frac{\text{Ampere}}{\text{kg}}$
	Dose equivalent rate	1 Sievert/h

▷ Still admitted:	Absorbed dose rate	1 rd/h or 1 rd/s
	Ionisation dose rate	1 R/h or 1 R/s
	Dose equivalent rate	1 rem/h or 1 rem/s

4. Dose Constant

The dose rate DR of a given activity A produced in a definite distance r may be calculated in case of

a) pure γ-emitter

b) point source

c) neglected absorption on the distance r.

$$\boxed{DR = D_{\gamma} \times \frac{1}{r^2} \times A}$$

Depending on the radiation energy the value of the dose constant D_{γ} defines the relation between activity and dose rate.

Table 8: Survey - Units in Radiation Protection

Variable	Symbol	Dimension	Unit	
			Recommended	Still Admitted
Activity	A	1/Time	1 Bq	1 Ci
Absorbed Dose	AD	Energy/Mass	1 Gy	1 rd
Absorbed Dose Rate	ADR	Energy/Mass x Time	1 Gy/s	1 rd/h
Ionisation Dose	ID	Charge/Mass	1 C/kg	1 R
Ionisation Dose Rate	IDR	Charge/Mass x Time	$1 \frac{C}{kg \times s} = 1 \frac{A}{kg}$	1 R/h
Dose Equivalent	DE	Energy/Mass	1 Sv	1 rem
Dose Equivalent Rate	DER	Energy/Mass x Time	1 Sv/h	1 rem/h
Quality Factor	QF	-	-	-

Table 9: Conversions

Variable	Unit	
	Recommended	Still Admitted
Activity	1 Bq = 2.7 × 10^{-11} Ci	1 Ci = 3.7 × 10^{10} Bq
Absorbed Dose	1 Gy = 10^{2} rd	1 rd = 10^{-2} Gy
Absorbed Dose Rate	1 Gy/s = 3.6 × 10^{5} rd/h	1 rd/h = 2.78 × 10^{-6} Gy/s
Ionisation Dose	1 C/kg = 3.88 × 10^{3} R	1 R = 2.58 × 10^{-4} C/kg
Ionisation Dose Rate	1 A/kg = 1.40 × 10^{7} R/h	1 R/h = 7.16 × 10^{-8} A/kg
Dose Equivalent	1 Sv = 10^{2} rem	1 rem = 10^{-2} Sv
Dose Equivalent Rate	1 Sv/h = 10^{2} rem/h	1 rem/h = 10^{-2} Sv/h

Introduction to the Experiment

To assure safety during handling of radioactive materials it is necessary to prevent the possibility of the organism to be irradiated from both internal and external sources.

When radioactive substances are manipulated as open radiation sources, attention must be devoted in particular to prevent these elements from entering into any organism.

This may be achieved, among others, by preventing or at least reducing to a minimum the possibility of radioactive contamination of the laboratory.

To determine the radiation and contamination levels that exist in such a laboratory, means that a continuous program of monitoring as follows is necessary:

1. Air monitoring: The air of the laboratory must continously be taken in over filters on which radioactive dust can be adsorbed and detected.
2. Dose monitoring: The β-γ-dose rate must be measured with a suitable dose monitor.
3. Contamination measuring: With a survey meter and by taking smear-tests you have to look for eventual contaminations.

In the following experiment, a table separated into three areas should be examined for eventual radiation and contamination.

Apparatus and Materials

- Dose monitor (ionisation chamber, β-γ-monitor)
- Contamination monitor (α,β,γ-counter, survey meter)
- Filter-paper for smear-test ($\simeq$ 5 cm ϕ)
- G-M counter (end-window type)
- Gloves
- β-standard source

Experimental Details

(1) Dose monitoring:

Measure the dose rate of each area with a β-γ-monitor and note it in table 10.

(2) Contamination measuring with survey meter:

Using the β-standard source determine the efficiency η_D of the survey meter as follows:

$$\boxed{\eta_D = \frac{R_M - R_o}{R_E} \times 100\ \%}$$

R_M = Measuring rate

R_o = Background

R_E = Emission rate of the source

Measure the count rate of each area with the monitor (attend to constant geometry of the survey) and calculate the strength of each contamination A $[Bq / cm^2]$.

$$\boxed{A\,[Bq / cm^2] = \frac{R_M - R_o}{\eta_D \times A_D \times 60}}$$

A_D = Area of the detector

(3) Contamination measuring with smear-test:

Determine the efficiency η_D of the G-M counter (see 2). wipe off about 100 cm^2 of each area using filter-papers and determine the count rate with the G-M counter (wear gloves!). Calculate the strength of the contamination A $[Bq/cm^2]$ and note it.

$$\boxed{A \ Bq/cm^2 = \frac{R_M - R_o}{\eta_D \times \eta_{WT} \times A_{WT} \times 60}}$$

η_{ST} = Efficiency of smear-test, part of dust you wipe off (about 40%)

A_{ST} = Wiped area (100 cm^2)

▷ Discuss the distinct results.

Table 10: Measuring in Contaminated Areas

Area	Dose Monitor DR [Gy/h]	Contamination Monitor		G-M counter for smear -test	
		[counts/min]	[Bq /cm^2]	[counts/min]	[Bq /cm^2]
I					
II					
III					
		R_o = counts/min η_D = % A_D = cm^2		R_o = counts/min η_D = % η_{ST} = 40 % A_{ST} = 100 cm^2	

Exercises to 3.3.2

1. What is the weight of the active species in samples containing 37 MBq (1 mCi) of activity, for ^{131}I, ^{3}H, ^{60}Co, (freshly separated) ^{238}U? (Experiment 14)

2. What weight of ^{234}Th and ^{234m}Pa will be present in 1g of an ^{238}U-sample in secular equilibrium? (Experiment 18)

3. One of the isotopes of gadolinium, ^{152}Gd, is radioactive. Its abundance in naturally occuring element is 0.2 %. A sample, consisting of 5.0 g of metallic gadolinium was found, by approximate methods, to emit 114 α-particles every 4 hours. Calculate the half-life of ^{152}Gd! (Experiment 14)

4. The daughter nuclide ^{137m}Ba has been separated from a ^{137}Cs-sample. The activity of ^{137}Cs immediately after separation amounts to 37 kBq (1 μCi).
   Calculate the values after 2 hours for
   a) the emission rate of the ^{137}Cs-sample!
   b) the number of γ-rays emitted!
   c) the number of conversion electrons emitted!
   d) the total electron emission! (Experiment 13)

5. Describe the difference between isotopic and non-isotopic carrier.
   In which cases non-isotopic carrier will be applied? (Experiment 18)

6. Enumerate the steps for the determination of ^{89}Sr and ^{90}Sr using either a Geiger-Müller or a Liquid Scintillation counter! (Experiment 26, Experiment 8)

7. In the following table the coefficients for the distribution of some fission and fissionable nuclides between Tri-n-butylphosphate (30 % in kerosene) and 3 M nitric acid solution are given.
Explain the different values and their consequences for PUREX-reprocessing of spent nuclear fuel! (Experiment 20).

Element	$D = \frac{R(org)}{R(aq)}$
Cs	0.0001
Ce^{III}	0.0008
Zr	0.2
U	40
Pu^{IV}	10
Pu^{III}	0.08

3.3.3 Application of Radioisotopes

Experiments:

28. Use of ^{252}Cf in Instrumental Neutron Activation Analysis

Objective: ^{252}Cf-neutron sources have to be applied for Vanadium determination in Cracking Catalysts and crude oil samples using on-line process analysis.

29. Radiochemical Activation Analysis - Determination of Ag and Tl in Technical Grade Lead

Objective: Radiochemical Neutron Activation has to be learnt and applied for tracer analysis in lead.

30. Tracer Technique - Solubility of PbI_2

Objective: The student has to apply radioactive iodine in tracer technique. The solubility of PbI_2 has to be determined.

31. Isotope Dilution Analysis - I^- Determination in Presence of Large Quantities of Cl^- and Br^-

Objective: The principal of Isotope Dilution Analysis is reviewed and its application in analytical chemistry presented.

32. Application of Radionuclides in Industry

Objective: The application of sealed radioactive sources in industry is shown in four different examples, including the determination of liquid levels, layer thickness and humidity and in X-ray fluorescence analysis.

33. Homogeneous Isotope Exchange Reaction of Ethyliodide

Objective: An example for the use of isotopes in kinetic exchange reaction is presented. The student has to study the homogenious iodine exchange in organic molecules.

34. Insuline Labelling with ^{131}I

Objective: Iodine-131 as foreign atom has to be introduced in nonisotopic labelling of insuline.

35. Naphtalene Labelling with Tritium

Objective: The reaction of Grignard-compounds with ^{3}H- containing H_2O is used for tritiating an organic molecule in a definite position.

36. Szilard-Chalmers Reaction I - Change of the Chemical Bond of Ethyl Iodide by (n,γ) Processes

Objective: The student should be able to understand the principle of Szilard-Chalmers reactions. The classical experiment with C_2H_5I has to be repeated.

37. Szilard-Chalmers Reaction II - Change of Oxidation State of Manganese by (n,γ) Processes

Objective: The chemical effects after irradiation of crystalline species has to be studied. The student has to determine the Szilard-Chalmers effiency, and the amount of retention with and without annealing.

38. Szilard-Chalmers Reaction III - Separation of the ^{80m}Br-Isomeric State

Objective: The knowledge about chemical effects after (n,γ) reaction should be extended. The rearrangements in the system bromo-benzene have to be understood.

39. Final Practical Work: Quantitative Analysis for Trace Elements in Samples by Neutron Activation (Coco-nut, Topas, Natural Uranium Ores)

Objective: The student should be able to apply instrumental neutron activation analysis on the problem of trace element analysis of coco-nut, topas and natural uranium ores.

40. Final Practical Work: Identification and Separation of an Unknown Mixture of Radionuclides

Objective: An unknown mixture of radionuclides has to be identified by instrumental methods and radiochemical separation. The student has to apply the equipment and methods used in the proceeding experiments.

Experiment 28: Use of ^{252}Cf in Instrumental Neutron Activation Analysis

Theoretical Introduction

Due to its spontaneous fission properties the man-made radionuclide Cf-252 with a half-life of 2.6y emitts 2.3×10^{12} neutrons/g s with a mean energy of 2.3 MeV. Although the available thermal neutron flux of 10^7 n/cm$^2 \cdot$ s is low compared to a research reactor Cf-neutron sources have practical advantages. With reasonable costs and low maintenance and radiation protection control the flux is sufficient for numerous applications of neutron activation analysis (NAA) in education and industry.

The following exercise gives some examples showing the practical application of the time function in activation analysis

$$f(t) = (1-e^{-\lambda t}) \times e^{-\lambda t'}$$

with t = activation time

t' = cooling time (time between end of irradiation and measurement).

a) Growth Factor

Due to its practical decay within irradiation the activity formed increases exponentially up to saturation A_S (figure 57b).

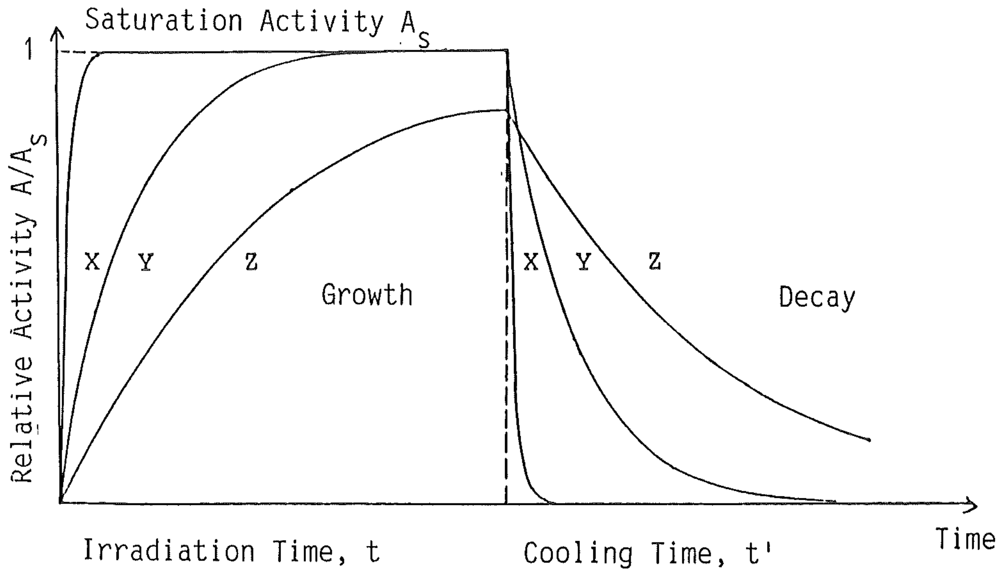


Figure 57b: Growth and Decay of Radionuclides
(X) Nuclide with short half-life
(Y) Nuclide with medium half-life
(Z) Nuclide with long half-life

In the first example Al-plates are irradiated with various time intervals. The Al-28-count rate related to its saturation value (measuring time 0.5 min, cooling time 1 min) is plotted against irradiation time.

Sample	R_N	Irradiation Time		R/R_S
	(Imp/0.5 min)	t	$T_{1/2}$ (^{28}Al)	
1		34 s	0.25	
2		1 min 8 s	0.5	
3		2 min 15 s	1	
4		6 min 45 s	3	
5		22.5 min	10	1

b) Determination of Vanadium in Catalyst Samples

In the second example the use of Cf-252-neutron activation for the determination of cracking catalysts is described. The method is quick, cheap and suffiently sensitive for most components of the catalyst as well as poisoning metals (e.g. V). Because of their low resolution the selection of appropriate irradiation and cooling time is essential when using NaI-scintillation detectors.

Procedure:

1.5 g of catalyst powder each is weighed and irradiated for 20 min (sample a) and 48 h (sample b), respectively.

Measuring conditions

- sample a: 5 min, no cooling time
- sample b: 1 h, no cooling time and
  1 h, 1.5 h cooling time

By known irradiation and activation data the amount of V in the catalyst sample is calculated.

c) On-line Vanadium-Determination in Crude Oil

In order to optimize the operation time of a cracking catalyst the amount of V in crude oil is precondition. It might be determined by use of neutron activation of a by-pass sample of the corresponding process stream (figure 57c).

In the third experiment three standard solutions with known V-amount are irradiated in a loop-arrangement (rate of flow 220 ml/min; activation time 12 min) and measured on-line by use of a NaI-detector (measuring time 12 min). From the calibration curve the V-amount of an unknown crude oil sample is determined.

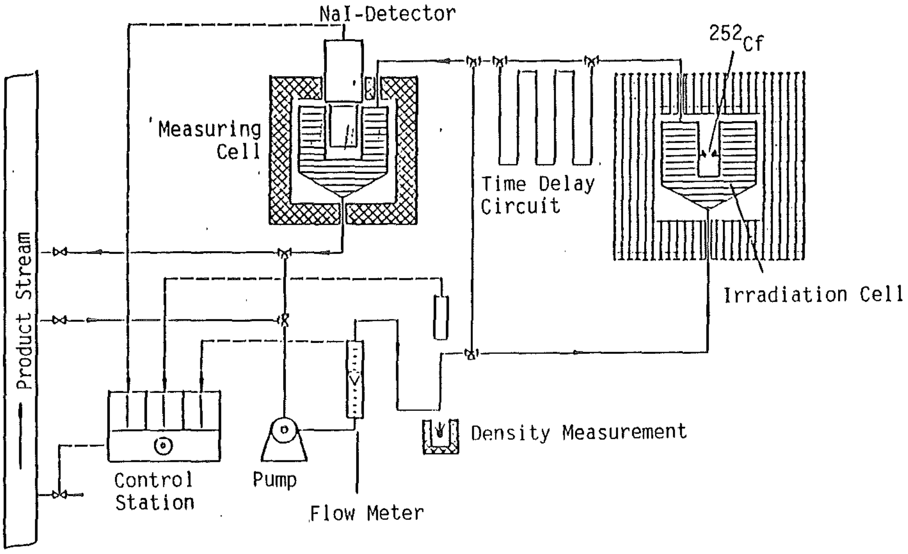


Figure 57c: On-line Loop Arrangement for Determination of Trace Elements in Process Streams

d) Analysis of "Warm" Superconductors

The recently developed so called "warm superconductors" (critical temperature higher than temperature of liquid nitrogen) consist mainly of mixed oxides of the elements Cu, La, Y, and/or Ba. Most of these elements are easily to be activated in a thermal neutron flux and thus might be determined. By variation of irradiation and cooling time the short lived copper isotope ^{66}Cu ($T_{1/2}$ = 5.1 m, E_γ = 1039 keV) and (or) the longer lived isotopes ^{140}La ($T_{1/2}$ = 40 h, E_γ = 1596 keV,....) and ^{139}Ba ($T_{1/2}$ = 83 m, E_γ = 166 keV) are activated as well (Figure 57d).

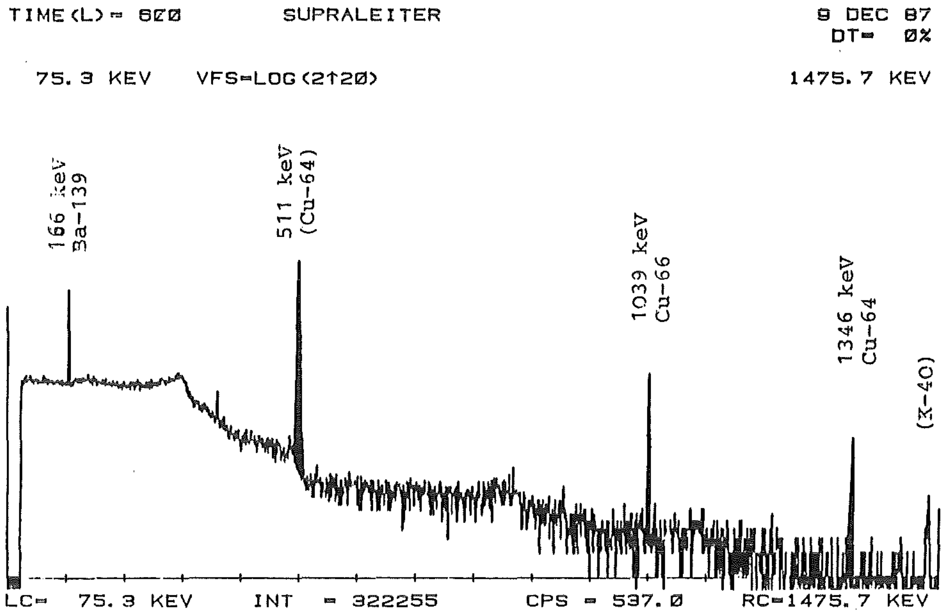


Figure 57d: γ-Spectrum of a n-activated "Warm Superconductor" (Y-Ba-Cu-Oxide, irradiation time 16 h, no cooling time, measuring time 10 m)

Experiment 29: Radiochemical Activation Analysis - Determination of Ag and Tl in Technical Grade Lead

Theoretical Introduction

For a general nuclear reaction

$$A + x \rightarrow y + B \qquad (1)$$

the rate of formation of the nuclide B is given by

$$\boxed{\frac{dN_B}{dt} = \sigma \cdot \phi \cdot N_A} \qquad (2)$$

where σ = Activation-cross-section
ϕ = Flux density of projectile
N_A = Number of target atoms

If the product nuclide B is radioactive its decay during time of irradiation, given by the decay constant λ, has to be considered

$$\frac{dN_B}{dt} = \sigma \cdot \phi \cdot N_A - \lambda \cdot N_B \qquad (3)$$

Integration between t = 0 and t = t (time of irradiation) for $t = 0 \rightarrow N_B = 0$ results in

$$N_{B(t)} = \frac{\sigma \cdot \phi \cdot N_A}{\lambda} (1 - e^{-\lambda t}) \qquad (4)$$

Since $$A = \frac{dN_B}{dt} = \lambda \cdot N_B \qquad (5)$$

equation (4) becomes

$$\boxed{A_{(t)} = \sigma \cdot \phi \cdot N_A \cdot (1 - e^{-\lambda t})} \qquad (6)$$

or

$$\boxed{A_{(t)} = \frac{m \cdot H \cdot N_L \cdot \sigma \cdot \phi}{M} (1 - e^{-\lambda t})} \qquad (7)$$

where m = Mass of irradiated element

H = Isotopic abundance

N_L = Avogadro's (Loschmidt's) number

M = Atomic weight

Because of the exponential decay of the product, saturation will occur after about $t = 10\,T_{1/2}$; longer time of irradiation will not increase activity considerably.

If measurements of the sample may not be executed directly after irradiation, decrease in activity has to be considered in the mean time t'

$$\boxed{A_{(t,t')} = \frac{m \cdot H \cdot N_L \cdot \sigma \cdot \phi}{M} \left(1 - e^{-\ln 2 \cdot \frac{t}{T_{1/2}}}\right) \cdot e^{-\ln 2 \frac{t'}{T_{1/2}}}} \qquad (8)$$

Introduction to the Experiment

To determine the amount of Ag and Tl in technical grade lead activation analysis has been suggested.

The Pb-sample together with a standard, containing known amounts of Ag and Tl is activated in a nuclear reactor (about 10^{12} neutrons/cm^2 x s) for at least one week. The following reactions will occur

$$^{109}Ag \xrightarrow[\sigma\,=\,3.5\text{ b}]{(n,\gamma)} {}^{110}Ag \xrightarrow[235\text{ d}]{\beta^-(\gamma)} {}^{110}Cd$$

$$^{203}Tl \xrightarrow[\sigma\,=\,8.0\text{ b}]{(n,\gamma)} {}^{204}Tl \xrightarrow[3.8\text{ a}]{\beta^-} {}^{204}Pb$$

After some time the short lived radionuclides will decay and ^{110}Ag and ^{204}Tl may be separated by chemical means.
Under identical conditions Ag and Tl are precipitated with carrier in standard and analyte.
After measuring, the amounts of Ag or Tl may be calculated by comparing the net rates of unknown (R_N) and of standard solution (R'_N) with the masses of the considered nuclide m and m'

$$\frac{R_N}{R'_N} = \frac{m}{m'} \qquad (1)$$

Masses m and m' may be expressed by the weights E resp. E' of the samples and their contents p and p' (percent amounts) of the corresponding nuclides

$$m = \frac{p \times E}{100} \quad (2) \qquad \text{and } m' = \frac{p' \times E'}{100} \quad (3)$$

Substitution in (1)

$$\frac{R_N}{R_N'} = \frac{E \times p}{E' \times p'} \qquad (4)$$

Finally, the amount of the unknown nuclide p' is given by

$$\boxed{p' = p \times \frac{R_N \times E}{R_N' \times E'}} \qquad (5)$$

Apparatus and Materials

- G-M counter (end-window type) with a suitable tube holder
- Scaler/timer
- NaI(Tl)-scintillation counter (well type)
- Multi- channel analyser
- Sample solution (1.1 mg Pb/ml)
- Standard solution (1.8 mg Pb/ml; 0.105 % Ag, 0.05 % Tl)
- HCl (12 M)
- NaOH (2 M)
- $KBrO_3$ (solid)
- 2 Centrifuge tubes (15 ml)
- 2 Beakers (100 ml)
- 2 Beakers (50 ml)
- Filtering apparatus (4 cm Ø)
- Fine filters and hard filters (4 cm Ø)

Experimental Details

(1) 1 ml of sample and standard solution, containing Ag and Tl-carrier ions, are placed into two marked centrifuge tubes (15 ml). Both should be prepared side by side and measured under exactly the same conditions.

(2) 1 ml HCl (12 M) and 10 mg $KBrO_3$ (for oxidation of Tl) are added. The solution is heated for about 3 minutes in a water bath until bromine gas disappears (caution: solution tends to brisk!)

(3) The solution is diluted to a volume of 12 ml with cold water and centrifuged. Remove the supernate into a beaker, stir the AgBr(Cl)-precipitate (containing the ^{110}Ag) with a dilute solution of $HCl/KBrO_3$ and centrifuge again. The supernate is poured into the beaker above.

(4) The γ-radiation of the ^{110}Ag in the centrifuge tubes is measured by means of a NaI(Tl)-detector (well type).

(5) In order to precipitate ^{204}Tl, NaOH (2M) is added dropwise in a beaker to the Tl-containing solution until it turns basic.

(6) After heating (water bath) the dark brown precipitate of TlOOH is separated with a fine filter supported with a hard filter. With a piece of tape the filtercake is placed on a suitable support and measured in a G-M counter (β-radiation of ^{204}Tl).

Experiment 30: Tracer Technique-Solubility of PbI_2

Introduction

Using a tracer method, the solubility of lead iodide at constant temperature has to be determined in the following experiment. Lead iodide is therefore labelled with ^{131}I, its relative specific activity calculated and the solubility determined by activity measurement.

Apparatus and Materials

- ^{131}I-solution (approx. 4 x 10^4 Bq/ml)
- Pb-acetate solution (100 mg Pb/ml)
- Potassium iodide
- Volumetric flask
- Pipettes (1 ml, 5 ml)
- Centrifuge tube (50 ml)
- Centrifuge
- Filtering apparatus
- Fine filters
- Test tubes
- NaI(Tl)-scintillation detector

Experimental Details

Preparation of the ^{131}I-labelled KI-solution and precipitation of PbI_2:

(1) To a 10 ml volumetric flask containing a definite amount of KI (about 50 mg) 1 ml of a carrier-free ^{131}I-solution is added and filled with H_2O (dist.) up to the mark.

(2) 1.0 ml of the solution is pipetted into a test tube and measured for activity ($\longrightarrow R_{M(KI)}$).

(3) After transferring the total labelled KI-solution into a centrifuge tube, PbI_2 is precipitated with 1 ml Pb-acetate-solution (100 mg Pb/ml).
The mixture is centrifuged, the supernate decanted and the precipitate washed twice with 3 ml H_2O each.

Determination of the solubility of PbI_2 at room temperature:

(4) The precipitate is mixed with 8 ml H_2O while heating up to 50-60°C (water bath). The centrifuge tube is removed from the water bath and cooled to room temperature

(5) After two hours (establishment of solubility equilibrium) a part of the solution (3-4 ml) is filtered and the temperature is noted. 1.0 ml of the filtrate is transferred into a test tube and measured for activity ($\longrightarrow R_{M(PbI_2)}$).
(Caution! Filtering apparatus, pipettes and test tubes must be clean and dry!)

Discussion

The solubility corresponds to the amount of PbI_2 (m_{PbI_2})

$$\boxed{m_{PbI_2} = \frac{R_{N(PbI_2)}}{\overset{*}{A}_{(PbI_2)}}} \qquad (1)$$

where

$R_{N(PbI_2)}$ = relative activity (net rate) of 1 ml saturated PbI_2-solution ($R_{N(PbI_2)} = R_{M(PbI_2)} - R_o$)

$\overset{*}{A}_{(PbI_2)}$ = relative specific activity of PbI_2 (= relative activity per mg PbI_2)

$$\overset{*}{A}_{(PbI_2)} = \frac{R_{N(KI)} \times 10}{m_{KI} \times \frac{MG(PbI_2)}{2 \times MG(KI)}} = \frac{R_{N(KI)} \times 10}{m_{KI} \times 1.39} \qquad (2)$$

With eq. (2) the solubility may be calculated via

$$\boxed{m_{PbI_2} = \frac{R_{N(PbI_2)} \times m_{KI} \times 1.39}{R_{N(KI)} \times 10}} \quad \text{in mg } PbI_2\text{/ml}$$

$R_{N(KI)}$ = net rate of 1 ml labelled KI-solution ($R_{N(KI)} = R_{M(KI)} - R_o$)

m_{KI} = amount of weighed KI in mg

$MG(PbI_2)$ = molecular weight of PbI_2 (461.0)

$MG(KI)$ = molecular weight of KI (166.0)

Using a thermostat for temperature control the solubility might be determined for other temperatures.

Experiment 31: Isotope Dilution Analysis- I^- Determination in Presence of Large Quantities of Cl^- and Br^-

Theoretical Introduction

Because of the high sensivity of radioactive tracers, isotope dilution analysis presents a suitable method for the determination of volumes and amounts of substances. Due to the fact that only a part of the concerning components has to be separated from the analysis system its application is essentially valuable when quantitative separation procedures are not available. The amount of the unknown component (m_x) is calculated by

$$\boxed{m_x = \frac{A_{In}}{A_s} \times m_s}$$

with
A_{In} = activity of added indicator
A_s = activity of subproduct
m_s = amount of subproduct

The activity may be substituted by the corresponding net rates in the case of identical measuring conditions for indicator and subproduct

$$m_x = \frac{R_{In}}{R_s} \times m_s$$

In the following experiment isotopic dilution with ^{131}I will be applied for the determination of I^- in presence of large quantities of Cl^- and Br^-. After addition of the ^{131}I-indicator chemical pure AgI is separated as subproduct by precipitation from strong ammoniacal medium. (Under these condictions the Ag^+-concentration is highly diminuished by the formation of comlex $Ag(NH_3)_2^+$-ions, in consequence only AgI is precipitated.)

To avoid weighing the active AgI, Ag^+ is precipitated by substoichiometric addition of 0.1 M $AgNO_3$-standard solution. The iodine amount then is calculated by multiplying the volume of added 0.1 M $AgNO_3$ with the stoichiometric factor:

1 ml $AgNO_3$-solution (0.1 M) $\hat{=}$ 12.69 mg I = m_s

Apparatus and Materials

- ^{131}Iodide-solution (2×10^4 Bq in 0.1 ml solution, carrier free)
- Analyte solution (KI, KBr and KCl, about 0.1 M)
- $AgNO_3$-solution (0.1 M)
- NH_4OH (conc.)
- NH_4OH (1 M)
- $NaNO_3$ (solid)
- Centrifuge tube
- Burette
- Beaker (50 ml)
- NaI(Tl)-scintillation detector

Experimental Details

(1) The centrifuge tube containing the ^{131}I-activity in 1 ml NH_4OH (conc.) is measured for activity in a well-type scintillation detector ($\longrightarrow R_{In}$).

(2) A definite amount of the analyte mixture (about 2.5 ml) is added from a burette.

(3) After intimately mixing Ag^+ is precipitated with 1.0 ml $AgNO_3$-solution (0.1 M). Some $NaNO_3$ is added and the mixture is heated in a waterbath for about 10 min.

(4) The solution is centrifuged, the supernate discarded and the precipitate washed with 2 ml NH_4OH (1 M).

(5) The net rate of the remaining AgI-precipitate is determined ($\longrightarrow R_s$).

Experiment 32: Application of Radionuclides in Industry

In the following experiment three examples are outlined for the technical application of radionuclides. They include

(a) Determination of Liquid Levels
(b) Determination of Layer Thickness and
(c) Radionuclide Activated X-Ray Fluorescence Spectrometry

(a) Determination of Liquid Levels

For control, measurement and regulation of liquid levels, the use of radionuclides is highly advantageous due to the absence of mechanical or electrical connections with the interior of the reservoir. γ-emmiters usually are preferred as radiation source due to their higher range. Source and detector are fixed at opposite sides of the tank (figure 58). The attenuation occurs both by the wall (constant contribution) and the filling material. When the liquid enters the path of rays the radiation absorption rises and causes a change of the count rate in the detector.

For the determination of unknown liquid levels a calibration curve has to be recorded by plotting the count rates of the detector against different levels of filling (figure 60).

(b) Determination of Layer Thicknesses

Backscattering of β-particles (see experiment 4) represents a method for non-destructive measurement of thin layers (about 1 mm down to some μm) on suitable supports. Basic condition is the difference in atomic number of layer and support. The cummulative β-count rate of the detector (figure 59) depends on the layer-thickness for a given support.

Using standard samples of known thickness, the calibration curve (count rate against layer-thickness) (figure 61) has to be plotted and the value of an unknown layer determined.

c) Radionuclide Activated X-Ray Fluoresecence Spectrometry

X-Ray Fluorescence Analysis (XRF) is based on the emission of characteristic X-rays after sample activation. As primary radiation source a sealed ^{241}Am-source (59.6 keV X-ray) is used in the arrangement (figure 62). The characteristic X-rays are detected by an intrinsic Ge-detector (better SiLi) with multichannel analyzer.

For the qualitative and quantitative determination of elements by XRF the spectrometer has to be calibrated with standard samples of known elements.

Element	Atomic No.	K_α- Energy [keV]
Fe	26	6.40
Ni	28	7.47
Zr	40	15.77
Mo	42	17.48
Cd	48	23.17

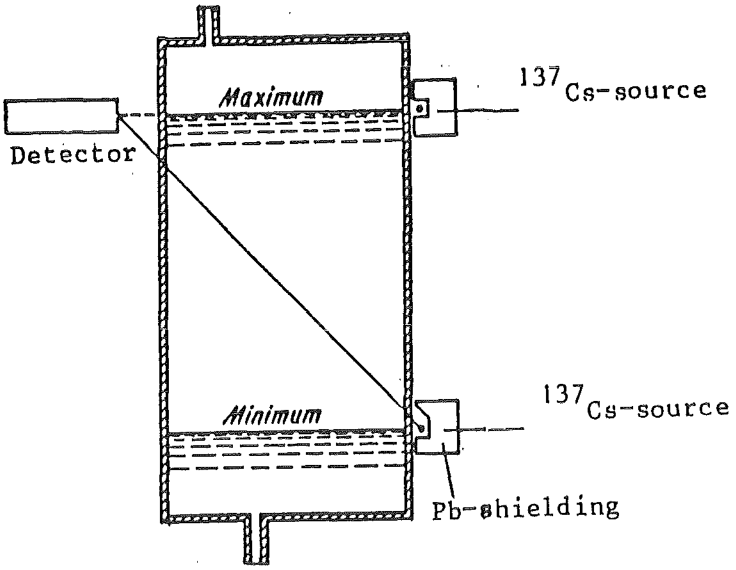


Figure 58: Arrangement for Measurement of Liquid Levels

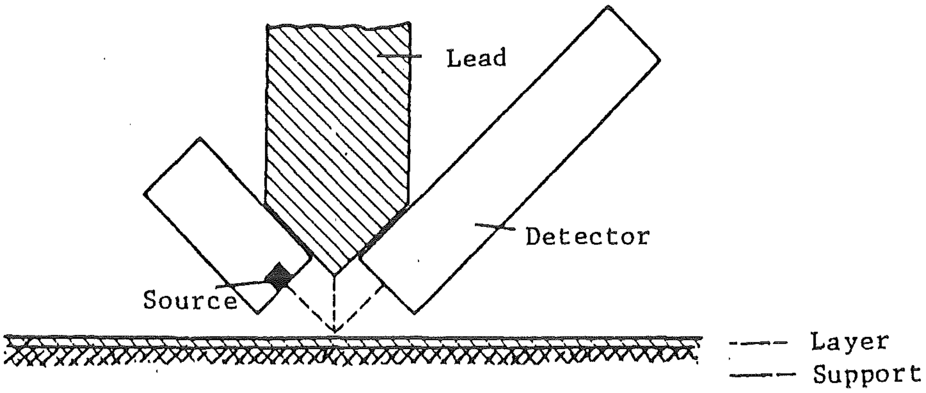


Figure 59: Arrangement for Measurement of Layer Thicknesses

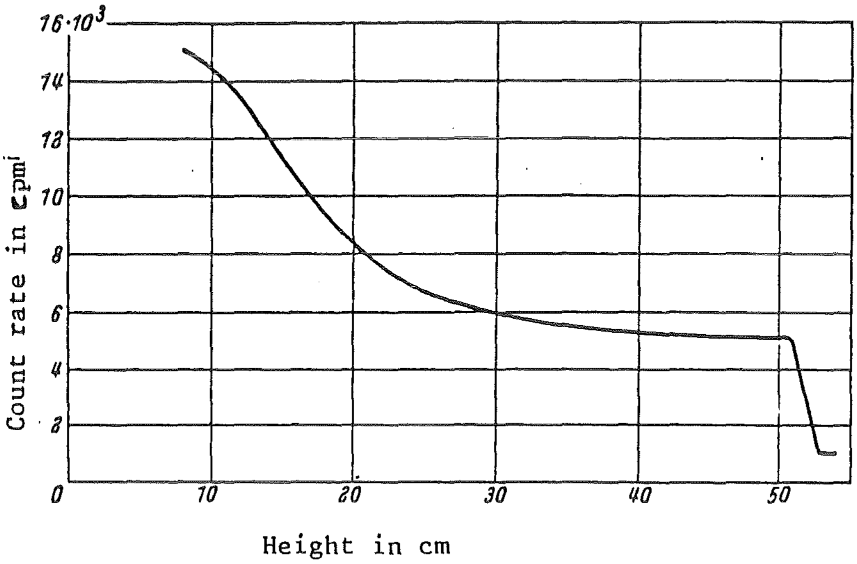


Figure 60: Typical Characteristic for Level Measurements (2-source-system)

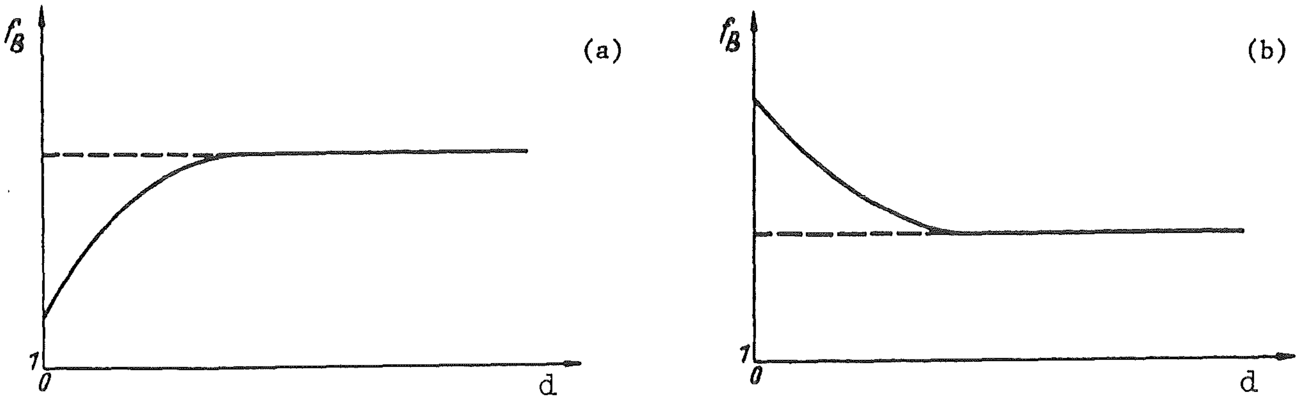


Figure 61: Backscattering Factor f_B vs. Layer Thickness d
(a) Z (layer) > Z (support)
(b) Z (support) > Z (layer)

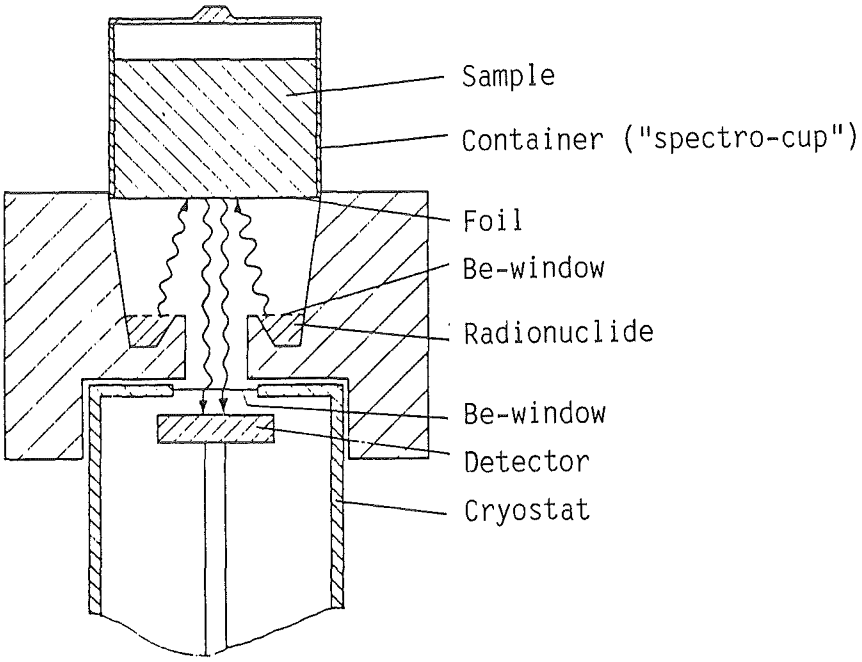


Figure 62: Radionuclide Activated XRF

Experiment 33: Homogeneous Isotope Exchange Reaction of Ethyliodide

Theoretical Introduction

The use of radionuclides enables one to distinguish between different isotopes of the same element. In consequence the physico-chemical exchange behaviour of different mixtures could be investigated when the distribution of an isotopic tracer is determined in different reaction phases.
Organic exchange processes in homogeneous phase occur in principal according to two different mechanisms:

- SN_1: monomolecular nucleophilic substitution, reaction rate is fixed by the dissociation step

$$RX \longrightarrow R^+ + X^-$$

- SN_2: bimolecular law, formation of compound complexes, reaction rate depends on both substrate RX and nucleophil Y

$$RX + Y^- \longrightarrow [X \cdots \overset{\backslash /}{\underset{|}{R}} \cdots Y]^-$$

The mechanism of the corresponding reaction depends on the conditions as well as the structure of the reacting agents.

For a homogeneous isotope exchange reaction of the general form

$$AC + BC^* \rightleftharpoons AC^* + BC \qquad (1)$$

the exchange rate R_V is calculated from equation (2)

$$R_V \cdot t = -\frac{a \cdot b}{a + b} \cdot \ln \left(1 - \frac{X_t}{X_\infty}\right) \qquad (2)$$

a and b relate to the concentration used for AC and BC^*, X_t and X_∞ to the concentration of the labelled molecules AC^* at time t and at reaction equilibrium respectively.

With $t_{1/2}$ ($\frac{X_t}{X_\infty} = 0.5$) as exchange half-life and the suggestion of a bimolecular reaction type, equation (2) may be simplified to

$$\boxed{R_v = k \cdot a \cdot b = \frac{a \cdot b}{a+b} \times \frac{0.693}{t_{1/2}}} \qquad (3)$$

or

$$\boxed{k = \frac{0.693}{(a+b)t_{1/2}}} \qquad (4)$$

The rate constant k of a bimolecular reaction (dimension l/mol x s) is independent on the concentrations of the reacting agents. It is calculated from the known concentrations of AC (a) and BC^* (b). From the plot of ($1 - \frac{X_t}{X_\infty}$) versus reaction time t on semilogarithmic graph paper, the exchange half-life is given from the slope of the straight line (in analogy to the half-life of the radioactive decay). Using different temperatures for the reaction, the activation energy of the isotope exchange can be determined additionally.

In the following experiment the iodine exchange reaction between C_2H_5I and NaI as example has to be investigated. The excellent exchange behaviour of iodide ions is practically applied in radiochemistry for the preparation of iodine labelled compounds (see experiment 34, Insuline Labelling with ^{131}I). The deviation of the mechanism from SN_2 in presence of water is due to the polar influence of the H_2O-molecules.

Apparatus and Materials

- NaI (Tl)-scintillation detector (well type)
- Stop-watch
- Separatory funnel (200 ml)
- Reflux condenser
- Volumetric flask (100 ml)

- Measuring cylinder (25 ml, 100 ml)
- Pipettes (0.5 ml, 10 ml, 20 ml)
- ^{131}I-solution (10^5 Bq/ml)
- NaI
- Ethyliodide
- Ethanol

Experimental Details

(1) In each of 3 volumetric flasks (100 ml) the following substances are added

- 3 g NaI + 0.1 ml ^{131}I-solution + 30 ml C_2H_5I
- 4.5 g NaI + 0.1 ml ^{131}I-solution + 30 ml C_2H_5I
- 4.5 g NaI + 0.1 ml ^{131}I-solution + 30 ml C_2H_5I + 1 ml H_2O

When ethyliodide is added, the stop-watch is started (beginning of the reaction). The flasks finally are filled up to 100 ml with ethanol.

(2) At different time intervals (5, 20, 40, 80 minutes) 10 ml of the reaction mixture is removed and equilibrated with 100 ml H_2O in a separatory funnel.

(3) 2 ml each of the heavier ethyliodide phase is transferred into a test tube and measured for activity ($R_N = X_t$).

(4) In order to determine the equilibration of the corresponding reaction 25 ml of each solution are heated under reflux, extracted with H_2O after cooling and the separated C_2H_5I measured as discribed above ($R_N = X_\infty$)

Experiment 34: Insuline Labelling with ^{131}I

Theoretical Introduction

Radioactive tracer compounds are usually used for solving problems in research and clinical diagnosis. In organic and biochemistry carbon-14 or tritium labelled compounds which may easily be prepared by exchange reactions or chemical synthesis are prefered.
For more complicated compounds labelling via sythesis is time consuming or even impossible. Due to their low energy ß-particles ^{14}C- and ^{3}H-labelling for nuclear medicine especially for in-vivo examinations is unsuitable.

For those cases it may be advantageous to introduce a molecule-foreign radioactive atom (nonisotopic labelling).

Nevertheless care must be taken that the introduction of foreign atoms does not change the chemical or biochemical behaviour of the initial molecule.
For the synthesis of insuline-^{131}I nonisotopic labelling is used.
Natural insuline exists of two peptide chains A and B (51 aminoacid groups) which are connected by two cytosine disulfide bridges (figure 63).

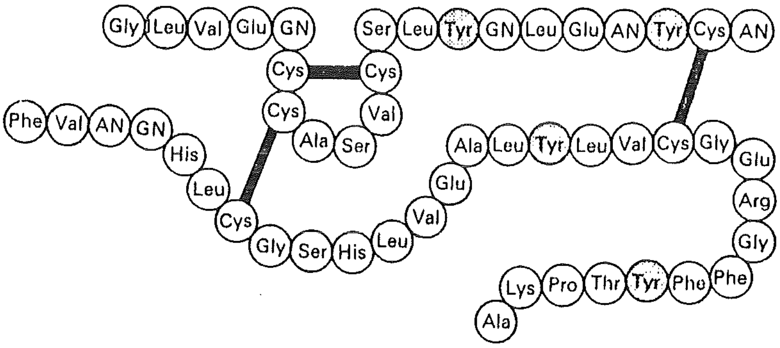
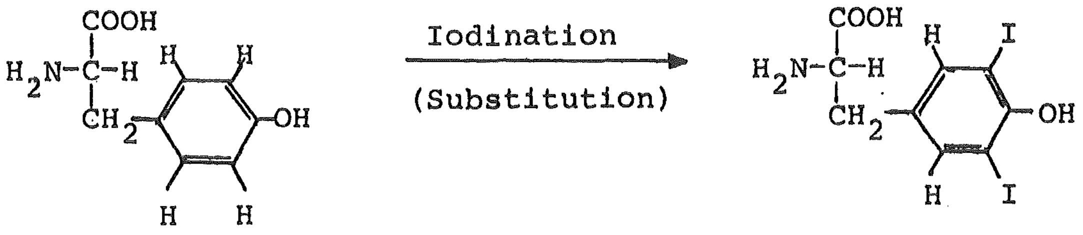


Figure 63: Aminoacid-sequence of Insuline (pancreas of a cattle)

Iodination takes place at the existing 4 tyrosine molecules (position 14 and 19 of chain A, 16 and 26 of chain B) in ortho-position to the phenolic hydroxyl groups of tyrosine resulting 3,5-Diiodtyrosine:



L(-)-Tyrosine

L-3.5-Diiodtyrosine

In the following experiment depot-insuline has to be labelled with ^{131}I by three different methods:

(1) with elementary iodine in potassium iodide solution
    (I / KI-Solution)

(2) with I-nasc. from KI, KIO_3 and acid

(3) with potassium iodide and chloramine-T

Iodination in each method has to be carried out under identical physical conditions (reaction temperature 40^{o}c and reaction time 20 min).

Apparatus and Materials

- 2 ml ^{131}I-solution (10^4Bq/ml)
- Depot-insuline (10 ml)
- HCl (0.05 M)
- Citrate buffer (0.5 M, pH 5.5)
- Iodine/potassium iodide solution (16.6 mg KI+12.7 mg Iodine/10ml)
- Potassium iodide solution (8.3 mg KI/10ml)
- Potassium iodate solution (2.1 mg KIO_3/10 ml)
- HCl (1 M)
- $Na_2S_2O_5$-solution (15 mg/10 ml)
- Chloramine-T (56.4 mg/10 ml)
- Graduated centrifuge tubes (15 ml)
- Test tubes
- Centrifuge
- NaI(Tl)-scintillation counter (well-type)

Iodination Mixtures:

(1) 0.5 ml iodine-potassium iodide solution
(2) 0.4 ml H_2O, 1 ml potassium iodide solution, 1 ml potassium iodate solution, and 0.1 ml 1 M HCl
(3) 1 ml potassium iodide solution, 0.5 ml chloramine-T solution, and 1.5 ml H_2O

To avoid losses of iodine the components should be combined just before iodination.
To avoid air contamination by oxidation of iodide the ^{131}I-containing waste solution should be gathered in bins free of oxidants!

Experimental Details

Preparation:

(1) The content of a vial depot-insuline (10 ml = 15.4 mg insuline = about 400 I.U.) is precipitated with 1 ml citrate buffer in a centrifuge tube on ice and centrifuged for 5 min. at 2500 rpm. The supernate is the precipitate dissolved in 2 ml 0.05 M HCl. The ^{131}I-solution (2 ml) used for iodination is measured in a well-type scintillation counter (⟶ $R_I(1)$).

Iodination step:

(2) The iodination substances are combined and mixed with the ^{131}I-solution. The mixture is transfered into a centrifuge tube containing the reprecipitated insuline solution. The empty test tube is measured for activity (⟶ $R_I(2)$).

(3) The tube is maintained at 40°C (water bath) for 20 min. (In case of KI and chloramine-T, excess chloramine-T has to be removed after iodination. $Na_2S_2O_5$-solution (1.5 mg/ml) is added dropwise to the mixture after cooling to room temperature.)

Purification step:

(4) After iodination the centrifuge tube is cooled (ice bath) and the insuline precipitated with 2.5 ml of cold citrate buffer. After further cooling (5 min) the solution is centrifuged at 2500 rpm for 5 min. The supernate and the precipitate washed with 1 ml citrate buffer and finally with 3 ml H_2O.

(5) For further purification the precipitate is dissolved with 2 ml 0.05 M HCl (water bath, < 40 °C), precipitated with 3 ml citrate buffer after cooling (ice) and centrifuged.

(6) The supernate is decanted, the precipitate washed with 3 ml citrate buffer and the suspension centrifuged (5 min at 2500 rpm).
The supernate is decanted, the precipitate washed once more with 2 ml H_2O, centrifuged and the supernate discarded.

(7) The purified precipitate finally is dissolved in 2 ml 0.05 M HCl transfered into a test tube and measured for activity (⟶ R_{Ins}).

Discussion

The activity A of the labelled insuline in Bq is calculated from

$$\boxed{A = \frac{R_{Ins} \times 100}{\eta_{\%} \times 60}} \quad [\mathrm{Bq}]$$

η = efficiency of the detector in % for ^{131}I

The labelling efficiency M [%] related to the total iodine activity R_I is

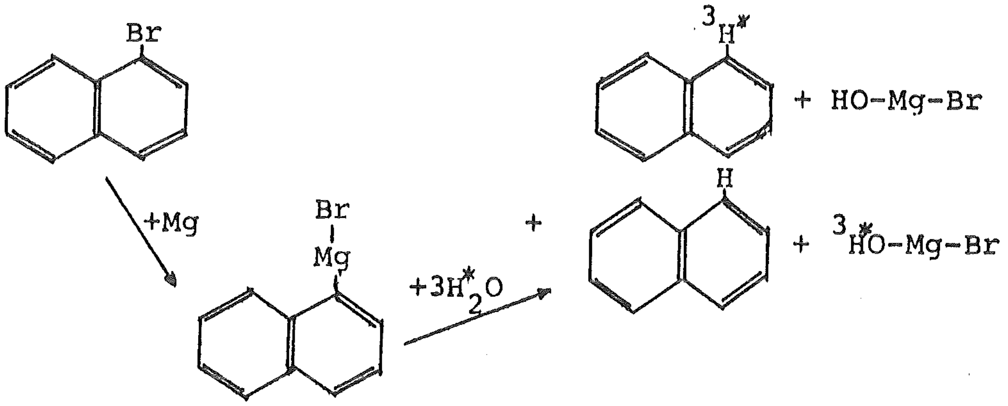
$$\boxed{M = \frac{R_{Ins}}{R_I} \cdot 100}$$

$$R_I = R_{I(1)} - R_{I(2)}$$

Experiment 35: Naphtalene Labelling with Tritium

Theoretical Introduction

The reaction of Grignard-compounds with ^3H-containing H_2O is one of the most simple methods for tritiating an organic molecule in a definite position. In the following experiment α-bromo-naphtalene is transfered into a Grignard-compound and finally decomposed by ^3H-containing H_2O.



The labelling efficiency M should be determined in comparing the total activity of α-^3H-naphtalene with the initial ^3H-activity.

Apparatus and Materials

- ^{3}H-containig H_2O in dioxan (2×10^5 Bq/ml)
- α-bromo- naphtalene
- Mg-cuts
- Ether (dry)
- Al_2O_3 (for adsorption)
- Benzene
- Petroleum ether (40 - 60°C)
- HCl (2 M)
- Round flask (100 ml, two-necked) with condenser and dropping funnel
- $CaCl_2$-drying tube
- Separation funnel
- Evaporating disk
- Chromatographic column (height 20 cm, Ø 1.5 cm)
- Cooling bath (ice)
- Liquid Scintillation Counter
- Scintillation cocktail

Experimental Details

(1) Into a 100 ml two-necked round flask 20 ml dry ether and 1 g Mg-cuts (activated with I_2 or C_2H_5I) are added. The flask is attached with a condenser, drying tube and dropping funnel.

(2) The funnel is filled with 4.2 g of α-bromo- naphtalene and the reaction started by adding some drops to the Mg-cuts (in most cases the reaction has to be warmed to 35°C, water bath!). The remaining α-bromo- naphtalene slowly is added and the solution further warmed (35°C) for about 45 min.

(3) To the cold mixture (ice bath) 1 ml of the tritiating solution of known specific activity is added (dropwise!).

(4) The remaining Grignard-compound is decomposed at 30 - 35°C by adding 20ml ether and 25 ml HCl (2 M).

(5) The mixture is transfered into a separating funnel, the organic phase separated and transfered to an evaporating disk. The ether is carefully (inflammability!) evaporated on a water bath.

(6) For purification the remaining crystals are dissolved in about 5 ml benzene and transfered onto an Al_2O_3-chromatographic adsorption column (Al_2O_3 suspended in petroleum ether is filled into a test tube to a height of approximately 15 - 18 cm). Eluating the column with petroleum ether, water and decomposition products remain on the column, while purified α-^3H- naphtalene leaves the tube.

(7) The chemical yield may be determined from the weight of naphtalene after drying the eluate (theoretical yield = 2.61 g).

(8) About 500 mg of the prepurified α-^3H- naphtalene is recrystallized from ethanol and dried. Aliquot parts (about 25 mg) are weighed, dissolved in 10 ml scintillation cocktail and measured for activity in a liquid scintillation counter.
The specific activity and labelling efficiency have to be calculated.

Experiment 36: Szilard-Chalmers Reaction I – Change of the Chemical Bond of Ethyl Iodide by (n, γ) Processes

Theoretical Introduction

In 1934 L. Szilard and T.A. Chalmers discovered radioactive iodide being extractable from ethyl iodide with water following irradiation of ethyl iodide with thermal neutrons. Moreover, when adding iodide carrier and silver ions to this aqueous phase, the radioactive iodide was precipitated with silver.
In consequence of this result the formation of ^{128}I must have been accompanied with bond rupture of this atom to the ethyl group.
The reaction, called Szilard-Chalmers process is of considerable interest to chemists as it involves the production of a new chemical species of high specific activity which is isotopic to the initial target atom.

decay	recoil energy (1 eV/Atom ≙ 96 kJ/Mol)
α	–some 100 keV
β	– 0,1 eV ... some 10 eV
γ	– <50 eV
-C-I-" Bond-Energy	– 190 kJ/Mol (≙ 2 eV/Atom)

Nature of the Reaction

The initial reaction carried out by Szilard and Chalmers may be written as

$$C_2H_5{}^{127}I + n \longrightarrow \left[C_2H_5{}^{128}I\right]^* \longrightarrow C_2H_5 + {}^{128}I + \gamma$$

The bond energy of iodine to carbon in C_2H_5I is about 2 keV (19.2kJ/mol). Since this exceeds the recoil energies of neutron capture, the bond breakage must have been resulted from the γ-emission of the compound nucleus following neutron capture and not from the capture process itself.

According to de Broglie

$$\lambda = \frac{h}{p} \tag{1}$$

λ = wave length
h = Planck's constant
p = m×v = impulse (momentum)

The impulse of a γ-quant (p_γ) is given by

$$\boxed{p_\gamma = \frac{h}{\lambda} = \frac{E_\gamma}{c}} \tag{2}$$

E_γ = energy of the γ-quant
c = light velocity

From the principle of conservation of momentum, the impulse of the recoil nucleus (p_R) is equal to that of the γ-quant.

$$p_R = p_\gamma \tag{3}$$

or

$$m_R \times V_R = \frac{E_\gamma}{c} \tag{4}$$

m_R = mass of recoil atom
v_R = velocity of recoil atom

With equ. (4) the recoil energy finally is calculated to

$$\boxed{E_R = \frac{m_R \times v_R^2}{2} = \frac{E_\gamma^2}{2m_R \times c^2}} \qquad (5)$$

or

$$\boxed{E_R = \frac{E_\gamma^2}{2 \times 931 \text{ a.m.u.}}} \; [\text{Me V}] \qquad (6)$$

if m_R is expressed in atomic mass units ($E = mc^2 = 931$ a.m.u. [MeV]).

With a.m.u. = 100 and $E_\gamma = 1$ MeV the energy of the recoil nucleus is 5.4 eV, which is equal to about 523 kJ /mol and exceeds the chemical bond energy.

Retention

With activation energies of 6 - 8 MeV for the compound nuclei bond rupture should be almost certainly 100 % effective. This is in contrast to the observed results. A certain proportion of the activity formed remains in the initial form of bond, known as "retention".

The percentage retention is extremely sensitive to traces of impurities and may be decreased when adding "scavengers" (e.g. free halogen).

A possible explanation is the reaction of the scavenger with the organic molecule fragments, thus supressing recapture of the radioactive atoms.

The radiation of solid crystalline species causes local melting zones of short life-time (10^{-11} s) in the direct neighbourhood of the recoil nuclei, initiating chemical reactions. When heating the species after irradiation "annealing" of the lattice dislocations occurs, thus increasing the percentage retention.

A further factor concerning the value of retention is the pH-value, due to acid dependence of consequent reactions of the recoil fragments.

Literature

G. Stöcklin "Chemie heißer Atome", Verlag Chemie, Weinheim 1969

T. Tominaga, E. Tachikowa "Modern Hot Atom Chemistry and its Applications", Springer Verlag, Berlin-Heidelberg-New York 1981

Introduction to the Experiment

When ethyliodide is irradiated with thermal neutrons free radioactive iodine as ^{128}I is obtained. In separating the extractable iodine from the organic phase high specific activity is obtained isotopic with the target.
In the following classical experiment free ^{128}I-atoms produced by irradiating ethyl iodide for 20 min with a n-source (Φ_{th} = 10^6 n/cm^2 x sec) should be separated and identified from their ß-maximum energy and half-life. The Szilard-Chalmers efficiency has to be calculated.

Apparatus and Materials

- G-M tube (end-window type) with tube holder and sample support
- Scaler/timer
- Set of aluminium absorbers of known thickness
- NaI(Tl)-scintillation detector (well-type)
- HNO_3 (2 M)
- $AgNO_3$ (0.5 M)
- KI-solution (40 mg KI/ml)
- $Na_2S_2O_5$-solution (0.05 M)
- $CHCl_3$
- Test tubes
- Al-planchettes
- Glass frit funnel (Ø 3 cm)
- Beaker (50 ml)
- Separation funnel
- Measuring cylinder

Experimental Details

(1) 5 ml of the irradiated ethyl iodide is transfered into a separation funnel and extracted with 10 ml $Na_2S_2O_5$-solution (0.05 M). The heavier layer (etyliodide) is drained off into a second separation funnel, further extracted with 10 ml $Na_2S_2O_5$-solution, separated and stored for further treatment.

(2) The aqueous layers (20 ml) are combined and washed with 10 ml $CHCl_3$. The organic phase is drained off and the upper aqueous layer stored.

(3) For determining the Szilard-Chalmers efficiency 2 ml of the extracted ethyl iodide and the aqueous layer each are measured for activity (NaI(Tl)-scintillation detector).

(4) The remaining aqueous extract is mixed with KI-solution (about 1 ml) and after addition of 2 M HNO_3 (about 5 ml) heated until SO_2 is completely removed. Finally iodide (^{128}I-carrier) is precipitated with excess of $AgNO_3$-solution, boiled up, filtered, sucked to dryness and mounted onto an Al- planchette.

Evaluation and Discussion

Because of the short half-life of ^{128}I, the measured values of the ß-absorption curve have to be extrapolated for the same measuring time:

(1) In order to obtain high net rates, the absorption measurement is started with the thickest Al-foil (800 mg Al/cm^2). For the determination of the decay curve for ^{128}I every 5 - 10 min a measurement is carried out without absorber.

(2) The data of the β-absorption are plotted in a diagram with measuring time as abscissa and log of net rate as ordinate. Parallels are drawn through the measuring values each with an inclination according to the half-life of ^{128}I (fig.64).

With aid of these straight lines the values are extrapolated for equal measuring time.

(3) The logarithm of these data is plotted in a second diagram against the surface density (mg Al/cm^2) as abscissa (fig.65). From the half-thickness or maximum range of the ß-radiation the maximum energy of ^{128}I is determined.

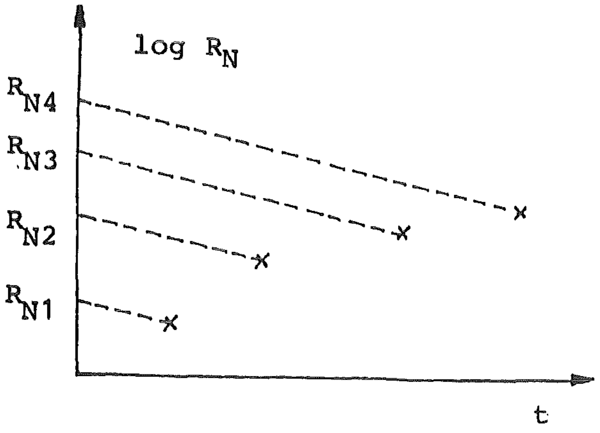


Figure 64: Scheme for Extrapolation of R_N

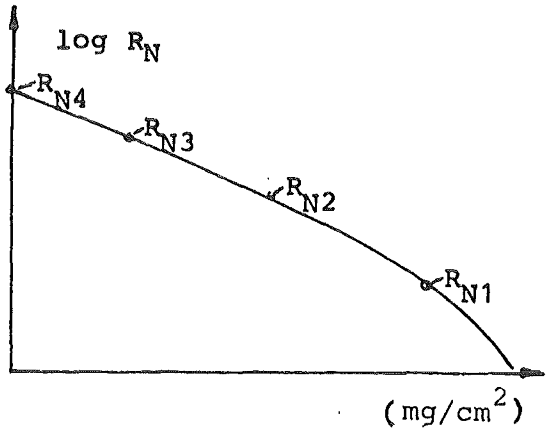


Figure 65: ß-absorption Curve

(4) The Szilard-Chalmers efficiency may be calculated from the percentage of activity extracted from the aqueous phase related to the total activity

$$\boxed{\text{Sz.Ch.-Eff.} = \frac{R_{N(aq)}}{R_{N(aq)} + R_{N(org)}} \cdot 100\ \%} .$$

Experiment 37: Szilard-Chalmers Reaction II - Change of Oxidation State of Manganese by (n,γ) Processes

Theoretical Introduction

Irradiation of $KMnO_4$ in solid form or solution causes a rupture of the chemical bond. In consequence an essential part of the formed ^{56}Mn-activity may be separated as MnO_2. The Szilard-Chalmers efficiency varies greatly with the pH-value of the medium during irradiation or on dissolve of the irradiated sample.
Directly after separation of one or more oxigen atoms due to γ-recoil ^{56}Mn remains as multiple positively charged ion:

$$MnO_4^- \longrightarrow MnO_3^+ \longrightarrow MnO_2^{3+} \longrightarrow MnO^{5+} \longrightarrow Mn^{7+}.$$

4-valent Mn (MnO_2) and 7-valent Mn (MnO_4^-) is finally formed by successive hydration- and oxidation-reduction reactions of the hot recoil fragments. The most probable reactions are:

$$MnO_3^+ + 2OH^- \longrightarrow MnO_4^- + H_2O \qquad (1)$$

$$4MnO_3^+ + 2H_2O \longrightarrow 4MnO_2 + 3O_2 + 4H^+ \qquad (2)$$

At pH $\approx$12 retention is almost 100%, the hydration reaction (1) predominates.
The increased retention in strong acid medium is probably the consequence of isotopic exchange between active MnO_3^+ and inactive MnO_4^- competing with the oxidation-reduction (2).

In the following experiment $KMnO_4$ in solid form is irradiated with thermal neutrons ($\approx$45 min, $\Phi \approx 10^5$ n/cm^2 x sec). One part of the sample is subsequently annealed (120^{o}C, about 1 h).
The distribution of the resulting ^{56}Mn between the oxidation states Mn^{4+} and Mn^{7+} has to be examined.

$$^{55}Mn\ (n,\gamma)\ ^{56}Mn \xrightarrow[2.6\ h]{\beta^-} \underline{^{56}Fe}$$

Apparatus and Materials

- NaI(Tl)-scintillation detector (well type)
- $KMnO_4$ (solid), irradiated
- $KMnO_4$ (solid), irradiated and annealed
- H_2SO_4 (3 M)
- H_2O_2 (30 %)
- Glass frit G 4
- Suction flask (250 ml)
- Filtering apparatus
- Measuring cylinder
- 2 Beakers (250 ml)
- Test tubes

Experimental Details

The two samples (irradiated, irradiated and annealed) are treated separately:

(1) The sample is dissolved in about 30 ml hot water and then is slowly sucked over a G 4-glass frit into a measuring cylinder

(2) The total volume is determined. 2 ml are pipetted into a test tube and measured for activity.

(3) The remaining active MnO_2-precipitate (fairly visible) is dissolved on the glass frit by adding dropwise a solution of 3 ml H_2SO_4 (3 M) + 0.5 ml H_2O_2 (30 %). Finally 3 ml H_2SO_4 (3 M) and 3 ml H_2O are sucked slowly.

(4) 2 ml of the solution likewise are measured in the scintillation detector.

➢ Caution: After each experiment the filtering devices have to be cleaned and freed carefully from H_2O_2/H_2SO_4!

Experiment 38: Szilard-Chalmers Reaction III – Separation of the ^{80m}Br-Isomeric State

Theoretical Introduction

The isomeric transitions which proceed by emission of γ-rays may not provide sufficient recoil energy to break covalent bonds. However, for low energy isomeric transitions, the internal conversion process is predominant. This results in vacancies in the lower electron orbitals. When electrons in higher orbitals move to fill the vacancies, the difference in electron-binding energies is sufficient to cause some ionization, resulting in relatively high charge states of the atom, which leads to bond rupture.

An interesting case of such a Szilard-Chalmers reaction is the (n,γ) reaction with an organic bromide. Apart from the useful tracer ^{82}Br, produced from ^{81}Br, two short lived products – ^{80}Br and ^{80m}Br respectively– are formed from ^{79}Br.

$$\begin{tikzcd}
 & {^{80m}\mathrm{Br}\ (T_{1/2} = 4.5\ \mathrm{h})} \arrow[d, "\mathrm{IT}"] \\
{^{79}\mathrm{Br}} \arrow[ur, "{n,\gamma}", "2.9\ \mathrm{b}"'] \arrow[r, "{n,\gamma}", "8.5\ \mathrm{b}"'] & {^{80}\mathrm{Br}\ (T_{1/2} = 18\ \mathrm{m})}
\end{tikzcd}$$

$$^{81}\mathrm{Br} \xrightarrow[2.4\ \mathrm{b}]{n,\gamma} {^{82}\mathrm{Br}}\ (T_{1/2} = 36\ \mathrm{h})$$

Extraction with water produces an aqueous sample containing both ^{80}Br and ^{80m}Br. Both ^{80}Br and ^{80m}Br also have some retention in the organic phase. (The ^{82}Br-activity formed by (n,γ)-process with natural ^{81}Br may be neglected due to the relatively long half-life ($T_{1/2}$ = 36 h) and short time of irradiation (1 – 2 h).). If, after a period of one hour, the extraction is repeated, only ^{80}Br is found in the aqueous sample, resulting from the reaction

$$\mathrm{R}\,{^{80m}\mathrm{Br}} \xrightarrow{\mathrm{IT}} \mathrm{R} + {^{80}\mathrm{Br}} + \gamma$$

Apparatus and Materials

- Bromo-benzene (irradiated)
- $Na_2S_2O_5$-solution (0.05 N)
- Diethylether
- Separatory funnel
- NaI(Tl)-scintillation detector
- Test tubes

Experimental Details

Separation of the Br-activity formed by thermal neutron irradiation:

(1) 5 ml bromo-benzene (irradiated) is dissolved with 10 ml diethylether in a separatory funnel and extracted with 5 ml $Na_2S_2O_5$-solution (0.05 N).

(2) After phase separation 2 ml of the aqueous (heavier) phase are drained off into a test tube and measured for activity (scintillation detector) at different time intervals (10min, later on 30 min).

Separation of the ^{80}Br-activity formed by isomeric transition:

(3) In the meantime the organic phase is washed twice with 5 ml $Na_2S_2O_5$-solution each (removing of the remaining extractable Br-activity).

(4) After storing for one hour, the organic phase is again extracted with 5ml $Na_2S_2O_5$-solution. 2 ml of the aqueous phase are drained off into a second test tube. The radioactive decay of ^{80}Br is finally recorded for about 2 hours.

☞ Caution: In case of phases getting difficult to separate due to losses of ether during extraction, some ether should be added.

Evaluation and Discussion

By analysis of the complex decay curve of the first extraction the half-life of the isomeric nuclides ^{80}Br and ^{80m}Br may be determined. The evaluation of the decay curve of each further extraction results in a half-life of $T_{1/2} = 17.6$ m., due to the ground state ^{80}Br.

From the net rates R_N extrapolated to the extraction time the amount of impurity V from the ^{80m}Br isomer has to be determined.

$$\boxed{V\ (^{80m}\mathrm{Br})\ [\%] = \frac{R_N\ (^{80m}\mathrm{Br})}{R_N\ \mathrm{total}}}$$

If the extraction will be repeated over longer periods, the half-life of ^{80m}Br($T_{1/2} = 4.4$ h) may be determined from the decrease of activity at each time of separation ("Interval Method" for half-life determination, figure 66).

For further investigations bromo-benzene may be irradiated under the same conditions after addition of 10 mg bromine or 5 % aniline respectively. What is the effect of aniline and molecular bromine to be expected for the recoil process?

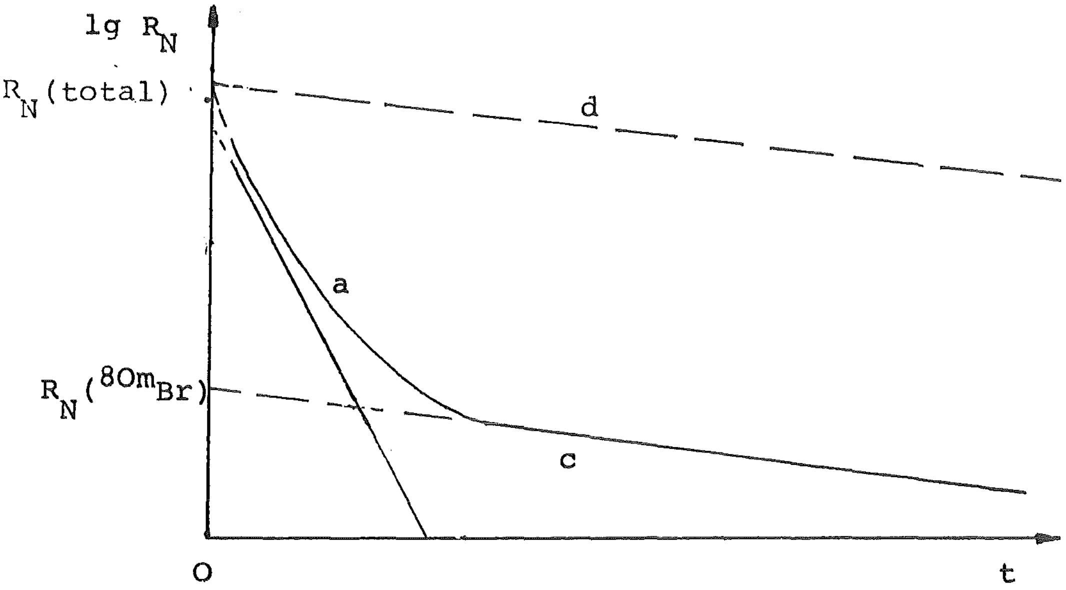


Figure 66: Decay Curve for the Isomeric System ^{80}Br/^{80m}Br

a: Complex Part of Aqueous Phase (1st Extraction)

b: Decay of Pure ^{80}Br ($T_{1/2} = 17.6$ m)

c,d: Decay of Pure ^{80m}Br ($T_{1/2} = 4.4$ h)

Experiment 39:

Final Practical Work: Quantitative Analysis for Trace Elements in Samples by Neutron Activation (Coco-nut, Topas, Natural Uranium Ores)

Theoretical Introduction:

Purpose of the final experiment is to determine the tracer elements in three different samples:

(a) Coco-nut

(b) Topas (geological material)

(c) Uranium Ore

A small amount of each sample has been activated in a beam of a strong neutron source ($10^{12} n/cm^2 \times s$). The radionuclides which have been produced, may be determined by their radiations, generally by use of a semiconductor counter with multichannel analyser. Radionuclides then may be identified by their characteristic γ-energy and half-life.

Experimental Details:

(1) The photopeaks should be analysed by use of a γ-ray table (start with the greatest peaks in the high energy region, compare if the other γ-rays of an identified nuclide are present in the spectrum according to the intensities).

(2) Compare now the half-life of the tabulated nuclide with the half-life from the graph: net rate of the photopeak measured at different time intervals against the time.

(3) From the given data of irradiation, mass of the corresponding irradiated sample and activity determined by γ-spectrometry, the amount of the tracer should be estimated.

Experiment 40 :

Final Practical Work :

Identification and Separation of an Unknown Mixture of Radionuclides

Theoretical Introduction

In order to identify unknown radionuclides the following data should be determined:

(a) half-life

(b) Type and energy of the emitted radiation and

(c) atomic number by chemical reactions.

In a synthetically prepared unknown radionuclide mixture two of the radionuclides given below are included and have to identified by the methods (b) and (c).

$^{14}\mathrm{C}$

$^{32}\mathrm{P}$

$^{35}\mathrm{S}$

$^{60}\mathrm{Co}$

$^{90}\mathrm{Sr}/^{90}\mathrm{Y}$

$^{106}\mathrm{Ru}/^{106}\mathrm{Rh}$

$^{110m}\mathrm{Ag}$

$^{131}\mathrm{I}$

$^{137}\mathrm{Cs}/^{137m}\mathrm{Ba}$

$^{144}\mathrm{Ce}/^{144}\mathrm{Pr}$

$^{204}\mathrm{Tl}$

After a rough survey using β-absorption measurements and multichannel analysis (table 11 and 12) a radiochemical separation scheme has to be evaluated and the resulting pure samples finally identified.

Apparatus and Materials

All chemicals and equipments used during the course should be available.

Experimental Details

Determination of Type and Energy of Radiation:

(1) About 1 ml of the unknown solution is evaporated onto an Al-planchette (don't overheat, ^{131}I and some oxides are volatile!)

(2) The dry sample is measured (GM-counter) using different Al-foils for β-absorption (see experiment5 and 6).

(3) From their maximum range and half-thickness the β-decaying nuclides are identified. A possible background indicates the presence of γ-radiation.

(4) By multi-channel analysis each photopeak resulting from γ-emission has to be identified, thus confirming the results from (3) (see experiment 7).

Chemical Separation and Identification:

(5) Carrier and hold-back carrier for each nuclide present in the liquid sample have to be added.

(6) All nuclides present are then separated and isolated according to the procedures used during the proceeding practical parts. A compilation of suitable methods is given in table 13.

(7) After each analytical procedure the β-maximum energy and/or γ-photopeak of the resulting separated radionuclide has to be determined.

Within the scope of our experimental problem, a nuclide will be considered as identified, if the initial energy values are reobtained after a selective chemical separation step (table 13).

Table 11: β-maximum Energies

E_β [MeV]	Nuclide	Half-life	Daughter-nuclide	Further β-energies [MeV]	E_γ [MeV]
3.55 (67,2%)	Rh-106	30 s	Pd-106(stab.)	3.05(12.5%), 2.39(17%)	0.51;0.62,...
2.99 (97.7%)	Pr-144	17.3 m	Nd-144	2,30(1.2%),0.81(1,0%)	0.697, ...
2.27 (100%)	Y-90	64,8 h	Zr-90 (stab.)	0.52(0.02%)	...
1,71 (100%)	P-32	14.3 d	S-32 (stab.)	---	---
1,16 (~100%)	Bi-210	5.0 d	Po-210	---	...
0.766 (98%)	Tl-204	3.8 a	Pb-204(stab.)	---	---
0,61 (87%)	I-131	8.05d	Xe-131(stab.)	0.33(9.3%),...	0.36,...
0,546 (100%)	Sr-90	28 a	Y-90	---	---
0,53 (36.9%)	Ag-110m	253 d	Cd-110(stab.)	0.085(62.5%!),...	0,66;0.89,...
0,51 (93.5%)	Cs-137	30 a	Ba-137m	1,18 (6,5%)	---
0,31 (~100%)	Co-60	5,26a	Ni-60 (stab.)	1.48 (0,1%)	1.17;1.33
0,31 (76%)	Ce-144	284 d	Pr-144	0,18 (24%)	0,134 ...
0.167 (100%)	S-35	88 d	Cl-35 (stab.)	---	---
0,156 (100%)	C-14	5730 a	N-14 (stab.)	---	---
0.085 (62.5%)	Ag-110m	253 d	Cd-110(stab.)	0.53 (36.9%), ...	0.66;0,89,...
0,039 (100%)	Ru-106	1.0a	Rh-106	---	---
0,015 (80%)	Pb-210	≈22 a	Bi-210	0.061(20%)	0.047

Table 12: γ-energies

E_{γ} [MeV]	Nuclide	Half-life	Further γ-energies [MeV]	$E_{\beta max}$ [MeV]
1.33 (100 +) 1.17 (100 +)	Co-60	5.26 a	...	0.31 (∼100%), ...
0.89 (73 +) 0.66 (100 +)	Ag-110m	253 d	0.94 (33 +) 1.38 (25 +)	0.085 (62.5%) 0.53 (36.9%)
0.697(100 +)	Pr-144	17.4 m	....	2.99 (97.7%)...
0.66	Ba-137m	2.6 m	---	---
0.62 (44 +) 0.51 (100 +)	Rh-106	30 s	1.06 (6 +), ...	3.55 (67.2%), ...
0.36 (100 +)	I-131	8.05 d	0.64 (9 +), ...	0.61 (87%), ...
0.134(100 +)	Ce-144	284 d	0.08 (18 +) ...	0.31 (76%), ...
0.047	Pb-210	22 a	---	0.015 (80%), ...

The numerical values in parenthesis for the ß-maximum energies refer to the abundance of the corresponding transition in % of decays, for the γ-energies to the relative abundance (most frequent line = 100 +) .

Table 13: Suggested Analytical Procedures

Nuclide	Separation and Characterization
^{14}C (org.)	extraction with diethylether from aqueous solution, evaporation of the ethereous extract
^{32}P	(a) precipitation as ammonium phosphomolybdate (b) precipitation as ammonium manganese phosphate (c) adsorption on freshly precipitated $Fe(OH)_3$ (unspecific, operation should be repeated) (d) separation from cations by ion exchange
^{35}S	(a) precipitation as $BaSO_4$ and purification by multiple reprecipitation (in presence of $^{137}Cs/^{137m}Ba$, the sample has to be stored for 20 minutes until the coprecipitated ^{137m}Ba has been decayed) (b) separation from cations by ion exchange
^{60}Co	(a) precipitation from weakly acidic solution as $Cs_3(Co(NO_2)_6)$ (b) separation by anion exchange (c) precipitation using α-nitroso-ß-naphtol (d) characteristic γ-lines
$^{90}Sr/^{90}Y$	(a) precipitation of Sr as $SrCrO_4$ from acetic acid solution (^{137m}Ba interferes unless it has been decayed).

Table 13: cont.

	(b) Sr-Y-separation by paper chromatography; ^{90}Y remains while ^{90}Sr migrates with the front of mobile phase (solvent: nitrate solution, pH > 5) (c) ^{90}Y is quantatively adsorbed on a 1 mm filter layer of freshly precipitated ammonium phospho molybdate (pH > 4) (d) extraction of ^{90}Y with 2- thenoyl-trifluoro-acetone, bis-2-ethylhexyl phosphoric acid or cupferron from aqueous solution
^{204}Tl	(a) adsorption as Tl^{+} in HCl (HNO_3) on a freshly prepared layer of phosphormolybdic acid (^{137}Cs is adsorbed equally, but contains the regrowing ^{137m}Ba-daughter) (b) coprecipitation with $Fe(OH)_3$ after previous oxidation to Tl^{3+} with $KBrO_3$
^{106}Ru/^{106}Rh	(a) distillation as RuO_4 from $\leq$ 6M HCl and identification in the destillate as - metallic Ru after reduction with Zn - coprecipitation of the ^{106}Rh-daughter with $K_3(Co(NO)_6)$ (b) separation by extraction
^{110m}Ag	(a) precipitation as AgI (boiling heat) and further reprecipiation (^{131}I when present has to be separated previously!) (b) adsorption on a 1mm filter-layer of freshly precipitated AgI from dilute nitric acid solution (^{131}I is adsorbed equally and interferes) (c) characteristic γ-lines

Table 13: cont.

^{131}I	(a) separation by distillation (nitrate as oxidant) (in presence of $^{106}Ru/^{106}Rh$ and $KBrO_3$, Ru has to be separated in the distillate as metallic Ru) (b) extraction with $CHCl_3$ and after previous reduction and stripping into the aqueous phase precipitation as AgI (c) adsorption on a 1 mm filter-layer of freshly precipitated AgI from dilute nitric acid solution (^{110m}Ag interferes) (d) characteristic γ-lines
$^{137}Cs/^{137m}Ba$	(a) separation from anions and Cl^--complex-forming cations on a anion exchanger (b) precipitation of ^{137m}Ba as $BaSO_4$ or $BaCl_2 \times 4\ H_2O$ and determination of the decay curve (c) adsorption of ^{137}Cs on a freshly prepared filter-layer of phosphor molybdic acid; after establishment of equilibrium the regrown ^{137m}Ba is eluted (^{204}Tl is equally adsorbed, at pH $>$ 4 also ^{90}Y) (d) adsorption of ^{137}Cs + ^{137m}Ba on a cation exchanger and elution of ^{137m}Ba with complexon (e) characteristic γ-lines
$^{144}Ce/^{144}Pr$	(a) coprecipitation with Ce $(IO_3)_4$ (b) separation by solvent extraction (c) separation from anions by cation exchange (d) Ce/Pr-separation (by ^{144}Pr, $T_{1/2}$ = 17.3 m) (e) characteristic γ-lines

Exercises to 3.3.3.

1. Calculate the activities of chlorine and tritium, produced by irradiation of 1 Mol LiCl with a slow-neutron flux of 10^{12} neutrons/cm^2 x s for 5 hours.
   What amount of activities remains 0.5, respectively 5 hours after end of irradiation? (Experiment 28)

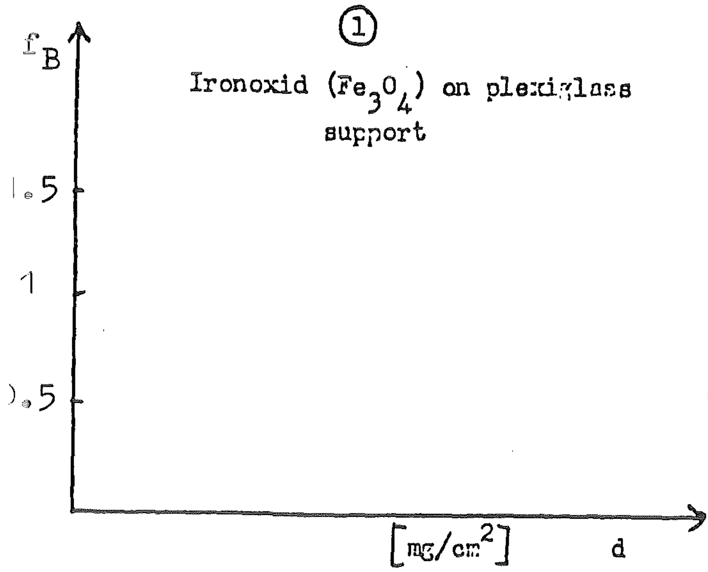
2. To determine the Cu-amount 1 gram of the sample is irradiated in a nuclear reactor for 10 hours with a flux of 10^{12} neutrons/cm^2 x s. After chemical separation of Cu (time 2h, yield 72%) a count rate of 23,5000 cpm was measured (efficiency of the detector 48%).

What is the amount of copper in ppm?

(2 hours after irradiation ^{66}Cu ($T_{1/2}$ = 5.1 m) has decayed completely; therefore only ^{64}Cu($T_{1/2}$ = 12.8 h) produced from ^{63}Cu (isotopic abundance 69.09%) with a cross section of 4.51 barn will be measured). (Experiment 29)

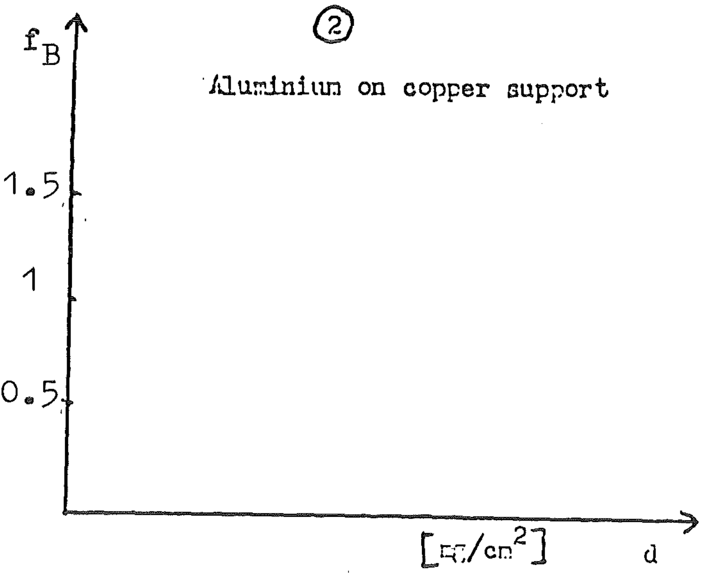
3. A 2ml sample of an aqueous solution containing 37 kBq per ml of ^{99m}Tc ($T_{1/2}$ = 6h) is injected into the blood stream of an animal. After complete circulatory mixture (6 h) a 1 ml aliquot of blood is removed and the count rate determined to 2,500 cpm ($\eta(^{99m}Tc)$ = 10%).
   Calculate the blood volume from the given data. (Experiment 32)

4. In order to determine the thickness of thin layers a calibration curve has to be plotted. Line out the shape of the graphs in the figures on the next page.



①

Ironoxid (Fe$_3$O$_4$) on plexiglass support



②

Aluminium on copper support

f_B = backscattering factor (= $\frac{\text{count rate with layer}}{\text{count rate without layer}}$)

d = layer thickness (Experiment 32)

5. For the performance of a Szilard-Chalmers reaction 100 g of ethyl iodide are irradiated for 1 hour at a neutron flux of 2×10^4 cm^{-2} x sec^{-1}. The radioactive iodine resulting from the nuclear reaction ^{127}I (n,γ) ^{128}I, is precipitated as AgI and measured.
Which is the count rate, if the amount of retention is 20%, the counting efficiency 10% and the separation time of the iodine 5 min after end of irradiation?
($\sigma_{n,\gamma}$ (^{127}I) = 62 b $\Longrightarrow$ 1.757 x 10^5 cpm;
activation equation A = $\frac{\sigma \cdot \varnothing \cdot N_L \cdot m \cdot H}{} \cdot (1 - e^{-\lambda \cdot t_1}) \cdot e^{-\lambda \cdot t_2}$).

(Experiment 36)

6. A sample of $KMnO_4$ (potassium permanganate) has been irradiated by neutrons. Due to the Szilard-Chalmers effect a part of the manganese +7 has been reduced to manganese +4.

(a) Describe the main steps for the determination of the Szilard-Chalmers efficiency!

(b) A part of the irradiated $KMnO_4$-sample has been tempered (100°C) for one hour before chemical separation. Explain the increased amount of retention! (Experiment 37)

4 Technical Terms

4.1. Radiation Measurements

Activity (A)	The number of decaying nuclei per unit time. Unit: 1 Becquerel(Bq) = 1 s^{-1} (1 Curie (Ci) = 3.7 x 10^{10} Bq)
Background (R_o)	The count rate registered by a measuring device without radiation source
Efficiency (η)	Efficiency of counting is a proportion of net rate to emission rate $\eta = \frac{R_N}{R_E}$ The value of efficiency is only sensible for a type of a definite energy of a radiation. Efficiency is influenced by the following factors:
- Absorption factor (f_A)	f_A describes the weakening of an emitted radiation by absorption between surface of source to the sensitive detector volume.
- Back-scattering factor(f_B)	f_B takes into account the amount of back-scattering
- Geometry factor (f_G)	f_G is a volume of solid angle effective in a measurement.
- Self-absorption factor (f_{SA})	f_{SA} causes reduction of net rate due to the finite thickness of the source.

- Scattering factor (f_{SC})	f_{SC} involves effects due to scattering but not from back-scattering at the bottom of the source.
Emission rate (R_E)	The number of particles and quanta, from radioactive source (emitting nuclides including the subsequent products) per unit time.
Measuring rate (R_M) or count rate	The value in a unit time shown by a measuring device registered with radiation source of interest.
Net rate (R_N) or corrected count rate	Net rate = measuring rate - background
Resolving time (τ) (dead-time, paralysis time)	f_τ engages the loss in count rate owing to finite temporal resolving time of the overall measuring arrangement (detector and electronics).

4.2 Nuclear and Radiochemistry , Radiation Protection

Activity, specific	Quotient of the activity of a substance and mass (or volume) of the substance, e.g. Ci/g or Bq/g
Alpha radiation	An α-particle is composed of 2 neutrons and 2 protons, identical to the nucleus of a helium atom. α-radiation is the least penetrating among the three types of the radiation, emitted by radioactive decay. It can already completely be absorbed by a sheet of paper. α-radiation is monoenergetic. Its energy is characteristic and lies between 4 and 8 MeV.
Becquerel (Bq)	see "activity"
Beta radiation	β-radiation is the emission of an electron with positive or negative charge in a radioactive decay. β-radiations have continuous energies with a specific maximum $E_{\beta_{max}}$. They are totally absorbed by 1-2 cm plastics or 1 cm aluminium .
Bremsstrahlung	Electromagnetic radiation originated, when electric charged particles are accelerated or slowed down. The spectrum of the radiations emitted, is composed of the kinetic energies of the produced particles from zero to a maximum energy. The loss of energy by Bremsstrahlung is roughly

	proportional to the square of atomic number of absorber and to the energy of the particle.
Čerenkov radiation	Light, with a maximum in blue spectrum part, produced, when a charged particle travels through a medium with greater velocity than that of light-velocity in the material ($v > c_o/ n; c_o$ = velocity of light in vacuum, n = refractive index). The threshold energy of electrons in water (n = 1.33) is 260 keV.
Contamination	Undesirable presence of radioactive substance on surface of working areas, apparatus, in room, water or air.
Controlled area	Area, in which there is a possibility of increased radiation (radioactive substances). A person working 40 hours/week in this area will receive radiation from external sources or by incorporation of radioactive substances with a dose exceeding 0.015 Sv/year (1.5 rem/year).
Curie (Ci)	see "activity"
Decontamination	Removal or decreasing of a radioactive contamination by means of chemical or physical techniques, e.g. by washing or by cleaning with chemicals. Decontamination of air and water could be done by filtration, vaporisation or precipitation.

Dose (D)	A measure of quantity of radiation, concerning energies of radiation which involve the interaction of the radiation with material. There are three types of doses: exposure (ionisation) dose absorbed dose (rad, Gy), and dose equivalent (rem, Sv).
Dose rate (D)	A quotient of dose and time.
Dose equivalent	A product of energy-dose and quality factor. Unit: Sv or rem. Dose equivalent is an indicator for interaction of an ionising radiation to a man. Different types of radiations caused by the same energy-dose creates different degrees of damage. Dose equivalent is then determined by quality factors.
Dose equivalent rate	A quotient of dose equivalent time Unit: Sv/h or rem/h.
Dosimeter	A device for measuring doses (exposure, radiation absorbed dose or dose equivalent): Ionisation chamber, film badge, phosphate-glass dosimeter, thermoluminescence dosimeter.
Dosimetry	Measurement techniques to determine dose (exposure, radiation absorbed dose or dose equivalent) produced by an ionising radiation in material.
Electron capture (ε or EC)	A type of decay occuring in a neutron-deficient radionuclide. Nucleus captures one of its orbital electrons, then converts

	a proton of the nucleus into a neutron. Electron capture competes with positron decay.
Electron volt (eV)	A unit of energy used in atomic and nuclear physics. An electron volt is the kinetic energy of an electron or other particle with mono-charge in vacuum moving through a potential difference of 1 volt. other magnitudes of the unit: keV = Kiloelectronvolt = 1,000 eV MeV = Megaelectronvolt = 1,000,000 eV GeV = Gigaelectronvolt = 100,000,000 eV
Equilibrium, radioactive	If the half-life of a parent nuclide is longer than that of the daughter, a radioactive equilibrium is reached, after a certain time being great compared to the half-life of the daughter. In this case the ratio of the numbers of atoms and consequently, the ratio of the activities of parent and daughter becomes constant. In "transient equilibrium", the daughter activity will be greater than the parent activity but both decay with the parent's half-life. If the half-life of the parent is much longer than that of the daughter, all of the activities are finally equal: This special system is called "secular equilibrium".

Exposure (ionisation)dose	A unit of exposure dose is coulomb per kilogram (C/kg): 1 C/kg is a quantity expressing the amount of ionisation corresponding to the production of ions (of one sign) carrying electrical charge of 1 coulomb per kilogram of air by an ionisation radiation of constant energy. The former unit: Röntgen (R): 1 R = 258 C/kg
Exposure (ionisation) dose rate	A quotient of exposure dose in a period of time and the period of time unit: A/kg or R/h
Gamma radiation	High energetic and short-wavelength radiation produced from a nucleus. Energies of gamma radiation lie between 0.01 and 10 MeV. X-rays have the same ranges of energy but they are not originated from nucleus but from electronic transition of an orbital electron or from slowing down of an electron in a material (Bremsstrahlung). γ-radiations are associated in most of α- and β-decays, always in nuclear fission. γ-radiation is attenuated by a material of higher atomic number (lead), but cannot be totally absorbed (exponential law).

Gray (Gy)	see "Radiation absorbed dose"
Half-life ($T_{1/2}$)	Time for which nuclei of a radionuclide decay into a half. Half-life of radionuclides lie between 1.4×10^{17} years (^{204}Pb) and 3×10^{-7} seconds (^{212}Po). Relations between half-life ($T_{1/2}$) and decay constant (λ) or average life (τ) are: $T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$ $T_{1/2} = \tau \times \ln 2 = 0.693 \times \tau$
Half-life, biological	Time for which, in a biological system, e.g. in a human-body or in an animal, an amount of a substance is decreased into a half by natural way.
Half-life, effective	Time for which, in a biological system, an amount of a radionuclide is decreased into a half by its radioactive decay and by biological process. $T_{1/2}(\text{eff.}) = \frac{T_{1/2}(\text{phys.}) \times T_{1/2}(\text{biol.})}{T_{1/2}(\text{phys.}) + T_{1/2}(\text{biol.})}$ $T_{1/2}(\text{phys.})$: half-life of radionuclide $T_{1/2}$ (biol.): biological half-life For example, effective half-life is 7.6 days for ^{131}I in thyroid grand ($T_{1/2}$(phys.) = 8d; $T_{1/2}$(biol.) = 138 d).

Half-thickness (D)	A thickness of a material which reduces intensity of a radiation into a half. Relation between half-thickness (D) and linear absorption coefficient (μ) can be expressed as (D) = $\ln 2 \times \mu^{-1}$.
Imission	Effect from impurity in air, noise and vibration on human, animal and vegetable.
Incorporation	General: Admission into a body. Special: Admission of radioactive substances into a human body. There are permissible (limited) activity-values for all radionuclides taken up into a body.
Neutron (n)	Uncharged elemental particle of mass of 1.67482×10^{-27} kg; being insificantly greater than mass of proton (p). A free neutron is unstable; it decays with half-life of 11.5 minutes into an electron, a proton and an antineutrino.
Positron (e^+)	Elemental particle of the same mass as an electron with positive charge ("anti-electron"). It is produced by β^+-decay. As antiparticle it combines with an electron as annihilation.
Rad	A unit of absorbed dose (rad: radiation absorbed dose. 1 Rad concerns absorption of radiation energy of 100 erg per gram of material.

	Recommended unit for absorbed dose is Gray. 1 Rad = 1/100 Gray.
Quality factor	A factor, used in calculation of dose equivalent, taking into account the different radiation risks.

Type of radiation	Quantity Factor
X-, γ-, β-, electron and positron	1
proton > 2 MeV	2
neutron < 10 MeV	3
neutron > 10 MeV	10
α-radiation, fission fragment and recoiling nucleus	20

Radiation absorbed dose (Rad)	Total absorbed energy in the unit of mass. Unit used is Gray (Gy). 1 Gray is energy deposit of 1 J in 1 kg of mass with constant flux of ionising radiation. 1 Gy = 100 Rad
Radiation absorbed dose rate (or absorbed dose rate)	A quotient of radiation absorbed dose and time. Unit: Gy/s or rad/h
Rem	A unit of dose equivalent (rem: radiation equivalent man). Dose equivalent is a measure of damage from radiation upon human. Different types of radiation create different degrees of damage by the same absorbed dose. So in the determination of

	dose equivalent, a quality factor (QF) is concerned by multiplying it with absorbed dose. Recommended unit of dose equivalent is joule per kilogram (J/kg) or Sievert (Sv). 1 rem = 1/100 J/kg (Sv).
Röntgen (R)	A unit of exposure, that amounts to a radiation that produces ions of an electrostatic charge unit in 1 cm^3 dry air under normal conditions (1.293 mg air), equivalent to 1 R = 258 C /kg.
Scintillation counter	An instrument for measuring the radiation by registering of light-flashes (scintillations). They are produced when radiation passes through some types of material - called "scintillator".
Sievert (Sv)	see "Rem"
Supervised area	An area, in which there is a possibility of radioactive material. A person working in this area would receive dose of higher than 1,5 m Sv/year (0.15 rem/year).

5 Literature Survey

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The exercises in this manuscript are adapted from our laboratory book

"Experimente zur Radiochemie"

and the laboratory manuals at Schule für Kerntechnik.

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Kernforschungszentrum Karlsruhe
Schule für Kerntechnik

EXPERIMENTAL COURSE ON NUCLEAR AND RADIOCHEMISTRY

C = Coffee Break
L = Lunch Break
S = Seminar, Demonstration

Part 1: Radiations and Their Measurement

Time	9.00 - 9.45	10.00 - 10.45	C 11.15 - 12.00	L 13.00 - 13.45	14.00 - 14.45	C 15.15 - 16.00
Monday	S: Nuclear Radiation - Formation, Interaction and Measurement		Detector Calibration (Gas Counters) - Characteristics - Efficiency		Errors and Their Correction - Self Absorption - Backscattering of β-Particles	
Tuesday	S: Absorption of Decay Particles	Absorption Measurements - Absorption of β-Particles (Range, Half-Thickness) - Attenuation of γ-Radiation (Half-Thickness)				S: Neutrons - Interaction and Detection
Wednesday	S: Scintillation and Solid Solid State Counters	S: γ-Spectrometry	Multi-Channel Spectrometry by Scintillation and Solid State Counters - Calibration - Identification of Unknown γ-Emitters			
Thursday	S: Liquid Scintillation Counting - Theory and Application		Liquid Scintillation Counting - Calibration - Quench Correction - Dual Labelling			
Friday	Identification of Unknown Radionuclides			S: Radiations and Their Measurement -Discussion-		

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EXPERIMENTAL COURSE ON NUCLEAR AND RADIOCHEMISTRY

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Part 2: Radiochemical Methods

Time	9.00 - 9.45	10.00 - 10.45	C 11.15 - 12.00	L 13.00 - 13.45	14.00 - 14.45	C 15.15 - 16.00
Monday	S: Units in Radiation Protection	S: Radiation Protection Measurement	Survey of Radioactivity in Air and Water		Measurements in Contaminated Areas - Dose Monitoring - Contamination Measuring	
Tuesday	S: Radioactive Decay - Genetic Relationships	Determination and Analysis of Radioactive Decay Curves - ^{137m}Ba		Half-Life Determination of ^{238}U		
Wednesday	S: Basic Methods in Radiochemistry	S: Separation of Radioisotopes	Radiochemical Separation Methods I - Scavenger-Precipitation - Precipitation With Non-Isotopic Carrier			
Thursday	Distribution Methods - Solvent Extraction With Tri-n-butyl-phosphate (PUREX) - Separation of Fission Products by Anion Exchange					S: Radionuclide Separation by α-Recoil
Friday	Separation and Analysis of Selected Fission Products (Sr,Cs,I)			S: Radio-chemical Methods -Discussion-		

Appendix 1 cont.

Kernforschungszentrum Karlsruhe
Schule für Kerntechnik

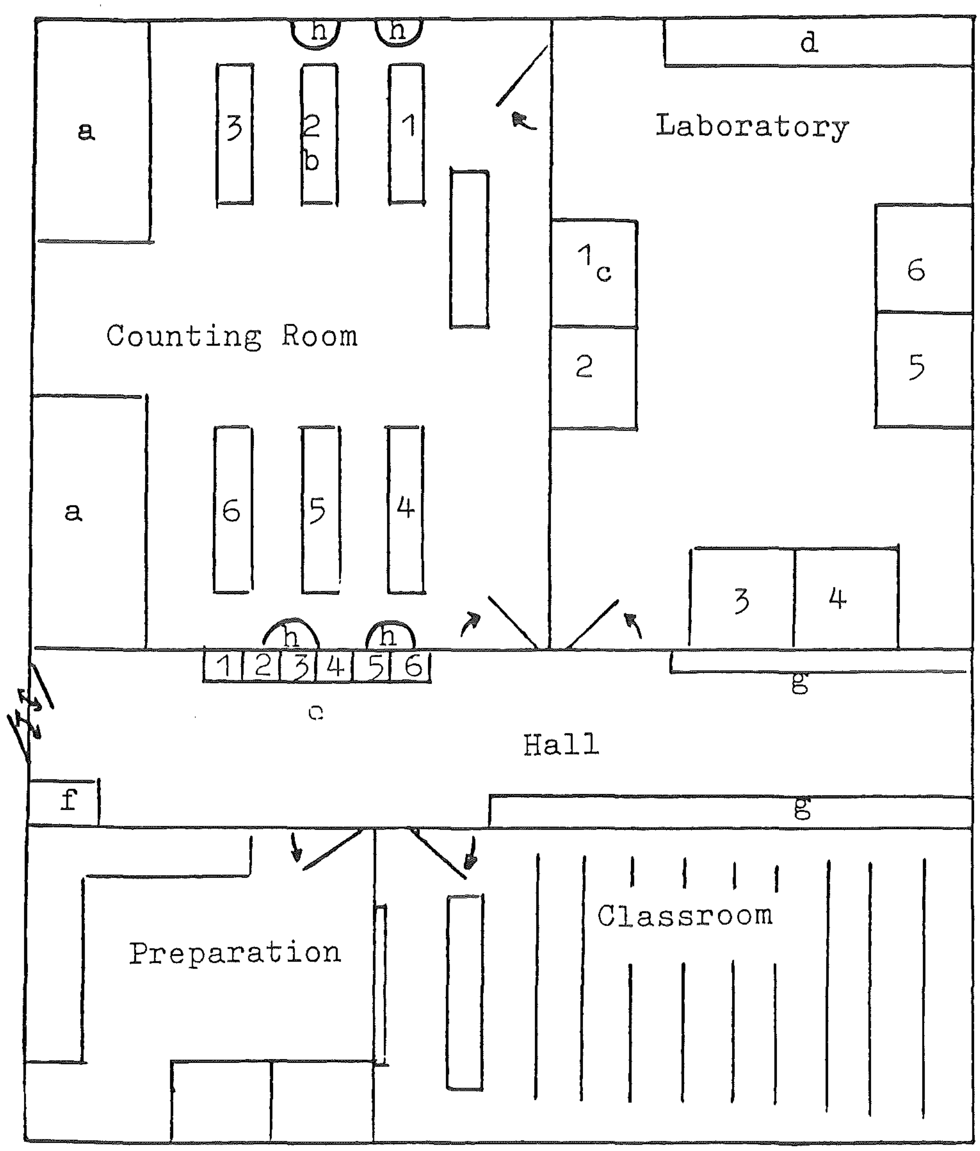
EXPERIMENTAL COURSE ON
NUCLEAR AND RADIOCHEMISTRY

C = Coffee Break
L = Lunch Break
S = Seminar, Demonstration

Part 3: Application of Radioisotopes

Time	9.00 - 9.45	10.00 - 10.45	C 11.15 - 12.00	L 13.00 - 13.45	14.00 - 14.45	C 15.15 - 16.00
Monday	S: Activation Analysis - Theory and Application	Activation Analysis - Determination of Ag and Tl in Technical Grade Lead - Indirect Neutron Activation Analysis				S: Mathematics in Activation Analysis
Tuesday	S: Radioisotope Labeling	For Choice: - Insuline Labeling With ^{131}I or - Naphtaline Labeling With Tritium				
Wednesday	S: Chemical and Physico-chemical Application of Radiotracers	Isotope Dilution Analysis - I$^-$ - Determination in Presence of Large Quantities of Cl$^-$ and Br$^-$		Tracer Technique - Solubility of PbI$_2$		S: Radio-nuclides in Industry
Thursday	S: Szilard-Chalmers-Effect	For Choice Backscattering of β-Particles and Its Industrial Application - Det. of Layer Thicknesses - Det. of Material Wear or Szilard-Chalmers-Reactions - Change of the Chemical Bond of Ethyl Iodide by (n,γ) - Change of Ox. State of Mn				S: Instructions for Further Investigations
Friday	Identification and Separation of an Unknown Mixture of Radionuclides			S: Course End Session		

Appendix 2



(a) Large Measuring Equipment
(b) Measuring Device (G-M Counter, Scaler/Timer, Absorber Foils)
(c) Fume Hood
(d) Laboratory Bench
(e) Locker
(f) Contamination Monitor
(g) Chemical Store
(h) NaI-Scintillation Detectors

Appendix 3

RULES FOR WORKING IN THE RADIOCHEMICAL LABORATORY

(1) No drinking, eating or smoking

(2) No mouth operations, all pipetting must be done with syrings.

(3) Laboratory coats and pocket chambers must be worn at all time.

(4) Gloves must not be worn in the counting room.

(5) Don't take calculators, books or other valuable things into the laboratory.

(6) All work with open sources (e.g. sample preparation) must be conducted over a tray.

(7) Solid waste must be placed in the active bin.

(8) Liquid waste must be poured into the "active residues" bottle.

(9) Gloves, coats and hands must always be monitored before leaving the laboratory.

(10) In the event of a liquid spill:
  a) Drop a handfull of paper tissues on the site of the spill.
  b) Put on gloves.
  c) Mop up the spill with paper tissue.
  d) Mark the spot.
  e) Report the spill immediately.
  f) Monitor the surface when dry.

Appendix 4

Counting Data

Name:..........................   Date:...................

Experimental Course:..

Background R_o = ...cpm   Notes:.....................

Sample	Counting Time t [min]	Measuring Rate R_M [cpm]	Net Rate R_N [cpm] = $R_M - R_o$