Studies in Environmental Science 22

ENVIRONMENTAL RADIOANALYSIS

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FOREWORD

Analytical applications of radioactivity have developed into a distinct branch of analytical chemistry, namely radioanalysis. One of the main reasons for its growth in recent years has been its usefulness in environmental research and control.

The present work has two aims. The first is to give a survey of the principles of radioanalysis in an analytically useful way; the second is to survey the important applications in the main fields of environmental research. In view of the ever-increasing flow of documentation, it is obvious that only examples which have proved to be of practical use can be cited here. It is the opinion of the authors that any recommendations on the use of radioanalysis in problems related to the environment can only be made on the basis of first hand practical experience.

The approach to radioanalysis and its subsequent practical applications described in this book have formed the main activity of the radiochemical laboratories of the Netherlands Energy Research Foundation (ECN) at Petten (N.H.), the University of Amsterdam and the State University at Utrecht. However the authors realise how much they are indebted to the many radiochemists all over the world who have contributed to this topic and whose studies are referred to in this work.

H. A. Das

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CHAPTER 1. INTRODUCTION

1.1. The status of radioanalysis

- Radioanalysis can be defined as the application of the phenomenon of radioactivity in analytical chemistry. It was originated in the '30's and has grown ever since. With the advent of cyclotrons in the '40's and nuclear reactors in the '50's and '60's, the field has expanded exponentially and ramified considerably. Long treated as one of the many branches of radiochemistry, the analytical use of radionuclides became a separate discipline by the sheer force of its usefulness. In essence, this use was three-pronged: Firstly, the application of radionuclides in the medical field especially that of diagnosis. Secondly, there was the age determination of organic samples by the ^{14}C-method. Finally the apparent geochemical applicability was stimulated by the ever increasing demand for uranium.

- The term "radioanalysis" was not coined prior to the mid '60's getting general recognition by the foundation of the Journal of Radioanalytical Chemistry and the Radiochemical and Radioanalytical Letters. A major impetus then came from the biological sciences which urged for more knowledge on the concentrations of trace elements in tissues as well as for the metabolism of many, primarily organic compounds. This was followed in turn by the same question from nearly all fields of environmental studies. Again an upsurge of procedures occurred, this time covering the whole scala of matrices which stretches from air via air-dust and sediment to hair and blood.

- Although radioanalysis had thus become of importance to many branches of science, its position was by no means secured. This was mainly due to the inherent limitations of the methods which were in principle four:

▣ The often high cost of irradiations.

▣ The use of - mostly open - radioactive sources which implies a radiochemical laboratory.

▣ The rather long turn-over time of many radioanalytical procedures.

□ The manual labour required in most of these procedures.

- The costs of irradiations are a problem in elemental analysis only. They have been tackled in two ways: Firstly by embedding the radioanalytical experiments in irradiation programmes of a wider scope. Thus a Materials Test Reactor which is operated almost continuously may well serve the purposes of radioanalysis at a rather low cost. The same reasoning holds for the time-sharing of cyclotrons and linear accelerators. A second approach was made by the advent of small research reactors like the "Triga" and "Slowpoke" combined with a marked increase in detection efficiency of high-resolution γ-ray detectors.
- It is understandable that the trend of the last years has been towards the reduction of the last two drawbacks. The turn-over time was reduced by a more systematic use of short-lived radionuclides. Moreover its effect is mitigated by the multielement character of most determinations. The time spent per analysis decreased drastically by the combination of high resolution detectors and sample changers. Eventually group separations are used to eliminate interfering radionuclides.
- Although radioanalysis is bound to remain a rather secluded area of analytical chemistry, it may be said now that its future is secured as long as there are irradiation facilities available, nuclear research reactors in particular. Then radioanalysis acts as a cost-saver. At the same time it is obvious that this can be fruitful only if a thorough grafting with the non-radiochemical methods is reached. We now have put forward the major theme of this text: The contributions which radioanalysis can make to environmental studies at a reasonable cost and within a reasonable time.

1.2. Scope of radioanalysis

- The scope of radioanalysis, even restricted to the field of environmental science, is very wide, as can be seen from table 1.I. The most important branches for environmental analysis are elemental analysis by activation and radiotracer studies.

  The potential of these sections of radioanalysis has not been fully explored yet. As there is much concern on the use of radiotracers in open systems nowadays, the trend in tracer experiments is towards the use of such stable nuclei as can be easily determined by activation analysis.

The applications of the activation techniques are of three types mainly:

- ☐ Instrumental multielement analysis.
- ☐ The determination of (a few) special elements which are hardly assayable by other methods.
- ☐ The use as a reference method.

- Multielement determinations by instrumental neutron activation analysis (INAA) are normally based on the simultaneous irradiation of many small samples, followed by γ-ray spectrometry. A "continuous" working reactor backed up by a smooth system of γ-ray spectrometry and the interpretation of the γ-spectra may process something in the order of 10^4 samples and yield about 10^5 data a year.

  The costs of the determination depend on the manual labour involved, on the computer charges and the equipment's write off. For purely instrumental analysis, this figures out at $\lesssim$ 10 dollars **per element** determination. For analysis involving chemical separations the costs are normally much higher. If a rapid group separation scheme is used however, followed by high resolution γ-ray spectrometry, the result may be as low as ~20 dollars per element determination. On may consider these group separations as a successful attempt to enlarge the scope of INAA.

- Alternatively prompt methods like proton induced X-ray emission (PIXE) or prompt capture γ-ray measurements (PGAA) are applied. As this implies the one-by-one irradiation of the samples, the capacity of these methods is limited by the irradiation-time and the manual labour. In the case of the determination of uranium by delayed neutron counting the annual production is of the order of 10^4 samples.

- Apart from INAA and PIXE the most important radioanalytical routine method in environmental analysis is X-ray fluorescence (XRF) with a tube or a radioactive source. In fact one should mention it before the two other methods as XRF is much more widely applicable. In practice however, XRF is largely performed by excitation with X-rays from tubes and thus a virtually independent field. Its most conspicuous applications are the elemental analysis of molten and pelletized silicates, of air-dust collected on cellulose filters and of trace elements from water, scavenged into a thin layer.

- Viewed from the point of practical application in environmental analysis, isotope dilution or radiometrical titration are of no appreciable importance. A development which may become useful is the application of radioactive reagents for certain groups of organic pollutants, followed by separation by HPLC and counting. This approach might extend the scope of radioanalysis to the domain of the molecule. Its succes will depend on the simplicity of the labelling procedure and the possibility of rapid on-line detection.
- One may compare the capacity of a routine INAA and PIXE group to that of an industrial analytical laboratory. As there are usually only one or two radioanalytical routine laboratories in each developed country against many industrial laboratories, it is obvious that radioanalysis covers a tiny part of the total analytical capacity only. Thus a proper use is essential. In general one should avoid all routine determinations which can be made by other methods. Overlap is justified only when INAA yields a few "extra" elements.

1.3. The task of the radioanalyst

- The gap between the capacities of radioanalysis and the combined other analytical techniques can thus be bridged by the combined effects of the high sensitivity for certain elements and the possibility of (instrumental) multielement analysis. It is the task of the radioanalyst to widen the opportunities for such applications. At least three aspects can be defined clearly:

  a. The definition of the requirements which should be met by the sampling procedure. Unknown biases in sampling are among the most frequent causes of analytical failure. This may be due to contamination of the sample by the tools used or by the substrate on which it is collected. Another reason for disappointment stems from the fact that radioanalytical methods often require small aliquots only. Conclusions drawn from these small samples may be untenable in view of the large masses they were taken from.

  b. The scope of the analysis. The (number of) elements determinable, the estimated accuracy and precision and the turn-over time of the analysis should be stated clearly. The claimed precision should be the overall reproducibility and not just the statistical error.

c. The presentation of data. Supplying a customer with a matrix of elemental concentrations often results in disappointment only as there is no obvious relation with the practical problem which triggered the analysis. Application of a standard statistical package to detect possible (sub-) groupings should be considered as part of the service.

1.4. Purpose and limitations of this monograph

- The main theme of the present monograph is the practice of a consistent system for the determination of the elemental composition of environmental samples by radioanalysis and its relation to other analytical methods. The experience gathered at the radioanalytical laboratory of the Netherlands Energy Research Foundation, ECN, at Petten, The Netherlands and the radiochemical laboratory of the University of Amsterdam has been used as a starting point. To this was added the important practical knowledge communicated by other Dutch radioanalytical laboratories, notably on PIXE. The emphasis has been laid on the methods. This body of practice has been compared to data from literature, issued during the last 5 years. In view of the rapid development of the environmental applications of radioanalysis, this period can be considered as representative. A monograph like this should, before all, incite thinking and thus make a subsequent literature search more fruitful. It will, however, not be able to make such a search superfluous.
- No attempt has been made to cover all radioanalytical techniques. The application of charged particle activation or X-ray fluorescence has been omitted. Table 1.II. gives the matrices and activation techniques which are considered. In addition, the use of radiotracers is surveyed.

Table 1.I. Survey of radioanalysis

- Radioanalysis
  - Use of radiation sources
    - Scattering analysis
    - Absorption measurements
  - Addition of radioactivity
    - Isotope dilution analysis
      - Classical isotope dilution
      - Reversed isotope dilution
      - Spiking isotope dilution
    - Radiometric titrations
    - Radiotracer measurements
  - Activation
    - Prompt techniques
      - Prompt capture procedures
      - γ-γ Resonance
      - PIXE
    - Delayed techniques
      - Delayed neutron counting
      - Activation analysis
        - with neutrons
        - with photons
        - with charged particles

Table 1.II. Scope of this text

Type of material	Radioanalytical technique			
	Activation analysis with neutrons	Delayed neutron measurements	Prompt capture γ-ray measurements	PIXE
Water	*			
Dry organic material	*			
Air dust and air	*			*
Fly ash and coal	*	*	*	
Silicates	*	*	*	

CHAPTER 2.

PRINCIPLES OF NEUTRON ACTIVATION ANALYSIS AND PROMPT TECHNIQUES, APPLIED IN ENVIRONMENTAL ANALYSIS.

SUMMARY

- From the point of view of environmental analysis, the most useful activation techniques are neutron activation and proton induced X-ray emission. Neutron activation is usually applied as a delayed technique: Aliquots are irradiated and counted later. Alternatively, the prompt capture γ-rays may be measured.
- This chapter deals with the principal features of these techniques, as far as they are encountered in environmental analysis.

List of symbols

A	Ideal result of measurement, in counts	[-]
A_{Fe}	Result of measurement of fluxmonitor, in counts	[-]
A_{norm}	Result of measurement, corrected for flux differences	[-]
A_{obs}	Result of measurement with extended counting-time	[-]
A_p	Number of counts in the pulser peak	[-]
$\left(Act\right)_o$	Activity of the sample at the end of the irradiation	[s^{-1}]
a	Isotopic abundance	[-]
a_d	Abundance of the γ-ray	[-]
C	True count-rate	[min^{-1}]
C_t	True count-rate at time t	[min^{-1}]
C'_t	Count-rate at time t	[min^{-1}]
$C_{t=0}$	True count-rate at $t = 0$	[min^{-1}]
c	Concentration of inactive species	[$M.g^{-1}$]
C_o	Natural background	[min^{-1}]
c_o	Total concentration	[$M.g^{-1}$]
D	Height of cylindrical aliquot Thickness of thin-layer aliquot	[cm]
D_o	Total dead-time fraction at the beginning of the measurement	[-]
D_t	Total dead-time at time t	[-]
E	Gamma-energy	[keV]
$F(t)$	Combined time-depending terms in activation equation	[min]
f	Factor representing the matrix influences in PIXE	[-]
f_a	Fractional absorption of radiation between source and detector	[-]
$\bar{f}_n$	Average neutron flux-depression	[-]
f_p	Influence of pile-up, as measured with an electronic pulser	[-]

f_τ	Influence of dead-time losses	[-]
f'_τ	Residual influence of dead-time losses at extended counting-time	[-]
G	Sample-weight	[g]
I	Resonance integral	[cm^2]
I_p	Proton beam-current	[s^{-1}] or [μA]
K	Constant proportional to the average neutron flux Specific count-rate in prompt techniques	[$cm^{-2}.s^{-1}$] [$min^{-1}.M^{-1}$]
M	Atomic weight	[g]
N*	Number of active nuclei	[-]
N_{Av}	Avogadro's number	[M^{-1}]
$(N_{cc})_i$	Number of nuclei per cm^3 of nuclide i	[cm^{-3}]
R	Radius of cylindrical sample	[cm]
R_{Cd}	Cadmium-ratio	[-]
r	Ratio number of radioactive nuclei/original number of stable nuclei	[-]
$S_{A/B}$	Advantage-factor in epithermal neutron activation	[-]
s	Suffix denoting the standard	[-]
t_1	Irradiation-time	[min]
t_2	Decay-time	[min]
t_m	Preset counting-time	[min]
t'_m	Extended counting-time	[min]
$t_{\frac{1}{2}}$	Half-life	[min]
V	Volume of sample	[cm^3]
x	Suffix denoting the sample	[-]
γ	Sensitivity	[-]
λ	Decay-constant	[s^{-1}] or [min^{-1}]
μ	Coefficient of absorption	[cm^{-1}]
Σ	Total macroscopic cross-section	[cm^{-1}]

$\sigma(E)$	Differential cross-section for neutron capture	$[cm^2]$
σ_i	Cross-section for neutron capture of nuclide i	$[cm^2]$
σ_o	Cross-section for thermal neutron capture	$[cm^2]$
ϕ	Neutron flux in the sample	$[cm^{-2}.s^{-1}]$
ϕ_o	Undisturbed neutron flux	$[cm^{-2}.s^{-1}]$
$\phi(E)$	Differential neutron flux	$[cm^{-2}.s^{-1}.keV^{-1}]$
ϕ_e	Epithermal neutron flux	$[cm^{-2}.s^{-1}]$
ϕ_{th}	Thermal neutron flux	$[cm^{-2}.s^{-1}]$

2.1. Neutron activation analysis

2.1.1. Principle

- Neutron activation analysis (NAA) depends on the induction of radioactivity by neutron capture which transforms a small fraction of the stable nuclei of a given isotope into unstable, radioactive, ones. The number of these transformed nuclei is proportional to the original number of the parent nuclei and thus to the concentration of the corresponding element.
  The rate of decay, the "activity", is in turn proportional to the number of active nuclei.

- The activity is usually measured in a relative way, that is as a count-rate and calibration is obtained by comparison to standards.

- NAA is by far the most important radioanalytical technique for elemental analysis. The irradiation capacity of a nuclear reactor or even of a neutron generator is very large.
  Then neutron activation offers the advantage of small and usually negligible matrix effects. Combination with high resolution γ-ray spectrometry may result in multi-element analysis.
  The influence of (self-)absorption is, as a rule, negligible as most analytically important lines have energies in the region $\sim$ 80-2000 keV [1,2].
- In NAA irradiation and measurement are separated. Thus the technique is a combination of two different disciplines. The precision and accuracy of both govern the final result.

- Neutron activation analysis may be divided into three sections according to the neutron energy used:
  Thermal, epithermal and fast neutron activation.
  The first variety is mainly based on thermalized reactor neutrons. The second uses epithermal reactor neutrons after elimination of the thermal neutrons by a Cd- or a B-shield. Fast neutrons are produced by a neutron generator.
  All these techniques are restricted to a nuclear centre or a laboratory which has access to it.

2.1.2. Formulation

- At the end of the irradiation a small fraction r of the stable nuclei has been transformed into radioactive, unstable ones.

The number of radioactive nuclei, N*, is thus equal to

$$N^* = r \cdot c_o \cdot G \cdot N_{Av} \qquad (2.1)$$

The related activity at the end of the irradiation is

$$(Act)_o = -\frac{dN^*}{dt} = \lambda\, N^* = \lambda \cdot r \cdot c_o \cdot G \cdot N_{Av} \qquad (2.2)$$

The ratio r = unstable/originally stable can be defined in terms of the irradiation conditions:

$$r = a \cdot \left[\int_o^\infty \sigma(E) \cdot \phi(E) \cdot dE\right] \cdot \left(\frac{1-e^{-\lambda t_I}}{\lambda}\right) \cdot \bar{f}_n \qquad (2.3)$$

It contains four factors:

- The isotopic abundance a. From this it is evident that (neutron) activation analysis refers to isotopes. Elemental compositions can be deduced only if the isotopic ratios are identical for samples and standards.

- The term in square brackets represents the influence of the neutron flux and the neutron spectrum. Although, in principle, this integral may be calculated from the flux-spectrum and the literature data on σ(E), it is common practice to use standards for comparison and to measure the ratio of the integrals for samples and standards.

- The integral $\int \sigma(E) \cdot \phi(E) \cdot dE$ is often written as

  $$\int \sigma(E) \cdot \phi(E) \cdot dE = \sigma_o \cdot \phi_{th} + I \cdot \phi_{epi} \qquad (2.4^a)$$

  Here ϕ_{th} and ϕ_{epi} stand for the thermal and epithermal neutron flux while σ_o and I give the thermal cross-section and the resonance-integral. Thus, by dividing the neutron-spectrum into two parts a formula without an integral can be obtained. The value of σ_o and I have been tabulated for use in a priori calculation of the induced activity [3].

Furthermore, for routine purposes, the integral can be rewritten as

$$\int_0^\infty \sigma(E) \cdot \phi(E) \cdot dE = K \cdot \frac{\int_0^\infty \sigma(E) \cdot \phi(E) \cdot dE}{K} \qquad (2.4b)$$

Thus it is split into two parts again: The constant K is proportional to the average neutron flux while the second term on the right hand represents the influence of the normalized neutron spectrum.
Usually the neutron-spectrum is well defined and constant so that only K has to be determined, preferably for each aliquot separately. This is done by means of a flux-monitor: Small but constant amounts of a metal are mounted in the irradiation capsules in an identical way. Annular iron wires are often convenient to this end [4]. The induced ^{59}Fe ($T\frac{1}{2}$ = 45.1 d) activities are measured separately. The precision and accuracy of these measurements govern the result of the analysis.

- ☐ The factor $\left(\frac{1 - e^{-\lambda t_1}}{\lambda}\right)$ represents the influence of the half-life.
- ☐ The influence of the depression of the neutron flux in the sample, due to absorption, is represented by the factor $\bar{f}_n$ which is defined by (2.5).

$$\bar{f}_n = \frac{\int \phi \cdot dV}{\phi_o \cdot V} \qquad (2.5)$$

For cylindrical samples $\bar{f}_n$ may be approximated by [2]:

$$\bar{f}_n \simeq 1 - 1.33 \, R \cdot \sum_i (N_{cc})_i \cdot \sigma_i \qquad (2.6)$$

For aliquots taken from the environment the sum-term is usually 10^{-4} cm^{-1} or lower.

So with R ≤ 0.5 cm, the influence will be ≤ 0.01% and thus negligible.

2.1.3. Standardization and flux monitoring

- Neutron activation is usually applied as a relative technique, that is by comparison to standards. This implies the preparation of standards and the monitoring of the neutron flux and its spectrum.

- The standards should be of approximately the same composition, shape and volume as the samples, to avoid systematic differences in neutron absorption and counting efficiency. Multielement standards of variable size may be prepared on the base of active carbon [5] or calcium carbonate [6].
- Flux-monitors should preferably be external; hence the use of small iron-rings. If this is not possible as when short-lived radionuclides have to be measured, this causes inconvenience. Addition of a radioelement which does not occur at an appreciable concentration in the sample nor does interfere in the γ-spectrometry may be suitable then. Thus, for the flux-monitoring of water samples one may use the reactions $^{86}Sr(n, \gamma)\, ^{87m}Sr$, $T\frac{1}{2} = 2.8$ h or $^{84}Sr(n, \gamma)\, ^{85}Sr$, $T\frac{1}{2} = 65$ d on enriched ^{84}Sr. With a neutron generator, the flux-monitor is often replaced by a fission-chamber which gives a signal proportional to the integrated neutron dose.

  If there exists any doubt on the constancy of the neutron-spectrum it can be monitored by way of the ratio between the activities induced in two monitors, one with a low and one with a high I/σ_o-ratio [7].

2.2. Count-rate

- Radioactive decay implies the emission of energy. Absorption in a detector may cause a momentary potential drop or "pulse". Usually the pulse-height is proportional to the energy absorbed. Both the count-rate, i.e. the frequency of these pulses, and the frequency distribution of their height, the spectrum, may be measured.

  For analytical purposes, only the complete absorption of the emitted photons is of interest. This complete absorption yields discrete lines which are broadened into "photo"-peaks due to the finite resolution of the apparatus. They are superimposed on a compton-continuum. Figure 2.1. gives a γ-ray spectrum of a silicate sample, taken after a decay-time of a few weeks [15].
- The ideal count-rate, in counts min^{-1}, can be defined as the number of pulses registered by an infinitely fast recording system. It is related to the activity of the aliquot by equation (2.7).

$$C = C_o + 60 \cdot \gamma \cdot (Act)_o \cdot a_d \cdot f_a \cdot e^{-\lambda t_2} \tag{2.7}$$

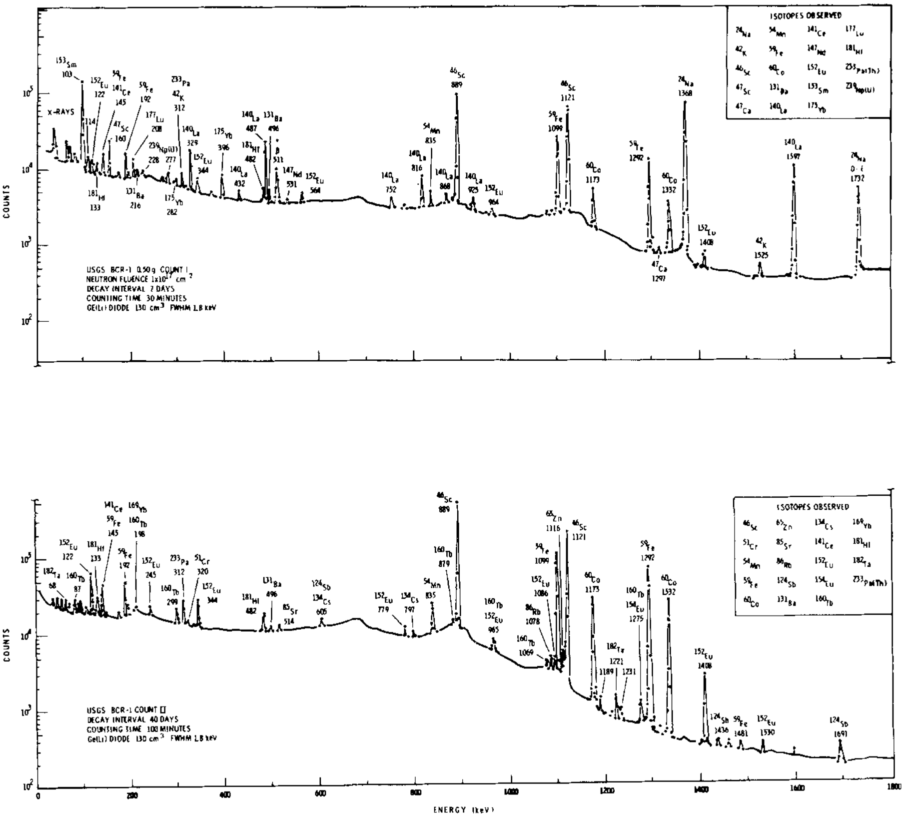

Figure 2.1. (Ref. [15]).

The γ-ray spectrum of a silicate a few weeks after its activation with thermal neutrons.

The term C_o denotes the natural background of the detector; γ is the efficiency, expressed in pulses per desintegration, a_d the fraction of the desintegrations which give rise to the desired radiation while the influence of absorption is represented by f_a. The decay-time is t_2.

Usually f_a is equal to unity for energies above ≈ 100 keV.

- Combination of (2.2), (2.3) and (2.7) yields

$$C - C_o = 60 \cdot a \cdot N_{Av} \cdot G \cdot K \cdot \left[\frac{\int_o^{\infty} \sigma(E) \cdot \phi(E) \cdot dE}{K} \right] \cdot \left(1 - e^{-\lambda t_1}\right) \cdot \gamma \cdot e^{-\lambda t_2} \cdot a_d \cdot f_a \cdot c_o \qquad (2.8)$$

With f_a equal to unity, there exists a simple proportionality between the net "ideal" count-rate $(C-C_o)$ and c_o. The natural background is usually negligible compared to the induced count-rate. The value of γ comes as a rule between 0.1 and 0.5.

- The count-rate is determined by integral counting or deduced from spectral measurements.

  The first case applies to aliquots which contain one radionuclide only. The total count-rate and the background are measured and subtracted. By far more frequent nowadays is the processing of γ-ray spectra which consist of the contributions of many radionuclides. There the count-rate is obtained by separating the photopeaks from the compton-continuum. This procedure causes an additional statistical and systematic error, which can be reduced by using appropriate computer-programmes. Whether one accepts the results of such a calculation or prefers to do a (further) chemical separation is a matter of personal decision. It can be taken after consideration of the analytical criteria discussed in chapter 6. The requirements which should be met by the separation are discussed in chapter 5.

2.3. Counting-result

- The integration of the count-rate over the measuring period, t_m should yield the (ideal) counting-result, A.

Thus:

$$A = \int_{o}^{t_m} C_t \, . \, dt \tag{2.9}$$

Insertion of $C_t = C_{t=o} \, . \, e^{-\lambda t}$ yields:

$$A = C_{t=o} \, . \, t_m \, . \left[\frac{1 - e^{-\lambda t_m}}{\lambda t_m}\right] \tag{2.10}$$

Usually, the counts under a photopeak are observed.

As the electronic apparatus is not infinitely fast, losses will occur. They are of two kinds:

a. The count-rate decreases, due to pile-up of pulses from C_t to C'_t. The fractional loss is independent of the pulse-height.

b. The total dead-time causes a fractional loss in the registration, of $(1-D_t)$. This causes a fractional loss-factor f_τ. To compensate for this, the γ-spectrometer automatically extends the counting-time from t_m to t'_m, defined by

$$t'_m = \int_{o}^{t_m} (1 - D_t) \, . \, dt \tag{2.11}$$

Thus (2.9) is transformed into (2.12).

$$A_{obs} = \int_{o}^{t'_m} C_t \, . \, (1 - D_t) \, . \, dt \tag{2.12}$$

- The fractional loss due to pile-up can be measured by introducing the 50 Hz electronic pulser signal of a convenient height into the pre-amplifier. The area under the resulting photopeak, A_p, is then related to the loss-factor, f_p, by

$$f_p = \frac{A_p}{3000 \; t_m} \tag{2.13}$$

- The automatic correction for dead-time losses is not sufficient if the decay during the measurement is appreciable, that is if $\lambda t_m \geq 0.1$. The residual loss-factor, f'_τ, can be defined in terms of λt_m and D_o [8].

However, D_o-values over $\simeq 0.25$ should be avoided.

- The observed counting result is thus proportional to the ideal counting result by

$$A_{obs} = A \cdot f'_\tau \cdot f_p \tag{2.14}$$

Equations (2.9) - (2.12) can now be rewritten as

$$A_{obs} = C_{t=o} \cdot t_m \cdot \left[\frac{1 - e^{-\lambda t_m}}{\lambda t_m}\right] \cdot \frac{f'_\tau \cdot A_p}{3000\ t_m} \tag{2.15}$$

Combination with (2.8) yields

$$A_{obs} = \left\{60 \cdot a \cdot N_{Av} \cdot G \cdot c_o\right\}\left\{K \cdot \left[\int_o^\infty \frac{\sigma(E) \cdot \phi(E)dE}{K}\right] \cdot \right.$$

$$\left.\left(1 - e^{-\lambda t_1}\right)\right\} \cdot \left\{a_d \cdot e^{-\lambda t_2}\right\} \cdot \left\{t_m \cdot \frac{f'_\tau \cdot A_p}{3000\ t_m} \cdot \gamma_o \cdot \left[\frac{1 - e^{-\lambda t_m}}{\lambda t_m}\right]\right\} \tag{2.16}$$

The four groups of factors represent the influence of the samples, irradiation, decay and measurement respectively.

- The A_{obs}-values of samples (x) and standards (s) are normalized by means of the annular iron-flux monitors (Fe) which have been irradiated with each sample and standard. The weights of the flux-monitors are equal within 0.3%. This variation might be eliminated by weighing. The normalization step is defined by equation (2.17).

$$A_{norm} = \frac{A_{obs}}{A_{Fe}} \cdot 10^5 \tag{2.17}$$

As $K_x = (K_{Fe})_x$ and $K_s = (K_{Fe})_s$, this step eliminates the influence of variations in the neutron-flux.

The ratio of the A_{norm}-values for samples and standards can be written down. We assume that the following conditions hold:

a. The neutron spectrum does not change during the irradiation.

b. The weights, decay-time and measuring-periods for the flux-monitors of samples and standards are equal.

c. The γ_o-values of samples and standards are equal.

d. The irradiation and counting-times of samples and standards are equal.

Then:

$$\frac{(A_{norm})_x}{(A_{norm})_s} = \frac{(c_o)_x}{(c_o)_s} \cdot \frac{G_x}{G_s} \cdot \frac{(e^{-\lambda t_2})_x}{(e^{-\lambda t_2})_s} \cdot \frac{(f'_\tau)_x}{(f'_\tau)_s} \cdot \frac{(A_p)_x}{(A_p)_s} \qquad (2.18)$$

In most cases $(f'_\tau)_x = (f'_\tau)_s = 1$ and $(e^{-\lambda t_2})_x \simeq (e^{-\lambda t_2})_s$.

Equation (2.18) can then be reduced to a simpler proportionality.

If samples and standards are irradiated separately and connected by the flux-monitors only, the applied neutron spectra may be somewhat different. This may necessitate a small correction.

2.4. Sensitivity

- Equation (2.16) may be used to estimate the sensitivity, defined as the number of counts per μg element. To this end, the product of flux and cross-section can, according to (2.4a), be approximated by

$$\int_0^\infty \sigma(E) \cdot \phi(E) \cdot dE = \sigma_o \cdot \phi_{th} + I \cdot \phi_e = \phi_{th} \cdot \left[\sigma_o + I \cdot {\phi_e}/{\phi_{th}}\right] \qquad (2.19)$$

The values of σ_o and I may be taken from literature compilations.

The values of ${\phi_e}/{\phi_{th}}$ depends on the irradiation position.

- Insertion of practical values for the constants yields 10^3-10^5 counts per ($\mu g.g^{-1}$) in the photopeak for 300-500 mg samples.

The factors which contain $t_{\frac{1}{2}}$, t_1, t_2 and t_m may be combined to one term, F(t). The (dimensionless) product λ . F(t) gives the ratio

$$\frac{\text{actual signal}}{\text{theoretical maximum signal}}$$

For each set of t_1, t_2 and t_m, it has an optimum value for a certain $t_{\frac{1}{2}}$.
For the conditions of t_1 = 12 h, t_2 = 24 h, t_m = 1 h, $\lambda F(t)$ is of the order of 10^{-3}-10^{-2} and has an optimum at $t_{\frac{1}{2}} \sim 10$ h.
For the subsequent measurement of long-lived radionuclides one has t_1 = 12 h, t_2 = 21 d and t_m = 1.7 h and the optimum at $t_{\frac{1}{2}} \sim 177$ h. Here λ . F(t) is of the order of 10^{-4}.

2.5. Special features of the three types of neutron activation

- The three variations of neutron activation feature some peculiarities. These follow from the differences in neutron spectrum and irradiation position.

- Thermal neutron activation is based on exothermic, mostly (n,γ), reactions. In a few cases the daughter-product of the formed radionuclide is measured. The integral over the product of cross-section and flux is usually replaced by the product of the flux in the thermal region (< ~ 0.4 eV) and an average "reactor" cross-section. As a rule the former lies between 5.10^{10} and 10^{14} $cm^{-2}s^{-1}$; the latter is of the order of 1 to 10.10^{-24} cm^2. Thus the reaction rate varies between 10^{-13} and 10^{-9} s^{-1}.

  Thermal neutron activation analysis is primarily used as a tool for trace element determination. It is applied in two ways:
  a. Instrumental thermal neutron activation which typically covers between 10 and 30 elements simultaneously.
  b. Single element determinations in - often small - aliquots.

- Epithermal neutron activation is usually based on the elimination of the thermal neutrons by a Cd-shield of ~ 1 mm thickness which removes neutrons with an energy of 0.4 eV. If the heat-production in the shield can be kept in check and aliquots can be taken out remotely, a useful extension of thermal NAA can be obtained. Although the sensitivity is obviously less, the precision and accuracy may be enhanced by suppression of interfering radionuclides. The elimination of ^{24}Na ($T\frac{1}{2}$ = 15 h) is the most conspicuous use of epithermal activation.

  The ratio of the induced activities without and with a Cd-shield is called the Cd-ratio:

$$R_{Cd} = (Act)without_{Cd}/(Act)with_{Cd} \qquad (2.20)$$

  It is obvious that the advantages of epithermal NAA for a particular radionuclide A over its interference B may be expressed by [9]:

$$S_{A/B} = \frac{(R_{Cd})_B}{(R_{Cd})_A} \qquad (2.20)$$

Now R_{Cd} decreases with I/σ_o. The greatest reduction in activity will thus be observed for reactions with a low I/σ_o-ratio; consequently the technique is applied for elements with a high I/σ_o-ratio primarily. Typical applications are the determination of iodine in biological material and of uranium in rocks.

Simultaneously, the Cd-shielded irradiation may be used for activation with fast reactor neutrons.

- Fast neutron activation is based on endothermic (n,2n), (n,p) and (n,α) reactions induced by energetic neutrons.

  Two approaches are used:

  a. 14.5 MeV neutrons produced in a neutron generator by the (d,α) reaction on tritium.

  b. "Fast" reactor neutrons with an energy distribution which decreases about exponentially to a maximal energy value of ~ 11 MeV.

  In the first case one has a rather low flux of 10^8-10^{10} $cm^{-2}s^{-1}$ and cross-sections of the order of 10^{-25} cm^2. Thus r is about 10^{-17}-10^{-15} s^{-1}. In the second situation the flux may be much higher but most of it falls below the threshold of the reaction so that the effective σ-value is small.

  The neutron generator is used for determinations by way of short-lived radionuclides; N by $^{13}N(T\frac{1}{2} = 10$ min), O by $^{16}N(T\frac{1}{2} = 7.3$ s), F by $^{18}F(T\frac{1}{2} = 110$ min) and Si by $^{28}Al(T\frac{1}{2} = 2.3$ min) are the most important examples.

  The reactor is applied for the production of long-lived radionuclides. The determination of Fe by way of $^{54}Mn(T\frac{1}{2} = 313$ d) and Ni by ^{58}Co $(T\frac{1}{2} = 71$ d) may be mentioned.

2.6. Prompt techniques

2.6.1. General

- Prompt techniques require a combination of irradiation and counting facilities. For the analysis of environmental samples the most important techniques are neutron induced prompt capture γ-ray measurements (PGAA) and proton induced X-ray emission (PIXE).

- Like NAA prompt techniques feature a proportionality between count-rate and concentration. However, the number of counts collected increases linearly with the counting-time as there is no half-life involved. This also implies that there is no variation of the total dead-time fraction over the measurement as the activity of the counting aliquot does not change. Again the flux should be monitored.

2.6.2. Neutron induced prompt capture γ-ray measurement (PGAA)

- The measurement of the immediate γ-radiation which is caused by neutron capture implies the irradiation of the aliquot in a "beam" of neutrons and detection of the emitted γ-rays by a detector under an angle of $\sim 90^{o}$.

  The emitted γ-ray spectra are complex and cover the energy region up to $\simeq$ 11 MeV. Compilations of the principal γ-rays and the analytically useful lines have been published [10,16]. Usually lines below $\simeq$ 3 MeV are applied in analysis as the detection efficiency decreases rapidly with energy.

  The technique is, in principle, quite versatile. In practice however, its applications are severely limited by the fact that convenient experimental facilities are scarce. This restricts the use to reference measurements or for the completion of NAA.

- For the prompt γ-ray production per second by aliquot under irradiation one can write

$$C = C_o + \gamma \cdot \frac{dN^*}{dt} \cdot a_d \cdot f_a \qquad (2.20)$$

where $\frac{dN^*}{dt}$ is the rate of activation given by

$$\frac{dN^*}{dt} = a \cdot \left[\int_o^\infty \sigma(E) \cdot \phi(E) \cdot dE\right] \cdot \bar{f}_n \cdot \left[\frac{c_o \cdot G \cdot N_{Av}}{M}\right] \qquad (2.21)$$

The factor $\bar{f}_n$ accounts for the loss of neutron-flux over the aliquot due to absorption and scattering. The second factor in brackets gives the number of reactive nuclei.

Combination of (2.20) and (2.21) yields the count-rate C as a function of c_o.

For practical purposes one writes, for samples of the same size:

$$(C - C_o) = K \cdot \bar{f}_n \cdot c_o \cdot G \qquad (2.22)$$

The constant $(K \,.\, \bar{f}_n)$, expressed in counts $.\text{min}^{-1}.g^{-1}$, is determined empirically. The changes of $\bar{f}_n$ with the matrix can be estimated from the relation

$$\bar{f}_n = 1 - e^{-\Sigma \,.\, D} \qquad (2.23)$$

where Σ is the total macroscopic cross-section, in cm^{-1}, and D the thickness of the aliquot in cm. By analyzing standard materials of known composition, the variation of $(K \,.\, \bar{f}_n)$ with $\bar{f}_n$ may be obtained. The blank C_o is often considerable, due to activation of the construction and shielding material. The reduction of the blank is tedious as it usually involves a complete rearrangement of the experimental array. The value of the detection efficiency γ is mostly low (< 0.1) as the distance between aliquot and detector is large.

2.6.3. Proton induced X-ray emission

- X-ray fluorescence may be induced by photon or charged particle irradiation, usually with protons. Thus one may distinguish between XRF (photons) and PIXE (protons). Figure 2.2. gives a schematic representation of these two possibilities [11]. The cross-section for both excitations are of the same order of magnitude. The beam-intensity however, differs considerably. In photon excitation it is $\sim 10^7 \, s^{-1}$ whereas proton beams of up to $5.10^{11} \, s^{-1}$ are feasible. The limiting factor here is the cooling of the target.
  Thus the sensitivity of PIXE is much higher than that of XRF. In both techniques there is an appreciable background; in XRF due to scattering, in PIXE to bremstrahlung, caused by the slowing down of the incident protons.

- Usually PIXE is applied to thin samples only. A layer of 0.1 to 2 $mg \,.\, cm^{-2}$ is spread out evenly over an inert support of ~ 5 $mg \,.\, cm^{-2}$. The protons penetrate the entire layer. It is supposed that the composition of the aliquot is homogeneous. This makes PIXE well suited for the analysis of air-dust or biological materials which can be spread out conveniently.
  The count-rate observed under the X-ray peak of a certain element in a given target may be written as

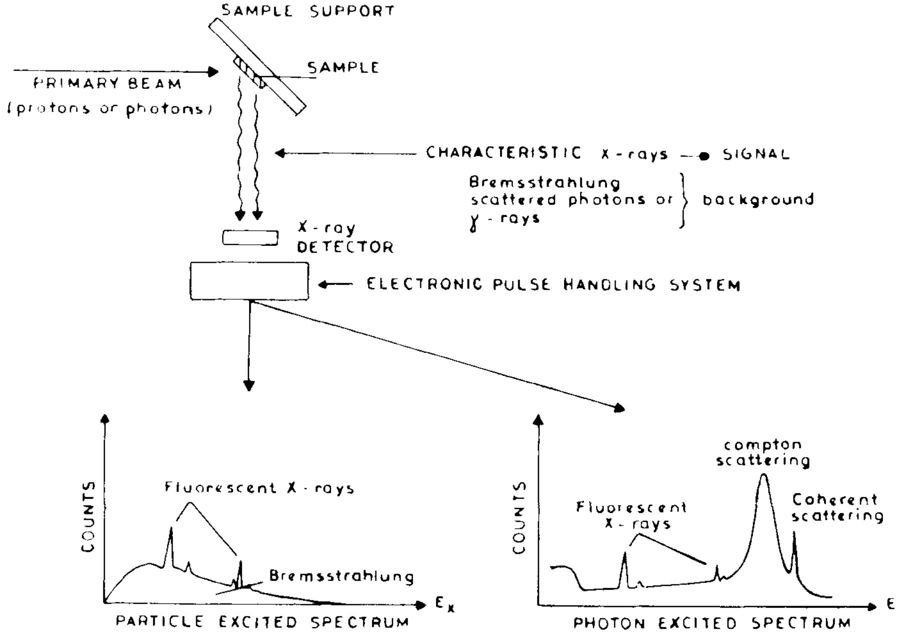

Figure 2.2. (Ref. [11]).

Schematic representation of the major components of an energy dispersive X-ray fluorescence analysis system.

$$C = C_o + \gamma \cdot \sigma \cdot I_p \cdot N_{cc} \cdot D \cdot f \qquad (2.24a)$$

σ = microscopic cross-section for X-ray excitation, in cm^2.
I_p = proton beam current, in s^{-1}.
N_{cc} = number of reactive nuclei per cm^3.
D = thickness of the thin-layer aliquot, in cm.
f = factor representing the matrix influences.

The blank count-rate is usually negligible. The value of γ is chiefly determined by the geometry of the array and is usually low.
The factor f represents the combined effects of

a. Beam attenuation.
b. X-ray emission due to secondary electron excitation.
c. X-ray absorption.

It is possible to calculate these effects [11,12]. In environmental analysis however, it is customary to use PIXE as a relative technique. For practical purposes equation (2.24a) is rewritten as (2.24b) with I_p expressed in µA.

$$C - C_o = K \cdot I_p \cdot f \cdot c_o \cdot G \qquad (2.24b)$$

The sensitivity, expressed in counts$\cdot(\mu g)^{-1} \cdot (\mu C)^{-1}$, is measured experimentally in such a way that the matrix corrections are small (and so can be applied by calculation) or even negligible. Thus in environmental analysis the application of PIXE is usually restricted to layers of $\simeq$ 100 µg . cm^{-2} to $\simeq$ 2mg . cm^{-2} [12,13] although infinite thick pellets may be used [12].

Two procedures are possible:

a. Within one sample one can obtain the mass-ratios of the elements relative to a suitably chosen reference element. Usually some element in the range from Mn(Z = 25) to Zn(Z = 30) is taken. Homogeneous thin standards are prepared and processed which yield, in terms of equation (2.24b), the ratios of the ($K \cdot I_p$)-values. Then the obtained peak-areas, eventually corrected for the matrix-effects, are transformed into mass-ratios.
b. By appropriate standardisation of the irradiation conditions it is possible to obtain the experimental K-values. This implies a reliable technique for the measurement of the total proton-dose per irradiated aliquot.

It can be done in three ways:

- o Measurement of the beam current behind the target with a Faraday cup.
- o Measurement of the incident beam-current from the back scattering caused by a thin (80 $\mu g \cdot cm^{-2}$) gold foil [13].
- o Evaluation of the bremstrahlung-spectrum of the support [12].

In any case the result is a measure of the total proton dose, $\int I_p \cdot dt$. The final calculation of the absolute mass of each element is done by equation (2.25).

$$\text{mass of element in sample} = \frac{A_x}{A_s} \cdot \frac{(\int I_p \cdot dt)_s}{(\int I_p \cdot dt)_x} \cdot \text{(mass of element in standard)} \qquad (2.25)$$

2.7. Conclusions

- The application of radioanalytical techniques in environmental analysis should be restricted to those cases where matrix-effects are negligible or small and the procedures are well standardised.
- Neutron activation analysis, especially that with thermal neutrons, is the most versatile of the radioanalytical techniques.
- Proton induced X-ray emission should be reserved for thin-layer aliquots, especially air-dust.
- Prompt capture γ-ray measurement is useful as a reference technique and for some carefully chosen routine applications.

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CHAPTER 3.

PRINCIPLES OF RADIOTRACER MEASUREMENTS IN ENVIRONMENTAL STUDIES

SUMMARY

The signal obtained from a radiotracer depends on the concentration and the specific activity of the compound or phase measured.
In case of a closed system a radiotracer experiment gives information on the rate of the net mass-transport which affects the concentration, and on the rate of isotopic exchange which influences the specific activity of the compound of interest.
In open systems one generally does not make this distinction but considers the variation of the signal and thus of the radiotracer concentration in relation to the volume or weight of the whole system.

The principles of those measurements which are frequently performed within the scope of environmental studies are summarized here and illustrated with some examples. For closed systems, the formalism is based on the three functions f_A, f_a and f_c which stand for the reduced counting-result, the reduced specific activity and the reduced concentration respectively.
For open systems it is based on the age distribution functions.

LIST OF SYMBOLS

A	Result of measurement, in counts	$[-]$
$A(t)$	Counting results of a radiotracer experiment on an open system	$[-]$
a	Specific activity	$[d.s^{-1}.g^{-1}]$
B	Total concentration of species B	$[M]$
C	Total concentration of species C	$[M]$
c	Concentration in the liquid phase	$[g.l^{-1}]$ or $[M]$
$E(t)$	Exit age distribution function	$[h^{-1}]$
E	Reduced exit age distribution function	$[-]$
$F(t)$	Specific mass transfer function	$[g.g^{-1}.h.^{-1}]$
$F_1(t)$	Leaching part of $F(t)$	
$F_2(t)$	Precipitation/adsorption part of $F(t)$	
f_A	Reduced result of measurement, A/A_o or A/A_∞	$[-]$
f_a	Reduced specific activity, a/a_o or a/a_∞	$[-]$
f_c	Reduced concentration in the liquid phase, c/c_o or c/c_{eq}	$[-]$
$f(x)$	Tracer distribution function	$[-]$
G	Weight of solid phase	$[g]$
k, k_1, k_2	Rate constants	various dimensions
m	Exchangeable mass	$[g]$ or $[Mol]$
m^*	Mass of radiotracer in the liquid phase	$[g]$
m_s^*	Mass of radiotracer in the solid phase	$[g]$
r	Availability ratio, defined by eq. (16)	$[-]$
t	Time	$[h]$
Δ_t	Time-interval	
V	Volume of liquid phase	$[ml]$
α	Rate constant	$[h^{-1}]$
γ	Sensitivity	$[-]$
ν	Reduced time $= t/\tau$	$[-]$
μ	First moment of tracer distribution defined by eq. (3.25)	$[h]$
σ^2	Second moment of tracer distribution defined by eq. (3.26)	$[h^2]$
τ	Average residence time	$[h]$

3.1. Basic equations of radiotracer experiments in a closed system and their applications

- Radiotracer experiments in a closed system refer to the interaction between two or more phases or compounds. Usually an amount of activity is added and the quantity which is present in one phase is measured as a function of time. If the reaction between two compounds in one phase is to be studied, a separation has to be performed prior to the measurement. Often an aliquot is taken for counting. In any case the result is a number of counts, A, which is related to the specific activity, a (desintegration . g^{-1} or desintegration . Mol^{-1}) and the concentration, c (g . l^{-1} or M) by

$$A = \gamma \cdot a \cdot c \qquad (3.1)$$

The constant of proportionality accounts for the volume of the aliquot taken as well as for the counting conditions. If all the radioactivity was introduced at time zero into the phase which is measured and if the counting conditions do not change over the experiment, one has

$$A_o = \gamma \cdot a_o \cdot c_o \qquad (3.2)$$

and thus

$$\frac{A}{A_o} = \frac{a}{a_o} \cdot \frac{c}{c_o} \qquad (3.3a)$$

If we now write $f_A = A/A_o$, $f_a = a/a_o$ and $f_c = c/c_o$ one has

$$f_A = f_a \cdot f_c \qquad (3.3b)$$

and thus, with $df/dt = f'$

$$f'_A = f_a \cdot f'_c + f_c \cdot f'_a \qquad (3.4)$$

Equation (3.4), the activity balance, forms together with the mass-balance, the base of all radiotracer experiments in a closed system. In kinetic studies the third obvious equation is the rate balance: At equilibrium the net rate of two opposing reactions must be zero.

- If there is no net mass transport $f_c \equiv 1$ and $f'_c \equiv 0$ and thus $f'_A = f'_a$ and consequently $f_A = f_a$.
  One can then measure the isotopic exchange. If on the other hand there is no isotopic exchange, the reverse holds and one has $f_A = f_c$.
  When both a and c change one must have extra information from outside the radiotracer experiment to solve (3.4). This may be a separate determination of f_c or a logical prediction of f_a.
  The various possibilities are summarized in table 3.I. together with some examples.

  One should make a clear distinction between the amount of radiotracer which is present in the system and the amount which is available. In leaching experiments on radioactivated solids the available amount increases (non-linearly) with time.
  The moment of introduction of the radioactivity does not have to coincide with the beginning of the experiment. By varying the moment of introduction a possible change in f_a with time may be detected.

  An equally clear distinction should be made between the conclusions which can be drawn from the empirical data, the mass- and the activity balance on one hand and model descriptions of the system on the other. Although one has to rely on the experiments and the balances only, the obvious advantage of a model is that it may bring forward parameters which otherwise may remain hidden by the technical limitation of the experiment.
  Moreover one may readily deduce from the model description what kind of measurements have to be performed and how frequent and how precise they need to be.

- The applications of radiotracer experiments in environmental studies within a closed system may be divided into two groups: Interaction between phases and interaction between compounds in one phase. As one may ask for net mass transfer and isotopic exchange in both cases, there are four possible combinations.

  ☐ The study of the mass transfer between two phases usually refers to the interaction between a solid and an aqueous solution. The precipitation and adsorption of toxic trace constituents on active carbon or their scavenging by ferric hydroxide are obvious examples. The reverse effects of leaching and adsorption have to be measured in the evaluation of the risks of industrial waste disposal.

☐ Isotopic exchange between two phases is equally studied on solid-liquid systems primarily. The additional information which can be drawn from it concerns the availability of the compound or element of interest in the solid.

☐ Mass transfer between two compounds comes into view when the decomposition rate of a substance has to be measured.

☐ The question whether a certain element can be exchanged between different chemical forms can be solved only by measuring the isotopic exchange between two compounds.

Combinations of these four situations occur in practice.
Table 3.I. summarizes the most important applications of radiotracer experiments in closed systems of environmental interest. The different cases will be treated more in detail now. The reader should compare his own problem to the examples expanded here to develop a proper solution.

3.2. Isotopic exchange in one phase

- This case has been treated in many textbooks [1, 2].
  The reaction to be studied is of the type

$$AB + A^*C \rightleftarrows A^*B + AC$$

The asterik indicates the radiotracer. One supposes that it is introduced as A*C at t = o. The kinetics of exchange are then described by equation (3.5):

$$\ln[1 - c/c_\infty] = -k \cdot (B + C) \cdot t \qquad (3.5)$$

c = concentration of A*B [M];
c_∞ = concentration of A*B at equilibrium ($t = \infty$) [M];
k = reaction rate constant [$M^{-1} \cdot s^{-1}$];
B = total concentration of B ⎫
C = total concentration of C ⎭ [M].

By measuring c as a function of t at known values of B and C one may obtain k. These measurements imply a chemical separation. If A*C is separated from the aqueous phase and the remaining count-rate is described by $f_A = A/A_o$, one has $c = (1 - f_A) \cdot [A^*C]_o$ and thus $c/c_\infty = (1 - f_A)/[1 - (f_A)_\infty]$.

TABLE 3.I. SURVEY OF RADIOTRACER EXPERIMENTS IN A CLOSED SYSTEM

Net mass transport?	NO	NO	NO	YES	YES	YES	YES
Changing specific activity?	NO Stable Situation	YES	YES	NO	NO	YES	YES
Changing total available amount of radiotracer?		NO	YES	NO	YES	NO	YES
Case		Isotopic exchange with radiotracer solution	Isotopic exchange between activated solid and a solution	Adsorption from a radioactive solution	Leaching of radioactivated solid with water	Leachable solid and radiotracer solution	Leaching of radioactivated solid with aqueous solution
Example		Exchange between CH_3Hg^I and HG^{II}(§ 3.2) Exchange of ^{32}P between H_2PO_4' and sediment (§ 3.3)		Active carbon and a spiked solution (§ 3.4)	Activated fly-ash and water (§ 3.4)	Fly-ash and a radiotracer solution (§ 3.5)	Activated fly-ash and an aqueous solution (§ 3.5)

- The interaction between CH_3Hg^+ and Hg^{II} ions in 1 N H_2SO_4 may be taken as an example [3]. In this case A*C = $^{203}Hg(NO_3)_2$; the radionuclide is ^{203}Hg, $T\frac{1}{2}$ = 45.1 d. The isolation of A*B = $CH_3{}^{203}Hg^+$ is performed by solvent extraction into benzene from a 1 M NaCl solution.
  Figure 3.1. visualizes the exchange of CH_3Hg^+ and H_g^{II} in 1N H_2SO_4 at concentrations around 10^{-3} M.

3.3. Isotopic exchange between a solid and an aqueous solution in a closed system

- Again this is a textbook-case [1, 2].
  The exchange of ^{32}P between a river sediment and a solution of H_2PO_4' can be taken as an example [1,2]. If there is mass equilibrium at the beginning of the experiment when a spike of $H_2{}^{32}PO_4'$ is added to the solution, the exchange reaction (3.6) starts

$$\left(^{32}P\right)_{solution} \underset{k_1}{\overset{k_2}{\rightleftarrows}} \left(^{32}P\right)_{sediment} \qquad (3.6)$$

to which the differential equation (3.7) corresponds:

$$\frac{dc^*}{dt} = k_1 \cdot m^* - k_2 \cdot m_s^* \qquad (3.7)$$

m^* and m_s^* are the masses of the ^{32}P in the solution and the solid respectively.

Equation (3.7) can be solved by using the rate balance (3.8) and the mass balance for the radioactive tracer (3.9):

$$k_1 \cdot m_\infty^* = k_2 \cdot \left(m_s\right)_\infty^* \qquad (3.8)$$

and

$$M^* = m^* + m_s^* = m_\infty^* + \left(m_s\right)_\infty^* \qquad (3.9)$$

Here M^* is the total mass of ^{32}P. The solution of (3.7)-(3.9) is

$$\ln\left[\frac{m^* - m_\infty^*}{M^* - m_\infty^*}\right] = -k_1 \cdot \left[1 + \frac{m_\infty^*}{\left(m_s\right)_\infty^*}\right] \cdot t \qquad (3.10)$$

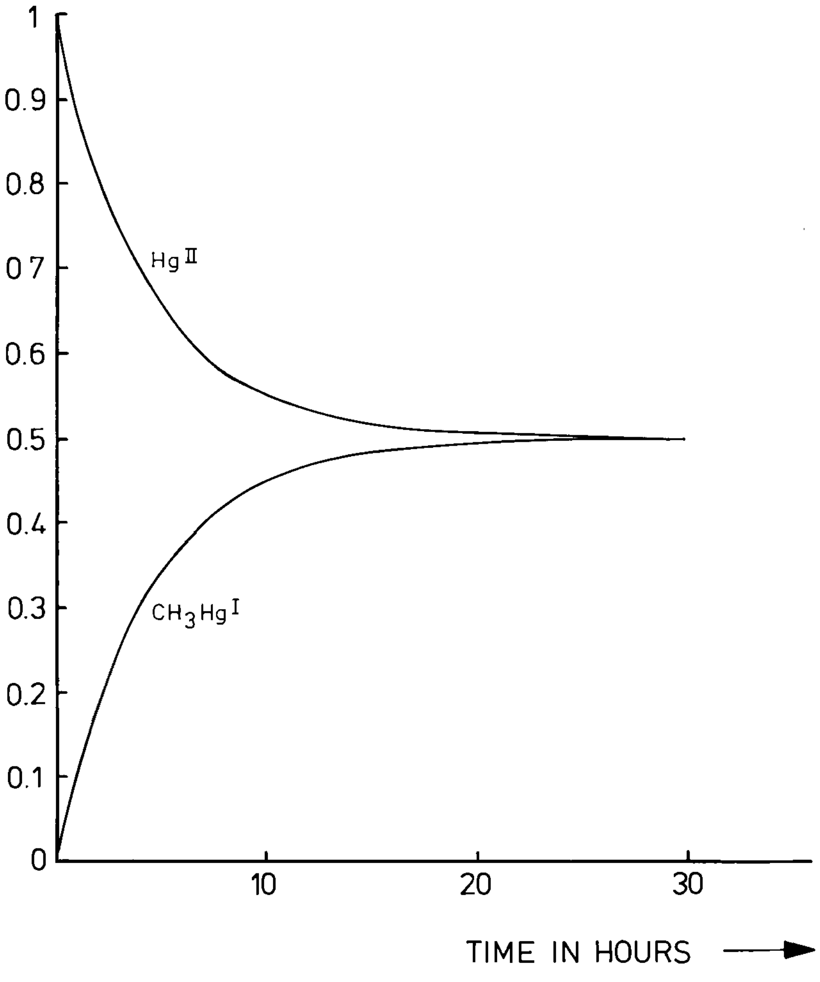

FIG. 3. 1: THE FUNCTION f_A FOR THE ISOTOPIC EXCHANGE BETWEEN $CH_3\,Hg^I$ AND $^{203}Hg^{II}$

The specific activity of the liquid is proportional to m*; so is the counting result. Reflecting that $\frac{m^*}{M^*} \equiv f_A$, one may thus rewrite (3.10) as:

$$\ln\left[\frac{f_A - \left(f_A\right)_\infty}{1 - \left(f_A\right)_\infty}\right] = \frac{-k_1}{1 - \left(f_A\right)_\infty} \cdot t \qquad (3.11)$$

From the experimental f_A-values one obtains the rate of exchange, $\frac{k_1}{1 - \left(f_A\right)_\infty}$, and the corresponding half-life.

Then k_1 can be calculated. It follows from (3.8) that

$$k_2 = k_1 \cdot \frac{\left(f_A\right)_\infty}{1 - \left(f_A\right)_\infty} \qquad (3.12)$$

- The determination of $\left(f_A\right)_\infty$ may be performed conveniently by plotting f_A against 1/t and extrapolation to 1/t = 0 [6].
- Using the described procedure, Vaas [7] identified three exchange processes between an aqueous H_2PO_4' solution of pH 7-8 and river sediment. The k_1 values are of the order of 10^{-3} h^{-1}; 5.10^{-3} h^{-1} and 5.10^{-2} h^{-1} respectively.

3.4. Net mass transport in a closed system

- The case of net mass transport at a constant specific activity and a constant total amount of activity is met frequently. Equation (3.4) now reduces to $f_A \equiv f_c$, while f_c can be described by an exponential. The adsorption of spiked metal ions from an aqueous medium to active carbon or the decomposition of a (labelled) metallo-organic compound in solution are examples. In the latter case a separation has to be performed prior to the measurement.
- A complication arises when the total available amount of radioactivity changes with time. An example of this is met in the leaching of a fly-ash sample which has been activated with thermal neutrons. The activity in the solution is measured as a function of time.

It is obvious that the specific activity will remain constant only when the fresh eluent does not contain this element of interest. The mass balance may be written as

$$V \cdot \frac{dc}{dt} = G \cdot F(t) \qquad (3.13)$$

where V = volume of eluent [ml];

c = concentration in the eluent $[g \cdot ml^{-1}]$;

t = time [h];

G = amount of solid [g] and

F(t) = specific mass transfer function $[g \cdot g^{-1} \cdot h^{-1}]$.

Measurements of c as a function of t yields F(t). The F(t) function contains a positive (leaching) and a negative (precipitation/adsorption) term which counter-balance each other at equilibrium. Thus:

$$F(t) = F_1(t) - F_2(t) \qquad (3.14)$$

As the leachable amount is finite, it is obvious that

$$F_1(\infty) = F_2(\infty) = o \qquad (3.15)$$

- The total amount which can be leached from one gram of solid is equal to $\int_o^\infty F_1(t) \cdot dt$.
  If $(c_s)_o$ stands for the original concentration in the solid one may define the availability ratio by (3.16):

$$r = \frac{1}{\left(c_s\right)_o} \cdot \int_o^\infty F_1(t) \cdot dt \qquad (3.16)$$

- A convenient F(t) function is

$$F(t) = k_1 \cdot e^{-\alpha t} - k_2 \cdot (c - c_{eq}) \qquad (3.17)$$

The leaching term is governed by the rate constants $k_1 [g \cdot g^{-1} \cdot h^{-1}]$ and $\alpha [h^{-1}]$. The total leachable amount per gram solid is k_1/α $[g \cdot g^{-1}]$ while for r one gets

$$r = \frac{k_1}{\left(c_s\right)_o \cdot \alpha}$$

The equilibrium concentration is written as c_{eq}; the counter current from the solution to the solid is supposed to be proportional to $(c - c_{eq})$. This fits with a linear adsorption isotherm as well as with precipitation.
The dimension of the rate constant k_2 is $[g \cdot g^{-1} \cdot h^{-1} \cdot (g \cdot ml^{-1})^{-1}]$.
The values of the four parameters depend on the grain size of the solid.

- The implications of equations (3.13) and (3.17) for the functions f_c and f_A are presented in table 3.II. It should be noted that f_c, f_a and f_A are defined here as c/c_{eq}, a/a_{eq} and A/A_{eq} respectively.

3.5. Combination of net mass transport and isotopic exchange in a closed system

- We continue our discussion of the fly-ash leaching.
  If the concentration in the fresh eluent, $c_o = 0$, one has $f_a \equiv 1$ and thus $f_A \equiv f_o$. When $c_o \neq o$, *the specific activity* and thus f_a *changes with time*. When one supposes that only the leached portion of the element will participate in the exchange, one has:

$$f_a = \frac{a}{a_{eq}} = \frac{c_oV + \int_0^\infty F_1(t) \cdot dt}{c_oV + \int_0^t F_1(t) \cdot dt} \cdot \frac{\int_0^t F_1(t) \cdot dt}{\int_0^\infty F_1(t) \cdot dt} \qquad (3.18)$$

Insertion of $F_1(t) = k_1 \cdot e^{-\alpha t}$ yields

$$f_a = \frac{[c_o \cdot V/G + k_1/\alpha] \cdot (1 - e^{-\alpha t})}{c_o \cdot V/G + k_1/\alpha \cdot (1 - e^{-\alpha t})} \qquad (3.19)$$

- When the four parameters k_1, α, k_2 and c_{eq} have been obtained by curve fitting, the availability ratio r can be calculated and the behaviour of the system at other values of c_o can be predicted. Figure 3.2. represents the leaching behaviour of a basic fly-ash for antimony.

TABLE 3.II. THE FUNCTIONS f_c AND f_A FOR THE INTERACTION BETWEEN AN ACTIVATED LEACHABLE SOLID AND AN AQUEOUS SOLUTION

c_o	= o	≠ o
F(t)	$k_1 \cdot e^{-\alpha t} - k_2(c - c_{eq})$	
$f_c = c/c_{eq}$	$\frac{k_1}{c_{eq}} \cdot \frac{G}{V} \frac{\left[e^{-\alpha t} - e^{\frac{-k_2G}{V} \cdot t}\right]}{\left(\frac{k_2G}{V} - \alpha\right)} + \left(1 - e^{\frac{-k_2G}{V} \cdot t}\right)$	$\frac{k_1}{c_{eq}} \cdot \frac{G}{V} \cdot \frac{\left[e^{-\alpha t} - e^{\frac{-k_2G}{V} \cdot t}\right]}{\left(\frac{k_2G}{V} - A\right)} + \left(1 - e^{\frac{-k_2G}{V} \cdot t}\right) + \frac{c_o}{c_{eq}} \cdot e^{\frac{-k_2G}{V} \cdot t}$
$f_A = A/A_{eq}$	identical to f_c	$\left\{\frac{\left[C_oV/G + k_1/\alpha\right] \cdot (1 - e^{-\alpha t})}{c_oV/G + k_1/\alpha \cdot (1 - e^{-\alpha t})}\right\} \cdot f_c$

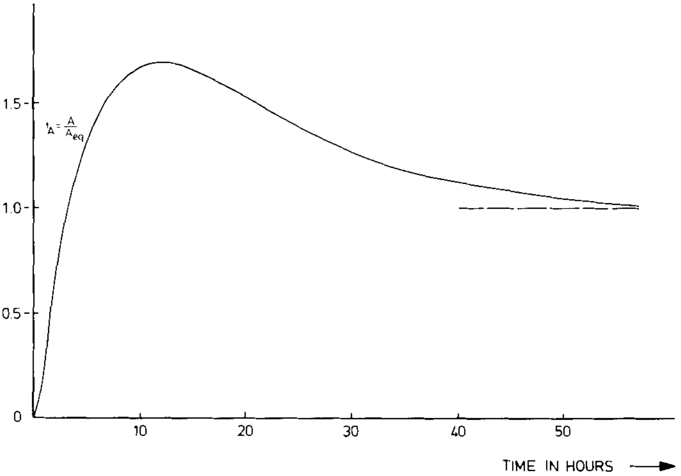

FIG. 3.2 : THE FUNCTION $f_A = \frac{A}{Aeq}$ FOR THE LEACHING OF 1 GRAM OF ACTIVATED "BASIC" FLY - ASH WITH 100 ml DEMINERALIZED WATER.

- When a leachable solid interacts with a radiotracer solution of the elements leached both f_c and f_a change for the eluent, while the total available amount of radioactivity remains the same. A practical example is found in the combination of fly-ash with a spiked solution. By following the radiotracer in the solution one may obtain information on the change in the leaching of the fly-ash over the interaction.

- The functions f_c, f_a and f_A are defined as c/c_o, a/a_o and A/A_o as all radioactivity is originally present in the solution. It follows from (3.4) that if the radiotracer is present at the beginning of the experiment one has

$$f_a = \frac{f_A}{f_c} \tag{3.22a}$$

while if it is added at $t = \Delta t$

$$f_a = \frac{f_A + [f_c(\Delta t) - 1]}{f_c} \tag{3.22b}$$

- Two approaches are possible now:

□ The functions f_A and f_c are determined separately

If the specific mass transfer function (3.17) applies, one may easily obtain from the mass balance (3.13):

$$\frac{c}{c_o} = \frac{k_1}{c_o} \cdot \frac{G}{V} \cdot \frac{\left[e^{-\alpha t} - e^{\frac{-k_2G}{V} \cdot t}\right]}{\left(\frac{k_2G}{V} - \alpha\right)} + \frac{c_{eq}}{c_o} \cdot \left(1 - e^{\frac{-k_2G}{V} \cdot t}\right)$$

$$+ e^{\frac{-k_2G}{V} \cdot t} \tag{3.23}$$

The four parameters may thus be derived from the f_c-measurements. Combination with the experimental f_A-data yields f_a by way of (3.22). The total exchanged mass, m, then follows from the activity balance:

$$m = \left[\frac{1}{f_a} - 1\right] \cdot c_oV \tag{3.23a}$$

for a tracer addition at t = o and

$$m = \left[\frac{1}{f_a} - 1\right] \cdot c_{\Delta t} \cdot V \tag{3.23b}$$

for an addition at t = Δt.

□ The function f_a is derived

One may write down f_a on the assumption that isotopic exchange is restricted to the leached portion of the fly-ash. Using expression (3.17) for F(t) one arrives at

$$f_a = \frac{a}{a_o} = \frac{c_o V + \int_o^t F_1(t) \cdot dt}{c_o V} = \frac{c_o V + k_1/\alpha \cdot (1 - e^{-\alpha t})}{c_o V} \tag{3.24}$$

Combination of (3.23) and (3.24) by way of

$$f_A = f_a \cdot f_c \tag{3.22a}$$

yields an expression which links the four parameters k_1, α, k_2 and c_{eq} with the experimental f_A-data.
The radiotracer should be present at t = o as addition at a later time will make (3.24) more complicated.

3.6. Radiotracer experiments in open systems

- Radiotracers are used in open environmental systems to measure flow-rate and/or time of residence as well as their distributions. This is invariably done by a one-time (delta-function) injection.
  Either the radioactivity is added to the system or induced by activation in small aliquots taken from the system.
  Unlike in experiments in a closed system, one considers f_c only. Thus $f_a \equiv 1$ and $f_A \equiv f_c$, implying that the radiotracer remains in its original phase.
- In principle, there is nothing particular in the use of a radiotracer as the tagging agent. Thus the formalism, developed by Danckwerts [8] and expanded in many recent textbooks like that of Levenspiel [9] may be used. The distribution of the radiotracer over the effluent, f(t), is determined. From this one calculates the first and the second moment.
  First moment or centroid, μ:

$$\mu = \frac{\int_0^\infty t \cdot f(t) \cdot dt}{\int_0^\infty f(t) \cdot dt} \tag{3.25}$$

Second moment or variance, σ^2:

$$\sigma^2 = \frac{\int_0^\infty t^2 \cdot f(t) \cdot dt}{\int_0^\infty f(t) \cdot dt} \tag{3.26}$$

It is obvious that μ is identical to the average residence time, τ. The value of σ^2 can be related to the degree of dispersion in the system.

- The practice of a radiotracer experiment in an open system consists of the following steps:

☐ A convenient radiotracer is chosen. Usually one tries to have a half life between 2 and 5 times the average residence time.

☐ The radiotracer is injected at t = o. Preferably an identical aliquot is preserved as a standard for the calculation of the activity balance.

☐ At regular time intervals a small aliquot is taken out of the system and counted under standardized conditions. This yields a number of counting results, A(t).

☐ The functions

$$E(t) = \frac{A(t)}{\Sigma A(t) \cdot dt} \tag{3.27}$$

and

$$\tau = \frac{\Sigma\, \tau \cdot A(t)dt}{\Sigma\, A(t)dt} \quad \text{are computed} \tag{3.28}$$

☐ The dimensionless function E is calculated:

$$E = \tau \cdot E(t) \tag{3.29}$$

and plotted against the reduced time $\nu = t/\tau$.

□ The function $\nu^2 \cdot E$ is plotted against ν and σ^2 is determined by equation (3.30):

$$\sigma^2 = \Sigma\nu^2 \cdot E \cdot \Delta\nu - 1 \tag{3.30}$$

- Most radiotracer experiments in open environmental systems refer to solid-liquid systems; next to that gas-solid systems are of interest. The radiotracers which are mostly used are:
  - □ ^{82}Br, $T_{\frac{1}{2}}$ = 35.3 h, added as Br' to an aqueous solution.
  - □ ^{41}A, $T_{\frac{1}{2}}$ = 1.8 h as a tracer for gases.

  Alternatively stable elements are added and determined by activation analysis.

3.7. Combination of radiotracer experiments in closed and open systems

Any environmental system may be studied by a combination of radiotracer experiments under laboratory conditions on small scale closed units, with in-field measurements of the average time of residence and its variance on the actual open system.

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CHAPTER 4.

SAMPLING IN ENVIRONMENTAL ANALYSIS

SUMMARY

This chapter deals with the practice of sampling the environment and the associated problems.
The six matrices mentioned in chapter 1, are examined separately.

4.1. Introduction

- Sampling is possibly the most critical step in the entire analytical process. Out of the environment one isolates a, usually tiny, fraction. Its composition then serves as a base for general conclusions on often considerable portions of our planet. Obviously the first requirement for a sample then is that it gives a true representation of the matrix which is sampled. This implies:

  (a) that one has a clear idea on the variation of the matrix composition with position and time and,

  (b) that the sampling at a given position and time be reproducible.

  It follows immediately that the (systematic) variation with position and time as well as the (statistical) reproducibility of the sampling are relative notions only which depend on the precision of the subsequent treatment and analysis.

  The process of sampling and the subsequent storage inevitably involves the use of tools and often of transport vehicles too. These equipments are sources of contamination and losses. The second criterion for the sample is thus accuracy, defined as the absence of an appreciable systematic bias. The word "appreciable" should be understood in terms of the standard deviations in the subsequent determinations, like discussed in section 6.6.

- The sampling process proper is often completed by some mechanical treatment like centrifugation, filtration, sedimentation or sieving, to separate the material into fractions. The step may follow the sampling immediately like in the case of airdust or performed separately as for water or silicates. In any event it constitutes a second source of risks which may affect both the requirements of representation and accuracy.

- In sampling, compromises are inevitable. Once the procedure has been found reproducible and free of apparent biases one may start to work with it. The next test must be the analysis of the data obtained for systematic trends with the obvious variables which are mentioned in the following sections, the check for sudden unexplainable "jumps" and, of course, the comparison with the results obtained by others. Finally, there is a little chance that a sampling-procedure will remain unchanged for more than a few years in view of the rapid development in environmental conceptions and the general trend towards narrower gauges. This necessitates the analyst to (re)check his adapted procedure time and again.

4.2. Sampling of sea and surface water

4.2.1. Definitions

- Water samples are collected by pumping or with a polythene bucket on nylon string. Sub-surface samples can be taken by pumping or with samplers, which are shut at the desired depth [1]. Surface water is often collected in a bucket [2-4].
  Ideally, the sample should then be separated into a soluble fraction (particle diameter $< 10^{-3}$ µm), a colloidal fraction (particle diameter $10^{-3} - 10^{-1}$ µm) and a particulate fraction (0.1 - 50 µm) but this is difficult to achieve [5]. Usually the soluble and colloidal fractions are taken together and the distinction is between "clear" water and a "suspended particulate matter"-fraction.
  The concentration of suspended material varies widely. In fresh water it is usually somewhere between 10 and 100 $mg.l^{-1}$; in coastal sea-water it may be still 10-20 $mg.l^{-1}$ while in open sea it is 0.5 $mg.l^{-1}$.
- It is common practice to define the sampling and the sample by some parameters which are determined in situ, thus one measures temperature, pH, salinity and often silicate and phosphate, the latter two by colorimetric procedures [6].
- The probability of interference by the sampler is a function of two parameters primarily:
  a. The ratio surface area/volume (S/V) of the sampler.
  b. The residence time in the sampler.
  If v is the flow rate through the pumping device and V its internal volume, one can define the residence time as $\tau = V/v$.

Table 4.I.

	Losses due to adsorption		Contamination	
Bucket	$\div (1 - e^{-\alpha\tau})$	(4.1)	$\div (1-e^{-\beta\tau})$	(4.2)
Pump	$\div \alpha\tau$	(4.3)	$\beta\tau + \gamma v$	(4.4)

The difference between (4.1) and (4.3) stems from the short residence time in the pump. The same holds for (4.2) and (4.4) while the second term in (4.4) accounts for the erosion of the pump surface. In case of pumping, the water has to be collected in a bucket.

4.2.2. Modes of separation between water and particulate matter

- Separation of the suspended matter can be performed by:
  a. Gravitational settling or sedimentation.
  b. Filtration.
  c. Centrifugation.

Gravitational settling

Sedimentation is based on the size and the density of the particles. When a sedimentation tank of one meter height is used, it takes ∿ 10 days to have particles with a diameter of more than 1 μm removed completely [7]. Consequently, sedimentation is used almost exclusively in model experiments on transport phenomena and hardly for the preparation of analytical samples.

Filtration

Membrane filters with a definite pore-width are applied widely. A pore diameter of 0.45 μm is most common [2-4,8], although occasionally other values are used [9]. Eventually the filter makes part of a standard equipment. For the filtration of sea water a 10 litre vessel of fibre glass, working at an overpressure of ≤ 5 atm. was used [2]. At a pressure drop of 0.9 atm. a specific filtration velocity of 65 ml cm^{-2} s^{-1} was observed. Preferably, however, teflon-vessels are applied.

Centrifugation

As in gravitational settling, separation of suspended matter by centrifugation is based on the size and the density of the particles. Continuous flow centrifuges of various types are available. At the ECN-laboratory, centrifuges with a maximal attainable revolution rate of ≃ 1500C r.p.m. are used.

The corresponding flow-rate is 1.2 ℓ $(\text{min})^{-1}$. To minimize contamination by the metal of the rotor, parts not subjected to friction are coated with teflon. Up to 300 ml of sediment can be collected.

4.2.3. The precision of sediment separation by filtration and centrifugation

- At a first glance centrifugation seems to be the best procedure for the separation between liquid and solid. The obvious drawbacks are the costs and the difficulty of applying centrifugation on board of moving ships. The latter objection may be overcome by mounting the centrifuge in gimbals. Figure 4.1. shows the equipment built at ECN for sampling in the estuaries. Thus a comparison must concentrate on the quality of the separation.
- The effective pore-width for filtration depends on the amount of suspended matter, which has been collected already, and its particle size distribution. The effect of clogging on the filtration efficiency can be estimated by plotting the weight of material, obtained per litre, against the filtered volume. For seawater with a low content of suspended matter no decrease is measurable, nevertheless the flow-rate decreases steadily.

  The variation of the flow-rate during filtration can be deduced from equation (4.5) |10|.

$$\frac{1}{v} = \frac{\eta}{\Delta P}\left[\frac{2D}{R_f^{2}.\varepsilon_f} + \frac{38\ \gamma.V}{r_s^{2}}.\frac{(1-\varepsilon_s)^{2}}{\varepsilon_s^{3}}\right] \qquad (4.5)$$

The symbols have the following meaning:

v = flow-rate in cm.s^{-1}

η = viscosity in $\text{dynes.cm}^{-2}.\text{s}$

ΔP = pressure drop in dynes.cm^{-2}

D = filter thickness in cm

R_f = hydraulic radius of filterpores in cm

r_s = hydraulic radius of filtered sediment particles in cm

V = filtered volume in ml

γ = factor of proportionality between the filtered volume and the resulting sediment layer on top of the filter in cm.ml^{-1}

ε_f = porosity of filter

ε_s = porosity of filtered sediment layer.

Figure 4.1. The continuous flow centrifuge mounted in gimbals

The value of γ can be determined separately. When the hydraulic radius of the filter pores changes during filtration, the porosity of the filter changes accordingly.

When it is assumed that the contribution of the second term in equation (4.5), which is related to the variation of v due to the growing sediment layer on the filter, is small in the early stage of the filtration, a proportionality of 1/v with R_f^2 must be expected. The relative change of R_f with V, the filtered volume can be estimated from a plot of 1/v against V.

This was tested with the mentioned filtration apparatus and filters with the following properties:

- surface area : 15.9 cm^2
- weight : 90 ± 8 mg (standard deviation)
- thickness : 140 μm
- porosity : 60 - 80%
- pore diameter: 0.45 μm or 8 μm

Results for the filtration of a fresh water sample with 35 mg . l^{-1} suspended matter are given in figure 4.2. If a 0.01 μm membrane filter is used, the initial rate is $v = 0.09$ cm.s^{-1} or $\frac{1}{v} = 11$ cm^{-1}.s. Thus both a 8 and a 0.45 μm filter will, after clogging, behave as one with 0.01 μm pores.

Obviously the spectrum of particle-sizes influences the picture too, like can be seen from the results for the 0.45 μm filter.

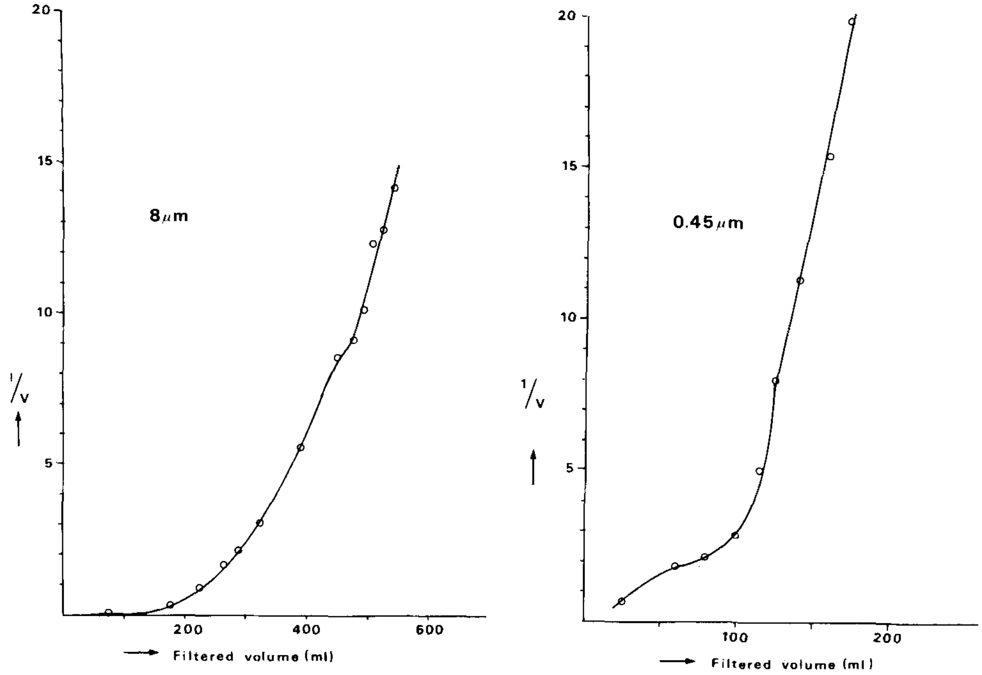


Figure 4.2. The variation of 1/v with the filtered volume (V) in the filtration of fresh water through an 8 µm and a 0.45 µm membrane filter

- The radius, r_p, of the particles which can be separated by a flow-through centrifuge may be estimated from equation (4.6a)

$$4.5 \frac{\Delta . \eta}{(\rho_p - \rho_w)} \cdot \frac{1}{\omega^2} \cdot \frac{1}{(R-\Delta/2)} \cdot \frac{1}{r_p^2} \leq \left[\tau - \frac{\rho_p \cdot r_p^2}{4.5\eta} \cdot (1-e^{4.5 \frac{\eta}{\rho_p} \cdot \frac{\tau}{r_p^2}}) \right] \qquad (4.6a)$$

where

r_p = hydrodynamic radius of particle (cm)
R = inner radius of centrifuge (cm)
Δ = thickness of water film (cm)
ρ_p = density of particle ($g.cm^{-3}$)
ρ_w = density of water ($g.cm^{-3}$)
η = viscosity of the water ($g.cm^{-1}.s^{-1}$)
ω = angular velocity (s^{-1})

τ = residence time in centrifuge (s)

The values of τ and Δ vary with ω; they may be determined experimentally from the time needed to centrifuge a large aliquot and the inner surface area of the rotor.
At 10^4 r.p.m ($\omega = 10^3.s^{-1}$) and R = 9 cm, one has $\tau \simeq 10$ s and $\Delta \sim 0.2$ cm, while the second term on the right hand may be neglected. Equation (4.6a) can now be simplified to:

$$r_p^{\,2} \geq 4.5 \; \frac{\Delta.\eta}{(\rho_p - \rho_w)} \cdot \frac{1}{\omega^2 . \tau} \cdot \frac{1}{(R-\Delta/2)} \qquad (4.6b)$$

At 20 °C, $\eta = 10^{-2}$ g.cm^{-1}.s^{-1}. With $\rho_p = 2$ g.cm^{-3} and $\rho_w = 1$ g.cm^{-3}, one gets $r_p \geq 0.1$ µm.
Thus the centrifuge is comparable to the filter.

4.2.4. The accuracy of sediment separation by filtration and centrifugation

- The concentration of suspended matter is determined either by filtration through a pre-weighed 0.45 µm membrane filter or by centrifugation at > 10^4 g and collection from the rotor. Comparative measurements on aliquots of one large sample gave the following results:
  Filtration : 43 ± 2 mg.ℓ^{-1} (30 ± 5% organic material).
  Centrifugation : 32 ± 2 mg.ℓ^{-1} (26 ± 4% organic material).
  Subsequent filtration: 4 ± 0.5 mg.ℓ^{-1} +
  36 ± 3 mg.ℓ^{-1}
- The blank values caused by the filter may be considerable. Table 4.II gives some data for membrane filters as determined by INAA [2]. After washing with 2N HNO_3 the leaching of trace constituents into the water is negligible.
  Centrifugation causes iron, chromium and vanadium to be released by the rotor. Without precautions the amounts added to a litre water are:

Table 4.II. Trace element contents in membrane filters

	Trace element content ($\mu g.g^{-1}$)			
	Type:	Millipore HAWP 04700	Selectron Ba 85/1	
	Filterweight:	87 ± 7 mg	85 ± 4 mg	
Element	Treatment:	none	none	2N HNO_3
Al		14 ± 2	42	2
V			0.004	
Cr			1.6	1.5
Mn			0.4	0.2
Fe		22 ± 3	9	6
Co		0.006	0.09	0.05
Cu		0.7±0.1	2	0.5
Zn		16 ± 1	8	5
Se			<0.05	
Mo			<0.1	
Cd		0.6±0.1	<0.1	< 0.2
W		< 0.01	<0.01	
Hg		0.12±0.02	0.15	
U		<0.01	<0.01	

Fe: 20-60 μg; Cr: 0.5-3 μg; V: 0.02-0.08 μg.

By applying rubber-sealed bearings and by coating the inner surfaces with teflon, this contamination can be reduced appreciably.

- Losses due to adsorption are serious in filtration only. Table 4.III gives the result of radiotracer experiments at ECN on the sorption of six heavy metals in their ionic state from spiked seawater, which had been previously filtered through a 0.2 μm filter.
  Radiotracer experiments on the effect of filtration in (artificial) seawater [2] confirm the data from table 4.III; the ions Cr^{III}, Fe^{III}, Hg^{II} and Pb^{II} are removed to a large extent.

4.2.5. Storage of seawater

- Sampling usually involves a certain storage time which may cause deterioration, primarily by adsorption to the container wall. This effect has been studied for various types of water and for the most common container-materials [8, 11, 12]. It appears that, in general, a contact time of more than a few minutes is not acceptable. To keep the storage time as low as possible, three techniques may be used:

. Freezing, eventually combined with freeze drying [13].
. Scavenging of the (chelated) ions [2].

Acidification of seawater is not to be recommended, due to the accompanying desorption from particulate matter. Of elements which are in cationic form most of the mass is, in equilibrium, located at the surface of the suspended matter. The equilibrium may be described as an exchange between H^+ and the metal cations [14].
Figure 4.3. gives the desorption of Hg^{II} as a function of time.

Table 4.III. Sorption of trace elements on 0.45 μm membrane filters

Element	Concentrations in $\mu g.\ell^{-1}$	Volume filtered (ml)	Sorption percentage (%)
Hg	0.2	100	19
	0.2	250	16
	0.2	500	16
	0.2	750	15
	0.2	1000	14
	0.4	1000	3.5
	0.9	1000	1.5
Pb	0.1	1000	11
	0.2	100	5
Zn	13	1000	0.5
Co	1	1000	<0.1
Fe	19	1000	33
Mo	14	1000	3

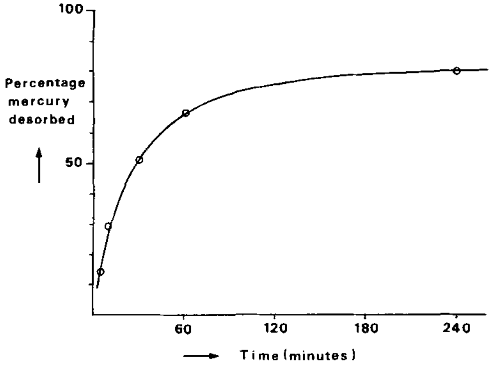


Figure 4.3. The desorption of mercury from suspended matter at pH 0.1 as a function of the contact time

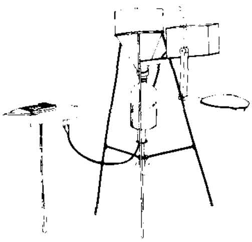


Figure 4.4. (Ref. [16]). A wet-only rain collector

4.3. Sampling of rainwater

- Rainwater is difficult to sample for at least three reasons:
  . The amounts available are often small.
  . Wet and dry deposition should be separated preferably.
  . The concentrations of trace constituents may be very low i.e. $<< 1\ \mu g.\ell^{-1}$.

Two sampling techniques are in use, the "open rain" and the "wet only" sampling. A polythene funnel mounted in an iron-tripod and connected to a large polythene bottle by means of a screw-cap may be used in the first case [15]. The " wet only" sample consists of an open sample and a lid, connected to a pneumatic rotator (fig. 4.4.); a description of this device is given in refs. [16] and [55].
Eventually, these tools may be transformed into sequential samplers by adding a sample changer and a timer [17].
A further refinement may be obtained by filtration of the samples. For this and for the storage, the same remarks apply as were made on sea- and surface water.

4.4. Sampling of organic material

4.4.1. General

- The term "biological material" is often used in radio-analytical literature. It comprises all materials, both fluid and dry, which can be obtained from the plant or animal kingdom as well as the industrial products derived from it. In a more strict state it refers to the dried residues of such materials.
- The bulk of living matter is formed by ∿ 15 elements of low atomic number. In principle all other elements are present in traces [18, 19]. In recent years interest has been concentrated on the elements with a concentration below 1 $\mu g.g^{-1}$, more especially on the trace elements which are supposed to be essential for life. These comprise at least F, Si, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Sn, Mo and I.

  This trend has an important analytical consequence: To make sure that an element is -possibly- essential for a certain organism or organ implies the analysis of many samples to obtain a frequency distribution of the concentration. It has been suggested that an essential element will feature a more concise and symmetrical distribution than a toxic or an "indifferent" element does [20].
- As organic material is often taken from a living organism or from a still intact structure, there is the additional problem of the anatomy of the matrix. Analytical chemistry as an auxiliary science has to adapt to the current state of the anatomical art.
- From a practical analytical point of view one may divide organic material into some subgroups of increasing difficulty.
  - ☐ Materials which in principle are homogeneous, of which large aliquots may be taken and for which contamination can be avoided easily. Examples are "industrial" products like flour, milkpowder, potatoes and coffee.
  - ☐ Materials which may be sampled readily but which suffer from previously deposited external contamination. Eventually the problem of the anatomy of the matrix poses itself.
    Examples are grass, leaves, hair and nails.
  - ☐ Some materials may be sampled readily but are extremely sensitive to outward contamination.
    Examples are urine, blood and milk.

☐ Finally, one has the matrices which can only be sampled under due reference to the anatomy, the inward and the outward contamination. Examples may be found in the medical field when it comes to biopsies and obductions.

The subject will be discussed in this order. It should be remarked in advance that it is desirable to have a "dust-poor" room, equipped with a laminar flow-box and a semi-microbalance available for all these categories and that this is mandatory for medical applications.

4.4.2. Sampling of homogeneous bulk materials

- The avoidance of outward contamination is the main problem here. This contamination stems from the sampling tools and the deposition of air-dust. The influence of the tools depends on their composition, the surface and the intensity of the contact. The degree of transfer may eventually be determined by experiments with a radioactivated tool. Table 4.IV gives an appreciation of the level of contamination by various materials [21]. Tools of teflon, quartz or carborundum (SiC) should be used.

  The influence of air-dust depends on the dust-concentration and composition as well as on the duration of the sampling. Immediate storage in clean polythene bags is now general practice.
- Pretreatment is often necessary to obtain a constant moisture content and to facilitate further handling. Drying at 60-90 °C and lyophilization have been proposed [21-25].

  For plant material Bowen [23] recommends drying at 90 °C for 20 hours while a more cautious advice is given by the National Bureau of Standards [24]: "Drying in air in an oven at 85 °C for 2 hours during at 105 °C or in vacuo at 25 °C should not be used as it gives rise to losses". The general reputation of lyophilization is that it does not cause losses [21-25]. It is advisable, however, to perform determinations on different aliquots of the same sample which have been subjected to lyophilizations of different duration.

  The loss of weight over lyophilization was studied for some bulk materials and the Standard Reference Material "Orchard Leaves" [26]. Figure 4.5. gives the result. It makes a difference whether the aliquots are frozen at -20 °C or at -196 °C prior to the lyophilization.

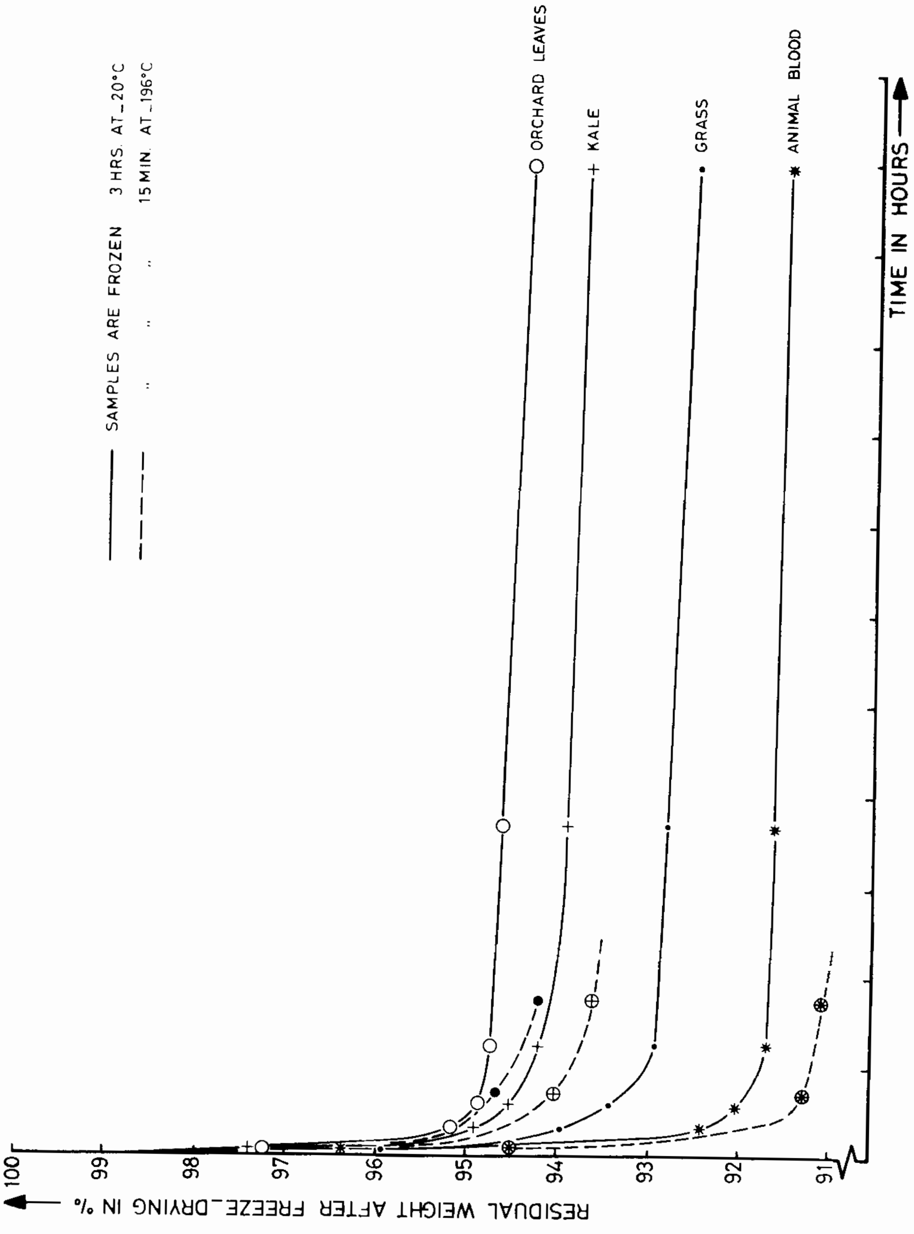


Figure 4.5. (Ref. [26]).

Loss of weight during lyophilization of some dry organic materials

It is necessary to store the lyophilized aliquots over a drying agent [21] and to determine the rate of moisture uptake upon exposure to the laboratory air.

Table 4.IV. Contamination of organic material during sampling with tools of various materials [21]

Material	Degree of contamination	Contaminating elements
Stainless steel	Large	Co,Cr,Fe,Mn,Mo, Nb,Ni,V,W,Ta
Aluminium	Medium	Al,Cu,Mg,Mn,Na, Sc
Pyrex glass	"	Al,B,K,Na,Si
Rubber	"	Mg,S,Sb,Zn
Quartz	Low	B,Na,Sb,Si
Polythene	"	Al,Cl,Ti,Zn
Teflon	Very low	F

4.4.3. Sampling of materials which are subject to external contamination

- The problem of the previously deposited external contamination can be reduced to that of sample definition. The analyst has to know whether the external contribution should be regarded as a part of the material. This is, for instance, the case with plants sampled to measure the degree of pollution by motorized traffic or the influence of volcanic emissions [27].
  Alternatively, the external contamination of hair is removed prior to the elemental analysis [28].
  The removal is usually effectuated by some kind of washing. It follows from the experiments with hair that the alkali elements and the halogens are invariably eluted from the interior of the sample material as well. Thus it does not make sense to determine these elements

after cleaning of the sample.

- As the specific surface area of this type of samples tends to be large and the total mass is often small, the remarks made in the previous section on the contamination by the sampling tools get more weight still. The use of a quartz knife or a titanium pair of scissors is mandatory. The same holds for the contamination by dust deposition. The samples should be stored in small polythene bottles with screw or snap cap immediately after collection.

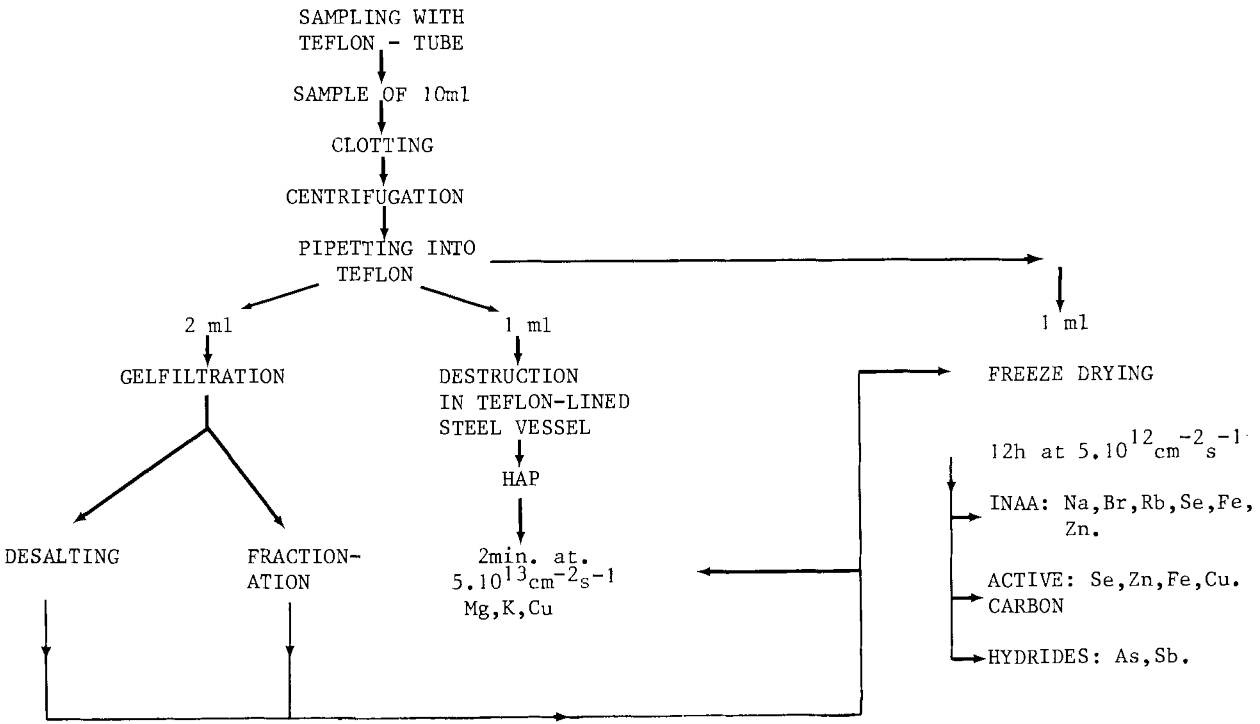
4.4.4. Sampling of urine, blood and milk

- The sampling of urine [29, 30] and milk [31] does not pose problems when the obvious precautions of sampling in a clean surrounding and direct collection into previously washed polythene vials are observed. The trace impurities in containers and the accompanying leaching are summarized in ref. [32].

  Freezing and lyophilization are advisable.
- Blood has to be sampled by venepuncture. Preferably this should be done with a plastic needle [33-38]; a teflon needle proved to be feasible [37]. The (sterile) cannula is unpacked at the spot. After puncture, it is rinsed with a few ml blood before the sample is collected in a teflon capsule with snap cap which has previously been cleaned with double distilled water in a "dust-poor" room to which the sample is transferred. If serum is to be obtained, the blood is allowed to clot and the supernatant pipetted into a weighted 20 ml teflon beaker to determine its mass. Aliquots for protein separation and determination by short-lived radionuclides are then taken with polythene pipettes into standard polythene irradiation capsules with snap cap and stored frozen. Tabel 4.V summarizes this.

  The necessity of a "dust-poor" room is illustrated by the poor accuracy of many determinations [38].

Table 4.V.



SCHEME OF THE ELEMENTAL ANALYSIS OF SERUM AND SERUM - FRACTIONS.

4.4.5. Biopsy and obduction samples

- This is the most difficult part of the environmental sampling and in fact a separate discipline. It may be doubted seriously whether it can be done outside a few specialized laboratories. The outfit comprises a dust-poor laboratory with a dissection table in a laminar flow box. Tools should be made of quartz and samples should be kept in plastic covers and stored frozen. For further details the reader is referred to refs. [32, 39, 40 and 41].

4.5. Sampling of aerosols

4.5.1. General

- Aerosols are formed (a) in the gaseous phase by chemical reactions and/or condensation like in the cases of smoke and fog; (b) by mechanical actions like the whirling of already existing dust or spraying. Formation through the gasphase yields particles which, in general, have a diameter of < 0.01 μm; by coagulation and condensation particles with a diameter of a few microns are formed.

  Mechanical actions yield particles with diameters of at least a few microns.

  Figure 4.6. gives a survey of the production and removal processes [42]. The submicronic dust changes in composition with increasing distance from the source: The original particles coagulate rapidly till diameters around ∿ 0.1 μm are reached. These small particles consist of ammonium nitrate and sulphate, organic compounds and soot.

  The hypermicronic particles have their origin in street- and coal-dust and come from agricultural activities and marine aerosol.
- For practical reasons the transport of aerosols is divided into three levels [43]:
  - ☐ Macro-transport over long distances. This holds for submicronic particles.
  - ☐ Meso-scale transport over a few kilometres. This phenomenon is especially important for the larger particles.
  - ☐ Micro-scale deposition for particles with a diameter of > ∿ 50 μm.

  It is customary to define the deposition processes in the following way [44, 45]:

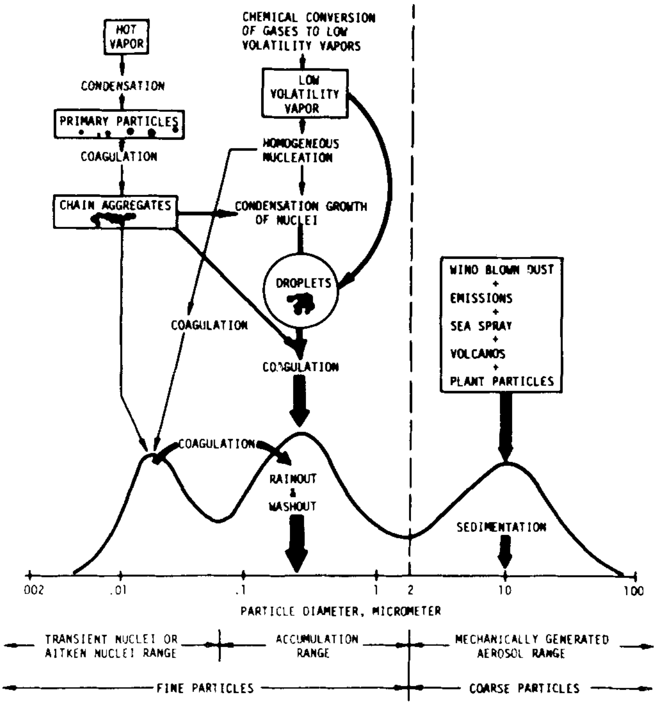


Figure 4.6. (Ref. [42]).

Idealization of an atmospheric aerosol surface area distribution showing the principal modes, main sources of mass for each mode, and the principal processes involved in inserting mass in each mode and the principal removal mechanisms.

- Dry deposition is the direct settling of dust particles on objects without the intermediary action of the atmospheric water.
- Wet deposition is caused by incorporation in the precipitation. When this takes place in the clouds it is called "rain out", when the dust is catched by the falling precipitation the term "wash out" is used.

- The sampling of aerosols as a function of the parameters of distance/ place, wind-direction and -velocity, dimension and wet against dry, is incited by studies on the effect of airdust on health [46], vegetation [44], visibility [47] and the climate [48,49].
  The nature of the deposition-processes is still imperfectly understood. This and the complexity of the natural situations makes it difficult to develop optimal sampling procedures. Thus the whole subject of aerosol sampling is primarily a matter of custom and formalism.
- It is obvious that aerosol sampling involves the measurement of, at least, two qualities: The amount of air sampled and the mass of the aerosol collected. The first datum implies that a calibrated air pump has to be used. A good survey of the pumps available and their calibration is found in ref. [50]. In general the pump should provide a high vacuum, have a large flow volume, cause little pulsation and be easily transportable.

The aerosol is collected on a filter. This should, in general, meet the following requirements:

- At least 99% collecting efficiency for particulates of ≥ 0.3 μm diameter.
- Low hygroscopicity: The efficiency of the filter changes considerably with the amount of water adsorbed. Moreover, the mass of the collected aerosol is determined by difference-weighing.
- A low (trace) element content:It is, in general, not feasible to separate the sample from the substrate. The filter constitutes a blank which should be kept low and constant.

The choice of the filter material is between glass, quartz, cellulose and various plastics. Table 4.VI, taken from ref. [50], summarizes the main possibilities. It should be noted that the collecting efficiency of a filter changes with the velocity of filtering and with the duration of sampling [51].

The blank values for the membrane filters, as reported in ref. [50], range from some hundreds of ng.cm^{-2} for Al, Na and Ca to 0.1 ng.cm^{-2} for Co and V.

A second criterion may be found in the difference in pore structure between cellulose-based filters: Nuclepore versus millipore.

Table 4.VI. Properties and applicability of various filters (Ref. [50]).

Material	Filter type	Por size (μm)	Electric charge*	Pressure loss**	Initial collecting efficiency***	Hygroscopicity****	Applicability**** for: Low volume air sampler	High voluem air sampler	Atomic absorption spectrometry	Activation analysis	Fluorescence X-ray analysis	Remarks
Glass fiber	Toyo GB-100R		o	o	o	o	o	o	o	*X*	Δ	
	Gelman type A		o	o	o	o	o	o	o	*X*	Δ	High Zn content
	Whatman type A		o	o	o	o	o	o	o	*X*	Δ	High Zn content
	Millipore AP-20		o	o	o	o	o	o	o	*X*	Δ	High Zn content
	MSA 1106 BH		o	o	o	o	o	o	o	*X*	Δ	
Quartz fiber	Tissue Quartz 2,500 QAST		o	o	o	o	o	o	o	Δ	Δ	SiO_2 99%
	Gelman Quartz Paper type I		o	o	o	o	o	o	o	Δ	Δ	SiO_2 98.5%
	Gelman Quartz Paper type II		o	o	o	o	o	o	o	Δ	Δ	SiO_2 99.5%
Polystyrene	Microsorban (sartorius)		o	Δ	o	Δ	o	Δ	o	Δ	*X*	
Polyvinyl cloride	Yumicron MF-100	1	o	Δ	o	o	o	Δ	o	*X*	o	High Cl and Ti content
Nitro-cellulose	Millipore-RA	1-3	Δ	*X*	o	Δ	o	*X*	o	o	o	
	Sartorius SM		Δ	*X*	o	Δ	o	*X*	o	o	o	
	Toyo TM-100		Δ	*X*	o	Δ	o	*X*	o	o	o	
Cellulose acetate	Gelman GA-3		Δ	*X*	o	Δ	o	*X*	o	o	o	
Fluorine resin	Polyfuron PF-3 (Toyo)		o	Δ	o	o	o	*X*	Δ	o	-	Fibrous
	Millipore Mitex LS		o	Δ	o	o	o	*X*	Δ	o	-	Fibrous
	Fluoropore AF-07P (Sumitomo Denko)	10	*X*	*X*	o	o	o	Δ	o	o	-	Membrane type
	Millipore Florinert FA	1	Δ	Δ	o	o	o	Δ	o	o	-	Membrane type

* o, Trace; Δ, moderate; *X*, too high for use.

** o, Very small; Δ, moderate; *X*, large.

*** o, Not less than 99%.

**** Moisture content: o, 0.1-0.5%; Δ, 1-2%.

4.5.2. Sampling of total aerosol

- Criticized by many investigators, the High Volume Sampler (HVS) is still the tool for samplings of a general nature [50, 52-54]. Typically, the apparatus consists of a rectangular metal frame which holds a filter of ∿ 50 to ∿ 500 cm^2 surface area. The flow-rate varies from ∿ 10 till ∿ 60 $m^3.h^{-1}$, pointing to a specific flow-rate of the order of 5 $\ell.min^{-1}.cm^{-2}$. With aerosol concentrations of 50-500 $\mu g.m^{-3}$ this leads to 0.3-3 mg aerosol per cm^2. Although microsorban is likely to be the best filter material, its high cost may be prohibitive in HVS application and the choice often falls on Whatman 41 [54].
  Low volume samplers usually operate at a flow-rate of 20-30 $\ell.min^{-1}$ [50]. To obtain a continuous time record, a "streaker" is used [82]. The material is deposited on a 2.5 mm x 250 mm teflon strip which passes the sampling orifice at ~2 mm . h^{-1}.

- Next to suction, collection of the precipitating dust is also applied [55]. The dry deposition is then collected in a large volume of double distilled water. This is filtered over a Whatman 41 filter and both filtrate and the solid fraction are analyzed.

4.5.3. Sampling of aerosol-fractions

- There is a growing tendency to sample air particulate matter according to particle size. Various devices have been constructed which separate particles according to their inertia against sinusoidal air movement. The material which is not able to follow the air is then catched on some filter. Finally the air is filtered to collect the finest fraction. These instruments, which are called "impactors", are described in detail in refs. [50, 56 and 57] and, in a concise form, in ref. [54] which also refers to the original papers, published by the various designers. Usually, the aerosol is separated into 3-8 fractions, varying in particle diameter from ∿ 10 μm to ∿ 0.5 μm. The flow-rate may be low, 0.1-5 $m^3.h^{-1}$, or high, around 30-60 $m^3.h^{-1}$. Refs. [53, 58-64] give some practical examples.
- From the point of view of the environmental analyst, this practice implies an inevitable increase in the ratio blank/sampled aliquot. The blanks of the impactor foils thus become increasingly important. Organic polymers such as polythene, polycarbonate, nylon and teflon are commonly used.

To obtain the limit of determination (cf. section 6.7.) one should first decide what the maximal acceptable relative standard deviation for the various elements should be. On the basis of the experimentally determined specific count-rates under the photopeak and the corresponding interval of the compton-continuum for both the loaded filter and the blank and using the equations from table 6.I, one can then determine the absolute standard deviations for the peaks from the blank (σ_b) and from the loaded filter (σ_ℓ).
The (absolute) error in the net-difference is now calculated as $[\sigma_b^2 + \sigma_\ell^2]^{\frac{1}{2}}$. This error increases with the square-root of the counting-time while the net-difference goes up linearly. For a given set of specific count-rates and a fixed counting-time, one may thus determine the minimal determinable amounts of the various elements. From these and the masses of the sampled aliquots follow the minimal determinable concentrations for the various fractions.

4.6. Sampling of silicates

- The technique of preparing homogeneous aliquots of silicates has been described long ago [65, 66]. Unfortunately, the environmental analyst seldom has the opportunity to follow these procedures completely. Most often the nature of the problem does not permit more than the simplest technique. In general, the analyst is asked to study the elemental composition of silicates as a function of (a) sampling location and (b) particle size.
  If a two-dimensional surface sampling is to be performed, simple grabbing techniques are used. Road dust was collected by vacuuming the gutter and the road way of streets [67]. For the sampling of harbor sediment a snapper grab sampler was used [68]. When cores are taken from a sediment-layer, these are usually cut into sections which are then dried, powdered and sieved [69, 70]. Eventually only one fraction is taken [71]. Sludge samples are air-dried and homogenized [72].
  In the case of surface-layer sampling from hard materials like glased or high-temperature fired pottery, tools made of tungsten carbide could be used, but the blank problem has to be considered seriously.
  Crushing in an agate mortar with a pestle of the same material [73] or hammering between polythene sheets [74] is applied for sherds of pottery.

A good summary of the current practice in silicate sample treatment can be found in ref. [75] from which the following passage is taken: "The principal problem in sample preparation is to provide a small, uncontaminated aliquot for analysis that is properly representative of the parent sample. Sufficiently small samples (< 20 mg) are analyzed whole, without being ground. Most rocks and mineral specimens are large enough and heterogeneous enough that grinding and splitting of a representative sample are required. Small (< 1 g) samples are crushed and ground in an agate mortar. Larger samples are crushed in an agate ball mill. Selection of equipment is crucial. For example, Co is a common contaminant of ceramic alumina mortars. Tungsten contaminates samples ground in tungsten carbide mortars, making analyses for several elements difficult or impossible".
In the sampling of fly-ash and the subsequent splitting into fractions, three problems are to be faced:

- Representative sampling.
- Separation of the sampled material into fractions.
- Surface enrichment of trace elements.

Samples should be as large as possible to be representative; they are usually taken from the electrostatic precipitators [76-78]. Simultaneous fractionation is possible [77]. Next to sampling from the ESP's, the particulate matter in the stack gas is sampled as discussed earlier.

Separation of the sampled material is usually performed by sieving; using a micro particle classifier, nine size fractions from 0.5 to 50 μm mass median diameter are obtained [79]. Alternatively a separation may be effectuated magnetically; the resulting two fractions of ferrite and the rest are then subjected to selective dissolution. Using concentrated HCl and dilute HF, one may end up with three fractions: glass (dissolved), mullite-quartz (solid) and magnetic spinel (dissolved) [80, 81].

Trace elements which are volatilized during the combustion process condense on the surface of the fly ash particles and thus cause a high surface-enrichment. This implies that the average concentration of a volatile trace element will tend to be a linear function of the inverse particle size and that fractionation is mandatory.

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CHAPTER 5.

PRECONCENTRATION AND DECONTAMINATION IN RADIOANALYSIS

SUMMARY

- The scope of environmental radioanalysis can be enlarged substantially by preconcentration. The techniques used may be characterized by a concentration- and a decontamination-factor.

  In addition the minimal representative sample-mass and the maximal acceptable aliquot-mass and dose-rate have to be considered.
- In general the best choice is an inorganic scavenger like active carbon or an automatized solvent extraction.
- This chapter deals with the principles and a general survey of the available techniques only. For applications to a specific case, the reader should also consult chapters 8-10.
- The approach given in this chapter was first expanded in the survey paper written upon request of the International Union of Pure and Applied Chemistry, mentioned in the last reference.

LIST OF SYMBOLS

A_i	Mass of analyte of species i	[g]
$\bar{C}_o$	Expected in concentration level in original sample	[μg.ml^{-1}] or [μg.g^{-1}]
$\bar{C}_1$	Average concentration in the preconcentrated aliquot	
D	Distribution constant	
D_1	D of compound of interest	[-]
D_2	D of interference	
G_0	Mass of the original aliquot	[g]
G_1	Mass of the preconcentrated aliquot	
k_i	Specific sensitivity for species i	[g^{-1}]
k_Q	Limit of determination/standard deviation	[-]
$(L_Q)_m$	Limit of determination, expressed as a mass	[g]
n	Number of unit operations	[-]
p	Ratio mass of reagent/mass of analyte	[-]
R	Recovery	[-]
r	Minimal acceptable ratio mass of analyte/blank	[-]
S_i	Specificity for species i	[-]
V_0	Volume of original aliquot	[ml]
V_1	Volume of preconcentrated aliquot	
X	Concentration factor	[-]
Y	Decontamination factor	[-]
ε	Porosity of a solid	[-]
$\sigma_{rel}(\bar{C}_1)$	Standard deviation in $\bar{C}_1$	[μg.ml^{-1}] or [μg.g^{-1}]

5.1. Analytical criteria for preconcentration in elemental analysis

5.1.1. General

The scope of any analytical method may be enhanced by preconcentration of the compound of interest and the elimination of interferences. Often these steps may be combined. Obviously, preconcentration makes sense only if the sample material cannot be analysed as such. This depends on

a) The limit of determination, $(L_Q)_m$, expressed in μg.

b) The maximal volume or weight, V_1 or G_1, which can be handled, in ml or g.

c) The expected concentration level, $\bar{C}_o$, expressed in $\mu g.ml^{-1}$ or $\mu g.g^{-1}$.

If the limit of determination for the untreated material is $(L_Q)_m$, the scope of the analysis without preconcentration is given by

$$V_1 \cdot \bar{C}_o > (L_Q)_m \qquad (5.1^a)$$

or

$$G_1 \cdot \bar{C}_o > (L_Q)_m \qquad (5.1^b)$$

If this condition is not fulfilled it may be reached by

a) increasing the concentration or

b) lowering the limit of determination.

- The preconcentration-step may be defined by four criteria:
  a) Concentration factor
  b) Decontamination factor
  c) Recovery
  d) Specificity

5.1.2. Concentration factor

- A concentration procedure reduces the original volume or weight, V_o or G_o, to new values V_1 or G_1, under constant, preferably quantitative, recovery of the compound of interest.

  It thus follows from equations (5.1) that

$$X.V_1 \cdot \bar{C}_o = V_1\bar{C}_1 \geq (L_Q)_m \qquad (5.2^a)$$

or

$$X.G_1 \cdot \bar{C}_o = G_1\bar{C}_1 \geq (L_Q)_m \qquad (5.2^b)$$

where X stands for the concentration factor and $\bar{C}_1$ for the average concentration in the preconcentrated aliquots.

- The actual concentrations of the individual samples will vary around the estimated average. If this variation follows a Poisson-distribution, $\sigma(\bar{C}_o) = \sqrt{C_o}$ and 99% of the samples will be covered by the analysis if equations (5.2^c) or (5.2^d) hold.

$$X.V_1 \cdot (\bar{C}_o - 2.5\sqrt{\bar{C}_o}) \geq (L_Q)_m \qquad (5.2^c)$$

$$X.G_1 \cdot (\bar{C}_o - 2.5\sqrt{\bar{C}_o}) \geq (L_Q)_m \qquad (5.2^d)$$

- The blank caused by the preconcentration step poses a third condition:

$$\frac{\text{blank}}{[\text{mass of analyte}]} = \frac{\text{blank (in µg)}}{X.V_1 \cdot \bar{C}_o} \text{ or } \frac{\text{blank (in µg)}}{X.G_1 \cdot \bar{C}_o} \leq \frac{1}{r} \qquad (5.3)$$

The minimal acceptable value of r depends on the uncertainty in the blank. A reasonably practical choice is $r = 2$. When the blank is caused by the reagents solely it is obvious that

$$\frac{1}{r} \geq (\text{blank concentration}) \cdot \frac{[\text{mass of reagent}]}{[\text{mass of analyte}]} \qquad (5.4^a)$$

5.1.3. Decontamination factor

The elimination of interferences which is caused by the preconcentration step may be expressed in terms of the decontamination factor Y, defined as the double ratio

$$Y = \left(\frac{\text{concentration element of interest}}{\text{concentration interference}}\right) \text{after/before} \qquad (5.5)$$

In general the value of $(L_Q)_m$ depends on that of Y. In spectrometric techniques a net peak-area is obtained by subtraction of a background which is due to the interferences. Moreover, the peak involved may be interfered by a similar peak of the interfering compound. Separation by a numerical

technique will cause an extra uncertainty and thus increase $(L_Q)_m$. If it is required that the peak of interest is at least as strong as that of the interference a minimal value of Y can be defined.
The relation between X and the minimal value of Y is "the X-Y line" in an X-Y graph. The position of this line depends on the preconcentration procedure.

- For each material there exists a minimal representative aliquot-mass which imposes a minimal X-value limited by the maximal aliquot-mass or -volume which can be handled. This is represented by a vertical line in the X-Y graph.
- Finally the maximal mass which can be handled in activation analysis due to counting limitations depends on Y. In trace analysis this relation is usually a simple proportionality. In the X-Y diagram this becomes "the decontamination line". Its shape depends on the sampled material and the irradiation.

5.1.4. Recovery

The recovery, R, is defined as 100.[amount collected]/[amount present]. One may consider R as a function of the ratio $p = \frac{[\text{mass of reagent}]}{[\text{mass of analyte}]}$ as shown in figure 5.1. In the ideal case of a complete reaction and with a stoichiometric ratio α one has

$$R = \frac{100}{\alpha} \cdot p \qquad (5.6)$$

Then equation (5.4^a) becomes

$$\frac{1}{r} \geq (\text{blank concentration}) \cdot \frac{\alpha \cdot R}{100} \qquad (5.4^b)$$

Thus for a quantitative recovery and a given value of α the choice of r sets the maximal acceptable value of the blank concentration in the reagent.

5.1.5. Specificity

The determination of the isolated compound should be free of an appreciable bias due to interferences. The specifity for compound i, S_i, may thus

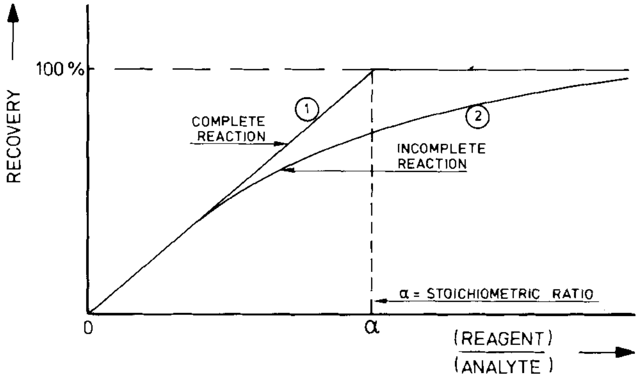


Figure 5.1 *THE RECOVERY AS A FUNCTION OF THE RATIO MASS OF REAGENT / MASS OF ANALYTE*

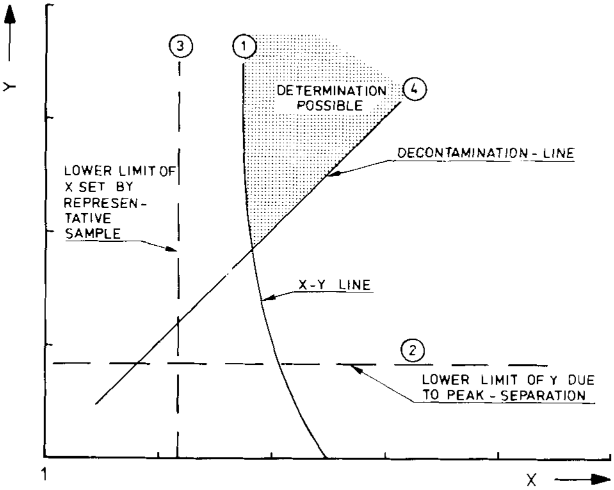


Figure 5.2. *PRINCIPLE OF THE X-Y DIAGRAM.*

be defined as

$$S_i = 100 \cdot \frac{k_i[A]_i}{\Sigma k_i[A]_i} \qquad (5.7)$$

where A_i is the mass of the analyte i and k_i the corresponding specific sensitivity.

5.1.6. The X-Y diagram

Figure 5.2. summarizes the features of the X-Y diagram. The area which represents the analytical possibilities lies to the right of the line 1 and 3 and above the lines 2 and 4. In addition to these requirements equation (5.3) has to be fulfilled.

5.1.7. Chemical speciation

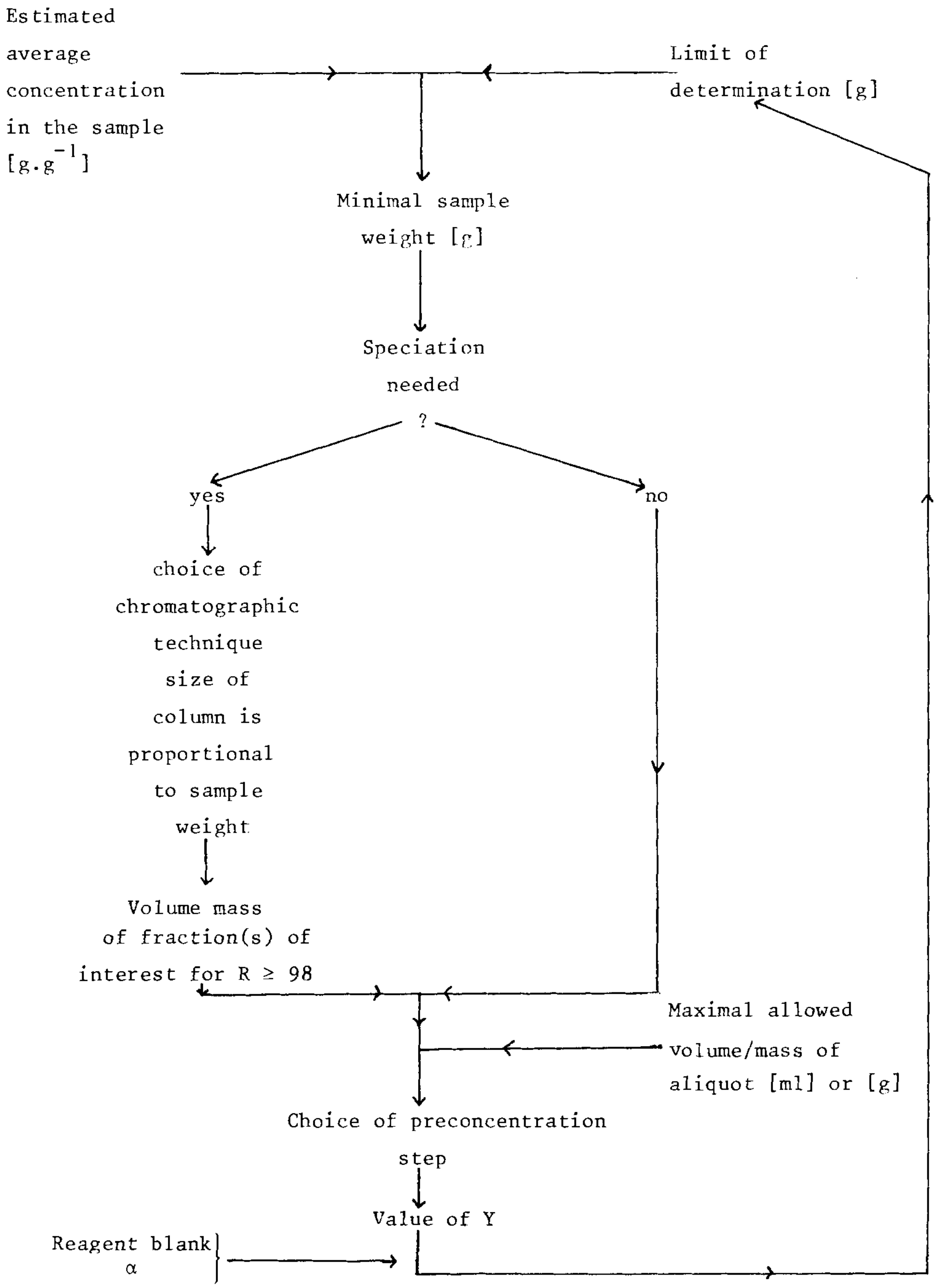
A special case is presented by the separate determination of the different chemical forms of one element. This may sometimes be done by separate procedures for each species. More often it is achieved by some sort of chromatography. Then the peak-width increases with the amount of material. This implies that the required column length, needed to obtain a certain separation factor, is about proportional to $(L_Q)_m^2$.
For a given separation technique the R- and S-values may be calculated from the experimentally observed separation factors and peak-widths.

5.2. Application to radioanalysis

5.2.1. Choice of the procedure

- The procedure which is followed in choosing a preconcentration/purification step is shown schematically in table 5.I. It is iterative by nature as $(L_Q)_m$ depends on Y. Whether the chosen procedure is feasible or not depends on the blank.
- In activation analysis two additional, closely related, factors have to be considered:
  a) The half-life of the radionuclide involved.
  b) The dose-rate at the time of handling.

Table 5.I. Scheme for the iterative choice of a preconcentration (-purification) procedure



In practice one gets the eight combinations shown in table 5.II. In cases 6 - 8 the analyst is in a conflicting situation. His choice depends on the local circumstances.

5.2.2. The limit of determination (cf. section 6.7.)

- The value of $(L_Q)_m$ follows from the total standard deviation in the final result of the analysis of the preconcentrated aliquot. One may write:

$$(L_Q)_m \geq k_Q \cdot G_1 \cdot \Sigma\, \sigma\, (\bar{C}_1) \qquad (5.8^a)$$

or

$$(L_Q)_m \geq k_Q \cdot V_1 \cdot \Sigma\, \sigma\, (\bar{C}_1) \qquad (5.8^b)$$

where G_1 and V_1 are the maximal processable mass and volume of the preconcentrated aliquot. To cover 99% of all samples $\bar{C}_1$ has to be replaced by $\bar{C}_1 - 2.5\sqrt{\bar{C}_1}$ (cf. equation 5.2^c and 5.2^d).

The factor k_Q is a matter of personal appreciation [1]; often one sets $k_Q = 10$. Inserting

$$\Sigma\, \sigma(\bar{C}_1) = \bar{C}_1 \cdot \Sigma\, \sigma_{rel}(\bar{C}_1) \qquad (5.9)$$

into (5.8), one obtains $(L_Q)_m$ as a function of the total <u>relative</u> standard deviation in $\bar{C}_1$:

$$L_Q \geq k_Q \cdot G_1 \cdot \bar{C}_1 \cdot \Sigma\, \sigma_{rel}(\bar{C}_1) \qquad (5.10)$$

Now $\Sigma\, \sigma_{rel}(\bar{C}_1)$ increases with decreasing $\bar{C}_1$ [2,3]. The minimal acceptable $\bar{C}_1$-value and thus $(L_Q)_m$ follows then from the relation

$$\Sigma\, \sigma_{rel}(\bar{C}_1) \leq \frac{1}{k_Q} \quad \text{(cf. figure 6.9)} \qquad (5.11)$$

- The total relative standard deviation is build up from the relative σ's in the peak-area determinations for sample and standard, in the relative flux- or beam-intensity measurements and in the electronic correction factors (cf. table 6.VI. and section 7.3.).

In X-ray and γ-ray spectrometry these correction factors are usually obtained by way of peak-area determination as well. The relative standard deviation in an individual photopeak can be calculated from the specific count-rate in the peak, the ratio compton background/peak, the counting time and the number of channels in the peaks [2,3].
The second parameter decreases with increasing Y. One may write the compton background as the sum of two or more terms, each with a characteristic half-life. The elimination of interfering radionuclides will reduce one or more of these contributions.

- Equally the maximal amount of sample which can be handled may increase by elimination of interfering radionuclides, if the dose-rate during handling is the governing factor. This is often the case when short-lived radionuclides have to be measured.

5.2.3. The use of the X-Y diagram

- The use of the quantities X and Y may be demonstrated on two extreme cases. In the first example, the value of X is of primordial importance while in the second the improvement is due to a large Y-value. In both cases the recovery is (nearly) quantitative.

- The first case deals with the determination of mercury in unpolluted air by thermal neutron activation [4]. Typical concentrations vary from 1 to 10 $ng.m^{-3}$. The available $(L_Q)_m$-value for instrumental neutron activation is $\simeq$ 10 ng while the maximal acceptable volume V_1 = 5 ml. Thus, according to (5.1^a), X must be $\geq 2.10^6$.
  The metal is present in elemental form and as organomercurials; it is collected by pumping $\simeq$ 5 m^3 air through $\simeq$ 2 g (= 5 ml) active carbon. Air dust is removed by a 0.20 μm membrane filter. This eliminates the interfering elements sodium and bromine; $Y \simeq 10^3$.
  The carbon contains < 1 $ng.g^{-1}$. The ratio blank/collected mass is thus well below 0.5 as required by equation (5.3). Determination is based on activation to ^{197}Hg ($T\frac{1}{2}$ = 66 h), assayed by way of the 77 keV photopeak. Due to the removal of ^{24}Na and ^{82}Br the compton-background is reduced by two orders of magnitude which decreases $(L_Q)_m$ by a factor of ~ 10. Consequently one needs $X \simeq 2.10^5$ now. The actual X-value obtained is $X = 4.10^5 - 10^6$. Figure (5.3^a) gives an account of the situation. The lines of the minimal X- and Y-values coincide with the X- and Y-axis.

The second example refers to the determination by thermal neutron activation of arsenic in the NBS Standard Reference Material "Orchard Leaves" [5].

The relatively short-lived radionuclide ^{76}As ($T\frac{1}{2}$ = 26.4 h) is measured by its 559 keV photopeak. It is interfered by the 554 keV line of ^{82}Br ($T\frac{1}{2}$ = 35.6 h). The concentrations of arsenic and bromine in Orchard Leaves are $\simeq$ 10 ppm [6]. Table 5.III gives the values of $(L_Q)_m$ and the minimal determinable concentration $\bar{C}_1$ as a function of the cooling time. Without separation the maximal acceptable weight due to the dose-rate after 48 hrs of cooling is $G_1 \simeq 1$ mg. This maximal weight increases proportional to the decontamination factor against ^{24}Na and ^{82}Br: G_1 (in mg) $\simeq$ Y. With an average mass of the concentrated aliquot of one gram, one has thus $Y \simeq 10^3$ X as the equation for the <u>decontamination line</u>.

The irradiation facility accepts sample weights up to ~ 0.5 g. A representative sample should be 100 mg at least. Thus the <u>minimal X-value</u> is $\simeq$ 0.5. The ratio of the specific count rates in the ^{76}As- and ^{82}Br-peaks is 1.5. This sets the minimal Y-value at $\simeq$ 2.

The arsenic is isolated by coprecipitation with $Fe(OH)_3$. For the decontamination from ^{24}Na and ^{82}Br $Y \geq 5.10^2$. The equation of the <u>X-Y line</u> is a horizontal.

Figure 5.3^b. visualizes the situation for a cooling time of 48 hours.

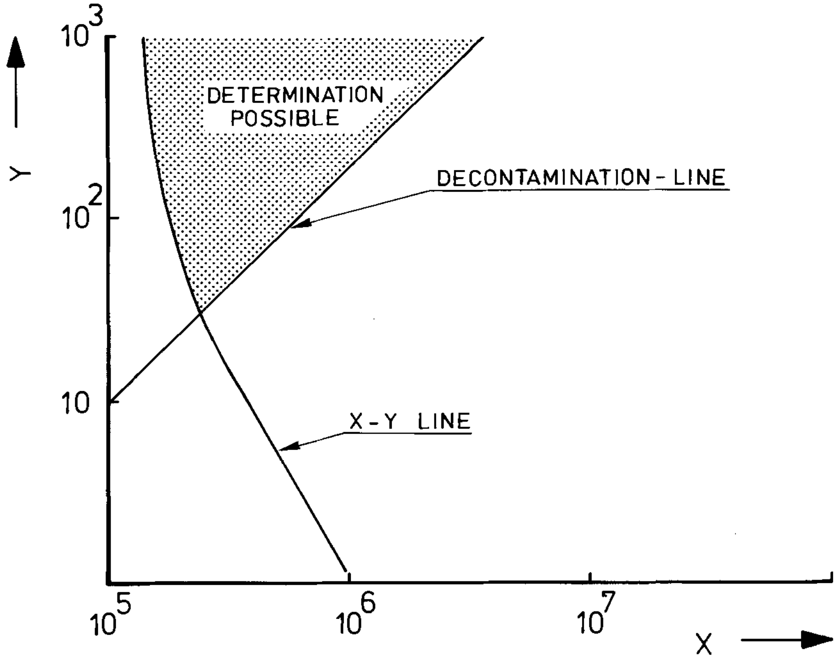


Figure 5.3^a.: *THE X-Y GRAPH FOR THE DETERMINATION OF MERCURY IN AIR.*

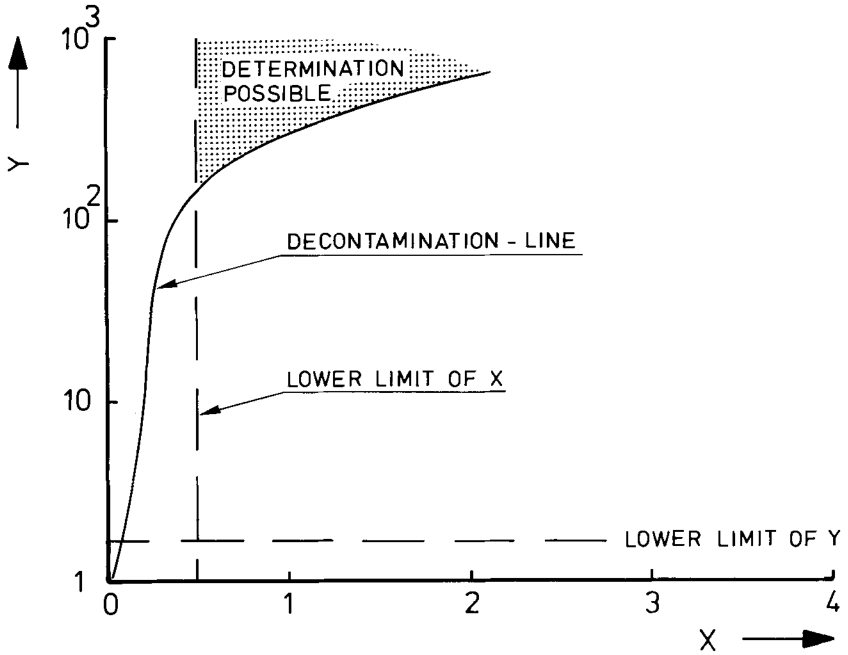


Figure 5.3^b.: *THE X-Y GRAPH FOR THE DETERMINATION OF ARSENIC IN DRY PLANT MATERIAL.*

Table 5.II. Survey of the eight different situations encountered in the determination of total element concentrations by neutron activation analysis

No.	Volume	Blank	Dose rate and Time	Concentration/ purification prior or after the irradiation	Remarks	Example
1				after	Separation necessary for the elimination of interfering radionuclides	Cr in dry biological material
2		x		after		W in silicates
3			x	prior		Trace elements in metallic mercury
4	x			prior		Trace elements in airdust
5	x		x	prior		V in seawater
6	x	x	x	prior	Depends on the purification of the tools and reagents. Otherwise impossible	Mn in seawater
7	x	x		prior		Lanthanides in surface water
8		x	x	prior	Depends on the time needed for return to the laboratory and that used in dissolution and separation	Al in blood

The x sign indicates that the corresponding criterion is not met.

Table 5.III. The values of $(L_Q)_m$ and $\bar{C}_l$ as a function of the cooling time for the determination of arsenic in dry plant material by thermal neutron activation analysis

Cooling time in hours	$G_l = 1$ $Y = 1$		$G_l = 10$ $Y = 10$		$G_l = 100$ $Y = 100$		$G_l = 400$ $Y = 400$	
	$(L_Q)_m$ in µg	$\bar{C}_l$ in ppm	$(L_Q)_m$ in µg	$\bar{C}_l$ in ppm	$(L_Q)_m$ in µg	$\bar{C}_l$ in ppm	$(L_Q)_m$ in µg	$\bar{C}_l$ in ppm
12	0.025	25	0.015	1.5	0.015	0.2	0.015	0.05
24	0.03	30	0.015	1.5	0.015	0.2	0.02	0.05
36	0.04	40	0.025	2	0.02	0.2	0.025	0.1
48	0.05	50	0.02	2	0.025	0.3	0.035	0.1
60	0.07	70	0.025	2.5	0.03	0.3	0.045	0.15
72	0.09	85	0.035	3.5	0.04	0.4	0.06	0.15
84	0.12	115	0.045	4.5	0.05	0.5	0.08	0.2
96	0.15	150	0.055	5.5	0.07	0.7	0.11	0.3
108	0.21	205	0.075	7.5	0.09	0.9	0.14	0.35
120	0.28	280	0.10	10	0.12	1.2	0.19	0.5

G_l = Mass of preconcentrated counting aliquot in mg.

Y = Decontamination factor from ^{24}Na and ^{82}Br, needed to make counting possible.

5.3. Preconcentration techniques in radioanalysis

5.3.1. General

- Preconcentration is performed on a sample to get a suitable aliquot for the analysis. Thus preconcentration is subject to the sampling technique. The sample has to be regarded as being homogeneous and representative. If, for instance, water has been sampled including the suspended particulate matter an eventual preconcentration should be capable of collecting the compound of interest from both phases in the sample.
- By the same token it is obvious that an eventual dissolution and mineralisation should be regarded as a separate step which, once again, by definition leads to a homogeneous material.
- On the other hand the dissolution and destruction have to meet the suppositions on which the separation technique is based. If, for instance, it becomes manifest that mineralisation has not been complete the whole analytical procedure has to be redressed.
- Preferably the (pre)concentration technique should not be the limiting factor in the total analytical procedure with respect to time, costs or blank value. These three requirements narrow down the possibilities appreciably.

5.3.2. Preconcentration by evaporation, freeze-drying and dry ashing

- Evaporation has been used frequently in the analysis of water samples by neutron activation analysis [7-9]. It only concentrates without any decontamination. The usual X-values are between 10^2 and 10^3.
- Drying, especially of "nearly dry" biological material, has been recommended to obtain well-defined sample weights [10,11]. In general the temperature should not exceed ~ 90 °C [11]. The resulting X is $\leq$ 1.5.

  Freeze-drying is generally applied for biological samples [12-15]. There is a slight influence of the freezing temperature on the weight loss [5]; usually the final weight is constant within 1%. The concentration factor may be as high as X = 10 (cf. section 4.4.2.).
- Dry ashing may lead to concentration factors of $X \leq 50$. Volatile elements

are easily lost but can be retained at a low temperature or trapped by a suitable agent. The recovery of lead from milk powder [16] and fluorine from plant material [17] can be quantitative.
An elegant technique is gradual dry oxidation with KNO_3 at a slowly increasing temperature [18].

5.3.3. Preconcentration by liquid-liquid extraction

- Extraction from an aqueous solution into an immiscible organic phase is an obvious technique for preconcentration. Usually a chelating reagent is added. The recovery R is related to the concentration factor X and the distribution coëfficient D by

$$R = 100 \cdot \frac{D}{X + D} \qquad (5.11)$$

The value of D depends on the equilibrium constants of the compound involved and of competitive reactions, as on the ratio [mass of reagent]/[mass of analyte].
It follows from (5.11) that D should be ≥ 49 X to obtain R ≥ 98.
Often part of the organic layer is left with the water to avoid contamination. The extraction may then be repeated to obtain a high R-value.

- The resulting X can be enhanced still by evaporation of the organic solvent or by back extraction. The decontamination factor depends on the distribution constants of the compound of interest (D_1) and the interference (D_2). It is obvious that

$$Y = \frac{D_1}{D_2} \left(\frac{X + D_2}{X + D_1}\right) \qquad (5.12)$$

- An elegant procedure is the pulsating column technique [19,20]. The column consists of a syringe of ≥ 20 ml volume which contains a cylindrical plug of polyurethane foam impregnated with a hydrophobic organic reagent. Pressing and releasing the plunge causes a fixed volume of the sample to enter and come into contact with the reagent-loaded foam. It follows that

$$X = \frac{\text{Sample volume } (V_0)}{\text{Geometrical volume of the foam column } (V_1)}$$

If the porosity of the foam is ε and the distribution coefficient remains constant one has, for the recovery after n pumpings:

$$R = \left(\frac{D}{X + D}\right) \cdot \left[1 - \left\{\left(\frac{X - \varepsilon}{X}\right) \cdot \left(\frac{D}{1 + D}\right)\right\}^n\right] \qquad (5.13)$$

It is obvious that at $n = \infty$, $R_\infty = {}^D/(X + D)$.
For polyurethane foam $\varepsilon \simeq 0.99$.
The required number of pumpings pulses, needed to reach R_∞ within one percent follows from (5.14)

$$n \geq \frac{-2}{\log\left[\left(\frac{X - \varepsilon}{X} \cdot \frac{D}{1 + D}\right)\right]} \qquad (5.14)$$

For $X = 10^2$ and $D = 10^4$ one needs $n \geq 460$. With a fixed pumping rate of $\sim 8.\mathrm{min}^{-1}$ [20] one reaches $X = 10^2$ in one hour.

- The practical procedures for preconcentration by extraction usually consist of three steps:
  a) The extraction itself, sometimes performed in several successive stages.
  b) Evaporation.
  c) Mineralization.

  Two representative examples of this approach may be cited.
  a) Using pyrrolidine-dithiocarbamate or diethylammonium-dithiocarbamate as the chelating reagents and extraction into chloroform, values of $R \geq 98$, $X = 10^2 - 2.10^2$ and $Y \geq 10^2$ are obtained [21,22].
  b) The application of pyridine ketoximes as a reagent for the determination of ultra trace amounts of cobalt leads to $R \geq 98$, $X = 10^2 - 3.10^2$ and $Y \geq 10^2$ [23].
- The application of the pulsating column to the determination in water samples of ^{131}I ($T\frac{1}{2}$ = 8.1 d), present as iodide, and ^{203}Hg ($T\frac{1}{2}$ = 45.1 d), probably present as Hg^{II}, has been reported [20].
- The use of extraction in post-irradiation chemistry is well known. The analysis of the NBS environmental Standard Reference Materials for

copper and cadmium was performed by extraction of the DDC-compounds [24]; $Zn\ (DDC)_2$ is used as the reagent. The resulting Y-values with respect to ^{24}Na and ^{82}Br are $\simeq 10^3$. The concentration factor is $X \simeq 0.1$. A system for multi-element solvent extraction based on DDC was developed by several authors [25,26]. The elements which are indeterminable by neutron activation are used as subsequent scavengers at increasing pH-values. The time needed is $\approx$ 2 hours. Starting with 40 ml sample solution it leads to $R \geq 98$ and Y (against ^{24}Na) $\geq 10^4$ at $X \simeq 2$.
Extraction is often applied in the elaborate group separation schemes for irradiated samples. Here the sole aim is decontamination.
Examples are found in the schemes of Samsahl [27] and its modification by Schramel [28] for biological material and that of Smet for rocks and minerals [29].

5.3.4. Preconcentration by ion exchange

- Ion exchange is often used for preconcentration. Moreover it is the backbone of many separation schemes which are applied in post-irradiation chemistry. The use for the isolation of single elements is restricted to a few cases where no other, more rapid, techniques are available.
- The application in preconcentration is almost entirely restricted to water samples. Moreover the trend is towards those types of ion exchangers which can be used directly in multi-element determinations. Thus resin-loaded papers have become popular as collectors in the determination of trace elements by X-ray fluorescence or instrumental neutron activation analysis in filtered fresh water. Preliminary work [30-34] led to procedures , based on cellulose-phosphate paper which contains DDC-groups (8 $\mu Mol.cm^{-2}$) at the surface [35] and on anionic resin loaded filters [36]. The DDC-filters have to be prepared afresh. Samples of 200 - 1000 ml are pH-adjusted and pumped through at a specific flow-rate of $\simeq$ 10 $ml.cm^{-2}.s^{-1}$. The observed capacities of 13 mm diameter filters range from 20 to 100 µg metal.
  Usually one has $R \geq 98$, $X = 10^2 - 10^3$ with $Y \geq 10^2$ against sodium, chlorine and bromine. The possibilities can be summarized as below. The collection from alkaline medium is of limited use due to the risk of hydroxide precipitations.

	Cellulose phosphate	Quaternary ammonium		Immobilized dithiocarbamate
Optimum pH	1	1		6 - 8
Medium	HNO_3 or HCl	HCl	$CN^-(10^{-4}M)$	HNO_3
Preconcentrated elements	Th, U, lanthanides	Au, Hg, Sb, Cd, W, U	Hg, Au, Zn, Cd, Cu, Co, U	Hg, Cu, Zn, W, U

Paper loaded with an anion-exchange resin was used for the collection of mercury ions as $HgCl_4''$ [37], leading to $R \geq 95$, $X = 50$ and $Y \geq 100$ from alkali-ions.

- The use of chelating resins opens up the possibility of preconcentration followed by atomic absorption spectrophotometry [38] or neutron activation analysis [39]. As a rule the chelating compounds are grafted on a cellulose support which may be a filter or a small column [40,41].
  If a column is used the elements are eluted with 1 M HCl. Results are: $R \geq 98$, $X = 10^2 - 2.10^2$ (column) or $\geq 10^3$ (filter) and $Y \geq 10^3$ against sodium.
  The obvious drawback of the filters is their low capacity ($\simeq 5.10^{-2}$ m Mol).
- The application of small columns of Chelex-100 resin for preconcentration in multi-element neutron activation [42] is hampered by their blank value [43]. For some single elements it may be feasible. Examply are uranium [44], the lanthanides, copper and zinc [45]. For uranium the resin is irradiated. The lanthanides are eluted with 2.5 M HNO_3. At $R \geq 98$ and $Y \geq 10^3$ for the decontamination from the alkalis and earth alkalis, one has $X \simeq 10^3$ for uranium and $X \simeq 10^2 - 5.10^2$ for the lanthanides, copper and zinc.
- Single element preconcentration with columns of other chelating resins are based on mixed anionic-cationic resins, eventually combined with a chelating reagent [46] or some specialized resin like the aniline sulfur ASH for mercury [47], Srafion NMRR [48-50] for the noble metals and

XAD-7 for cesium [51].
Usually R is ≥ 95, $X \geq 10^2$ and $Y \geq 10^3$ against the major interferences. The elimination of interfering elements prior to the irradiation in case of determination by short-lived radionuclides belongs to this class also. An example is the assay of vanadium in biological material by ^{52}V ($T\frac{1}{2}$ = 3.8 min). The element can be concentrated on a cation-resin with R = 93, $X \simeq 0.5$ and $Y \simeq 20$ [52]. Eventually the adsorbed elements may be eluted prior to the counting to avoid most of the resin's blank.

- In post-irradiation chemistry ion-exchange is the base of most of the laborious schemes for group separation which were designed for NaI-counting [53]. The development of the Ge(Li) detector and the increasing labour costs have tended to reduce the number and complexity of the separation steps and to automatize the whole procedure.
  The modifications of Samsahl's scheme for dry biological material [27] by Schramel [28] and Tjioe et al. [54] feature still 7 - 10 fractions. That of Smet et al. for the determination of 24 elements in rocks and minerals [29] implies 21 fractions. The alternative to these systems is a combination of a rapid scavenging procedure for all trace elements, like that with active carbon (see below), completed by a few single element determinations. The choice of these elements follows from the analytical criteria mentioned above and of the costs involved.

- For some separations of single elements or one group, ion-exchange remains the best technique. The ion-exchanger "Srafion NMRR" which is specific for noble metals can be used for a group separation of the noble metals [55]. It leads to R ≥ 95 (except for Pt^{IV}) and $X \simeq 0.1$ with $Y > 10^3$ from ^{24}Na, ^{32}P and ^{82}Br. The application to the determination of copper [49] and molybdenum [50] in dry biological material, silicates and coal yields the same R, X and Y-values.

5.3.5. Preconcentration by coprecipitation, isotopic exchange and adsorption

- Collection of a microcomponent by coprecipitation belongs to the oldest part of radiochemistry [56]. In its ideal form, coprecipitation becomes cocrystallization and it follows Hahn's rule: "A microcomponent is carried down by a solid formed by crystallization or precipitation if it enters into the normal lattice formation".
  Often however, the collecting precipitate acts as a scavenger by the

combined actions of coprecipitation, inclusion, adsorption and ion-exchange.
Distribution between a suitable solid phase and a solution may be used as an alternative. Finally isotopic exchange may be applied in radiochemistry.
In practice the behaviour of the collector can best be described by the empirically determined relation between the recovery R and the ratio p = [mass of precipitate]/[mass of analyte] as shown in figure 5.1. In the ideal case of cocrystallisation the two straight lines are obtained.

- Cocrystallisation may yield impressive concentration factors. A determination of copper and manganese by cocrystallisation with oxine [27] yields R = 100, X = 10^3 and Y ≥ 10^3 with respect to ^{24}Na and ^{82}Br.
  The distribution of cesium and strontium between the hexacyanoferrates and an aqueous solution may be used to separate the fission products ^{137}Cs and ^{90}Sr from water samples, yielding X-values of 10^2 - 10^4 [57].

- Isotopic exchange is of interest in post-irradiation chemistry. It depends on the application of a large excess of the inactive element in a suitable form. The collection of ^{203}Hg from an acid solution by adding a droplet of mercury metal [58] and that of ^{128}I by exchange with a solution of iodine in carbon tetrachloride [59] work well. The collection of the lanthanide ions by isomorphic exchange with La-oxalate [60] is another example. In all cases R ≃ 100 and Y ≥ 10^2 from the interfering radionuclides.

- The collection of trace elements by scavenging has become important with the development of multi-element analytical techniques [61]. The scavenger is either formed "in situ" by precipitation or it is added.
  Iron hydroxide is often used as an "in situ" scavenger; hydroxides of metals of the third and fourth group like aluminium or lead are applicable too [62].
  The agent is characterized by determining the R versus p diagram. The pH, ionic strength and precipitation rate are used as parameters [63].
  Applications of ferric hydroxide are the determination of arsenic in water [64] and thorium in large samples of soft tissues [65] leading both to X ≃ 10^2. The collection of fall-out radionuclides from river water by flocculation of aluminium hydroxide gives X ≃ 4.10^4 [66].

- The action of an added solid scavenger is based on adsorption and ion-

exchange at one hand and collection of precipitate particulates at the other.
Van der Sloot et al. [67,68], Jackwerth [69,70], Lieser [71,72] and van Grieken [73] developed the use of active carbon for preconcentration of trace elements from sea- and surface water. The ions are chelated and scavenged into a small aliquot. The carbon may be stirred through the sample and filtered off or the water may be filtered through a carbon layer.
The carbon is submitted to neutron activation [67] or, in the case of uranium, to delayed neutron counting [74]. Alternatively the elements are desorbed into dilute nitric acid and determined optically [70,76]. Commercial active carbon may be used [67] but it is possible to prepare a purer brand [75]. The best procedure is found by independent variation of the concentration of the chelating agent, amount of carbon, pH and stirring-time or rate of filtration. Results are: $R \geq 95$, $X = 10^2 - 10^3$ and $Y \geq 10^2$ from ^{24}Na, ^{32}P and ^{82}Br.
Active carbon is used for collection from the gas phase, notably for the halogens [77] and mercury [4], resulting in X-values of 10^4 or more. An elegant application is the determination of uranium by way of ^{222}Rn ($T_{\frac{1}{2}}$ = 3.8 d) [78].

- The use of active carbon for the collection of trace elements from a neutron irradiated sample leads to a rapid multi-element determination [5,79].
  Figure 5.4 summarizes the effect in the case of "Orchard Leaves". The features of this technique are: $R \geq 95$, $X \simeq 5$, $Y \geq 2.10^2$ from ^{24}Na, ^{32}P and ^{82}Br.

5.3.6. Volatilization techniques

- Trace constituents which are volatile or can be transformed into volatile compounds may be isolated by evaporation and subsequent ad- or absorption. This principle is applied in post-irradiation chemistry primarily. Mutual separation has been restricted to the fractionation of the halides [80] and the hydrides [81].
- The primordial importance of the technique lies in a few determinations which cannot be matched by other procedures and which yield Y-values well

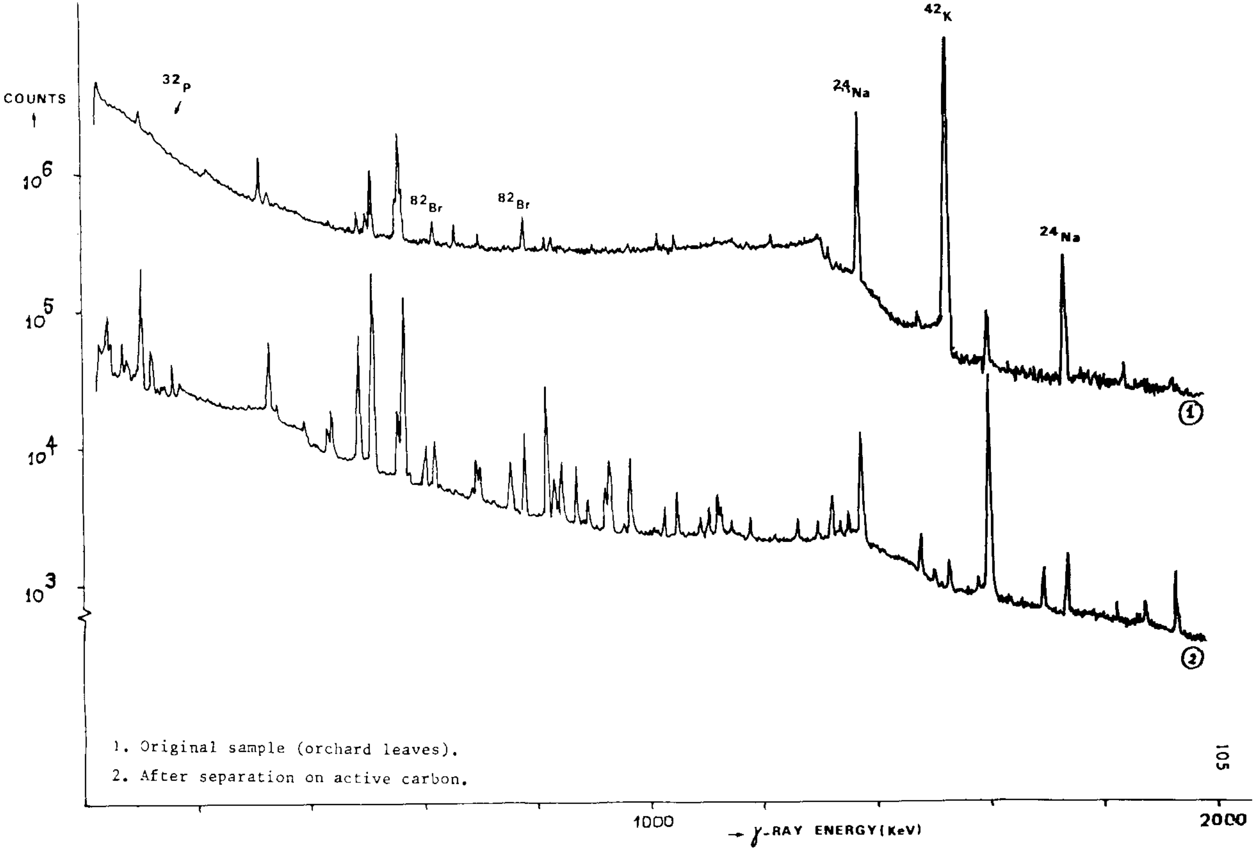


Fig.5.4. The γ-ray spectra of orchard leaves and the combined carbon fraction obtained from this material.

above 10^3 at $R \simeq 100$.

These are:

a) The distillation of chromium as $CrOCl_2$ [54].
b) The isolation of osmium and ruthenium as their oxides [82].
c) Hydride formation of arsenic, antimony and germanium [83,84].
d) Hydride formation and fractionation of organotin compounds [81].

5.3.7. Electrochemical preconcentration

- Electrolysis and amalgamation are primarily applied in post-irradiation chemistry. An exception is the collection of mercury from a gas stream. Electro deposition on pyrolitic graphite is applied for the determination of heavy metals in seawater by atomic absorption [85,86]. The procedure is slow and concentration factors do not exceed $X = 10^2$ at complete recovery. The blank of the graphite limits the applicability in neutron activation.
- Simple electrochemical displacement can be used in post-irradiation chemistry for quantitative collection of the noble metals except ruthenium, osmium and iridium, on copper powder [87]. The technique is rapid and gives $X \simeq 10^2 - 10^3$.

5.4. Practical conclusions

- Preconcentration comes between sampling and analysis. It should be able to keep pace with the sampling and eventually be carried out in the field. This presses for simple, rapid and reliable techniques. Moreover it should be possible to store the resulting aliquots without risk of contamination or deterioration. If the preconcentration is performed in the laboratory it is possible to use slow but easily controllable techniques. It should be realized that a longer processing time implies a longer exposure to contamination, notably by dust.

  Post-irradiation chemistry is restricted to the laboratory. Considerations of radiation burden and radioactive contamination again press for simple and rapid procedures. Here sample dissolution, radiation level and half-life of the radionuclide of interest set the limits.

  For preconcentration in the field the best general choice seems to be scavenging with active carbon or liquid-liquid extraction with a pulsating column. The use of metal hydroxides as scavengers is more restricted due to blank values.

  If a considerable time-gap may occur between the preconcentration and the analysis, the preconcentrated aliquots should not deteriorate during storage.

  From this point of view liquid extraction seems somewhat less useful than ion-exchange or scavenging with active carbon.

- The processing of irradiated samples in the radiochemical laboratory can best be based on the combination of a general scavenging technique with the separate determination of a few elements.

  If too less sample is present for that, the scavenging procedure is usually preferable as it leads to more information.

  If only one element is wanted the chemical separation may be slow and laborious. If the choice is possible one should prefer the procedure which is most open to automation.

- The costs of preconcentration and post-irradiation chemical separation within the total analytical procedure may be estimated only. The following data apply to the Dutch situation in 1981. They are an illustration of the need for multi-element techniques.

	Preconcentration in the field No chemical separation	Preconcentration in the laboratory No chemical separation	No preconcentration Post-irradiation group separation	No preconcentration Single element determinations
Total costs per sample	$ 100 - 150	$ 150 - 175	$ 150 - 175	$ 175 - 225
Total costs per element	10	10	10	20 - 100
Sampling	20 - 35%	20 - 30%	20 - 30%	15 - 30%
Preconcentration	15 - 20	30	-	-
Irradiation	15 - 20	15	15	15
Post-irradiation separation	-	-	20 - 35	40 - 60
Counting	10	5 - 10	5 - 10	5 - 10
Calculation	10	10	10	10
Overhead	15 - 20	15	15	15

Absolute values refer to 1981 situation

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CHAPTER 6.

ANALYTICAL CRITERIA IN RADIOANALYSIS

SUMMARY

In this chapter the main criteria are considered which should be used in designing radioanalytical procedures for environmental projects.
They are of three kinds: analytical, occupational and financial. If used with caution, the systematic check of these parameters will lead to the optimal procedure for each goal. Alternatively, the value of published data may be evaluated along the same lines. A practical example is discussed briefly.

LIST OF SYMBOLS

A	Net peak area obtained by linear interpolation	[-]
A_{sp}	Specific net peak area	$[g^{-1}]$
a	Count-rate (under the photopeak) (eq. 6.6)	$[min^{-1}]$
	Constant in the linear approximation of the compton-background (eq. 6.21)	[-]
a_{sp}	Specific count-rate under the photopeak	$[min^{-1}.g^{-1}]$
B	Area of the compton-continuum in the peak-interval	[-]
B_{lim}	Area of the compton obtained by linear interpolation	[-]
B_{extr}	$B - B_{lin}$	[-]
b	Count-rate of the natural background in the photopeak-interval (§ 6.3)	$[min^{-1}]$
	Count-rate of the compton-continuum in the photopeak-interval (§6.6)	
b_{sp}	Specific count-rate of the compton-continuum in the photopeak-interval	$[min^{-1}.g^{-1}]$
c	Total count-rate (eq. 6.1)	$[min^{-1}]$
E	Gamma-ray energy	[keV]
E_o	Energy of original photon	
f	Concentration	$[g.g^{-1}]$
G	Mass of aliquot	[g]
k_1	Constants in the empirical relation between count-rate and mass of aliquot	[min]
k_2		[min.g]

k_α, k_β	Constants defining the maximal accepted errors of the first and second kind	[-]
k_Q	Minimal acceptable ratio limit of determination/ standard deviation	[-]
L_c	Limit of decision	[-]
$(L_c)_f$	L_c expressed in f	[g.g^{-1}]
$(L_c)_m$	L_c expressed in mass	[g]
L_D	Limit of detection	[-]
$(L_D)_f$	L_D expressed in f	[g.g^{-1}]
$(L_D)_m$	L_D expressed in mass	[g]
L_Q	Limit of determination	[-]
$(L_Q)_f$	L_Q expressed in f	[g.g^{-1}]
$(L_Q)_m$	L_Q expressed as mass	[g]
N	Number of channels in the photopeak	[-]
n	Channel number, counted from the peak-top	[-]
	Number of independed measurement of the standard	
T_1	Contents of channel no. 1	[-]
T_N	Contents of channel no. N	[-]
T_n	Contents of nth channel, counted from the top of the photopeak	[-]
T_E	Contents of channel corresponding to energy E (keV)	[-]
T_0	Contents of topchannel of the photopeak	[-]
t_m	Preset counting-time	[min]
n	Excentricity of a result (eq. 6.18)	[-]

u_1, u_2	Excentricities of the edges of an interval	[-]
x	Ratio B_{lin}/A	[-]
y	$\frac{B_{extr}}{B_{lin}}$	[-]
Δ_{rel}	Relative systematic bias (eq. 6.14)	[-]
$\Delta_{rel}(f)$	Relative systematic bias inf (eq. 6.17)	[-]
δ_{rel}	Acceptable relative error	[-]
λ	Decay-constant	[min^{-1}]
σ	Standard deviation of gaussian photopeak	[keV]
$\sigma(A)$	Standard deviation in A	[-]
$\sigma(B)$	Standard deviation in B	[-]
$\sigma_{rel}(A)$	Relative standard deviation in A	[-]
$\sigma_{rel}(A+B_{extr})$	Relative standard deviation in $(A+B_{extr})$	[-]
$(\sigma_{rel})_f$	Relative standard deviation in f	[-]
$(\sigma_{rel})_o$	Minimal relative standard deviation	[-]
w	Channel-width	[keV]

6.1. Survey

- Analytical data refer to a certain matrix. Part of this is isolated to get a sample from which an aliquot is obtained. Even if these steps are performed without appreciable bias the radioanalyst is faced with two questions:

  Will it make sense to apply radioanalysis to this particular sample or aliquot?

  In case the analysis is performed, what will be the use of the data in solving the original problem?

  Both questions should be considered "a priori". In addition however, the analyst is often faced with already existing sets of data and then has to decide whether it would make sense to add his own effort to it. Here an "a posteriori" consideration is necessary.

  In both cases the judgement should be based on a number of criteria which are, in principle, of three different natures: analytical, occupational and financial.

  Analytical criteria comprise:
  - Sensitivity;
  - Blank value;
  - Matrix effects;
  - Chemical yield;
  - Accuracy;
  - Precision;
  - Limits of decision, detection and determination;
  - Turn-over time;
  - Capacity.

  Occupational criteria deal with health burdens of various kinds, including radiation doses. Financial criteria have to do with the cost per datum and the long term investments.

  Most of these criteria overlap considerably. One could for instance define the turn-over time as a financial feature in cases where the data are needed urgently, only to find that its reduction entails a substantial increase of the radiation burden.

- In addition to the mentioned criteria, there are factors which cannot be quantified properly.

The application of radioanalysis is relying heavily on nuclear reactors which are available at a few places only. The total number of nuclear reactors which can be applied in radioanalytical practice did, in 1980, not exceed 80. Of these, about 20 are in the European Community, and another 20 in the USA and Canada.
This implies that the samples have to be sent to one of a few nuclear centra to be analysed there. By the same token these determinations are off-line and thus tend to aim at some faraway goal like trend-setting rather than at rapid back-coupling to an industrial process. This sets a considerable barrier to the use of radioanalysis. In addition, the large majority of these reactors and nuclear centres are owned by governments or universities; the number of purely industrial reactors does not exceed 5. Thus radioanalysis is primarily a government or university-controlled activity. This is reflected by the affiliations of the scientists who participate in international scientific meetings on radioanalysis: Less than 10% are from industry.
As the control of the environment is a concern of governments primarily, it is understandable that the relative importance of radioanalysis in this field is rather large. It is equally logical that the emphasis has been on the determination of distribution patterns and ranges of "normal" concentration-values for the trace elements. Preferably the analysis is performed purely instrumentally for a number of elements simultaneously. The latter feature is not only the main attraction for government-sponsored work. It is likely to provide a future for activation analysis as a tool for "in situ" industrial analysis, based on small reactors like the "Slowpoke", developed by the AEC of Canada.
Thus, the consideration of the analytical criteria often boils down to one question only: "Is it possible to perform the analysis purely instrumentally?"

- Viewed from this angle, the scope of environmental radioanalysis on the matrices mentioned in chapter 1 may be condensed to:
  - o From 10 to 40 elements by instrumental neutron activation analysis.
  - o Uranium analysis by the delayed neutron technique.
  - o Up to 10 elements by prompt capture γ-ray measurements.
  - o Up to 10 elements in thin aliquots by PIXE.

Added to this come the radiotracer experiments.

6.2. Sensitivity

- The sensitivity should always be determined experimentally as the specific count-rate under well defined conditions of irradiation and measurement. Calculations based on equation (2.8) may only serve as an estimate.

  Even when based on experimental observations, the sensitivity may be used only to estimate the theoretical limits of determination, based on Poisson-statistics of the isolated (radio)nuclide. In practice these limits may be approximated only if a rigorous chemical separation is applied. In case of instrumental analysis the limitations set by the compton-background and the maximal acceptable sample-weight, due to geometry or total count-rate considerations, will invalidate the naive conclusions.

  From this it follows that one should use published data on specific count-rates only if they are based on experiments and then solely as a first estimation.

6.3. Blank value

- Blanks of four different origins limit the applicability of radio-analytical techniques:
  - Natural background and noise;
  - Stray radiation;
  - Compton-continuum;
  - Sample contamination.

- Natural background and noise effects all measurements. In practice however, it is of primordial importance only in the assay of natural radioactivity. Figure 6.1. gives the background γ-ray spectrum in the region 0-2 MeV for a 100 cm^3 coaxial Ge(Li) detector, shielded with 5 cm "old" (i.e. ^{210}Pb-free) lead, lined with 1 mm Cd and 1 mm Cu and surrounded by an inner shield of 10 cm "old" lead. The detector is mounted on a rubber math to reduce vibrations and surrounded by polystyrene foam to reduce noise. The visible photopeaks are due to ^{40}K and the $^{235/238}$U and ^{232}Th-series [1].

  Detector shields range from 0.5 to 50 tons depending on the choice of the shielding material and the application. Preferably, the detector-array is situated in a room with potassium-low concrete walls. If a sample-changer is used there should be a good shielding and/or a considerable distance between the detector and the sample-storage. Figure 6.2. gives the array around a $100\,cm^3$ well-type coaxial Ge(Li) detector. The natural background of a well-shielded Ge(Li)-detector usually amounts to $10^{-2} - 10^{-1}$ $c(min)^{-1} \cdot (keV)^{-1}$ depending on the energy.

In the (few) cases that integral counting is applicable, the optimal threshold-setting follows from elementary statistical considerations: If the count-rate of the sample is a and that of the background b $c.min^{-1}$, the expression $\frac{1}{a}(1 + \frac{2b}{a})$ should be made minimal.

- Stray radiation from the irradiation facility is the major source of natural background in the case of neutron-induced prompt capture γ-rays. Neutrons are scattered by the guide-pipe and the shielding.
  In the determination of uranium by delayed neutron counting one encounters the same problem. Again one should try to minimize the function $\frac{1}{a}(1 + \frac{2b}{a})$, as far as this is permitted by practical conditions.
- Compton-continuum Although the compton-continuum is due to the counting-aliquot itself it acts, from a practical point of view, as a blank value which has to be subtracted. The substantial improvement in γ-ray spectrometry due to the introduction of the coaxial Ge(Li) detector is demonstrated by fig. 6.3 [2]. Both the peak/compton-ratio and the peak-width have improved by a factor of ten.
  If a further reduction of the compton-continuum is needed there are, in principle, three ways:
  - o The use of an anticoincidence compton-shield. This array is an expensive solution but it reduces the compton-continuum by a factor of ten. Figure 6.4 gives the principle of the counter while figure 6.5 displays the γ-ray spectra obtained for a basalt sample in the normal (coincidence) and the anticoincidence mode [2].
  - o The influence of the compton-continuum may be reduced somewhat further by the use of a planar Ge(Li) detector due to the better resolution of these detectors, if at the price of a substantially longer counting-time. In practice this only pays off below $\leq$ 200 keV.
  - o Alternatively one may apply chemical separation, either of the single element or of a group. Figure 5.4 of chapter 5 demonstrates the effect of collecting chelated trace elements on active carbon.

Sample contamination is an obvious source of blank. Next to the effect of the pre-irradiation treatment, the counting aliquot may be

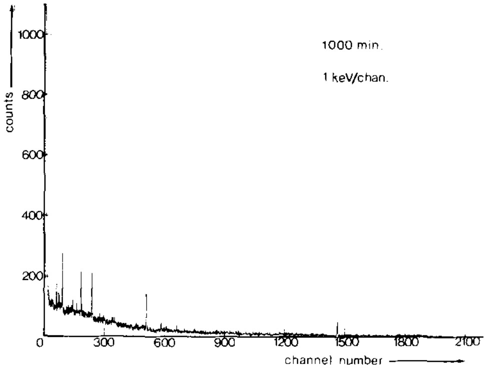


Figure 6.1. (Ref. [1]).

The background γ-ray spectrum in the region 0-2 MeV for a 100 cm^3 coaxial Ge(Li) detector, shielded with 5 cm "old" lead, lined with 1 mm Cd and 1 mm Cu and surrounded by an inner shield of 10 cm "old" lead.

The photopeaks are due to ^{40}K and the $^{235/238}U$ and ^{232}Th-series.

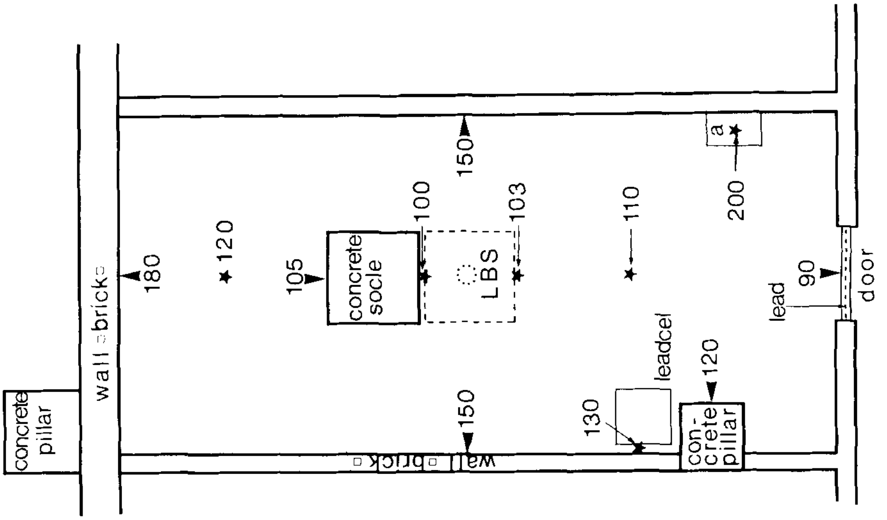


Figure 6.2. (Ref. [1]).

The array of a 100 cm^3 coaxial Ge(Li) detector, ("LBS").
The numbers indicate the relative total background level.

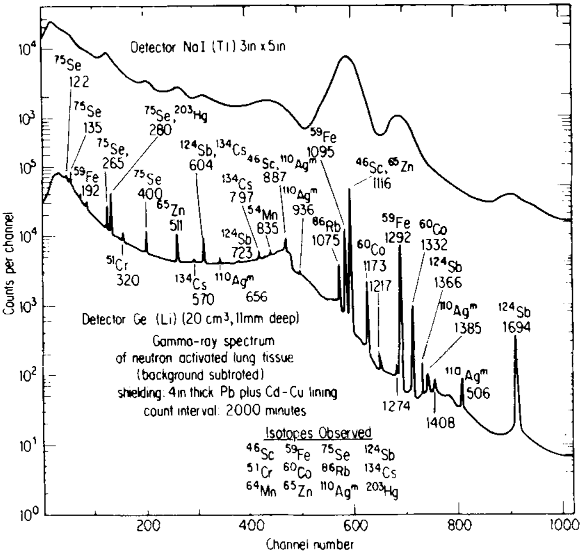


Figure 6.3. (Ref. [2]).

Comparison of the typical resolution in gamma spectra of a neutron-irradiated sample counted with a NaI(Tl) (top curve) and a Ge(Li) detector (bottom curve).

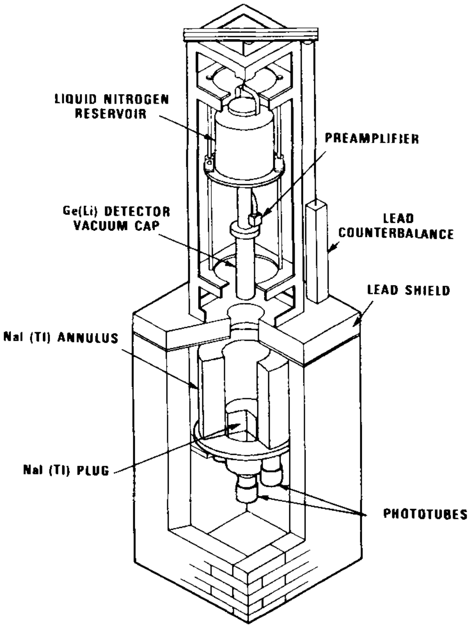


Figure 6.4. (Ref. [2]).

A schematic diagram of coincidence and non-coincidence [Ge(Li)-NaI(Tl)] systems

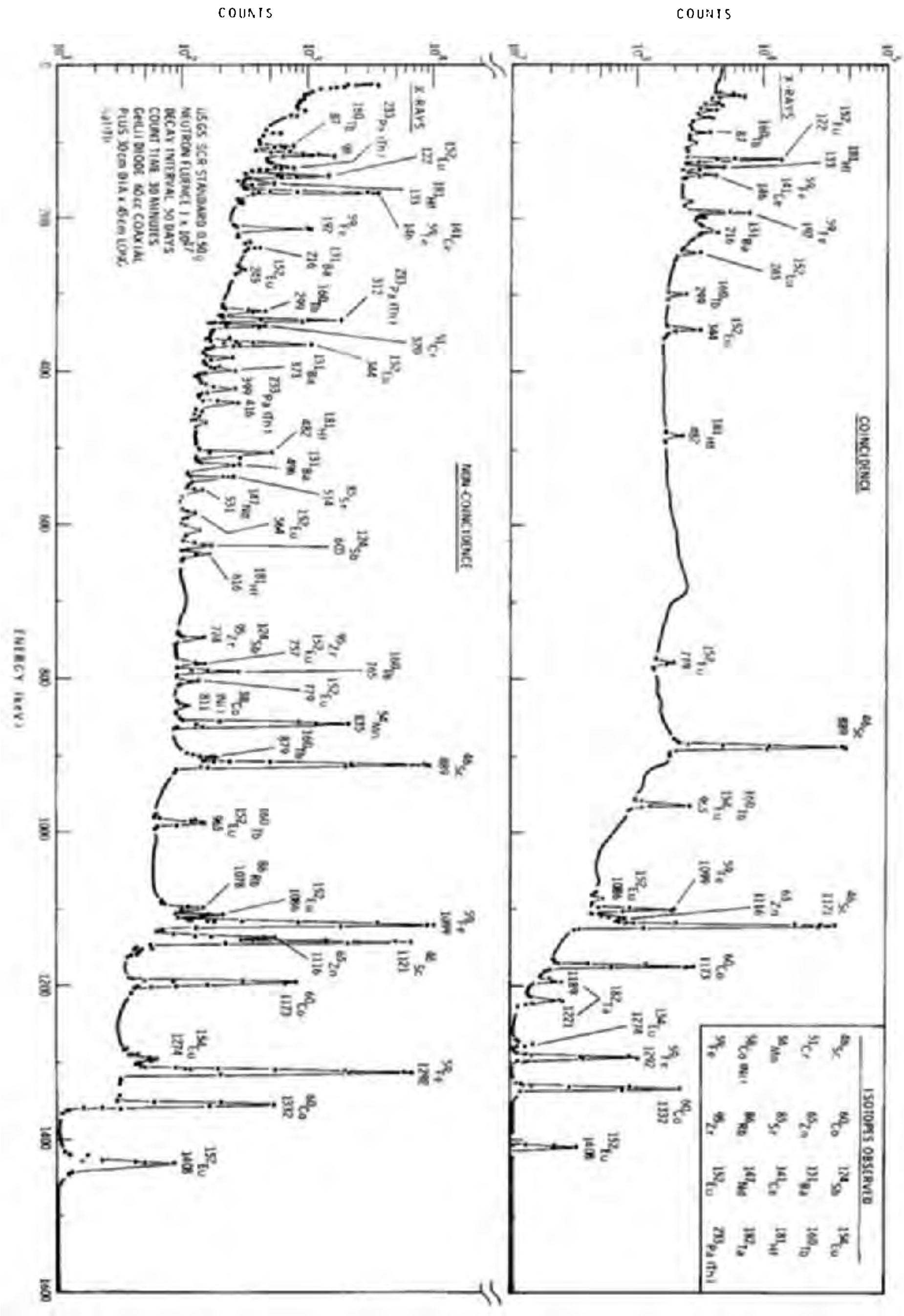


Figure 6.5. (Ref. [2]).

Ge(Li) γ-ray spectra of the long-lived radionuclides in a basalt sample, irradiated with thermal neutrons.

Top : Coincidence between Ge(Li) and NaI.

Bottom: Anti-coincidence.

contaminated by radioactivity from the container material or cross-contamination during handling in a lead-cell or glove box.

6.4. Matrix effects

- One of the outstanding advantages of radioanalysis is its relative insensitivity towards matrix composition. Self-absorption of neutrons may in general be neglected for samples taken from the environment. This small effect may be estimated from equations (2.5) or (2.23). They cancel out if the aliquots for standards and samples are identical.
- Self absorption during measurement is the next obvious phenomenon. Its extent can be measured by spiking an aliquot with a radionuclide which features a number of γ-rays in the low energy region, like ^{133}Ba [3], or by using an X-ray tube [4]. It appears that the effect becomes important below ∿ 100 keV. Again, if the counting aliquots for samples and standards are made exactly equal and the counting position is defined equally well, it is possible to extend γ-ray spectrometry till below 50 keV.
- The variation of counting geometry with the mass of the aliquot can be determined experimentally. Often only the height of the (cylindrical) aliquot varies as the counting vials contain more or less sample material. Then the empirical relation between count-rate (c) and mass of aliquot (G) is of the type

$$\frac{1}{c} = k_1 + \frac{k_2}{G} \qquad (6.1.)$$

were the constants k_1 and k_2 can be determined by linear curve-fitting.

- Finally, the influence of the total dead-time fraction and of pile-up should be mentioned. Although automatical correction of dead time is applied in any modern γ-ray spectrometer, there is a residual systematic bias if short-lived radionuclides are measured, i.e. if the ratio preset measuringtime/half-life exceeds ∿ 0.1 [5,6]. Pile-up correction requires a pulser (cf. 2.3).

6.5. Chemical yield

- Irradiation may cause losses of certain volatile elements, notably mercury and the halogens, which eventually may penetrate into or through the container material. This is probably due to the production of the elemental state by Szilard-Chalmers reactions. Thus the intensity of this phenomenon depends on the specific surface area of the sample material and on the permeability of the capsule material. The effect should be measured for the irradiation facility involved by standard addition of the chemical species which are probably present.

- The inevitable side-effect of a chemical separation is a chemical yield of limited constancy. The average value will act as a systematic error which can be corrected for. The residual variation will add to the statistical error. The procedures described in literature can be judged by considering their precision and variation with parameters like pH, contact-time, mode of stirring, filtration-rate etc.

6.6. Accuracy and precision

- The total error in quantitative radioanalysis can be defined in terms of the standard deviations in the various quantities involved. Here, INAA based on equations (2.1 - 2.18) is taken as an example; the situation for PIXE based on (2.25) is analogous.
- The main source of error is the peak-area evaluation. The problem in its simplest form is summarized in figure 6.6. The begin and end-channel are defined by the properties of the counting-system. They may be detected by the steepness of increase and decrease of the channel-content or by way of the peak-top position and the known resolution of the detector. The generally applied linear interpolation will result in a systematic error represented by B_{extr}. If one neglects this phenomenon, the ensuing standard deviation follows from the formula given in table 6.I. It should be noticed that here and in the following tables of this chapter the concentration is defined as a fraction, f, of the aliquot-mass.

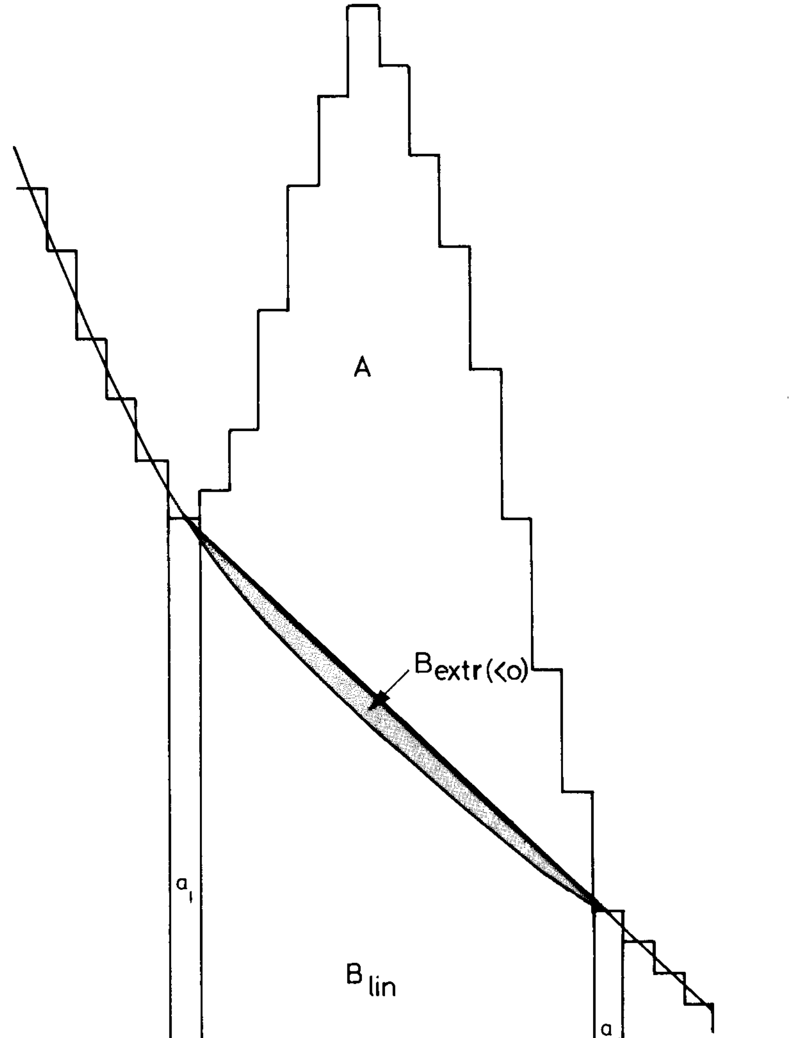
  The statistical error is governed by:

  The "minimal" relative uncertainty $(\sigma_{rel})_o$ associated with the net number of counts.

  The ratio a/b = (specific) count-rate under the peak/(specific) count-rate of the compton-background.

  The concentration, f, expressed as a fraction.

  When the systematic error due to B_{extr} is considered, the formulae



AREA DETERMINATION FOR A SINGLE PHOTOPEAK from table 6.II apply. Now the quantity $y = B_{extr}/B_{lin}$ as well as its relative standard deviation $\sigma_{rel}(y)$ govern the statistical error. The latter parameter stems from the fact that y has to be determined experimentally.

If the photopeak is interfered the total statistical variance in the final result will be composed of that due to background subtraction and that from peak-separation. For a given calculation-procedure the latter follows if the peak-shape, channel-width and total number of counts are known. It is good practice however to test the programme experimentally, preferably against other options. More in particular, the comparison of a programme based on a simple algorithm, like the ratio of the contents of adjacent channels, to a (semi-)gaussian fitting is of practical interest. The simple programme will be less costly and should be applied whenever possible (cf. section 7.3).

Table 6.I

Peak-area determination of a single photopeak by linear interpolation in the case of a linear compton-background

The total content, T, of the energy-interval is

$$T = A + B \qquad (6.1)$$

A = peak-area

B = compton background

One computes B as

$$B = \frac{N}{2} \cdot (T_1 + T_N) \qquad (6.2)$$

where N = number of channels and T_i=content of channel i. From this it follows that

$$\sigma(B) = \frac{N}{2} \cdot (T_1 + T_N)^{\frac{1}{2}} = (\frac{N}{2} \cdot B)^{\frac{1}{2}} \qquad (6.3)$$

Combination of (6.1) and (6.3) yields for the absolute standard deviation in the net peak-area:

$$\sigma(A) = [A + (1 + \frac{N}{2}) \cdot B]^{\frac{1}{2}} \qquad (6.4)$$

Thus $\sigma_{rel}(A)$, the relative standard deviation in A, is given by:

$$\sigma_{rel}(A) = \frac{1}{A^{\frac{1}{2}}} \cdot [1 + (1 + N/2) \cdot B/A]^{\frac{1}{2}} \qquad (6.5)$$

or

$$\sigma_{rel}(A) = \frac{1}{\left|a \cdot t_m \cdot (\frac{1-e^{-\lambda t_m}}{\lambda t_m})\right|^{\frac{1}{2}}} \cdot \left[1 + (1 + N/2) \cdot b/a\right]^{\frac{1}{2}} \qquad (6.6)$$

where

t_m = measuring-time [min], λ = decay-constant [min^{-1}] and a and b are

Table 6.I continued

the count-rates [c.min^{-1}] under the peak and the compton-continuum in the energy-interval involved.

- We now introduce the specific count-rates a_{sp} and b_{sp} by means of equations (6.7) and (6.8).

$$a = a_{sp} \cdot f \cdot G \qquad (6.7) \qquad\qquad b = b_{sp} \cdot G \qquad (6.8)$$

with f = fractional concentration of the trace constituent [g.g^{-1}] and G = mass of aliquot [g].

We abbreviate $\frac{b_{sp}}{a_{sp}} = x$. One should realise then, that $A/B \equiv x/f$.

Furthermore we write

$$(\sigma_{rel})_o = \left[a \cdot t_m \cdot \left(\frac{1-e^{-\lambda t_m}}{\lambda t_m} \right) \right]^{-\frac{1}{2}} \qquad (6.9)$$

where $(\sigma_{rel})_o$ denotes the minimal relative standard deviation, associated with the observed net peak-area. Then equation (6.6.) transforms into

$$\frac{\sigma_{rel}(f)}{(\sigma_{rel})_o} = \left[1 + (1 + N/2) \cdot \frac{x}{f} \right]^{\frac{1}{2}} \qquad (6.10)$$

as one may set $\sigma_{rel}(f)$ equal to $\sigma_{rel}(A)$. Thus the influence of N, x and f on the ratio $\sigma_{rel}(f)/(\sigma_{rel})_o$ can be computed.

Table 6.II

Peak-area determination of a single photopeak by linear interpolation in the case of a non-linear compton-background

- As in table 6.I on has

$$T = A + B \tag{6.1}$$

We now define B as

$$B = B_{lin} + B_{extr} \tag{6.11}$$

in accordance with figure 6.6. The area B_{extr} is - erroneously - added to the net-peak. Equations (6.4.) and (6.6.) now change into

$$\sigma(A + B_{extr}) = \left[A + B_{extr} + (1 + N/2) \cdot B_{lin}\right]^{\frac{1}{2}} \tag{6.12}$$

$$\sigma_{rel}(A + B_{extr}) = \frac{\left[1 + \frac{x}{f} \cdot y\right]^{\frac{1}{2}}}{\left[a \cdot t_m \cdot \left(\frac{1-e^{-\lambda t_m}}{\lambda t_m}\right)\right]^{\frac{1}{2}}} \cdot \left[1 + (1 + N/2) \cdot \frac{x/f}{1 + \frac{x \cdot y}{f}}\right]^{\frac{1}{2}} \tag{6.13}$$

where a, t_m and λ have the same meaning as in table 6.I while $x = \frac{B_{lin}}{A} = \frac{m b_{lin}}{a}$, the ratio of the count-rates in the peak and the linear-part of the compton-continuum and $y = b_{extr}/b_{lin}$, the corresponding ratio for the two parts of the compton-continuum.

- The peak-area obtained is subject to a bias. Its relative (fractional) value, Δ_{rel}, is defined by equation (6.14).

$$\Delta_{rel} = 1 + \frac{x \cdot y}{f} \tag{6.14}$$

One may try to correct for this systematic error using experimentally determined values of x and y.

As these values are of a limited precision only, this procedure will cause an additional statistical error. Using the abbreviation $\sigma_{rel}(A+B_{extr}) = \sigma_{rel}$, the total relative standard deviation in the corrected result will then become

Table 6.II. (continued)

$$\Sigma\sigma_{rel}(A) = \left[(\sigma_{rel})^2 + \frac{x \cdot y}{1 + x \cdot y} \cdot \left\{\sigma^2_{rel}(x) + \sigma^2_{rel}(y)\right\}\right]^{\frac{1}{2}} \qquad (6.15)$$

Introduction of the quantities a_{sp}, b_{sp} and $(\sigma_{rel})_o$ by equations (6.7) - (6.9) and setting $\Sigma\sigma_{rel}(f) = \Sigma\sigma_{rel}(A)$ leads to

$$\frac{\Sigma\sigma_{rel}(f)}{(\sigma_{rel})_o} = \left[\frac{f + (1 + N/2) \cdot \frac{fx}{f + xy}}{f + xy} + \frac{xy}{f + xy}\left\{\sigma^2_{rel}\left(\frac{x}{f}\right) + \sigma^2_{rel}(y)\right\}\right]^{\frac{1}{2}} \qquad (6.16)$$

Thus it is possible to calculate the ratio $\frac{\Sigma\sigma_{rel}(f)}{(\sigma_{rel})_o}$ as a function of N, x, y and f.

- The relative systematic bias, Δ_{rel}, can also be written in terms of of the x, y and f-values of sample (x) and standard (s):

$$\Delta_{rel}(f) = \left[\frac{f_x + (xy)_x}{f_s + (xy)_s} \cdot \frac{f_s}{f_x} - 1\right] \qquad (6.17)$$

One may define $\Delta_{rel}(f)$ as an excentricity

$$u = \frac{\Delta_{rel}(f)}{\Sigma\sigma_{rel}(f)} \qquad (6.18)$$

If a relative error of δ_{rel} is allowed, the chance that the experimental result lies in the $(1 + \delta_{rel})$ interval is determined by the excentricities u_1 and u_2, defined by

$$u_1 = u - \frac{\delta_{rel}}{\Sigma\sigma_{rel}(f)} \qquad (6.19)$$

and

$$u_2 = u + \frac{\delta_{rel}}{\Sigma_{rel}(f)} \qquad (6.20)$$

This is illustrated by figure 6.7.

- The subtraction procedure affects the accuracy of the peak-area determination in two ways:
  - o The limits of the peak energy-interval as determined by a computer-programme may vary with the ratio B/A = compton background/net peak area.
  - o The non-linear variation of the compton-continuum causes a B_{extr} and thus a systematic bias.

  The first source of error can, in general, be neglected if the statistics of the measurement are sufficient. At a B/A-ratio of < 5 and a ratio σ/ω = (peak standard-deviation/channel-width) of 3, the systematic error is less than 0.5%, (cf. table 6.III).

  The influence of B_{extr} is defined in table 6.II. It should be realised that the ratio $y = B_{extr}/B_{lin}$ cannot be determined exactly as one has to rely on tentative interpolations.

  As with the statistical error, the systematic bias may be enlarged substantially in the case of peak-separation applied to multiplets. Experimental tests are mandatory here. First synthetic spectra should be processed, then a real one which features both single photopeaks and multiplets of various degrees of complexity (cf. section 7.3). The effect of a systematic bias can be visualized in terms of figure 6.7. The chance that the result of the determination will fall in the $(1 \pm \delta_{rel})$ range, is determined by the excentricities u_1 and u_2, defined in table 6.II.

- The contribution to the standard deviation and the systematic bias by the other factors in equations (2.16 - 2.18) and (2.25) can be kept small in comparison to that of the peak-area determination. In the case of neutron activation analysis, the determination is based on the measurement of 4 spectra and thus on 4 photo- and 4 pulserpeaks:
  - o 2 photopeaks of the radionuclide in the standard and the sample-spectrum;
  - o 2 photopeaks of the flux-monitors;
  - o a pulserpeak for each of the 4 spectra.

  The statistical error in the photopeak of the standard may be reduced considerably by repeated analysis of different standard aliquots. The variation in the weight of the annular (∿ 25 mg) iron fluxmonitors, used at ECN, is < 0.3%; the standard deviation due to counting-statistics

Table 6.III

Accuracy of automatic peak-area determinations of gaussian-shaped peaks

- The spectrum can be approximated by the combination of a gaussian and a linear background. Then the channel-content can be described as a function of the energy E by (6.21) in which E_o is the original photon-energy

$$T(E) = T_o \cdot e^{-(E-E_o)^2/2\sigma^2} + a - b(E-E_o) \qquad (6.21)$$

This continuous function is measured with a channel-width ω keV. If the channels are counted form the peak-top, equation (6.21) transforms into (6.22), with n = channel-number. The $\pm$ sign refers to the left (+) and right (-) sides of the peak.

$$T(n) = T_o \cdot \omega \cdot e^{-\frac{n^2\omega^2}{2\sigma^2}} + [a \pm n\omega b]\,\omega \qquad (6.22)$$

- In principle, there are two criteria to find the peak-position and peak-extent: $\frac{\partial T(n)}{\partial n} = o$ and $\frac{\partial^2 T(n)}{\partial_n 2} = o$. Both expressions depend on the dimensionless groups a/T_o, $b\sigma/_a$ and σ/ω. The first criterion leads to the total peak-width, the second to its σ-value. In practice one has to allow for a certain interval around zero due to the finite channel-width and the limited counting-statistics.

  Instead of the first derivative, one may use the criterion $T_n/T_{n+1} \geq 1 + \delta$, where δ is either fixed, somewhere around $5 \cdot 10^{-2}$, or equal to $3(T_{n+1})^{-\frac{1}{2}}$.

  The use of the second derivative implies the scanning of the spectrum with a rectangular wave-function, as described in ref. [7].
- The use of the ratio-criterion $T_n/T_{n+1} \geq 1 + \delta$ is sufficient for single peaks. At the usual conditions of $\omega/\sigma \simeq 1/3$, $b.\sigma/a \simeq 10^{-2}$ and $a/T_o \simeq 5$ one arrives, for $\delta = 0.05$, at a systematic bias of less than 2% which is usually negligible in comparison to the total relative standard deviation in the peak-area determination (cf. equations (6.19) and (6.20)). Similar criteria may be developed for multiplets. Thus the computer-programme REKEN, developed at ECN, is capable of covering more than 90% of all coaxial Ge(Li) spectrometry by applying simple ratio-criteria

Table 6.III (continued)

[8]. The obvious advantage of this procedure is in the low computer-costs. However, it is necessary to have a more sophisticated programme available for the low-energy region, like encountered in PIXE, or for the resolution of difficult multiplets. Such programmes are based on fitting-procedures. Good examples of these programmes are given in refs. [7] and [9].

In any case the use of a large off-line computer is mandatory if the programmes are to be applied routinely. A survey of current programmes is given in ref. [10]. It should be realised that any peak-separation procedure causes an error which adds to those defined in tables 6.I and 6.II.

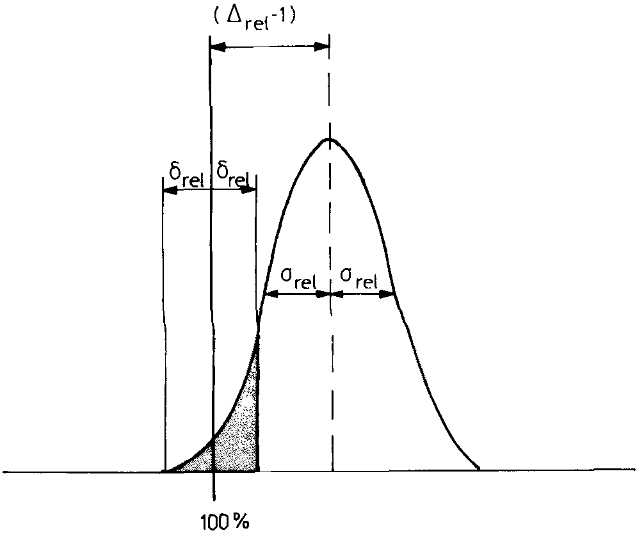


Figure 6.7. (Ref. [1]).

Accuracy and bias

and peak-subtraction is < 0.5% for the monitors.

If a 50 Hz pulser is used and if the peak is situated in the "flat" high-energy part of the spectrum, the total standard deviation in the net pulser peak area is < 0.2% while the systematic bias can be neglected.

The total relative standard deviationin the concentration, calculated by means of equation (2.18), due to peak-area determinations, can now be approximated along the lines given in table 6.IV. Thus it is possible to estimate the total relative standard deviation as a function of $x = \frac{sp}{a_{sp}}$ and f. Figures 6.8 and 6.9 illustrate this. These calculations may be used for "a priori" estimations. Situations which look feasible should then be tested experimentally. Table 6.V gives the case of the determination of iron by the 1292 keV photopeak of ^{59}Fe ($T\frac{1}{2}$ = 45 d) in various Standard Reference Materials. It can be seen that occasionally the experimental data may be appreciably different from the predictions.

- Standards and samples should be of identical size to avoid systematical errors. This may be achieved by using standards based on active carbon or another suitable inert support.

  Table 6.VI summarizes the error-budget for the system of instrumental neutron activation analysis, based on relative measurements, separately processed standards and annular iron flux-monitors. It is necessary for each laboratory to set up such a list.

6.7. Limits of decision, detection and determination

- Following the approach of Currie [14] it is possible to define limits of decision, L_C, detection, L_D, and determination, L_Q [15].

  All three criteria may be expressed in terms of counts, of the mass of the element to be determined or in terms of the concentration.

- The case of the limit of decision, L_C, is considered in table 6.VII. It is of practical interest only if the ratio $y = B_{extr}/B_{lin}$ and its standard deviation are known. Then it is possible to use the background-data to define a concentration which may be taken as an upper level with a certain probability.

- The limit of detection, L_D, is obtained by adding another safety barrier to L_C. Table 6.VIII gives the formulation.

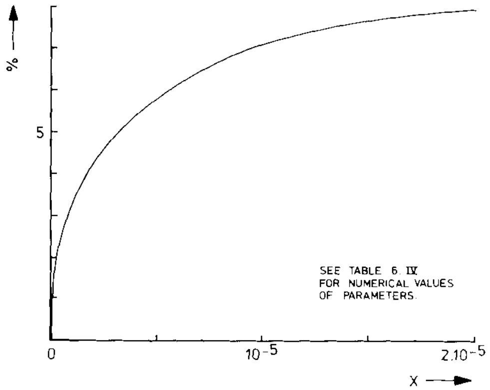


FIG. 6.8 THE TOTAL RELATIVE STANDARD DEVIATION AS A FUNCTION OF THE RATIO OF THE SPECIFIC COUNTRATES IN THE COMPTON-BACKGROUND AND THE PHOTO PEAK (X).

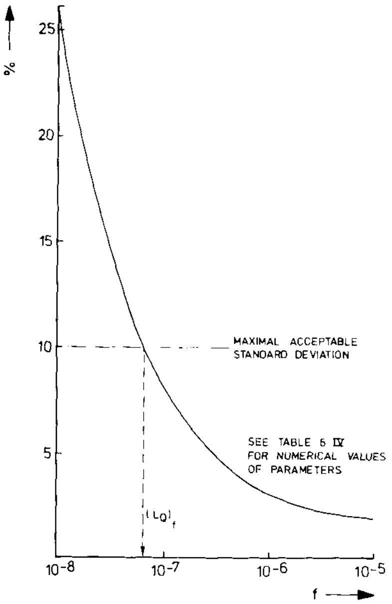


FIG. 6.9 THE TOTAL RELATIVE STANDARD DEVIATION AS A FUNCTION OF THE CONCENTRATION IN $\mu g \cdot g^{-1}$.

Table 6.IV

Total relative standard deviation in gamma-ray spectrometry of single peaks

- To the total relative standard deviation, defined in tables 6.I and 6.II, the corresponding error in the standard is added. If the (similar) standards have been counted separately (n-times), the total variance becomes $(1 + \frac{1}{n}).\Sigma^2_{rel}(f)$.
- The contribution by the fluxmonitors stems from the variation in their weight. With a σ_{rel} of 0.4% the added variance is $\simeq 5 . 10^{-5}$ or $\simeq 0.5(\%)^2$.
- The four 50 Hz pulserpeaks for sample, standard and their flux-monitors add a variance of $(3000. t_m)^{-1}$ each, where t_m = measuring-time in minutes.
- A estimate of the total error may be obtained easily now. Let Fe denote the flux-monitor. A not unusual case is now that:

$f = 10^{-6}$ (= 1 ppm)
$y = 5 . 10^{-2}$
t_m for samples and standards = 100 min
$(t_m)_{Fe}$ = 10 min
N = 10
n = 10
$(\sigma_{rel})_o = 10^{-2}$ (10^4 counts net)
$((\sigma_{rel})_o)_{Fe}$ for the fluxmonitor = $3 . 10^{-3}$ (10^5 counts net)
$x_{Fe} = 5 . 10^{-2}$
$y_{Fe} = 10^{-2}$
$\sigma_{rel}(\frac{x}{f}) = 5 . 10^{-2}$
$\sigma_{rel}(y) = 5 . 10^{-2}$
$\sigma_{rel}(x)_{Fe} = 5 . 10^{-2}$
$\sigma_{rel}(y)_{Fe} = 5 . 10^{-2}$

Figure 6.8. gives the total relative standard deviation in the determination as a function of x.

- For $x = 10^{-6}$, $y = 0$ and $A = 10^4$ counts collected at $f = 10^{-6}$ (1 ppm), the total relative standard deviation varies with f as shown in figure 6.9.

Table 6.V The determination of iron in some Standard Reference Materials

Material	Concentration found	Total relative error observed	Standard deviation calculated	Certified (or literature) value of f
Animal muscle IAEA H-4	45 ± 1 $\mu g.g^{-1}$	2.2 %	10.8 %	(43-49) [11]
Bowen's kale	117 ± 3	2.6	4.7	(103-118) [12-13]
Pine needles NBS SRM 1575	170 ± 10	5.9	3.5	200 ± 10
Orchard leaves NBS SRM 1571	285 ± 5	1.8	2.4	300 ± 20
Bovine liver NBS SRM 1577	293 ± 8	2.7	2.4	270 ± 20
Spinach NBS SRM 1570	557 ± 8	1.4	1.8	550 ± 20
Tomato leaves NBS SRM 1573	706 ± 12	1.7	1.7	690 ± 25
Animal bone IAEA A-3/1	1300 ± 50	3.9	1.5	(1520)
Animal blood IAEA A-2	2980 ± 50	1.7	1.4	-

Table 6.VI Error budget for instrumental neutron activation analysis based on gamma-ray spectrometry

Quantity	Statistical error	Systematic bias
Concentration of the standard	$\leq$ 0.01 %	-
Weight of standard	< 0.1 %	-
Weight of sample	< 0.1 %	Depends on lyophilization procedure. Usually $\leq$ 1 %
Geometry	< 0.5 %	None if volumes are equal
Irradiation-time	< 0.1 %	-
Decay-time	< 0.1 %	-
Counting-time	< 0.1 %	-
Peak-area of sample	1-10 %	Usually $\leq$ 5 %
Peak-area of standard	∿ 1 %	-
Peak-area of iron flux-monitor	< 0.5 %	-
Peak-area of pulser peak	< 0.5 %	-
	3-10 %	$\leq$ 5 %

Table 6.VII The limit of decision, L_C

The value of L_C depends on the standard deviation in the linearly interpolated background, B_{lin}, and on that in the correction-term, B_{extr}. It is defined by equation (6.23) where k_α is the abcissa of the standardized normal distribution corresponding to the probability level $(1-\alpha)$, with α as the accepted error of the first kind.

$$L_C = k_\alpha \{\sigma (B_{lin}) + B_{lin} \cdot \sigma (y)\} + |y| \cdot B_{lin} \tag{6.23}$$

As was derived in table 6.I, linear interpolation between the begin- and end-channel leads to

$$\sigma (B_{lin}) = (\frac{N}{2} \cdot B_{lin})^{\frac{1}{2}} \tag{6.2}$$

Furthermore, $\sigma(y)$ may be written as $y.\sigma_{rel}(y)$. Thus

$$L_C = k_\alpha \left(\frac{N}{2} \cdot B_{lin}\right)^{\frac{1}{2}} + |y| \cdot B_{lin}\{1 + k_\alpha \cdot \sigma_{rel}(y)\} \qquad (6.24)$$

It is convenient to express L_C in terms of the mass, $(L_C)_m$, or the concentration $(L_C)_f$. The specific counting-result is denoted by A_{sp}.

$$(L_C)_m = \frac{L_C}{A_{sp}} \; [g] \qquad (6.25)$$

$$(L_C)_f = \frac{L_C}{A_{sp} \cdot G} \; [g.g^{-1}] \qquad (6.26)$$

Introducing $B_{lin} = (B_{lin})_{sp} \cdot G$ (6.27)

and

$$(B_{lin})_{sp} = (b_{lin})_{sp} \cdot t_m \qquad (6.28)$$

and

$$A_{sp} = a_{sp} \cdot t_m \qquad (6.29)$$

one obtains the L_C-quantities as a function of G and t_m. Thus

$$(L_C)_f = \frac{k_\alpha \, [N/_2 \cdot (b_{lin})_{sp}]^{\frac{1}{2}}}{t_m^{\frac{1}{2}} \cdot G^{\frac{1}{2}} \cdot a_{sp}} + |y| \cdot \frac{(b_{lin})_{sp}}{a_{sp}} [1 + k_\alpha \cdot \sigma_{rel}(y)] \qquad (6.30)$$

It should be realized that the choice of k_α is a matter of personal preference.

Table 6.VIII The limit of detection, L_D

The definition of L_D is:

$$L_D = L_C + k_\beta \cdot \sigma(\text{net signal})$$

or (6.31)

$$L_D = L_C + k_\beta \cdot \sigma(A + B_{extr})$$

Again, k_β is the abcissa of the standardized normal distribution, corresponding to a probability level $(1 - \beta)$.

The sum $(A + B_{extr})$ in the net peak is left by subtraction of a linearly interpolated background.

We rewrite equation (6.12), table 6.II as

$$\sigma(A + B_{extr}) = [A\{1 + (1 + \frac{N}{2}) \cdot \frac{x}{y} + \frac{xy}{f}\}]^{\frac{1}{2}} \tag{6.32}$$

Insertion of (6.24) and (6.32) into (6.31) yields (6.33).

$$\begin{aligned} L_D = {} & k_\alpha \, (\frac{N}{2} \cdot B_{lin})^{\frac{1}{2}} + |y| \cdot B_{lin}\{1 + k_\alpha \cdot \sigma_{rel}(y)\} \\ & + k_\beta[A \cdot \{1 + (1 + \frac{N}{2}) \cdot \frac{x}{f} + \frac{xy}{f}\}]^{\frac{1}{2}} \end{aligned} \tag{6.33}$$

As with L_C, it is possible to define $(L_D)_m$ and $(L_D)_f$. Furthermore it follows from (6.27) to (6.29) that in the limiting case of $f = (L_D)_f$ one has:

$$\frac{x}{f} = \frac{(b_{lin})_{sp}}{a_{sp}} \cdot \frac{1}{(L_D)_f} \tag{6.34}$$

Combination of (6.33) and (6.34) leads to an implicit equation for $(L_D)_f$. Rearrangement leads to a quadratic form in $(L_D)_f$ with a positive and negative root which can be solved easily.

The numerical value of L_D depends on the net contents of peak and compton-background as well as on their ratio.

- The limit of determination, L_Q, follows directly from the computation of the total relative standard deviation, given in table 6.IV. The formulation is summarized in table 6.IX. It is analogous to drawing the straight horizontal line of the maximal acceptable error in figure 6.9.
- Finally it should be stressed once again that the calculations of the limits as well as of the attainable precision and accuracy, although based on experimental data, have to be checked by repeated analysis of Standard Reference Materials. Moreover, the mentioned calculations do not include the influence of a blank, such as encountered in the analysis of aliquots collected on some support.

6.8. Turn-over time and capacity

- For the majority of the determinations by neutron activation analysis the decay-period governs the turn-over time, even if a chemical separation is applied. This sets a limit to the scope of neutron activation analysis, both in terms of speed and capacity.
  A decay-time of ∿ 3-5 weeks is usually applied before measuring the long-lived radionuclides.
  If use is made of a large facility which accepts up to 50 samples and which is loaded twice or thrice a week this means that up to 15 series may be processed simultaneously, be it in different stages. This is a heavy administrative burden.
  With 2-3 series of 50 samples per week and an average of 15 elements determined the output of an INAA laboratory could come at $\simeq 2.10^3$ data a week, but processing of data will stop this soon.
  In the case of pneumatic rabbit irradiations and subsequent measurement of short-lived radionuclides pretreatment, calculation, control and administration are the decisive steps. The same holds for delayed neutron counting and PIXE-based determinations. For prompt capture γ-rays the irradiation/counting-time is the limiting factor.
  The turn-over time is seldom shorter than ∿ 1 week while the capacity is usually smaller than 10^3 data a week for rabbit irradiations and ∿ 10^2 for capture γ-ray measurements. It should be noted that for

Table 6.IX The limit of determination, L_Q

The limit of determination is governed by the acceptable statistical error.

$$L_Q \geqq k_Q \cdot \sigma(\text{net signal}) \qquad (6.35)$$

Again, the value of k_Q is a personal preference and again one may express L_Q as $(L_Q)_m$ or $(L_Q)_f$.
Insertion of the identity

$$\text{Total } \sigma \text{ in } f = f.(\text{Total relative } \sigma \text{ in } f)$$

yields

$$\text{Total relative } \sigma \text{ in } f \leq 1/k_Q \qquad (6.36)$$

The value of the total relative standard deviation in f follows from the calculation outlined in table 6.IV.
The value of $(L_Q)_f$ is found by plotting the total relative error as a function of f and drawing the horizontal line corresponding to $1/k_Q$, like is done in figure 6.9.

short-lived radionuclides the capacity may be limited further by health-physics considerations.

- The output is small if compared to that of other analytical techniques like AAS. This presses for application in selected cases only. The obvious choices are instrumental multielement analysis of materials which are not easily dissolved, and the determination of a few selected elements for which radioanalysis is obviously the best technique. Thus one comes to a short list of topics as was already mentioned in 6.1.

6.9. Occupational criteria

The most conspicuous hazard in radioanalysis is the personal radiation dose. Although the average personal dose has decreased throughout the development of radioanalysis, potential risk has become more emphasized in recent years due to the growth of popular concern with radiation hazards.

Thus it is hardly feasible to perform routine analysis based on short-lived radionuclides in which considerable manipulation is involved. The determination of tungsten in silicate samples based on ^{187}W ($T\frac{1}{2}$ = 24 h) and post-irradiation chemistry [16] implies, if performed daily, a weekly dose of $\sim$ 50 mRem and is thus limited to a few weeks a year only.

The preconcentration of trace elements from seawater serves the same purpose in avoiding high dose-rates due to ^{24}Na ($T\frac{1}{2}$ = 15 h) and ^{38}Cl ($T\frac{1}{2}$ = 37 min). The determination of manganese in seawater became possible only after the development of a sufficiently pure scavenger to permit pre-irradiation concentration [17].

6.10. Financial criteria

- There are a few reactors only which are operated on a purely commercial base for the sake of radioanalysis alone. They are owned by large industries and primarily used for in situ production of radiotracers.

  The great majority of irradiation facilities however is subsidized by governmental or educational authorities and often designed

for other reasons like materials testing or isotope production. From this it follows that environmental radioanalysis is based on motives rather than on money.
It is, however, advisable to calculate going-rates for the routinized analyses.

- The price is built up from three parts: Sampling and pretreatment; irradiation and handling costs; man-hours and overhead. The data which pertain to the radiochemical laboratory of ECN are given in section 5.4 of the preceding chapter. It can be seen that, in 1981, purely instrumental routine analysis came down at ∿ $10 per element.

6.11. A practical case: The determination of vanadium in rainwater

- Application of the mentioned criteria should result in an analytical procedure which meets the requirements of the environmental project of which it has to make a part. The determination of vanadium in rainwater offers a good example of the approach to an optimal procedure.
- The analysis is based on the reaction $^{51}V(n,\gamma)^{52}V$ ($T_{\frac{1}{2}}$ = 3.8 min) and measurement of the 1434 keV γ-ray. It is purely instrumental. The available sample-volume is 2 ml.
  The limit of determination is controlled by the compton-continuum from ^{38}Cl mainly. Systematic errors stem form the -possible- blank and the residual influence of the total dead-time fraction. Following the approach of ref. [6] the latter effect is found to be $\leq$ 5%.
- The essential feature of the required procedure is a large capacity. Thus, it is necessary to compromise between speed and counting statistics and, so, precision.
  Table 6.X summarizes the two procedures which were developed. The "routine" analysis is useful for concentrations down to ∿ 0.5 $\mu g.l^{-1}$ while it gives an order of magnitude for the remaining samples. For most environmental scannings this is quite sufficient as < 0.5 $\mu g.l^{-1}$ is equivalent to "unpolluted". For a closer investigation of samples around 0.5 $\mu g.l^{-1}$ the slower "precise" procedure may be used.
  It can be shown that the latter conditions are optimal [18].
  Figure 6.10 gives the results obtained for rainwater from the province of North-Holland. The frequency-distribution is markedly skew,

the high values being caused by the samples taken in the vicinity of the state steel mills.

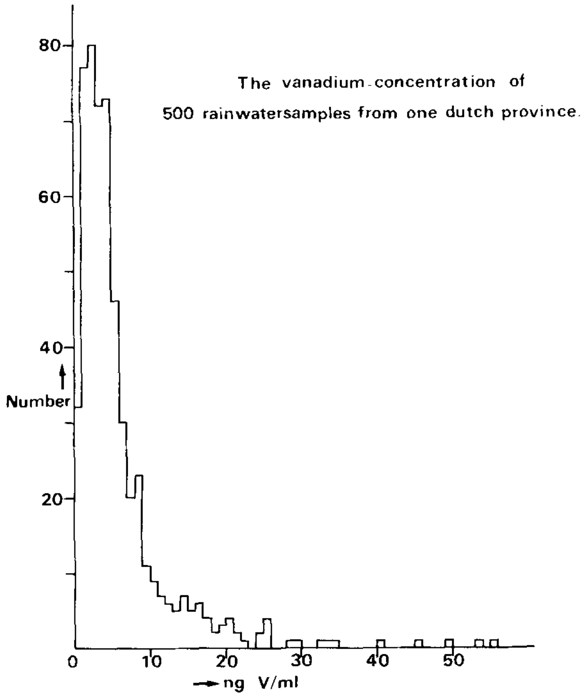


Figure 6.10. (Ref. [6]).

Table 6.X Two procedures for the determination of vanadium in rainwater by instrumental neutron activation analysis [6]

	"Precise" procedure	"Routine" procedure
Volume of aliquot	2 ml	0.5 ml
Irradiation-time	4 min	3 min
Decay-time	5 min	1 min
Detector and counting-equipment	90 cm^3 well-type coaxial Ge(Li)	40 cm^3 flat coaxial Ge(Li)
Counting-time	5 min	2 min
Geometry	in the well	on top of the detector
Mode of assay	Total area of the 1434 keV photopeak assuming a straight base-line. Comparison with standard solutions.	
Specific count-rate at the beginning of the measurement	2.3×10^2 $c.(ngV)^{-1}.min^{-1}$	1.6×10^2 $c.(ngV)^{-1}.min^{-1}$
Sensitivity	7.6×10^2 $c.(ngV)^{-1}$	3.2×10^2 $c.(ngV)^{-1}$
Time needed per determination	15 min	5 min
Number of determinations per hour	4	16-20 (irradiation is begun during counting of the previous sample)
Dose-rate per sample received on the hands	≤ 0.05 mR	≤ 0.1 mR

Neutron flux: $\Phi_{thermal}$ $5.10^{13} cm^{-2} s^{-1}$

$\Phi_{fast}/\Phi_{thermal} \simeq 0.1$

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CHAPTER 7.

PRACTICE OF ENVIRONMENTAL RADIOANALYSIS

SUMMARY

This chapter deals with the routing of radioanalysis and the requirements imposed by the radiochemical discipline. The implications of the irradiation facilities used are discussed. Some advices on the presentation of the data are given.

Finally a practical classification of ratiotracer experiments is considered.

7.1. The radioanalytical laboratory

- Radioanalysis implies the handling of "open" radioactive sources and thus of an adapted laboratory. Moreover, the environmental analyst is confronted with samples of a widely different nature which may eventually cause cross-contamination. This presses for an appropriate lay-out of the laboratory. Both requirements may be met, even on a modest space if a good understanding exists between the analyst and the technical service department(s).

- The laboratory has to contain the radioactivity and to be guarded against contamination and inrushing visitors by a sluice system. It should consist of the following units [1]:

  a. Lab-rooms

  These areas are kept at an underpressure of ≃ 4-5 mm water towards the corridor. At the same time they are guarded against in-flow of dust: The windows are single-paned and of double glass and cannot be opened; the air-inlet to the whole building or wing is by way of a filtration-system which eliminates particles of ≥ 5 μm diameter. The average residence time of the air is < 10 minutes. The floor is covered by a needless high-resistence plastic cover which bends up at the walls.
  The entrance is through a hall where the β-γ monitor is located and the white-coats are kept. A ~ 30 cm high threshold marks the entrance to the lab which can be closed effectively by sliding or turning doors. The hall also gives access to a sitting-room.

  The labs (fig. 7.1.) are equipped with an "island"-table, one or more fume-hoods, a lead-walled storage for small radioactive sources and various washing-units. It is mandatory to collect all water in a special tank for decontamination by decay, eventually followed by scavenging with $Fe(OH)_3$. Solid radioactive waste is collected in steel drums, liquid waste in various separate glass vessels to avoid unwanted reactions.

  At ECN a sequence of five separate labs of 7 x 9 m^2 and 3.30 m high each are used: they lie along a central corridor. In the first the irradiated aliquots arrive either by pneumatic tube or in a lead container for irradiations in batch-facilities (cf. section 7.2.).

Figure 7.1. Part of a radioanalytical lab-suite.

They may be stored in holes within a concrete shield. The lab is further used for dissolutions and subsequent chemical separations.
A second laboratory serves for the preparation of the aliquots for INAA, prompt capture γ-measurements or PIXE and of the accompanying standards of all matrices except dry biological material.
Another laboratory is used for radiotracer experiments on (chromatographic) separations.
Finally there are, at both extremities of the central corridor, the lab for radiotracer experiments with silicates and the dust-poor room. The latter is equipped with a double-door sluice (fig. 7.2.) and has no under-pressure towards the corridor. It features a laminar flow-box and an automatic semi-micro balance with punch-tape read-out and adjustable tarra.
The radiotracer lab for silicates contains the facilities for batch and column-experiments on leaching and adsorption.

b. A balance-room

At ECN the separate balance room is equipped with one or more fast mono-scale weighers and semi-micro balances. In addition it has an automatic semi-micro balance with punch-tape read-out and adjustable tarra. All instruments are placed on separate stone pedestals.

c. Counting-rooms

Three types of counting-rooms are used at ECN:

- ☐ Concrete shielded for routine INAA measurements (fig. 7.3.). The equipment comprises the central magnetic tape unit centre for storage and off-line processing of the γ-ray spectra from the various multichannel analyzers (cf. section 7.3.) a (home-made) sample-changer for solids and two more systems for liquid aliquots.

  A separate room houses a 90 cm^3 coaxial Ge(Li) well-type detector with a test-tube sample-changer (fig. 7.4.).
  The intrinsic Ge planar detector for low-energy region measurements on pelletized aliquots and accordingly equipped with a special sample-changer, has its own room due to the relatively high-activity of the counting-aliquots.
- ☐ A low-potassium concrete shield surrounding the counting-room for radiotracer measurements.

Figure 7.2. Sluice of the dust-free laboratory.

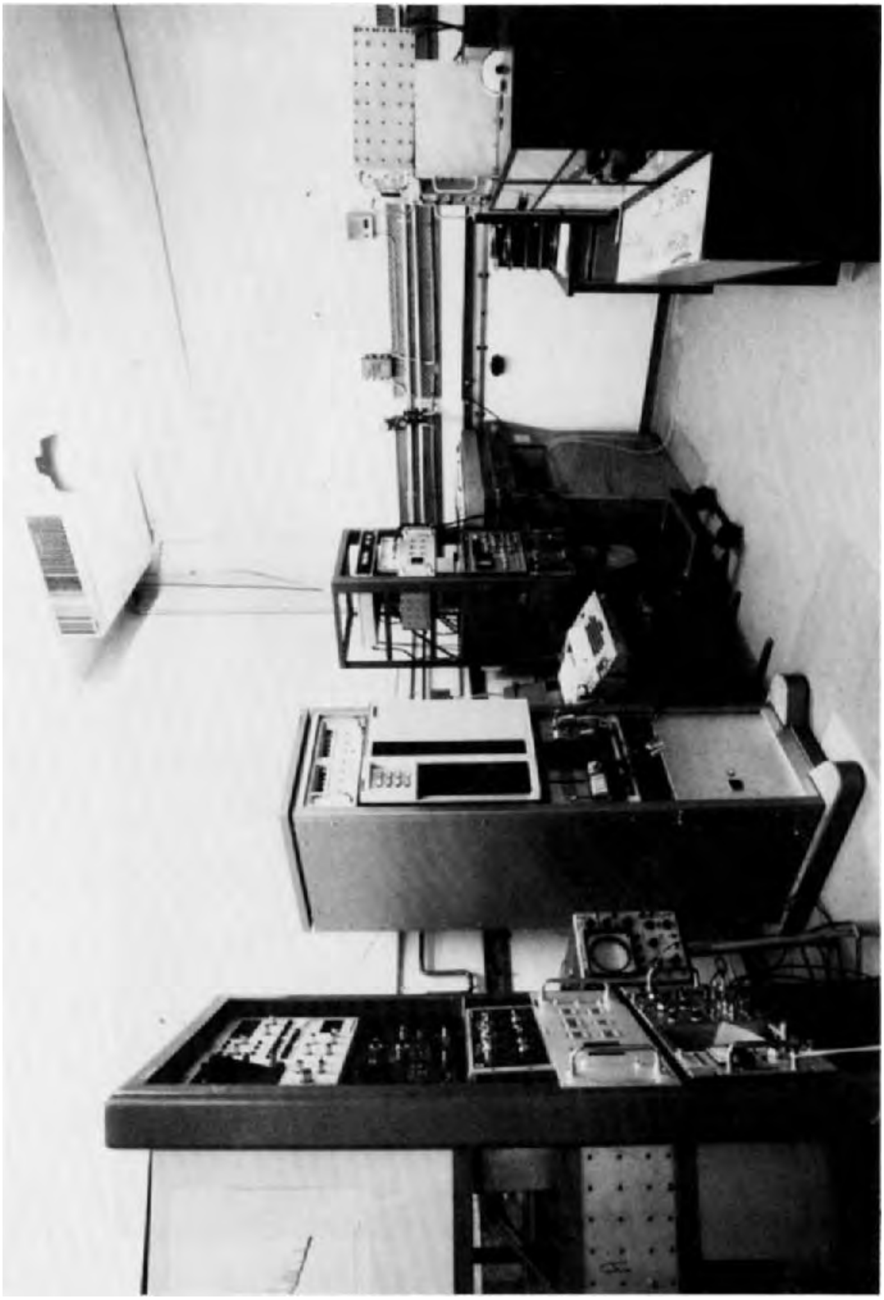


Figure 7.3. Concrete-shielded counting-room with the central magnetic tape unit in the middle and multi-channel analyzers with sample-changers.

Figure 7.4. Shield and test-tube sample changer of the well-type 90 cm^3 coaxial Ge(Li) detector.

- ☐ For special cases a low level counting-room, shielded with old lead and located far from the labs, may be used.

Counting equipment further includes coaxial Ge(Li) detectors in the range of 30-90 cm^3, solid and well-type NaI detectors, end-window and liquid-scintillator β-counters.
It is preferable to have both off and on-line spectra-processing available. All measurements on radionuclides with half-lives above ~ 12 h are processed off-line. For measurements with fast rabbit systems the spectra are dumped on magnetic tape directly after recording and processed off-line.
The on-line option is used in connection with the slow pneumatic rabbits of reactor and neutron generator (cf. section 7.2.) for the evaluation of simple peaks.
The off-line mode implies storage of the γ-spectra on a (central) magnetic tape (fig. 7.3.). The on-line possibility at ECN relies on a 4000 channel analyzer with a 48 k bytes/16 bits computer with floppy-disk storage.

- Radioactive discipline implies regular checks with β-γ monitors and determination of the activities which can be wiped off from the surfaces of lab floors, benches and equipment.
  Personal badges are worn on the chest; during manual radiochemical work wrist-badges record the dose-rate on the hands.

7.2. Irradiation facilities for NAA

- For routine (I)NAA it is mandatory to have a good modular system of polythene capsules and corresponding shuttles. Capsules are of high-pressure polyethylene and prepared in a specialized workshop to prevent contamination.
  For occasional long irradiations in a high flux it is necessary to use quartz capsules or ampoules, stored in Al-cans. Figure 7.5. gives a survey of the shuttles and capsules used at ECN.

- Irradiations are carried out in two ways:
  - ☐ Batch-wise in cans or capsules which are placed in fixed positions near the reactor core or in (slow) rabbit systems.
  - ☐ One by one in fast rabbit systems.

A complete radioanalytical laboratory needs both modes. Batch-wise

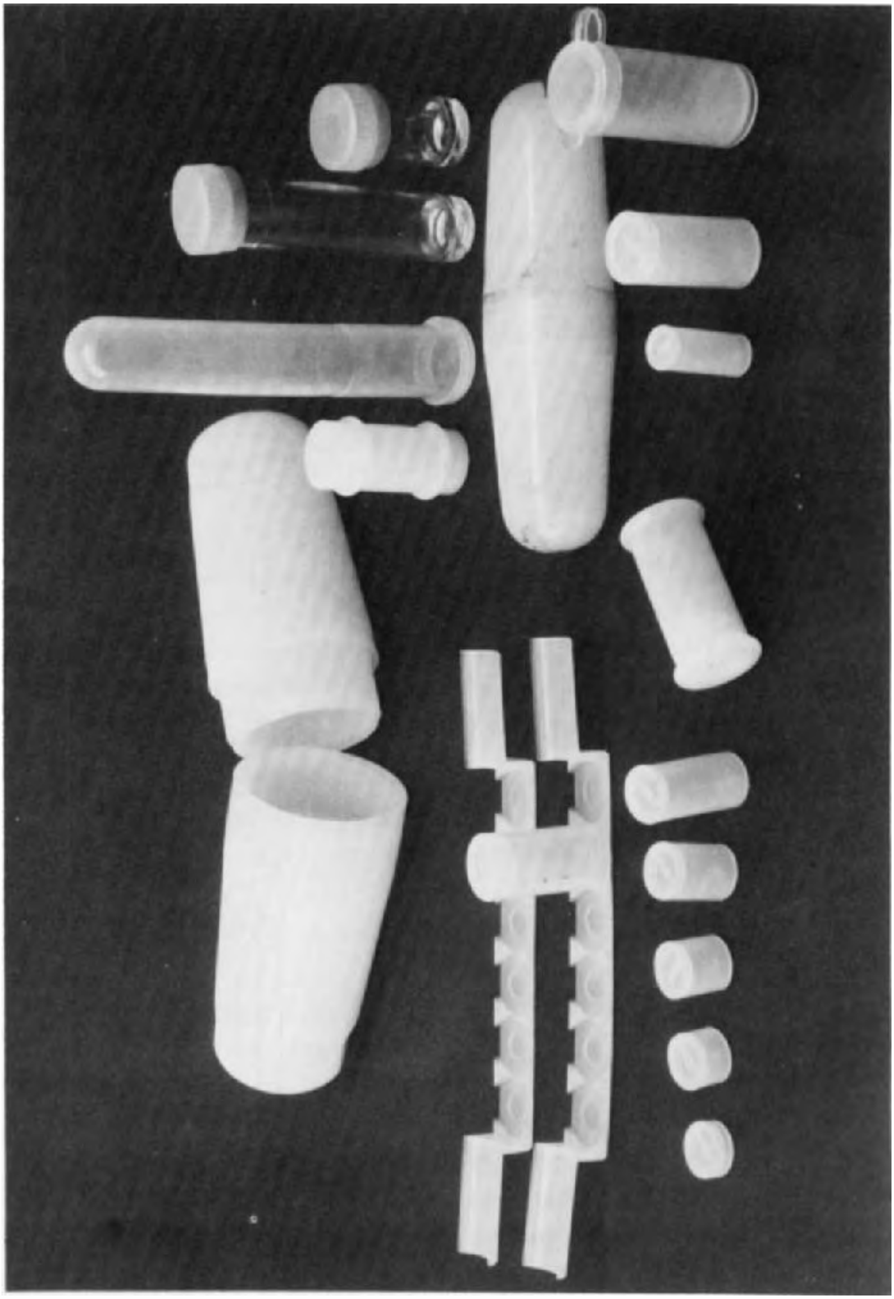


Figure 7.5. Shuttles and capsules used at ECN.

irradiations are usually applied for the production of radioisotopes with $T\frac{1}{2} > \sim 5$ h and in small research-reactors with a supple irradiation-regime for even shorter-lived isotopes.
Rabbit systems are mostly of the pneumatic type with return-times in the order of seconds.
Batch irradiations constitute the bulk of activation capacity.

- The quality of the radioanalytical laboratory is primarily governed by that of the irradiation facilities. To judge these, four factors must be considered:
  - □ Spacial capacity.
  - □ The (average) neutron flux } and its variation.
  - □ The neutron spectrum } and its variation.
  - □ Gamma-heating.

  For one by one irradiations in fast rabbit systems two other criteria are added:
  - □ The reproducibility of the return at the counting-position.
  - □ The contamination due to scraping from the shuttle tube.

- It appears that up to 40 aliquots can be handled as one series. Thus a batch facility should have enough space to contain about 60 aliquots, provided that multi-element standards are used (cf. section 7.3.).
  The device PROF used in the poolside of the HFR 45 MW reactor at ECN consists of a 400 ml polythene flask (fig. 7.6.) in a dry aluminium-pipe which is shielded by 2 cm lead and turned at ~ 1 r.p.m. during irradiation.
  The obvious drawback of such a large facility is variation of the neutron-flux. The alternative, used in medium-size research reactors is the "Lazy Suzan" facility which rotates around the core [2]. The vertical flux-gradient however, remains. For a Triga Mark III reactor it is $\sim 0.4 - 0.5\%.\text{mm}^{-1}$. As such a reactor has a very reproducible flux over long-periods, the flux-gradient may be eliminated by calibrating the positions within the capsules [27,30]. A more general solution which is mandatory for high-flux reactors is the use of separate fluxmonitors as discussed in the next section. The principle is simple: The reaction-rates r (cf. equations 2.3 and 2.4^a) in the sample and the standard are compared to that of their respective fluxmonitors. The standards may have been irradiated earlier.

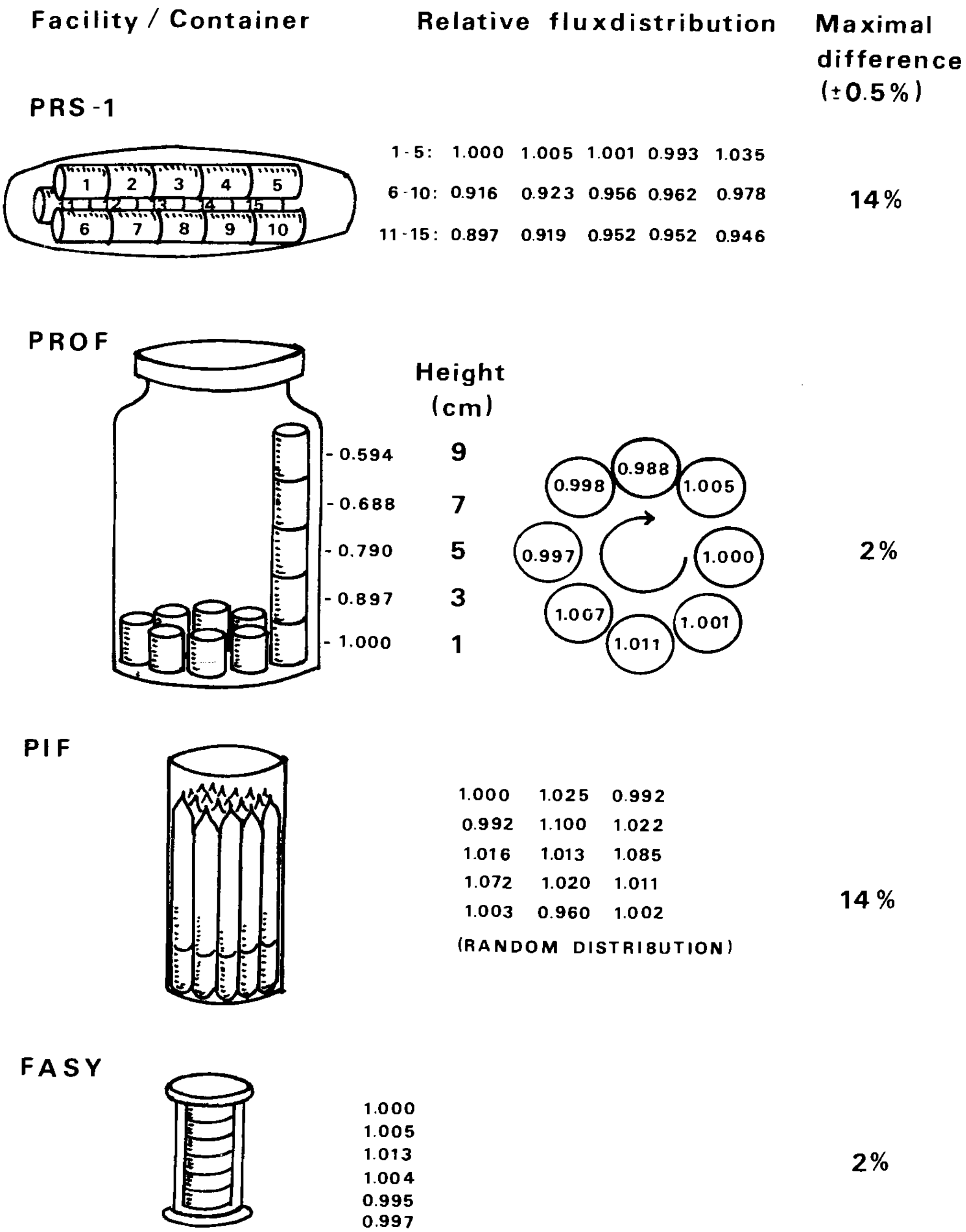


Figure 7.6. Relative flux distribution over some irradiation facilities at ECN.

PRS-1 = Slow pneumatic rabbit ϕ_{th} ~ $5.10^{13} cm^{-2} s^{-1}$

PROF = Poolside rotating facility ~ 5.10^{12}

PIF = Poolside isotope faciltiy ~ 8.10^{13}

EASY = Fast rabbit system ~ 5.10^{13}

If "e" denotes the element, "m" the monitor, "x" the sample and "s" the standard, one has:

$$\frac{r_x}{r_s} = \frac{\sigma_e + I_e \cdot (\phi_{epi}/\phi_{th})_x}{\sigma_m + I_m \cdot (\phi_{epi}/\phi_{th})_x} \cdot \frac{\sigma_m + I_m \cdot (\phi_{epi}/\phi_{th})_s}{\sigma_e + I_e \cdot (\phi_{epi}/\phi_{th})_s} \qquad (7.1.)$$

Thus a fluxmonitor based on a single nuclear reaction will do only if the neutron-spectrum does not change with the position or in time [9,39]. A fluxmonitor should thus be:

☐ Reactive to thermal, epithermal and, if possible, fast neutrons, giving rise to different radionuclides.
☐ Of low self-absorption.
☐ Of reasonable activity at the end of the irradiation.
☐ Of reproducible weight.
☐ Easy to handle.
☐ Cheap.

A convenient choice is pure iron as small rings of 10-30 mg which may be clamped around the capsules or inserted in the snap-caps. The reactions involved are $^{58}Fe(n,\gamma)^{59}Fe$, $T_{\frac{1}{2}}$ = 45 d and $^{54}Fe(n,p)^{54}Mn$, $T_{\frac{1}{2}}$ = 313 d. For the 25 mg rings, used at ECN, the standard deviation in the mass is ≤ 0.3%. Iron rings are not suitable for rabbit irradiations.

- A variation of the neutron-spectrum is much more serious than that of the flux as it affects each nuclear reaction differently. The problem has been discussed thoroughly by various authors, e.g. [3-8]. The obvious check on spectral variations is to measure the ratio of the rates for reactions with highly different I/σ_0-ratios. A suitable combination is $^{58}Fe(n,\gamma)^{59}Fe$, $T_{\frac{1}{2}}$ = 45 d, $I/\sigma_0 = 1$ [10] and $^{123}Sb(n,\gamma)^{124}Sb$, $T_{\frac{1}{2}}$ = 60 d, $I/\sigma_0 = 54$ [11]. In routine analysis such a double monitor can be best added as a multi-element standard. This implies that not each aliquot has its spectral-monitor and thus that one has to avoid regions of changing flux.
- Irradiations in higher fluxes than ~ $10^{13} cm^{-2} s^{-1}$ for longer than ~ 1 h imply the use of quartz capsules in an aluminium can. The energy-uptake in the 10^{14}-zone of a high-flux reactor is of the order of 3-5 $W.g^{-1}$.
- The use of a slow rabbit system entails the handling of the irradiated

shuttle in a lead-cell. Flux-monitoring may be done by calibration of the positions within the shuttle or, better, by adding an internal monitor. As such a spike of enriched ^{86}Sr may be applied to get the reaction $^{86}Sr(n,\gamma)^{87m}Sr$, $T\frac{1}{2}$ = 2.8 h and to measure the 388 keV photopeak, eventually after decay of the short-lived activity.

Rabbit systems which transport the irradiated aliquot directly to the counting-position pose the already signalled problems of positional reproducibility and contamination by scraping. Constructional details can be found in refs. [11] and [44]. A measuring position next to the reactor has to be shielded appropriately. Figure 7.7. shows the fast rabbit system FASY in the 45 MW HFR at ECN (cf. fig. 7.6.). In this device the aliquot-capsule is separated from the shuttle just before it reaches the measuring position.

The application of fast rabbit systems in environmental analysis is scanty, the outstanding example being the determination of Se in hair by ^{77m}Se ($T\frac{1}{2}$ = 18 s). In most other cases, the γ-spectra are dominated by ^{28}Al, ^{38}Cl etc.

Fluxmonitoring at a neutron generator may be done by a fission-chamber, if the irradiation-position is reproducible enough. Figure 7.8. gives the situation for the 400 kV neutron generator at ECN.

- Epithermal activation is performed in batch and rabbit-systems. In the latter a simple Cd or B_4C-cover is used [12]. The shuttle is perforated and filled with solid CO_2 for cooling. Batch systems in a reactor pool imply a cadmium-shield, lined with nickel to prevent contamination of the water. Great care has to be taken of the neutron-spectrum and its variations [13-16]. Again, iron-rings may be used as fluxmonitors. Flux-shifts are detected by the double-monitor technique, mentioned above. For correction one may then use the empirically established relation between each specific count-rate, normalized to one of the ^{59}Fe-peaks, and the ratio of the two activities induced in the double monitor.

  The lower limits of determination for As, Au, Ba, Br, Cd, Mo, Ni, Sb, Se and U are decreased with respect to thermal activation [25].

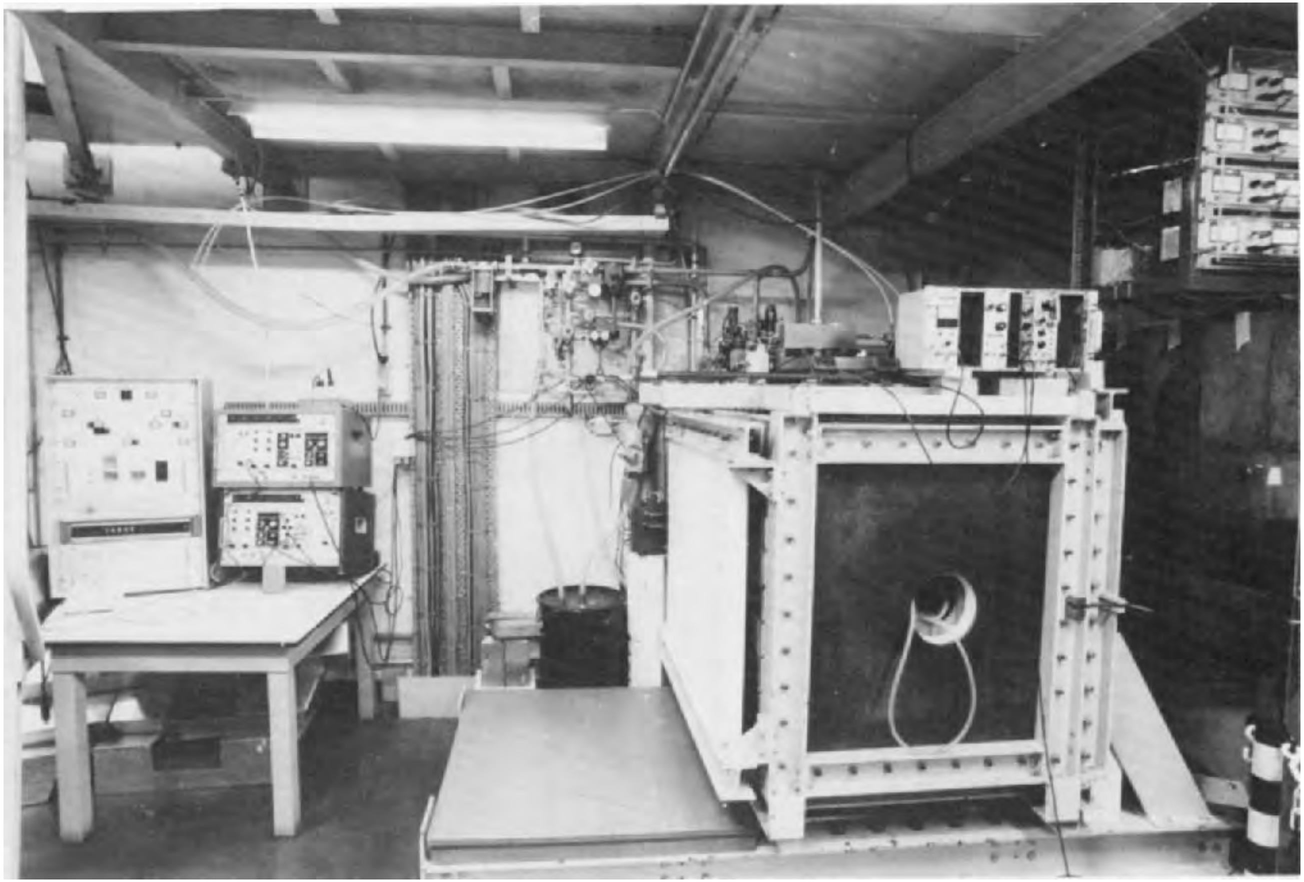


Figure 7.7 The fast rabbit system FASY in the 45 MW HFR at ECN.

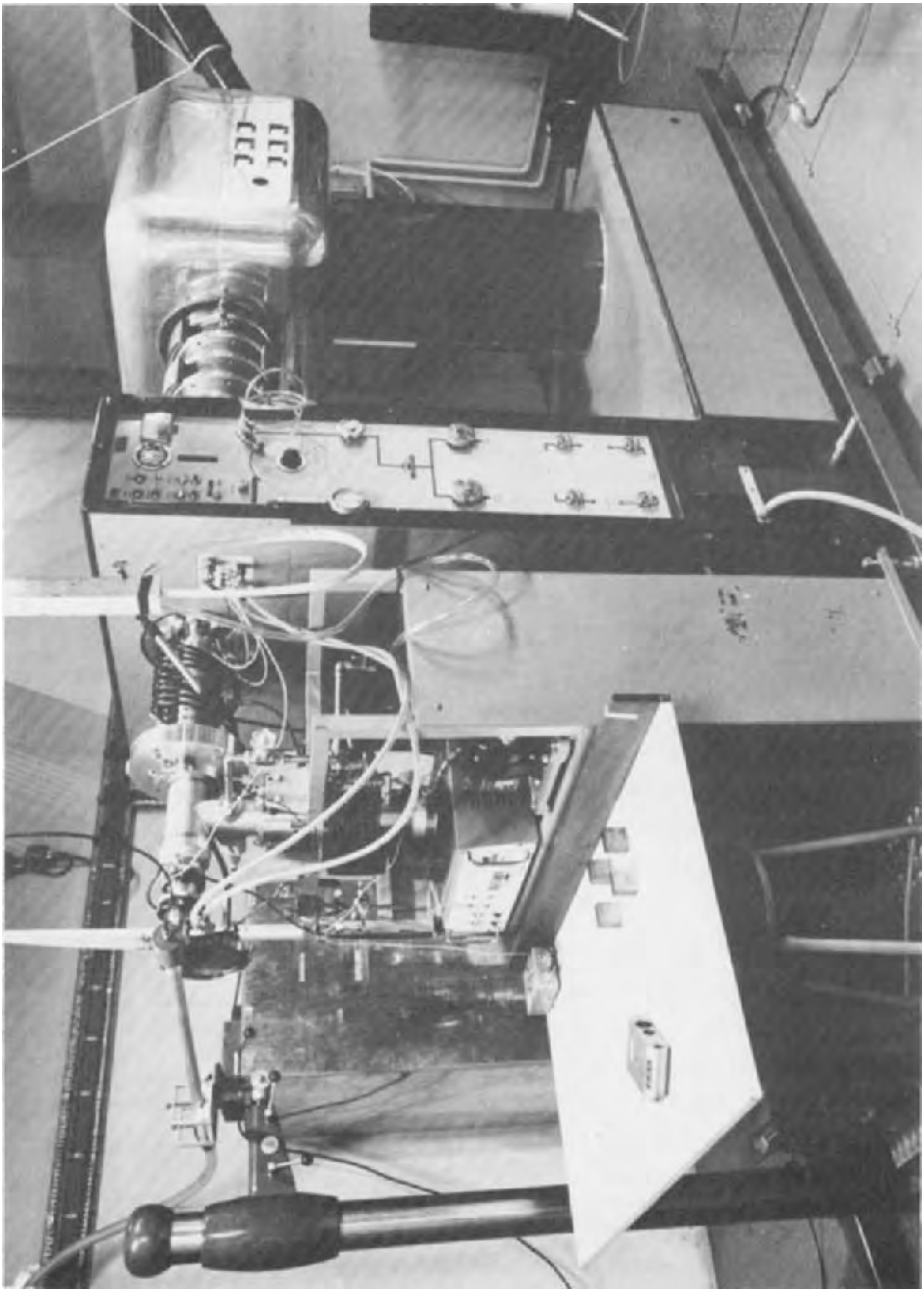


Figure 7.8. The neutron generator at ECN. The beam hits the upper end of the rotating target. The shuttle of the pneumatic rabbit system is kept in front of the beam-spot.
To the right the monitoring fission-chamber is visible.

7.3. Routing of NAA

- Table 7.I. gives the flowsheet of routine activation analysis by batchwise irradiation at ECN. It combines three data-streams:
  - ☐ The codes of the samples and the standards with the weights of the corresponding aliquots.
  - ☐ The specific count-rates of the fluxmonitors.
  - ☐ The γ-spectra.

  The first two converge in the left hand branch of the scheme; the γ-spectra follow the central line while the right branch comprises the (updating of the) specific count-rates and the control by in-house standards and SRM's.

- The storage of samples requires an accurate administration as well as various amenities, from closed plastic boxes kept in closed cupboards to freezers. It is mandatory to store biological samples in a separate area.

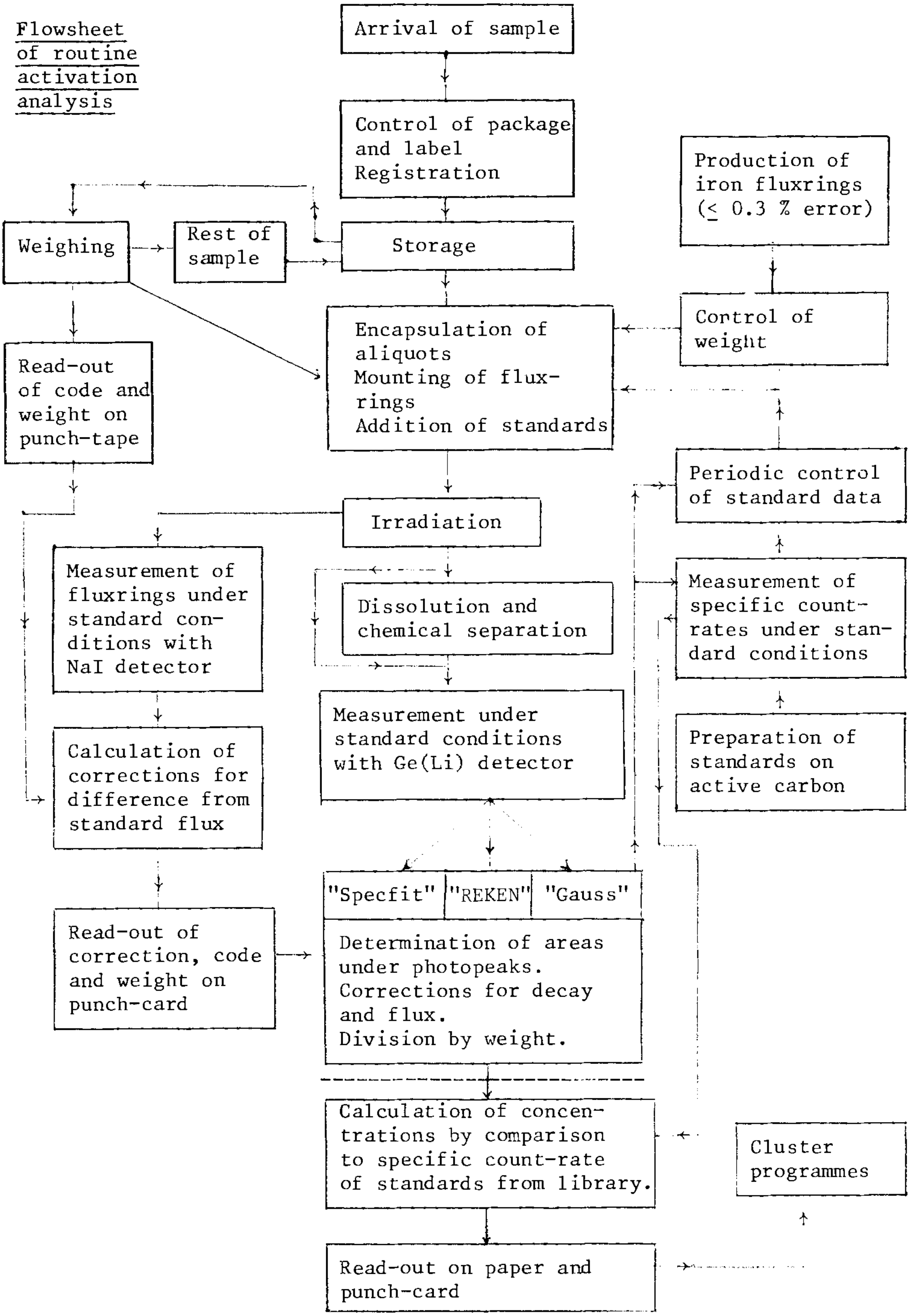
- Standard irradiation-time in the batch-facility PROF (figure 7.6.) is 12 hours; standard counting-time is 10^3 seconds. The γ-spectra of all analysers are stored on one central magnetic tape (fig. 7.3.). Each analyzer is equipped with a data-unit to label the spectra. Moreover, each series gets the code-numbers of the detector, the analyst and the geometry used. The time of the end of measurement is recorded for each spectrum.

  The channel-width, ω, in keV.channel^{-1}, should reflect the compromise between high resolution and good statistics (cf. table 6.I.). At ECN ω = 1 keV.channel^{-1} is the usual choice for coaxial Ge(Li) detectors; for the planar detector ω = 0.3 keV channel^{-1}.
  A small ω implies the necessity of a large memory to store the spectrum in. Thus the choice of ω = 1 is also inspired by the limitation imposed by the computer.

- Counting-geometry is limited to a few standard positions which are all calibrated in terms of the specific count-rates. These data have been stored in the computer.
  The use of a planar detector implies a meticulous care for the geometry. The use of pelletized aliquots is necessary [21,22,26].

Table 7.I.

Flowsheet of routine activation analysis



- Peak-area determination is mostly done off-line, preferably by a simple non-iterative programme "REKEN" (cf. table 6.III.) [17]. Alternatively the iterative fitting-programme "SPECFIT" is used; it is based on the combination of gaussians and exponential tails and a quadratic compton background [18] comparable to "SAMPO" [19,20]. In both cases a large computer is necessary. The limitation to the programme set at ECN is 7.10^4 octal words. The costs of "REKEN" are about one tenth of that of "SPECFIT". The result comprises the locations, widths and interpretations of the peaks; the latter according to a library adapted to the irradiation involved. A tolerance of ± 2 keV is usually applied; as a result there are multiple options which are all recorded.
  The specific contents of the photopeaks are given, corrected for decay from a given time (usually the end of the irradiation), pile-up by a 50 Hz pulser peak and flux-differences relative to a standard countrate of the flux-monitors.
  Selection of a portion of the spectrum is possible.
  Processing of the γ-spectra takes place during the night making results and the next days.

  It is desirable to have an interactive option available for detailed and/or rapid processing. To this end the fitting-programme "GAUSS" is used which resembles "SPECFIT".

  The performance of a computer-programme should be tested. For this three options are convenient: the IAEA test spectrum [35]; a mixed lanthanide-spectrum in the region 50-300 keV and, finally, γ-spectra of SRM's or rank and file samples. One should obtain linear relations between the results of each pair of programmes, with slopes around unity. Trying out on the SRM "NBS Fly Ash 1633^{A}" resulted, for the long-lived isotopes in the region 86-1408 keV, in

$$R = 1170 + 1.005\ S \qquad (7.2.)$$

and for peaks of $\geq 10^4$ counts

$$G = -1250 + 1.015\ S \text{ for peaks of } \geq 10^4 \qquad (7.3.)$$

  G, R and S standing for "GAUSS", "REKEN" and "SPECFIT" respectively. For the lower-energy region and for complex multiplets a curve-fitting programme is mandatory.
- At this point it should be remarked that each laboratory has to make a short-list of reliable γ-lines, if necessary for each matrix separately. Use can be made of compilations like refs. [89] and [90]. Such short-

lists can be found in many publications (cf. table 10.II).

- The results from the peak evaluation are stored in a file and printed out for inspection (dotted line in table 7.I.). A selection of peaks is now made and fed into a second programme for concentration-calculation. This is based on the specific count-rates obtained earlier for synthetic standards and stored in the computer.
  The output is controlled by the data obtained for the "in-house" standard (see below). It may be arranged in report-form or on punch-cards for further processing by statistical programmes.
- Synthetic standards may be prepared by loading pure active carbon [23] with known amounts of standard solutions.
  The principal combinations are listed in table 7.II. Aliquots are irradiated with each batch for controlling and updating. Moreover, an "in-house" standard material is applied. As such a homogeneous batch of illite is used.
  Final checks are made by one or two aliquots of some SRM.

  Other carriers for multielement standards are filter paper [24,34], Al-foil and $CaCO_3$ [31]. The use of filter paper may cause losses [32,33]; in the Al-foil the elements should be present as an alloy. The $CaCO_3$-based standards have to be checked against AAS or XRF in view of the carrier-blank [31].
- Absolute techniques for routine determinations depend on absolute calibration of the detector and precise knowledge of the decay-scheme [29]. They imply a rigorous standardization including neutron-flux and-spectrum [37,38].

7.4. Neutron induced prompt capture gamma-measurements (PGAA)

- A survey of the literature on practical aspects of PGAA can be found in ref. [40]; a recent description and a short-list of gamma-rays are found in refs. [41] and [42]. The systems usually consist of:
  - ☐ A neutron source. Most often this is a beam-tube of a reactor with a thermal neutron flux of 10^6-10^9 $cm^{-2}s^{-1}$. For field applications a ^{252}Cf-source can be used [43].
  - ☐ A neutron-moderator. Mostly this is the water of the reactor pool; blocks of concrete or paraffin are applied too.
  - ☐ An epithermal neutron filter; at ECN this is a liquid-nitrogen cooled bismuth crystal.

Table 7.II. Multi-element standards based on active carbon

Standard	Element	Concentration in $\mu g.g^{-1}$
I	Sc	1.24
	Cr	107.4
	Fe	7750
	Co	10.74
	Br	3.85
II	Zn	467.2
	As	1.12
	Rb	111.6
	Cs	10.6
	La	1.23
	Ce	48.9
	Sm	0.44
III	K	142.9
	Mn	6.0
	Zn	100.2
	As	1.00
	Ce	52.4
	W	2.56
IV	Cu	19.9
	Mo	25.0
	Cd	39.8
	Te	116.9
	Nd	101.6
	Hg	1.00
V	La	0.44
	Pr	14.5
	Sm	0.24
	Eu	0.026
	Dy	2.94
	Ho	0.51
	Yb	0.44

- A rotatable beam-shutter. It consists of some combination of a polymer and boron, iron or lead. In some cases a second movable neutron-absorber of $^6Li_2CO_3$ is applied.
- A collimator consisting of some combination of steel, boron and $^6Li_2CO_3$. The beam-spot is 2-4 cms in diameter. The collimator also acts as a biological shield and a background-suppressor.
- A sample-holder and, preferably, a sample-changer. Various forms of holders are used; in any case the whole aliquot should be covered by the beam.
- A Ge(Li) or intrinsic Ge-detector. This should be as large as possible in view of the low detection efficiency for high-energy photons.
- A beam-stop. It consists of a thick neutron absorber followed by ≥ 10 cms of lead. It is advisable to have a BF_3-counter in front of the beam-stop to monitor the neutron-beam.

- Analytical applications of PGAA are based on equation (2.22). From this it follows that the facility should meet four requirements:
  - The undisturbed neutron flux is constant and/or be monitored.
  - The blank is low and constant.
  - Differences in sample-position are negligible.
  - Self-absorption is small.

The radioanalyst is hardly ever in a position to change the existing facility appreciably. He can only standardize and define his procedure by the four mentioned criteria. Differences in sample positioning may be detected by separate radiotracer experiments with a switched-off beam.

The overall precision is determined by repeated measurements on the same aliquot.

Possible influences of self-absorption are determined by plotting the specific count-rates (cf. in equation 2.22), observed for well-defined matrices like the SRM's, against the product of the total macroscopic cross-section (Σ_T) and thickness (D) [45].

One expects

$$\bar{f}_n = \frac{1 - e^{-\Sigma_T \cdot D}}{\Sigma_T \cdot D} \simeq 1 - \frac{\Sigma_T \cdot D}{2} \qquad (7.4.)$$

- Routing of PGAA is similar to that of INAA. The most important differences are the complexity of the γ-spectra and the doubt on some lines reported in early compilations. It is advisable to prepare one's own list of the strongest lines and check it against ref. [41]. Such a list will, typically, contain 20 to 50 entries.

7.5. Proton induced X-ray emission

- There are about 20 facilities for PIXE in the world [47]; the majority uses 2-4 MeV Van der Graaff's, a few are cyclotron-based. Constructional details on the first group of facilities can be found e.g. in refs. [48-56]. Most of these articles have been published at the occasion of one of the International Conferences on PIXE.
  Data on cyclotron-based systems are given in refs. [57-59].

  As in PGAA, the radioanalyst has to work with the existing apparatus. He may press for a pulsed mode to reduce pile-up and bremstrahlung [58-60]. For the rest there remain the four phases of target preparation, mounting, counting and processing. Only thin-target (< 1 mg.cm^{-2}) applications are considered here.

- As the main application of PIXE in environmental analysis is on air-dust, just a piece of the loaded filter is used as the target there (cf. section 4.5.).
  Independent checks of the homogeneity by INAA demonstrated that deviations up to 5% may occur.
  Liquids are usually applied by the multi-drop technique in which 0.2-0.3 ml is deposited in drops of 10-15 µl. The most convenient procedure may be mixing with ethanol and dropping on a rotating support [59].
  Figure 7.9. gives the principle. The support should be homogeneous and consist of light elements ($Z < 11$). It should be reasonably resistent against treatment and wettable. Usually the support is a "Mylar"-foil of 10 µm (0.5 mg.cm^{-2}) thickness. Alternatively cellulose filters can be used; here the thickness is 5-10 mg.cm^{-2}.

  Solid powdered samples may be treated in the same way [57]. Hair and lyophilized biological material is pulverized first by the "brittle fracture technique" [61] using a teflon-lined ball mill.

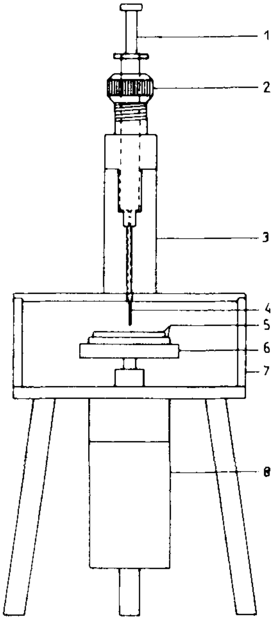


Figure 7.9. Taken from ref. [59]. Apparatus for target preparation from liquid samples.

(1) microdispenser,
(2) height adjuster,
(3) centering column,
(4) tip of dispenser,
(5) target (frame),
(6) rotating table,
(7) perspex house,
(8) motor.

- The loaded supports are mounted in a frame. For routine use the application of slide-frames and of a modified slide-projector is attractive [59]. A target ladder for a few aliquots is the usual practice in multi-purpose scattering chambers [57]. It is advisable to let one frame open to check the beam-position without disturbing the vacuum. The influence of the pressure on the "bremstrahlung"-background has to be determined experimentally [59,62].
  The detector is either of the Ge(Li) or the high-purity Ge-type. It usually faces the target under 20-45°. Beryllium or aluminium-filters are applied to eliminate the low X-rays. A conical filter to "flatten" the sensitivity-curve [64] is applied in the routine facility at the Eindhoven Technological University cyclotron [59].
  The beam is monitored by a Faraday-cup. For quantitative work this measurement is often too inaccurate. The use of an internal standard [57], back-scattering from a 80 $\mu g.cm^{-2}$ gold foil [56] and the intensity of the bremstrahlung of the support [59] have been tried out. The signal should have become constant before the recording starts. When a narrow beam is used which likely burns a pinhole in the target, the count-rate will be variable until the hole has been formed [63]. Usual counting-times are 100-1000 seconds. Filters loaded with standard solutions are irradiated to obtain the specific count-rates for the various elements.

- The routing of the PIXE spectra is based on the presence of an operator during the irradiations. Thus it is common practice that he inspects the spectrum prior to its registration. It is then stored on a floppy disk and processed both on- and off-line. A detailed description can be found in ref. [59]. The on-line programme yields the peak-locations and areas, corrected for absorption and enhancement. The quantities which must be given are:
  - ☐ Incident proton energy.
  - ☐ Energy-degradation coefficients of the matrix material.
  - ☐ Target-thickness.
  - ☐ Enhancement due to secondary electrons.
  - ☐ Mass-absorption coefficients of the target.
  - ☐ Absorber-thickness and material.
  - ☐ Geometry: Whether or not a conical filter is used.
  - ☐ Detector efficiency.

The energy-degradation and the enhancement are obtained from separate experiments. The energy is calibrated by standard targets of Al, Ti, Cr, Fe, Cu, Mo and Ag.
The programme then supplies the peak-locations and corrected-areas and their relative intensity with respect to the Mn K_α-line.
The off-line treatment may be interactive or delayed. It is invariably based on a curve-fitting programme like SPECFIT [18], TRACE [65] or PROFANAL [59]. The first is used for delayed batch-wise processing, the other two programmes are interactive.
Finally equation (2.25) is applied if the correction for the integrated flux is available. If not one has to give concentration-ratios.

7.6. Presentation of data

- The presentation of the data should be such that the essential information can be extracted from it at a glance. Thus it is obvious that the best way to present the data depends on the problem involved. At least four situations can be distinguished:
  - ☐ The interest is in a single element only and each sample is represented by one aliquot.
    An example is the determination of V in rainwater or of Hg in hair.
  - ☐ A single element is considered and the sample is divided into several aliquots.
    The determination of trace elements in soil samples, split according to grain-size is of this type.
  - ☐ Multi-element analysis is used to find the relation between one concentration and all the others. Examples are met in physiological and geochemical studies.
  - ☐ Fingerprinting by multi-element analysis. Examples are the characterization of hair, drug samples, potsherds etc.
- Single element determinations in one or a few samples should be reported with their standard deviation, the result for a Standard Reference Material obtained in the same way and its certified value.
  For large series the frequency distribution can be shown (fig. 6.10.).
  Given large numbers of data on single elements, which partly consist of limits of determination, one may assume a log-normal distribution and thus include the non-determined concentrations in the calculation of

the mean value and its standard deviation [34,36].

The procedure is simple:

- ☐ Plot y = log (cumulative frequency in %) against x = log (concentration) and determine the best linear fit y = a + bx.
- ☐ Extrapolate the line to the 50%-frequency level (y = 1.7) and determine the corresponding concentration, which is the median-value.
- ☐ The standard deviation is obtained as the difference between the median-value and the concentration at 84% (y = 1.92) or 16% (y = 1.20).

For markedly skew distributions the arithmetic mean may still provide an unbiased estimation of the expected value [69,88].

- The relation between the concentration of a single element and the other parameters determined is done by factor analysis [66]. Possible relations between two elements are detected by application of standard regression techniques.

  Multielement characterization by n simultaneous determinations may be visualized by using one of the pattern recognition techniques [70]. The n-dimensional space in which the samples are points is reduced to a plane. This procedure may be the "Minimal Spanning Tree" [67] followed by "Non Linear Mapping" [68] or "Cluster" [71].

  In the latter case a "similarity factor" is defined which is used as the discriminating tool. Figure 7.10. gives the result for "Cluster"-processing of the INAA-data on 21 elements in 27 tobacco samples [72]. The letters refer to the countries of origin. From the data on duplo-aliquots the lower level of significance can be found.

7.7. Radiotracer experiments

- Practice of radiotracer experiments depends on the scope of the system and the rate of the transport-phenomena to be measured. The distinction according to scope is that between field and laboratory.

  The reaction-rate of environmental transport processes is usually low.

- The apparatus needed for injection experiments in the field have been discussed thoroughly long ago [73-75] and more recently in ref. [76].

  In practice three groups of experiments may be distinguished:

  - ☐ With stable, activable tracers.
  - ☐ With active tracers.
  - ☐ Based on fall-out or natural radionuclides.

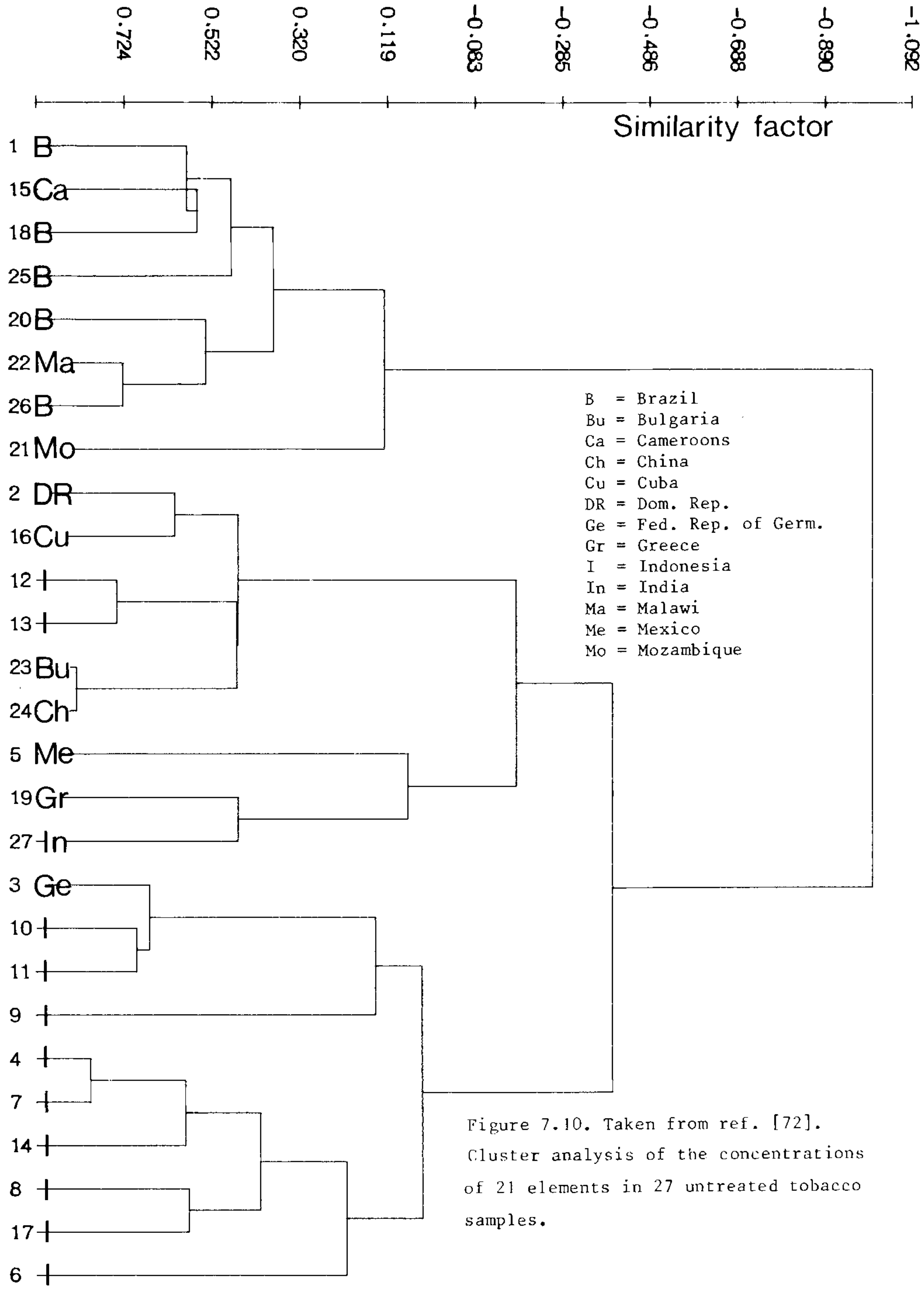


Figure 7.10. Taken from ref. [72]. Cluster analysis of the concentrations of 21 elements in 27 untreated tobacco samples.

In the case of water the first group is restricted to the halogenides and some chelates [76,77]. Bromide is the most common choice; the amounts used may be of the order of a few hundred kilogrammes. For air both indium and dysprosium have been released as aerosols [78,79].

The second type of experiment is of very limited applicability. The most obvious choice for water is tritium. The added activity may be some tens of Curies. The results from bromide and tritium are usually in good agreement. Other field applications are rare. The use of ^{54}Mn to measure phase-transformations of particulate manganese [80] and labelling of fly-ash with ^{99m}Tc [81] are examples.

The use for tracer experiments of naturally occurring radionuclides or of such as are released continuously by nuclear plants as well as of fall-out differs appreciably from single-injection experiments (cf. section 3.6. and ref. [82]. Sedimentation-rates measurement by fall-out implies the taking of undisturbed profiles and careful cutting [83]. Release of noble gases from chimney stacks may be used if the gases are concentrated on active carbon [85-87].

- Laboratory experiments usually deal with mass-transport and isotopic exchange in solid-liquid systems. In most cases the reaction-rate is slow enough to permit off-line measurements.
  Batch, backmix and column-reactors can be used.
  Batch-reactors are closed vessels with known amounts of solid and liquid. At t = 0 the contents are mixed and a tracer-spike is added. Usually the liquid phase is sampled either after settling or by taking an aliquot of the mixture and centrifuging. In the former case a separate batch is needed for each different contact-time.

  In back-mix reactors the eluent is renewed continuously. Thus the measurement of leaching (cf. section 3.4.) may be done without appreciable interference by adsorption. The required retention of the solid phase from the outgoing stream may be effectuated by a mini-cyclone.

  Column-experiments imitate field conditions. They comprise adsorption-measurements, in which the radiotracer is introduced at t = 0, and leaching-experiments which rely on INAA of the eluate, in conjunction with other analytical techniques. Prior to the injection of the tracer it is necessary to check whether the column is in equilibrium. For soil-water or fly-ash-water systems this may be done by pH-measurements. Then the number of plates has to be determined. In the case of leaching studies this is done by a separate tracer experiment with, for instance, bromide. The mass-balance equation may then be solved numerically for each successive plate.

For solids with a low porosity it is advisable to apply up-flow to prevent clogging. Typical conditions for leaching-experiments on fly-ash are:

Porosity ~ 30%; specific flow-rate 5.10^{-2} $ml.h^{-1}.cm^{-2}$; duration of the experiment ~ 10 months.

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CHAPTER 8.

RADIOANALYSIS OF WATER

SUMMARY

- Water is the most abundant component of the environment. For practical analytical reasons it may be divided into sea, rain, fresh surface and waste water.
- Sea and fresh surface water may be successfully analysed for trace elements by neutron activation if some rapid and quantitive preconcentration procedure is available. The use of some scavenging procedure like that with active carbon is preferable.
  Waste water may be analysed in the same way but the chemical yield should be controlled for each individual case.
- Rainwater presents a distinctly different matrix in that it is easily accessible to many non-radioanalytical techniques. Radioanalysis may be used to assay the halogens and a number of trace metal ions.
- The data obtained may serve to elucidate transport processes and to detect intercorrelations.

8.1. General

- Water is one of the major components of the environment. From the analytical point of view, four types of water may be distinguished. They are, in order of increasing influence of human activities:
  Seawater, rainwater, fresh surface water and waste water.
- Water always contains some suspended matter. The concentration of this solid fraction varies widely. In seawater it is between 0.5 and 5 $mg.kg^{-1}$ at full sea while in coastal waters it may exceed 50 $mg.kg^{-1}$. Surface waters feature values up to 10 $g.kg^{-1}$ while waste waters may eventually contain even higher concentrations.
  In planning, performing and reporting an analysis it should be clearly defined whether "water" comprises the solid matter or not.
- The application of radioanalysis to environmental water studies are trace analysis and measurement of mass transport and isotopic exchange between water and suspended matter. As demonstrated in table 8.I., "trace" means a concentration of 1 $mg.kg^{-1}$ or less.
- Trace analysis by neutron activation is usually based on some sort of preconcentration. The main procedures are mentioned in chapter 5.

  In this chapter the emphasis is laid on simple techniques like freeze-drying, solvent extraction and scavenging with active carbon of the chelated trace elements.

  In terms of sampling, sea, fresh and waste-water form one group and rainwater another, as for the latter the available amount is often strictly limited.

8.2. Seawater

8.2.1. Sampling and preconcentration

- The composition of -unpolluted- seawater is remarkably constant [1]. The total salt concentration varies with the water temperature, the inflow of fresh water and evaporation from 33 to 37 $g.kg^{-1}$. "Trace elements" refers to concentrations below 1 $mg.kg^{-1}$. The average trace concentrations are given in table 8.I. About 0.45 $mg.kg^{-1}$ or more than 90% of the total amount of trace is due to five elements only: Li, P, Rb, I and Ba.

- The concentration levels of trace elements in seawater are influenced in different ways:
  a) By natural mass-transport processes like erosion and subsequent sedimentation.
  b) By pollution due to volcanic events. Mercury is released in large quantities during submarine volcanism [7].
  c) By pollution due to discharge of industrial and domestic waste, either by the inflow of contaminated rivers or the direct discharge into estuaries and the sea and by aerial fall-out. Two well-known examples of serious pollution are the mercury poisoning in the Minamata region, Japan, in 1961 [9] and the contamination of Dutch coastal waters with copper in 1965 [8].

The current analytical investigations are usually directed towards the following aims:

a) Variation of concentrations with depth.
b) Variation of concentrations near bottom sediments.
c) Behaviour of trace elements during their transport to sea.
This implies the measurement of concentrations in sediments as well as the plotting of the data for the water against salinity.
A deviation from linearity points to sediment-water interaction.

From the combination of these measurements with other analytical data one may derive conclusions on the factors which control the distribution and transport of the elements involved.

TABLE 8-I *TRACE ELEMENT LEVELS IN SEAWATER*

Element	Symbol	Average concentration ($\mu g.kg^{-1}$)	Predominant inorganic form(s) in solution
Lithium	Li	170	Li^+
Beryllium	Be	6×10^{-4}	$Be(OH)_2$
Aluminium	Al	5	$Al(OH)_2^+$
Phosphorus	P	70	PO_4^{3-}
Scandium	Sc	7×10^{-4}	$[Sc(H_2O)_5\,OH]^{2+}$ [2]
Titanium	Ti	1	$Ti(OH)_2^{2+}$
Vanadium	V	1.9	HVO_4^{2-}, VO_3^-
Chromium	Cr	0.2	CrO_4^{2-}, $[Cr(H_2O)_4(OH)_2]^+$
Manganese	Mn	0.4	Mn^{2+}, $Mn(OH)^+$
Iron	Fe	1.5	$Fe(OH)_4^-$, $Fe(OH)_2^+$ [3]
Cobalt	Co	0.1	Co^{2+}, $CoCl^+$, $Co(OH)^+$
Nickel	Ni	0.7	Ni^{2+}, $NiCl^+$, $Ni(OH)^+$ [3,5]
Copper	Cu	0.9	Cu^{2+}, $CuCl^+$, $Cu(OH)^+$
Zinc	Zn	2	Zn^{2+}, $ZnCl^+$ [3,4]
Gallium	Ga	0.03	?
Germanium	Ge	0.06	$Ge(OH)_4$
Arsenic	As	2.5	$HAsO_4^{2-}$, AsO_4^{3-}, AsO_3^{3-}
Selenium	Se	0.09	SeO_3^{2-}, SeO_4^{2-}
Rubidium	Rb	120	Rb^+
Yttrium	Y	0.3	$Y(OH)^{2+}$
Zirconium	Zr	0.02	?
Niobium	Nb	0.01	?
Molybdenum	Mo	10	MoO_4^{2-}
Ruthenium	Ru	7×10^{-4}	?
Silver	Ag	0.29	$AgCl_2^-$
Cadmium	Cd	0.11	$CdCl^+$, $CdCl_2$, Cd^{2+}
Indium	In	0.1	$In(OH)_2^+$?
Tin	Sn	0.8	$Sn(OH)^+$, $Sn(OH)_2^{2+}$
Antimony	Sb	0.3	$Sb(OH)_2^+$, $Sb(OH)_6^-$
Iodine	I	60	I^-, IO_3^-
Cesium	Cs	0.3	Cs^+
Barium	Ba	30	Ba^{2+}

TABLE 8-I (Continued)

Element (continued)	Symbol	Average concentration ($\mu g.kg^{-1}$)	Predominant inorganic form(s) in solution
Lanthanum	La	1.2×10^{-2}	$La(OH)^{2+}$, $La(OH)_2^+$
Cerium	Ce	5.2×10^{-3}	$Ce(OH)^{2+}$
Neodymium	Nd	9.2×10^{-3}	?
Hafnium	Hf	$<8 \times 10^{-3}$	?
Tantalum	Ta	$<3 \times 10^{-3}$	?
Tungsten	W	0.1	WO_4^{2-}
Rhenium	Re	8×10^{-3}	ReO_4^-
Gold	Au	0.01	$AuCl_4^-$
Mercury	Hg	0.03	$HgCl_4^{2-}$
Thallium	Tl	<0.01	Tl^+
Lead	Pb	0.03	Pb^{2+}, $PbCl^+$
Bismuth	Bi	0.02	BiO^+, $BiOCl$, $BiCl_4^-$
Radium	Ra	1×10^{-7}	?
Thorium	Th	4×10^{-4}	$Th(OH)_2^{2+}$
Uranium	U	3.3	$UO_2(CO_3)_3^{4-}$ [6]

- Sampling procedures are discussed in detail in "Reference Methods for Marine Radioactivity Studies" [10]. Water samples from the surface are taken by pumping or with a polyethylene bucket. Sampling at various depths is performed by pumping or by using Nanssen bottles, which can be shut at the desired depth.

  Sediment samples are collected by dredging, grabbing or coring. The latter is preferred, although it is difficult to keep the superficial layer undisturbed.

  The separation between water and suspended matter is best achieved by filtration, centrifugation or gravitational settling. Often however, filtration through a 0.45 μm membrane filter is applied.

- Preconcentration may be based on one of the following procedures:
  a) Freeze-drying. This results in a salt residue which may be irradiated directly [11, 28, 68]. The obvious implication is the very high initial activity of the irradiated aliquot, due to ^{38}Cl ($T_{\frac{1}{2}}$ = 37.2 min) and ^{24}Na ($T_{\frac{1}{2}}$ = 15 h). An alternative to freeze-drying is evaporation at a relatively low temperature [63].
  b) Coprecipitation. Often $Fe(OH)_3$ is applied [26, 32, 33, 37]. Alternatives are CuS [41, 42] or MnO_2 [38]. Quinolinol was used for Cu and Mn [65]. Direct irradiation is not feasible here [60].
  c) Scavenging. Active carbon is used to collect the - previously chelated - trace elements [15, 30, 70]. The obvious advantage of active carbon is its inertness under neutron irradiation.
     The trace elements may be desorbed into dilute mineral acid for AAS determinations. Alternatives are many [70]. An example is CdS, used for the collection of Hg [44]. For some elements the blank of the active carbon may set a limit; an example is Mn [87].
  d) Ion-exchange. Three types of ion-exchanges are used:

o Cation	For V [25].
o Anion	For V [24]; Mo [34, 35]; W [34], Hg [40] and U [47-49].
o Chelating ("Chelex-100")	For V [21]; Co, Cu, Zn, Cd [29]; Cu, Cd [28]; Cu, Ni [64] and U [97].
o Exchange with an inorganic salt	The exchange with sulfides has been applied to collect 13 trace elements for XRF analysis [66].

e) Liquid extraction. For V [22, 23]; V, Mo, U [12]; Cr [27]; Cu, Zn, Cd [31] and Mo [36].

f) Electrodeposition. Using pyrolytic graphite as the cathode most trace metals can be isolated [13, 14, 68, 69].

Amalgamation by copper powder is very quick but of limited applicability [67]. Amalgamation with Au or Ag-wire is used for Hg [39, 43]. It implies the previous destruction of organo-mercuric compounds and is sometimes used as a second step after volatilization [43].

g) Volatilization. The reduction of mercuric-compounds to metallic Hg [43, 45, 70, 88, 92] and that of As and Sb to their hydrides (cf. [89]) provides sensitive and rapid procedures for the determination of these elements.

8.2.2. Analytical techniques

- Obviously, techniques with a sensitivity sufficient to allow a direct determination of trace elements in seawater are to be preferred. At present only Cu, Zn, Cd and Pb can be measured directly using anodic stripping voltammetry (ASV) [16-19]. Attempts are made to perform direct multi-element analysis by the inductively coupled plasma technique [93]. All other procedures imply either a preconcentration or, in case of radio-analysis, a post-irradiation chemical separation.

- Post-irradiation separation is usually based on liquid-extraction [46, 61, 62], ion-exchange of the interfering ^{24}Na with hydrated antimony pentoxide [61] or (co)precipitation [65].

- Table 8.II. gives a comparison of the techniques applied in the determination of trace elements in (sea)water. The limits of determination are divided into three classes, ranging from 1 to 10^{-6} $mg.l^{-1}$. The obvious use of neutron activation analysis (NAA) is multi-element determination. This may be completed by a few separate procedures for single elements or species which are of particular environmental interest. As the most obvious drawback of NAA is its turn-over time, rapid and simple techniques should be used.
  This, and the need to preconcentrate as soon as possible to prevent sample deterioration leads towards scavenging or liquid extraction as the preparatory step. It was found [70] that 25 elements may be concentrated in a chelated state on active carbon.

TABLE 8-II *COMPARISON OF ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN (SEA) WATER*

Technique		Limit of determination*			Advantages	Limitations
		A	B	C		
Atomic absorption spectrometry (AAS)	flame		Cd,Zn,Ni Co,Cu,Cr	Pb,Mo V,	Rapid and relatively simple. Applicable to many elements.	Simultaneous multi-element analysis not feasible. Serious matrix effects in seawater [20].
	graphite furnace	Cd,Zn	Cu,Mo,Co Pb,Cr,Ni Fe,Al,V	Sb,As,Hg Se		
Anodic stripping voltammetry (ASV)		Cu,Cd,Zn Pb			Direct measurement of seawater possible. Rapid.	Not suitable for a wide range of elements. The technique requires considerable skill.
Neutron activation analysis (NAA)		Hg,Co,V Sb	Se,As,Mo W, U, Cr Cd,Al,Cu	Zn,Ni,Fe [Pb]	Not subject to contamination by reagents. Also applicable to suspended matter and bottom sediments.	Total time for multi-element analysis may be long. Elimination of bulk NaCl is necessary, when elements forming radionuclides with short- or medium half-lives are to be determined. [61]

Technique (Continued)		Limit of determination			Advantages	Limitations
		A	B	C		
Spectrophotometry	Colorimetry		Cu,Pb,Cd Co,Sb,Fe	Hg,As,Mo V, Ni,Cr Zn	Simple measurement. Simple equipment.	Single element analysis. Preconcentration is necessary. Quenching by interfering elements.
	Fluorometry		Cu,As,Al U	V, Cd,Mo		
Emission spectrography (DC-arc)			Cu	Co,Cr,[Fe],[Hg] Mo,Ni,Pb,[Sb]	Multi-element technique.	Preconcentration necessary.
X-ray spectrometry	wavelength dispersive			Pb,Cu,Zn,V Fe,Cd,Hg Mo,Cr,Ni [Al]	Can be non-destructive.	Wavelength dispersive X-ray spectrometry: single element analysis. Preconcentration necessary. Thin samples required (e.g. resinloaded paper, filters).
	energy dispersive				Multi-element technique.	

* A: 10^{-6} - 10^{-4} mg.l^{-1}
B: 10^{-4} - 10^{-2} mg.l^{-1}
C: 10^{-2} - 1 mg.l^{-1}
The elements given in brackets exhibit a poor sensitivity with the technique concerned.

Bruland et al. [64] used extraction of the dithiocarbamates of Cu, Cd, Zn and Ni.

If properly combined with AAS and ASV, NAA based on scavenging with active carbon may be a decisive help in the monitoring of seawater. The outline of the last procedure is given in section 8.4.

8.3. Fresh water

8.3.1. Sampling and preconcentration

- The composition of fresh water varies greatly. Accordingly, the chemical speciation of the trace elements may vary as well [71, 90]. In general, the elements Na, Mg, Si, P, S, Cl, K, Ca, Fe and Br are present in concentrations of 1 $mg.kg^{-1}$ or higher. Attempts have been made to describe the behaviour of the minor constituents and some traces in water by computer models [91]. The results of such calculations may be used as a guide in setting up the analytical procedure. Parellel with this speciation of the soluble fraction of the trace elements, settling models have been proposed to describe the removal of trace elements by the deposition of sediment [94].
- The composition of fresh surface water may be effected by human activities in many ways. Pollution effects can be divided into acute "peak"-shaped increases in concentration and long term trend-effects. The applications of radioanalysis are almost entirely directed towards the latter phenomena. Examples of such investigations are given by Wyttenbach [62] for ice-cores from the Alpine region and Boutron [63] for artic snow. The control of the trace element content of river water over (part of) its course [72-74] is another application.
- Sampling is usually perfomed with a "teflon" or polythene bucket. The collected water is filtered immediately over a cellulose or "teflon" millipore filter, preferably in a closed system [75]. Alternatively centrifugation in a flow-through centrifuge is applied [70].
- Preconcentration is often based on freeze-drying [79]. This implies loss of the volatile elements, notably Hg, As and the halogens. Alternatively, the active carbon method may be used [70, 76]. Unlike with seawater, fresh water is sometimes irradiated as such. The rel-

atively low salt content makes it possible to perform post-irradiation chemistry on the laboratory bench.
The collection of trace elements on other inorganic scavengers may be of interest for non-radiochemical methods [66] or in post-irradiation chemistry [73, 78].

8.3.2. Analytical techniques

- Table 8.II. applies to fresh as well as to seawater. However, the possibilities of AAS tend to be considerably larger here due to smaller matrix effects [77]. The same holds for XRF where the preconcentration on thin sulphide layers gives good results for Cu, Cd, Ag, Te, Hg, Bi and Pb [66].
- The use of anodic stripping voltammetry for the speciation of Cu, Zn, Cd and Pb has been demonstrated on river and tap water [90]. The metal speciation scheme involves ASV measurements of "labile" and total metal concentrations in sample filtrates using (a) original water, (b) water passed through a chelating resin column (c) U.V. irradiated water and (d) U.V. irradiated water, passed through a chelating resin column.
- Neutron activation analysis is used for the simultaneous determination of many elements. Purely instrumental multielement analysis is possible but at the cost of very long counting-times [109]. Both the active carbon procedure and freeze-drying cover ~ 20 elements [70, 76]. With the carbon procedure it is sometimes possible to determine separate species. Usually this is based on the differences in complexation constants for chelation reactions. Combination of the hydride gas stripping technique [79] for Se^{IV} and Se^{VI} with subsequent adsorption of the volatilized hydrides on active carbon is possible too. Post-irradiation separation is applied often. It is based on (co-) precipitation with sulfides [73, 78], liquid extraction of the dithiocarbamate complexes [62] or ion-exchange with Chelex-100 [64].
  Bart et al. [73] irradiate 100 ml water at a thermal neutron flux of $\sim 7.10^{12}$ $cm^{-2}.s^{-1}$, followed by addition of 5 mg of carrier for each element to be analysed and evaporation to 7-8 ml. The interfering ^{24}Na is eliminated by a small column of 1 g hydrated antimony pentoxide (HAP) while the other elements are eluted with 10 ml 6 N HCl. They are then scavenged, either from an acid solution with Sb_2S_3 or from an

alkaline solution with $Fe(OH)_3$. Alternatively Thatcher [78] irradiates 20 ml and precipitates the combined sulfides from a homogeneous solution by adding thioaceetamide at pH = 1-1.5. This is followed by an oxide precipitation at pH = 9-9.5 with MgO [78].

In both cases, bulky aliquots have to be irradiated, after pretreatment to prevent wall-adsorption. This situation has been discussed in chapter 5. Usually HNO_3 is added to bring the pH at ≤ 1.5 [73, 78, 80]. For Hg it is preferable to add an oxidizing agent as well; the combination of 1% H_2SO_4 and 0.05% $K_2Cr_2O_7$ has been proposed [81] but this is hardly feasible for neutron activation analysis, due to the interference by ^{51}Cr ($T_{\frac{1}{2}}$ = 27.7 d) and the possible losses of traces in the HAP column from a SO_4''-containing solution [82].

8.4. The active carbon procedure

8.4.1. General

- The use of active carbon for the scavenging of chelated metal ions from aqueous solutions has been applied in several laboratories as a first step towards NAA [70, 83], AAS [84] and XRF [85]. For uranium determinations, delayed neutron counting may be used [86].
- The surveying radioactivation experiments done at ECN [70] are summarized in table 8.III. Ammonium pyrrolidine dithiocarbamate (APDC) and l-ascorbic acid are used as the chelating agents. The corresponding γ-spectra are given in figure 8.1. By a suitable combination of pH's and reagents it is possible to collect most trace elements.
- It follows from radiotracer experiments that the scavenging of the (chelated) trace elements may be described by a Freundlich adsorption-isotherm:

$$y = m \cdot \alpha \cdot c_e^{\beta} \qquad (1)$$

y = amount collected (g)
m = amount of carbon (g)
c_e = equilibrium concentration in the solution (M)
α and β are parameters.

At equilibrium-concentrations below 10^{-6} or 10^{-7} M the exponent β is usually equal to unity. At higher concentrations it may decrease

TABLE 8-III EXPERIMENTS ON THE ABSORPTION OF TRACE ELEMENTS FROM SEAWATER ON ACTIVE CARBON

Irradiation facility	Radionuclide observed	Adsorption conditions: Reagents: None	APDC	l-ascorbic acid
Rabbit Systems	^{28}Al		pH1.45-3.2-5.1	pH 4
	^{52}V	pH 3.2	pH 3.2	
	^{56}Mn		pH 8.05	
	^{66}Cu		pH 8.05	
	^{115}In (from ^{115}Cd)		pH 8.05	
	^{128}I	adsorbed under all conditions studied		
Low Flux facility (5.10^{12} cm^{-2} s^{-1})	^{122}Sb		pH 1.45	pH 3
	^{115m}In(from ^{115}Cd)		pH 8.05	
	^{99m}Tc(from ^{99}Mo)		pH 1.45	
	^{239}Np (from ^{239}U)	pH3.2-5.1		pH 3-4
	^{122}Sb		pH 1.45	pH 3
	^{198}Au	pH3.2-5.1		
High Flux facility (8.10^{13} cm^{-2} s^{-1})	^{141}Ce ^{103}Ru ^{95}Zr ^{140}La(^{140}Ba) } from U-fission	pH 3.2-5.1		pH 3-4
	^{233}Pa (from ^{233}Th)	pH 8.05		
	^{46}Sc	pH 8.05		
	^{59}Fe	pH 8.05		
	^{65}Zn		pH 8.05	
	^{60}Co		pH 8.05	
	^{58}Co (from ^{58}Ni(n,p))		pH 8.05	
	^{51}Cr	pH 8.05		pH 1.45
	^{181}Hf	pH3.2-5.1-8.05		pH 3-4
	^{124}Sb		pH 1.45	pH 3
	^{75}Se			pH 2
	^{203}Hg	pH 1.45-3.2	pH 1.45	
	^{110m}Ag	adsorbed under all conditions studied.		
	^{152}Eu			pH 3-4

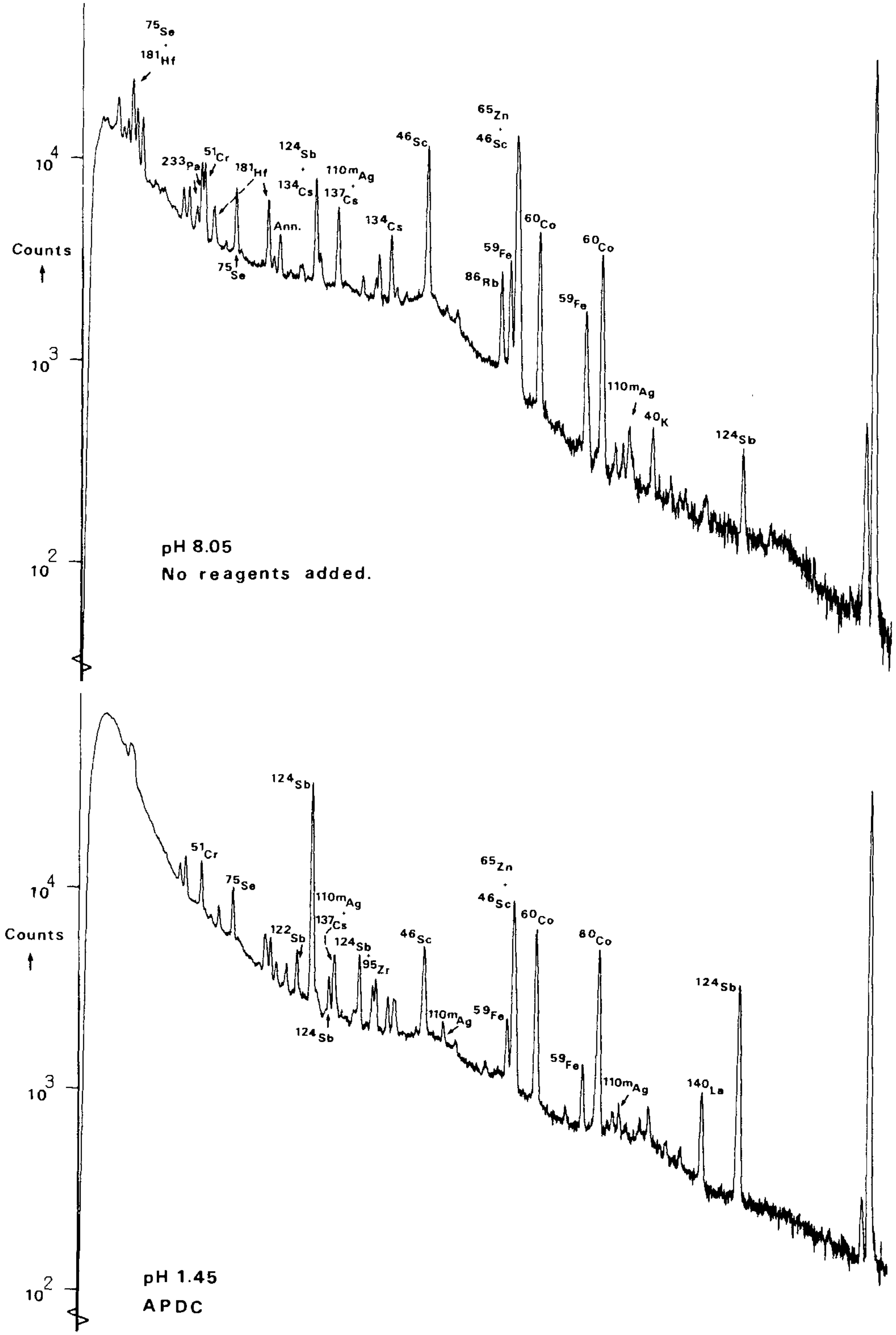


Fig. 8.1. Gamma ray spectra of carbon samples and a carbon blank

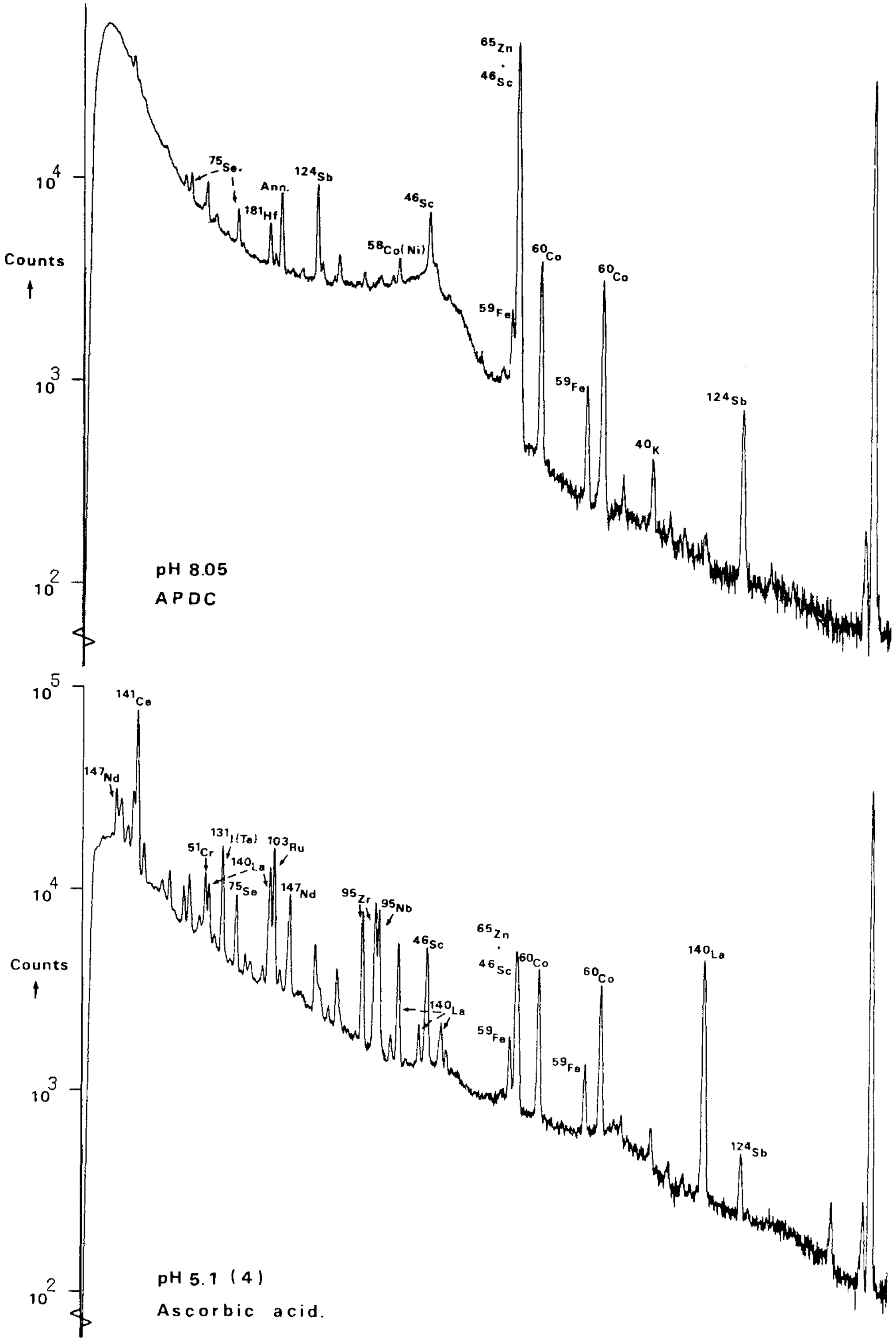


Fig. 8.1. Continued

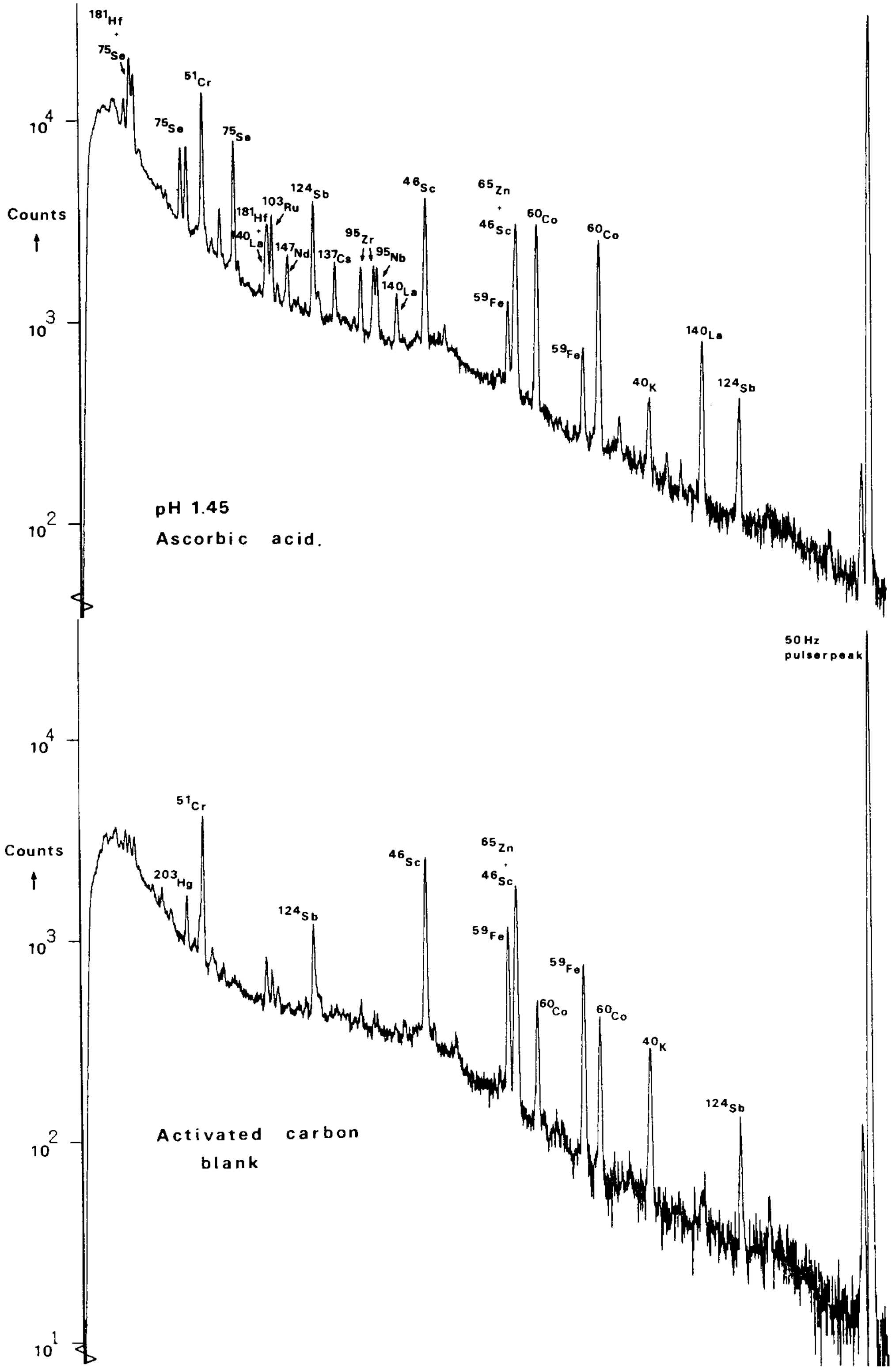


Fig. 8.1. Continued

abruptly to some value between 0.5 and 1.
Figure 8.2. gives the relation between y/m and c_e for Cu, Mo and Hg. For some other elements β increases with c_e, indicating the formation of larger adsorbable molecules. An example is Cr^{III} (figure 8.3).

8.4.2. Detailed procedures for single elements

- The carbon may be added to the solution, stirred through and filtered off. Alternatively the solution may be led through a layer of carbon on a support.
  The optimal conditions for the collection of a trace element in its ionic form are obtained by independent variation of the following parameters, starting from a reasonable first guess:
  o Concentration of chelating agent;
  o Concentration or amount of active carbon;
  o pH;
  o Stirring-time or rate of filtration.

- Separately, the blank of the procedure has to be considered. An example of an unfavourable case is the determination of Mn [87]. The blank of commercially available active carbon is between 1 and 10 $\mu g.g^{-1}$. At a concentration of 40 mg carbon per 100 ml water this corresponds to 0.4 - 4 $\mu g.l^{-1}$. Use of an ultrapure brand of carbon (cf. section 7.3) is mandatory here.

- The optimal conditions proposed by van der Sloot [70] are summarized in table 8.IV.
  The range of elements may be extended with the lanthanides, using oxalic acid as the reagent but at the cost of a partial recovery of ~ 60% [95].

- A special case is presented by mercury. The inorganic species is isolated by reduction with 10 mg $SnCl_2$ per litre and aeration at a flowrate of 3 - 6 $l.min^{-1}$. The volatilized mercury is collected on 2 g of active carbon. Recovery is complete after 5 minutes. Organomercurials are not collected.
  Passage of water through a small column of active carbon yields a complete recovery of the total mercury content.
  Eventually the collected mercury is purified further by a second volatilization.

Chemical form: Cu^{2+}
V = 100 ml seawater
m = 20 mg carbon
stirring time: 20 minutes
pH: 8

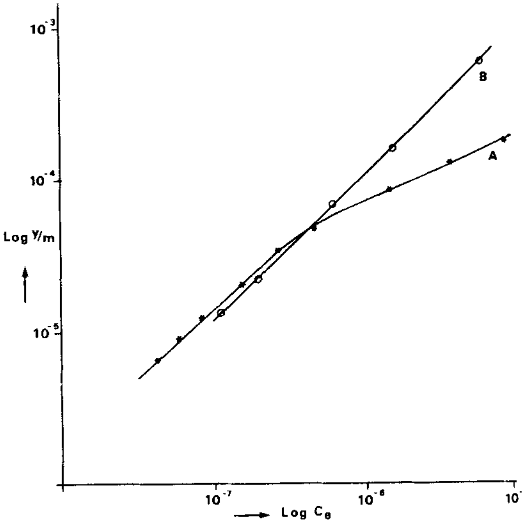


Figure 8.2.a The adsorption isotherm of copper (A) and copper-APDC complex (B) on activated carbon.

Chemical form: MoO_4^{2-}
V = 100 ml seawater
m = 20 mg carbon
stirring-time: 20 minutes
pH: 3.5

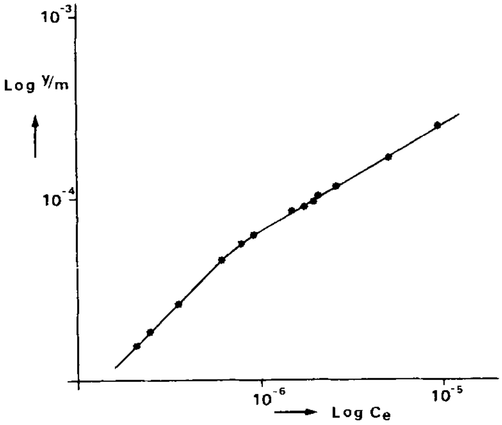


Figure 8.2.b The adsorption isotherm of molybdenum on activated carbon.

- The active carbon technique fails when the water contains a high concentration of organic compounds. Yet it proved possible to apply the procedure to Dutch sea and surface water which was highly polluted by the discharge of the potato-based amylose industry.

Chemical forms: Hg^{2+} and CH_3HgCl.
V = 100 ml seawater
m = 250 mg and 150 mg carbon
respectively
flow-rate through the carbon
column: 0.4 $ml.min^{-1}$ by means
of a peristaltic pump.
pH: 2

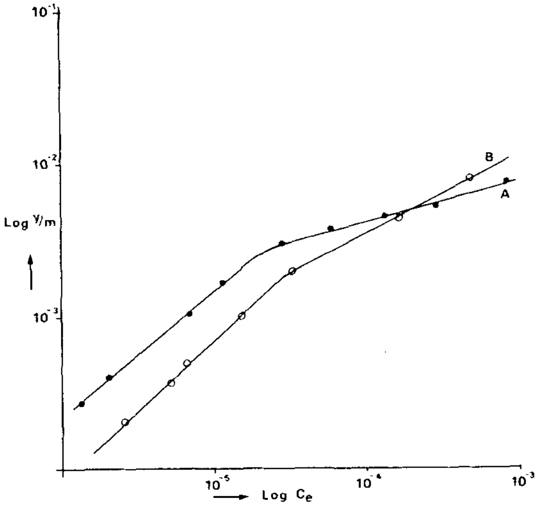
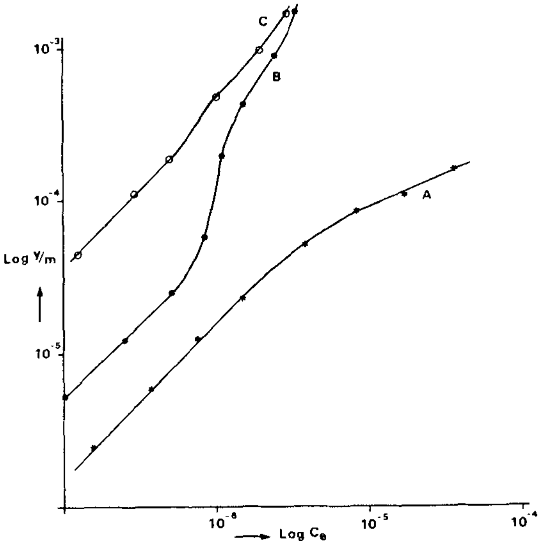


Figure 8.2. c *The adsorption isotherms of Hg^{2+} (A) and CH_3HgCl (B) on activated carbon.*

Figure 8.3. The adsorption isotherms for chromate and tervalent chromium on activated carbon
Curve A: chromate
Curve B: tervalent chromium from seawater stored at its natural pH (7.5 - 8.5)
Curve C: tervalent chromium from seawater stored at pH 1.5



Chemical forms: Cr^{3+} and CrO_4^{2-}
V = 100 ml seawater
m = 20 mg carbon
stirring-time: 20 minutes
The respective pH values are 8 and 3.5

Table 8.IV. Summary of the procedures for the determination of some trace elements by collection on active carbon and neutron activation analysis.

Element	Species	Volume of aliquot in ml	pH	Reagent	Reagent concentration in $mg.l^{-1}$	Stirring (S) or filtration (F)	Amount of carbon in mg	Stirring time in min	Chemical yield in %	Average concentration in seawater in $\mu g.l^{-1}$	Concentration range in fresh surface water in $\mu g.l^{-1}$	Remarks
V	total V as VO_3'	100	3.6 ± 0.1	APDC	75 ± 10	S	20	10 ± 3	93 ± 2	2	1-6	- Amount of carbon (in mg) is $10 + 0.1 \times$ (aliquot-volume) - For concentrations below 0.5 $g.l^{-1}$ a modified procedure is used, including ^{48}V ($T_{½}$ = 16 d) radiotracer.
Cr	total Cr^{III}	300	8 ± 0.5	APDC	-	S	20	30	95 ± 2	0.7	1-6	- Previous reduction of CrO_4'' with 50 $mg.l^{-1}$ SO_3'' at pH = 1.5 during ≥ 30 minutes for the total Cr-determination.
Mn	total	100 - 200	5-9	APDC	250	F	40	-	95 ± 2	0.4	50-500	- The use of ultra-pure active carbon is mandatory [87]
Co Cu Zn Cd	total	500 (seawater) 200 (fresh water)	7.8 ± 0.5	APDC	50 ± 5	F	20	-	97 ± 3	0.5 4 10 0.4	0.1-1 1-50 10-500 0.01-1	- A separate procedure for Cu, using the short-lived ^{66}Cu ($T_{½}$ = 5.1 min) is possible.
Se	total SeO_3''	500	2.1	1-ascorbic acid	3000	F	100	-	90 ± 3	0.1^5	0.05-0.5	- Selenate is reduced by refluxing of a pH = 1.5 HCl-solution.
Mo and W	total	500	1.3 ± 0.2	APDC	150	S	70	40-60	97 ± 2	11 and 0.1^2	0.5-5 and 0.01-0.1	- For W it is preferable to perform a post-irradiation separation as described in [34]

Table 8.IV. Summary of the procedures for the determination of some trace elements by collection on active carbon and neutron activation analysis. (continued)

Element	Species	Volume of aliquot in ml	pH	Reagent	Reagent concentration in $mg.l^{-1}$	Stirring (S) or filtration (F)	Amount of carbon in mg	Stirring time in min	Chemical yield in %	Average concentration in seawater in $\mu g.l^{-1}$	Concentration range in fresh surface water in $\mu g.l^{-1}$	Remarks
U	UO_2^{II}	200	4	1-ascorbic acid	800	S	20	15-20	92 ± 2	3.4	0.1-1	- The chemical yield tends to vary with the ionic strength A separate determination is necessary [96].
Hg	total	500	1.5	-	-	F	2000	-	99 ± 1	0.055	0.01-0.1	- Column (10x100 mm) of ≃ 2g carbon. Flow-rate ≤ 4 $ml.min^{-1}$. Purification by a second volatilization.
	Hg^{II}	1000	natural	$SnCl_2$	10	Aeration	2000	Aeration time 5min	99 ± 1	0.005	0.005-0.05	

8.5. Rainwater

8.5.1. General

- The elemental analysis of rainwater may yield information on the extent and origin of atmospheric pollution. Particles with a diameter of less than ~ 10 µm are removed from the atmosphere by wet precipitation mainly. Monitoring the composition of rainwater over a period of several years discloses possible trends.

- In comparison to sea and surface water, rainwater presents the additional difficulty of the scarcity of the sample material.

  The splitting up of rain showers into many fractions, according to time of deposition and direction of the wind, leaves the analyst with the task to determine as many trace constituents as possible in a total sample which is often much less than 50 ml. Under these conditions the application of scavenging techniques like that with active carbon is hardly feasible. Only in the exceptional case of a large (~ 100 ml) integral sample the procedures mentioned in the previous section should be considered too.

- Moreover, rainwater is an ideal matrix for various other analytical techniques, especially (atomic) absorption spectrophotometry, and ion-sensitive electrode measurements [98-100]. Table 8.V. gives a summary of the non-radioanalytical analytical techniques used in some systematic rainwater investigations. The applications of radioanalysis are therefore restricted to purely instrumental analysis, mostly INAA, and some multi-element determinations, involving a simple group separation. Table 8.VI. summarizes the literature data. Part of these procedures is not always applicable to large series of samples, as the turn-over time is too long or the irradiation capacity too small. Evaporation is the obvious technique for preconcentration.

8.5.2. Instrumental neutron activation analysis

- The γ-spectrum obtained by counting with a 45 cm^3 coaxial Ge(Li) detector after a short irradiation in a thermal neutron flux of 5.10^{13} $cm^{-2}.s^{-1}$ is shown in figure 8.4. while the corresponding specific countrates and the corresponding relative limits of determination are given in table 8.VII. Both are taken from ref. [108].

Table 8.V.

SOME NON-RADIOANALYTICAL METHODS FOR THE DETERMINATION OF TRACE ELEMENTS IN RAIN WATER.

Authors	Sample volume	Element	Method	Limit of determination (µg.l^{-1})	Concentration-range found	Remarks	Ref
Harriss et al. (1969)	-	F	Ion-selective electrode	20	20 - 1000 µg.l^{-1}	Preconcentration is sometimes necessary.	[101]
		Cl		100	0.25 - 34 mg.l^{-1}		
		Br		100	4 - 650 µg.l^{-1}		
					average concn.		
Lazrus et al. (1970)	100 ml	Pb	A.A.S.	1	34 µg.l^{-1}	Elements are preconcentrated by extraction.	[102]
		Zn		1	107 µg.l^{-1}		
		Cu		1	21 µg.l^{-1}		
		Fe		1	-		
		Mn		1	12 µg.l^{-1}		
		Ni		1	4.3 µg.l^{-1}		
Drozdova et al. (1970)	100 ml	Mn	Emission spectroscopy	-	1 - 43 µg.l^{-1}	Preconcentration by evaporation is necessary.	[103]
		Ni		-	1 - 20 µg.l^{-1}		
		Pb		-	1 - 48 µg.l^{-1}		
		Fe		-	3 - 200 µg.l^{-1}		

*) - = not mentioned

Table 8.V. (continued)

Rattonetti (1974)	50 µl	Pb	A.A.S.	0.2	1 - 50 µg.l^{-1}	Preconcentration is necessary for Ag and In.	[104]
	50 µl	Cd		0.03	0.03 - 20 µg.l^{-1}		
	5 ml	Ag		0.001	0.002 - 0.2 µg.l^{-1}		
	10 ml	In		0.01	-		
Slanina et al. (1978)	3.0 ml	NO_3^-	spectrophotometry	50	0.1 - 30 mg.l^{-1}		[98-100]
	4.0 ml	SO_4^{2-}	nephelometry	500	0.5 - 50 mg.l^{-1}		
	3.0 ml	NH_4^+	ion-selective electrode	50	0.05 - 200 mg.l^{-1}		
	0.5 ml	F		10	0.02 - 100 mg.l^{-1}		
	0.5 ml	Cl		500	1 - 1000 mg.l^{-1}		
	5.0 ml	Na	A.A.S.	10	0.05 - 20 mg.l^{-1}		
	1.0-5.0 ml	Fe		20	0.01 - 2 mg.l^{-1}		
	50 µl	Cd		0.01	0.1 - 10 µg.l^{-1}		
	50 µl	Pb		1	2 - 200 µg.l^{-1}		
	50 µl	Zn		0.01	0.01 - 2 mg.l^{-1}		
	50 µl	Cu		0.1	2 - 200 µg.l^{-1}		
	1.0-5.0 ml	Ca		10	0.05 - 10 mg.l^{-1}		

- not mentioned

A.A.S.: atomic absorption spectrophotometry

Table 8-VI

SOME RADIOANALYTICAL METHODS FOR THE DETERMINATION OF TRACE ELEMENTS IN RAIN WATER

Authors	Method	Elements	Limit of determination (μg.l^{-1})		Concentration-range found			Ref
Cawse (1974)	Instrumental neutron activation analysis after preconcentration of 100 ml rain water by evaporation.	Na, Al, Cl, Sc, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Rb, Cd, In, Sb, I, Cs, La, Ce, W, Au, Hg, Th.	Na: 100	Br: 30	Na	1.7 - 108	mg.l^{-1}	[105]
			Al: 100	Rb: 20	Al	0.06 - 150	mg.l^{-1}	
			Cl: 600	Cd: 200	Cl	2.7 - 200	mg.l^{-1}	
			Sc: 0.005	In: 0.5	Sc	0.01 - 0.7	μg.l^{-1}	
			V : 4	Sb: 0.3	V	1 - 38	μg.l^{-1}	
			Cr: 2	I : 40	Cr	0.6 - 34	μg.l^{-1}	
			Mn: 7	Cs: 0.1	Mn	1.2 - 77	μg.l^{-1}	
			Fe: 10	La: 3	Fe	63 - 2700	μg.l^{-1}	
			Co: 0.15	Ce: 0.3	Co	0.08 - 23	μg.l^{-1}	
			Zn: 15	W : 10	Zn	18 - 380	μg.l^{-1}	
			As: 5	Au: 0.8	As	1.0 - 2.0	μg.l^{-1}	
			Se: 0.3	Hg: 0.7	Se	0.2 - 1.6	μg.l^{-1}	
				Th: 0.1	Br	22 - 970	μg.l^{-1}	
					Sb	0.1 - 1.5	μg.l^{-1}	
			These limits of determination are based on rain water samples from industrial areas.		Ce	0.1 - 2.7	μg.l^{-1}	

Table 8-VI (Continued)

Bogen (1974)	Instrumental neutron activation analysis after preconcentration of 1 - 25 liter rain water by evaporation	Na, Cl, K, Sc, Cr, Mn, Fe, Co, Br, Ag, In, Sb, La, Sm.	-	Na 0.18 - 1.65 mg.l^{-1} Cl 0.16 - 3.45 mg.l^{-1} K 0.39 - 1.97 mg.l^{-1} Sc 0.01 - 2.8 μg.l^{-1} Cr 0.1 - 12 μg.l^{-1} Mn 4.6 - 77 μg.l^{-1} Fe 27 - 4020 μg.l^{-1} Co 0.07 - 4.2 μg.l^{-1} Br 1.4 - 21 μg.l^{-1} Ag 0.07 - 9.1 μg.l^{-1} In 1.4 - 2.6 μg.l^{-1} Sb 0.73 - 4.6 μg.l^{-1} La 0.13 - 1.9 μg.l^{-1} Sm 0.04 - 0.41 μg.l^{-1}	[106]
Duce (1965)	Neutron activation analysis of 8 ml of rain water. Separation of Cl, Br and I.	Cl, Br, I	-	Cl 1.37 - 4.23 mg.l^{-1} Br 8.4 - 15.0 μg.l^{-1} I 3.4 - 7.6 μg.l^{-1}	[107]

TABLE 8-VI (Continued)

			LIMITS OF DETERMINATION						
Luten (1974)	Instrumental neutron activation analysis on a 2.5 ml sample	Na, Al, Cl, Cr, V, Mn, Fe, Co, Cu, Zn, Br, Sb, I.	Na	10	$\mu g.l^{-1}$	Br	2	$\mu g.l^{-1}$	[108]
			Al	3	$\mu g.l^{-1}$	I	0.03	$\mu g.l^{-1}$	
			Cl	15	$\mu g.l^{-1}$	Cr	0.002	$\mu g.l^{-1}$	
			V	0.1	$\mu g.l^{-1}$	Fe	1.5	$\mu g.l^{-1}$	
			Mn	0.2	$\mu g.l^{-1}$	Co(^{60}Co)	0.003	$\mu g.l^{-1}$	
			Co(^{60m}Co)	0.5	$\mu g.l^{-1}$	Zn	0.07	$\mu g.l^{-1}$	
						Sb	0.01	$\mu g.l^{-1}$	
	NAA on a 10 ml sample. Separation by isotopic exchange	Br, I, IO_3	Br	0.2	$\mu g.l^{-1}$				
			I	0.02	$\mu g.l^{-1}$				
			IO_3	0.02	$\mu g.l^{-1}$				
	NAA on a 10 ml sample. Separation by solvent extraction	V, Co, Cu, Zn, In	V	0.03	$\mu g.l^{-1}$	Zn	17	$\mu g.l^{-1}$	
			Co	0.07	$\mu g.l^{-1}$	I	0.005	$\mu g.l^{-1}$	
			Cu	0.65	$\mu g.l^{-1}$				

Table 8.VII.

THE SPECIFIC COUNT RATE AND LIMIT OF DETERMINATION OF SOME SHORT-LIVED RADIONUCLIDES FOR INAA OF RAIN WATER

Element	Radionuclide	$T_{\frac{1}{2}}$	Gamma ray measured (keV)	Specific count rate* (counts.min^{-1}.µg^{-1})	Determination limit** L_Q (µg.l^{-1})
Sodium	^{24}Na	15 h	1368	2.2×10^3	10
Aluminium	^{28}Al	2.3 min	1779	1.3×10^5	3
Chlorine	^{38}Cl	37.3 min	1642	2.1×10^3	14
Vanadium	^{52}V	3.75 min	1434	5.8×10^5	0.1
Manganese	^{56}Mn	2.6 h	847	1.6×10^5	0.2
Cobalt	^{60m}Co	10.5 min	58.5	1.4×10^5	0.5
Copper	^{66}Cu	5.1 min	1039	1.4×10^4	7
Bromine	^{80}Br	17.6 min	617	2.3×10^4	2.1
Iodine	^{128}I	25.2 min	443	1.9×10^5	0.3

* At the end of the irradiation

**Experimental conditions:

Irradiation time 4 minutes at $\phi_{th} \approx 5 \times 10^{13}$ cm^{-2}.s^{-1}

Cooling time 4.5 minutes.

Counting time 10 minutes.

Detector 45 cm^3 coaxial Ge(Li)

Rain water sample volume 2 ml.

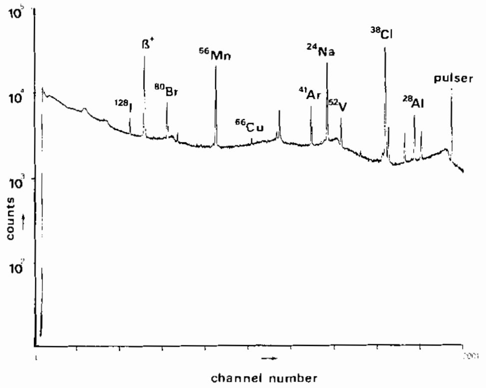


Figure 8.4. *A GAMMA-RAY SPECTRUM OF A RAIN WATER SAMPLE AFTER A SHORT IRRADIATION*

Experimental conditions: $\phi_{th} = 5.10^{13}$ cm^{-2}.s^{-1} irradiation time 4 minutes, cooling time 4.5 minutes, counting time 10 minutes.

Detector : 45 cm^3 coaxial Ge(Li).

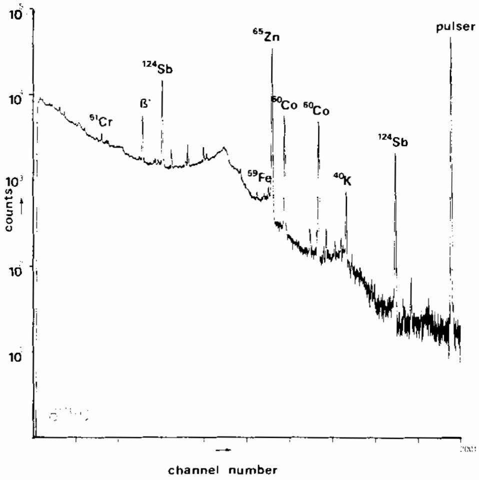


Figure 8.5. *A GAMMA-RAY SPECTRUM OF A RAIN WATER SAMPLE AFTER A LONG IRRADIATION IN THE POOLSIDE FACILITY OF THE HFR.*

Experimental conditions: irradiation time 2 days, cooling time 3 weeks, counting time 50 minutes. ϕ_{th} : 8 x 10^{13} cm^{-2}.s^{-1}

Detector 45 cm^3 coaxial Ge(Li).

The elements Cu and I are not always determinable.

- The situation for the long-lived radionuclides is shown in figure 8.5. and table 8.VIII. A 100 ml rainwater sample was preconcentrated by evaporation to dryness.

Table 8.VIII.

THE SPECIFIC COUNT RATE AND LIMIT OF DETERMINATION OF SOME LONG-LIVED RADIONUCLIDES FOR INAA OF RAIN WATER

Element	Radio-nuclide	$T_{\frac{1}{2}}$	Gamma-ray measured (keV)	Specific count rate* (counts.h^{-1}.μg^{-1})	Determination limit** L_Q ($\mu g.l^{-1}$)
Chromium	^{51}Cr	27.8 d	320	5.7×10^5	0.002
Iron	^{59}Fe	45 d	1099	3.3×10^3	1.5
Cobalt	^{60}Co	5.26 y	1173	1.3×10^6	0.003
Zinc	^{65}Zn	245 d	1115	5.0×10^4	0.07
Antimony	^{124}Sb	60.3 d	602	6.2×10^5	0.008

* At the end of the irradiation

** Experimental conditions: Irradiation time 2 days $\phi_{th} = 8 \times 10^{13}$ $cm^{-2}.s^{-1}$ Cooling time 3 weeks; Counting time 50 minutes; Original sample volume 100 ml. Detector 45 cm^3 Coaxial Ge(Li).

8.5.3. Neutron activation analysis including chemical separation

- Post-irradiation chemical separations are based on liquid extraction and ion-exchange primarily. Both techniques require a rather large aliquot of ≥ 10 ml.

- Solvent extraction procedures are similar to those used in AAS and based on chelation with APDC mainly [110].

  Table 8.IX. and figure 8.6. give the results for the extraction from 11 ml rainwater, containing 0.2% APDC, into 5 ml MIBK after a short irradiation in a thermal neutron flux of 5.10^{13} $cm^{-2}.s^{-1}$ [108]. It provides a sensitive determination for 5 elements.

  Isotopic exchange with a solution of Br_2 and I_2 in CCl_4 after a short irradiation with thermal neutrons leads to a rapid and quantitative isolation of the radionuclides ^{80}Br, $T_{\frac{1}{2}}$ = 17.6 m and ^{128}I, $T_{\frac{1}{2}}$ = 25 m [111].

- The application of anion-exchange makes it possible to separate I' and IO_3' and thus to determine the enrichment of the iodine-species in rain compared to seawater [112].

8.5.4. An analytical scheme and the interpretation of the experimental data

- The combination of different analytical techniques, including radioanalysis, is demonstrated in the work of Luten [108] and Slanina [98-100].

Table 8.IX.

THE SPECIFIC COUNT RATE AND LIMITS OF DETERMINATION OF V, Co, Cu, Zn, In *AND* U *IN RAIN WATER*

Element	Radio-nuclide	$T_{\frac{1}{2}}$	E_γ-measured (keV)	Specific count rate* (counts.min^{-1}.μg^{-1})	Determination limit** L_Q ($\mu g.l^{-1}$)
Vanadium	^{51}V	3.75 min	1434	5.8×10^5	0.03
Cobalt	^{60m}Co	10.5 min	58.5	1.4×10^5	0.07
Copper	^{66}Cu	5.1 min	1039	1.4×10^4	0.7
Zinc	^{69m}Zn	13.9 h	439	60	17
Indium	^{116m}In	54 min	417	3.8×10^5	0.005
Uranium	^{239}U	23.5 min	74.7	2.3×10^5	0.03

* At the end of the irradiation.

**Experimental conditions:

Irradiation time 4 minutes at $\phi_{th} = 5.10^{13}$ $cm^{-2}.s^{-1}$.

Cooling time 10 minutes.

Counting time 15 minutes for V, Co, Cu, In and U.

Counting time 60 minutes for Zn.

Rain water sample volume 10 ml.

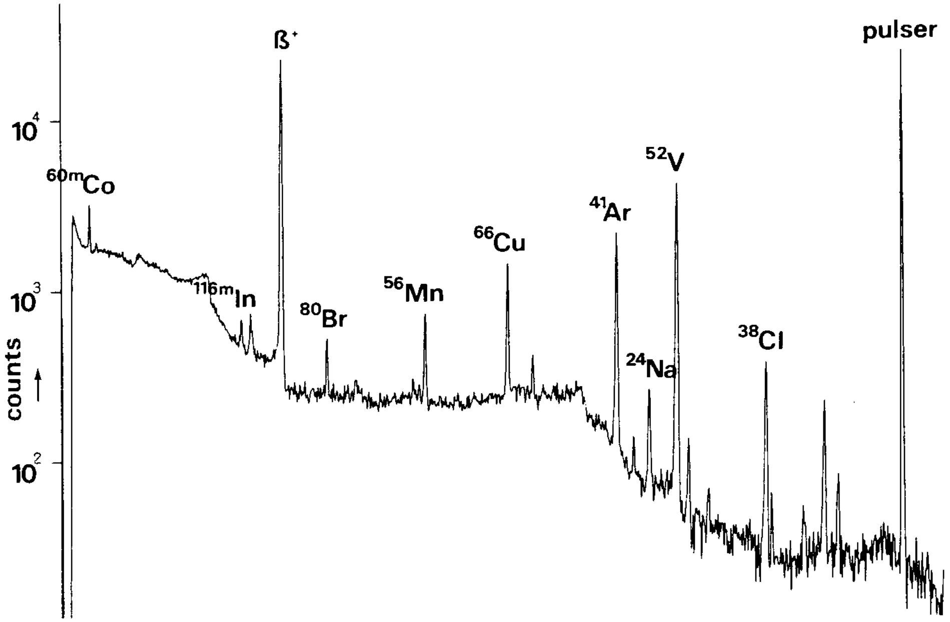


Figure 8.6. THE GAMMA-RAY SPECTRUM OF AN APDC/MIBK EXTRACT AFTER A SHORT IRRADIATION.

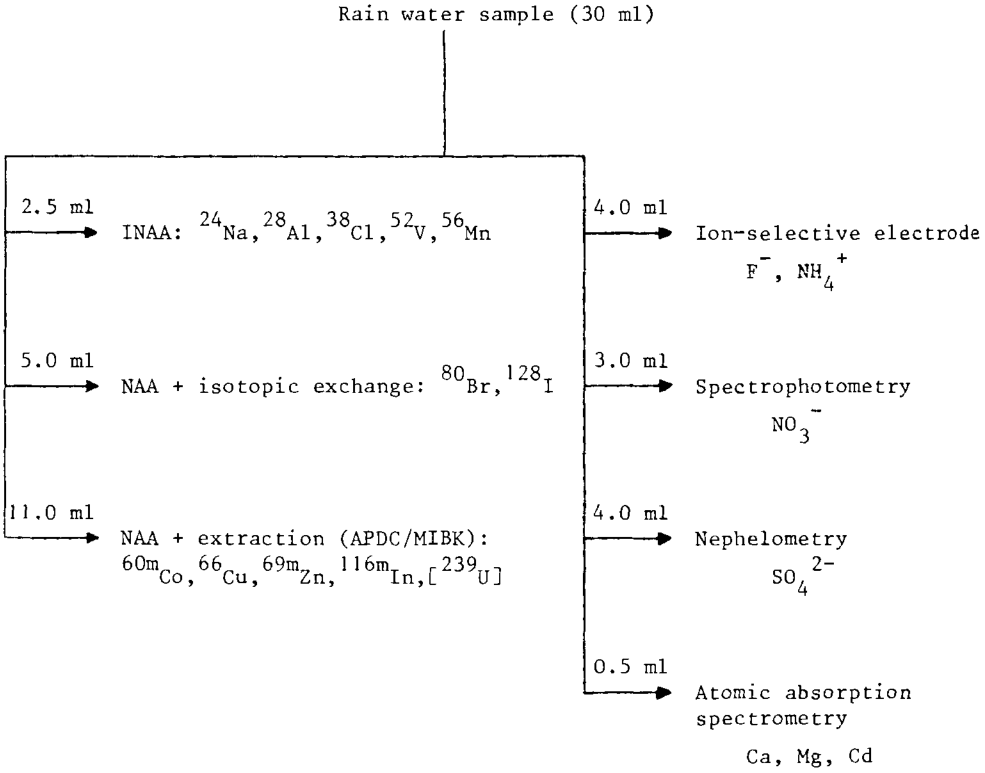
Experimental conditions: irradiation time 4 minutes, at $\phi_{th} = 5.10^{13}$ $cm^{-2}.s^{-1}$, cooling time 15 minutes, counting time 5 minutes
Detector 45 cm^3 coaxial Ge(Li).

Table 8.X. gives a simplified picture of these combinations [108], based on a 30 ml rainwater sample, obtained with a sequential sampler.

- The data one used to elucidate processes of "rain out" (interactions within the clouds) and "wash out" (on the way to the earth's surface). Concentrations are either plotted against the depth of rain fall [113, 114] or screened for possible intercorrelations [115].

TABLE 8.X.

SIMPLIFIED SCHEME FOR THE ELEMENTAL ANALYSIS OF RAINWATER



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CHAPTER 9.

THE ELEMENTAL ANALYSIS OF DRY BIOLOGICAL MATERIAL

SUMMARY

- The interaction between living organisms and their environment is reflected in their elemental composition, especially in the trace element contents. Thus the determination of the elemental concentrations is important for the environmentalist as well as for the physiologist.

  Most of the samples taken from plant or animal are dried to some extent prior to the analysis. This, and the fact that the aliquots taken for analysis are usually small, makes activation analysis and proton induced X-ray emission convenient tools.
- The applications of activation analysis on "dry" biological material are directed to multielement characterization and to the determination of a few important trace elements. To this end it is necessary to have a rapid and simple system of group separation as a preparation for Ge(Li) counting. This should then be completed by some simple chemical techniques, performed on separate aliquots and aimed at a few elements which are missing from the general system. A suitable combination is presented in this text.
- The achievements of radioanalysis in the six main groups of biological material are summarized. The accuracy of the results depends on the sampling procedure primarily.

9.1. Introduction

- The collective term "biological material" is often used in (radio-) analytical literature. It comprises all samples, both fluid and dry, which can be obtained from the plant or animal kingdoms. In a more strict sense, it refers to the dried residues of such samples. From the viewpoint of elemental analysis, the following classes may be distinguished:
  1) Dried plant material.
  2) Whole blood and serum.
  3) Dried animal tissues.
  4) Bone and teeth.
  5) Tartar, bile, kidney and bladder stones.
  6) Hairs and nails.
- The demand for information on the distribution of minor constituents through living organisms has increased continuously during recent years [1-6]. This has caused the rapid improvement of analytical methods and, consequently, tended to lower the concentration level below which an element is referred to as a "trace". In samples taken from living organisms, the interest has shifted towards concentrations below ~ 1 $\mu g.g^{-1}$. There is however, no apparent need to change the old definition of a "trace" element as having a concentration below ~ 100 $\mu g.g^{-1}$, as this is still in accordance with analytical practice at the moment. Elements with concentrations between ~ 100 $\mu g.g^{-1}$ and 10 $mg.g^{-1}$ can be referred to as "minor constituents".
- The bulk of living matter is constituted by ≃ 15 elements of low atomic weight. In principle all other elements are present as traces [7,8]. It is now generally assumed that some elements are required by living organisms [9]. These elements are called "essential". All major and minor constituents belong to this group. Until 1957 only seven trace elements were recognized as essential for animals: Mn, Fe, Co, Cu Zn, Mo and I. At least seven were added in recent years: Se (1975), Cr (1959), Sn (1970), V (1971), F (1971), Si (1972) and Ni (1973).

  Elements of which only a harmful effect is known are referred to as "toxic". Examples are Be, Tl, and the α-emitting radionuclides. This is primarily a matter of concentration as many elements become toxic above a certain threshold.

Elements which, at present, have no known function nor feature toxicity may be labelled "indifferent". They still comprise the majority of the trace elements [10].

- An essential element will show, for a certain organ within a certain species, a normal or log-normal distribution. A toxic element will feature a more irregular and markedly skew distribution whereas for an indifferent element a wide range may be expected [11].
  Thus information on the environmental impact can be obtained by the analysis of many small aliquots only [12-15]. This in turn implies the availability of (a) a reliable method of sampling and sample pretreatment and (b) internationally accepted standard materials for the various classes of dry biological material.
  Pretreatment should result in a material with a known moisture-content and which can be handled conveniently.
  The analysis should be multi-elemental, precise within 5% at the utmost and without appreciable systematic bias. The turn-over time for series of medium size, say 50-100 samples, should not exceed 1 month and the time spent per sample should be kept within ≃ 2 hours.
- The requirements which should be met by the analytical system can now be summarized:
  1) Elements of interest : At least the elements which are presently known as essential or toxic and as much of the possibily essential elements as can be realized.
  2) Limit of determination : Trace elements ≤ 0.1 ng or 1 to 10 $ng.g^{-1}$
     Minor constituents ≤ 1 μg or 10 to 100 $\mu g.g^{-1}$.
  3) Accuracy : < 5%.
  4) Precision : ≤ 10%.
  5) Turn-over time : ≤ 1 month.
  6) Man-hours needed per sample : ≤ 2 hours.

Activation analysis with neutrons and photons, as well as proton induced X-ray emission may meet these requirements.

9.2. Analytical techniques

- Comparison of the limits of determination, observed for neutron activation analysis (NAA) at a flux of ~ 10^{13} $cm^{-2} \cdot s^{-1}$ with the those for the most important other analytical techniques reveals that in many cases some other technique is more sensitive [10]. This situation is unlikely to change as higher neutron fluxes are hardly applicable to biological material. Furthermore, the turn-over time of NAA is often longer.
  However, the innate advantages of high sensitivity together with matrix- and contamination-independence make NAA an attractive technique for trace element determination, if the range of elements covered is wide enough. Instrumental neutron activation analysis (INAA) of dry biological material will give reliable results for a few elements only: Na, Cl, K, Sc, Fe, Co, Zn, Br, La, Ce, Eu and Th. The elements Al, V, Cr, Mn, Rb, Cs, Sb, Hf, Hg and U may be assayed sometimes. Occasionally Au is within reach [16]. Sophisticated spectrum-treatment may increase the range somewhat but usually at the cost of precision.

- Instrumental photon activation analysis (IPAA), using ≤ 50 MeV photons, can be applied for the determination of C, Mg, Ca, Ti and Sr and to a range of traces [17-19]. For the last group its sensitivity is decidedly less than that of (I)NAA.

- Proton induced X-ray emission (PIXE) is usually based on a ≃0.01-1 μA beam of 2-3 MeV protons and a cross-section of a few cm^2 on a thin sample of ≤ 2 $mg.cm^{-2}$, on an inert support like "Mylar" or "Hostaphan" of ~ 5 $mg.cm^{-2}$ [120,121]. The vacuum should be kept moderate.
  Details on dose-measurement and standardisation are discussed in section 7.5. Standard addition [120] absolute calibration combined with beam-current measurements [139] as well as calibration against INAA [121] are possible. The elements which are determinable in biological material range from Cl to Sr [122]. Usually Mn, Fe, Cu, Zn, Br, Rb and Sr are assayed.
  The advantage of PIXE lies in its speed and the fact that only small aliquots are needed. Its limitations are the requirement of the thin and even distribution of the material over the support and the rather small range of elements.

- From the average contents in dry biological material and the reported sensitivities for (I)NAA, IPAA and PIXE it follows that, in principle, all elements of interest may be determined in an aliquot of ~ 100 mg dry mass while for a chosen set of elements even less material is needed. This presses for representative sampling. Furthermore, this wide scope can be realised only if some system of chemical (group) separation is available. The feasibility of such a system is governed by (a) the radiation burden and (b) the time spent per analysis. A high radiation dose-rate implies that the work should be done in a hot-cell [25]. This is the case when short-lived radionuclides have to be separated. Such cumbersome work may be avoided by pre-irradiation separation under carefully controlled blank-conditions [129] (cf. section 4.4.4.).

9.3. Sampling and sample pretreatment

- The subject of sampling has been treated in chapter 4. A few remarks on biological material in particular can be added here.
  The aliquot taken should be representative. This is primarily a matter of definition. At least three levels of representation may be distinguished, as follows from the next example:
  a) A mixture of leaves from various trees may be homogenised and used as a standard reference material for the analysis of dry plants.
  b) The same tissue may be collected from various leaves and pooled. This may result in a sample which is representative for that particular tissue.
  c) Finally, one single leaf may be dissected and the various parts analysed separately to obtain data on the element distribution over a leaf.

  The smallest aliquots are obtained with case (c). They may be of the order of ~ 10 mg dry weight. The other approaches will give larger samples, usually of the order of ~ 100 mg.

  If only an aliquot of the sample is analysed, this involves both a systematic and a statistical error.
  The systematic error can be avoided by homogenisation of the sample prior to the taking of the aliquot. The material will then consist of a homogeneous mixture of small particles of - possibly - different

composition. The relative standard deviation around the average concentration will be inversely proportional to the square root of the number of particles per gram. With an average particle diameter of 100 µm, a sample of 10 mg will contain ~ 5.10^3 particles which points to a statistical error of ≤ 2%. For 50 mg, the relative error is ≤ 1%.

The samples should be handled in a laminar flow box in a dust-free room. For storage and encapsulation polythene bottles and capsules with screw- or snap cap should be used. The samples should be stored in a cool and dark place.

- Pretreatment is necessary to obtain a constant moisture content and to enable further handling. Drying at 60-90°C and lyophilization have been proposed [26-31].
  Bowen [28] recommends for standard kale powder drying at 90°C for 20 hours. A more cautious advise is given by the National Bureau of Standards [31]: "Drying in air in an oven at 85°C for 2 hours. Drying at 105°C or in vacuo at 25°C should not be used as it gives rise to losses".
  Lyophilization is usually applied and recommended [26-28, 31] as a generally applicable method.

9.4. Mineralization

Chemical treatment implies dissolution of the sample. Five methods may be used:

1) Dry ashing in an open system.
2) Dry ashing in a closed system.
3) Wet ashing in an open system.
4) Wet ashing combined with distillation.
5) Wet ashing in a closed system.

1) Dry ashing in an open system can be used except in the case of the halogens, especially I and Br, and elements which form volatile halogenides [26,32]. The losses of the latter group depend strongly on the halogen content of the sample. In general losses increase with temperature. An elegant method is gradual dry oxidation by heating the sample with KNO_3 at slowly increasing temperatures [33]. The advantage of the method is its simplicity. The results of ashing

in an oxygen plasma at low temperature (LTA) are often disappointing [26,34].

2) Dry ashing in a closed system is performed in the oxygen flask [35,36]. The rapid complete combustion is followed by absorption of the vapours in a suitable solution. The method is simple and fast but applicable to small samples (≤ 100 mg) of certain materials only [34]. Moreover, severe losses are observed for some elements [26].

3) Wet ashing in an open system is widely applicable after activation and if carrier has been added [37-40]. Then there is no risk of contamination from the destructing agents while losses are reduced effectively by the added carrier. A further improvement is the use of a reflux apparatus [41,42] or of long quartz-tubes, the upper ends of which are kept cool [43]. The use of a concentrated $Mg(NO_3)_2$ solution for the mineralization of dry biological material opens up the possibility of processing large samples up to ~ 5 gram [44]. This is of importance if the minimal representative aliquot is too large for mineralisation in a closed system and does not permit dry ashing either

4) Wet ashing combined with evaporation or distillation has been applied by many authors [22,24,45-62,140]. The usual reagents are conc. H_2SO_4 and HNO_3. Samples up to ~ 1 gram can be handled. The method is attractive in that it brings about a first separation. The halogens, B, Si, Ge, As, Se, Ru, Sn, Sb, Re, Os and Hg are evaporated or distilled by addition of conc. HBr [63]. Both terms are used indiscriminately in most publications. The practical applicability depends largely on the design of the apparatus. The separated phases should be recovered quantitatively and cleaning of the apparatus should be simple. The method is used after irradiation only. In view of the irradiation conditions, the limits of determination and the average concentrations, this separation is of interest for Br, As, Se, Sb and Hg primarily.

5) Wet ashing in a closed system is the most versatile method. It can be performed in a teflon covered stainless steel pressure bomb [26] or a Carius-tube [64]. Destruction takes 1-2 hours and can often be effectuated by conc. HNO_3 alone. The maximal sample weight is ~ 1 gram for the steel vessel and ~ 500 mg for the Carius-tube. Losses by evaporation during the recovery of the destruate from the vessel

or tube can be avoided by cooling in liquid nitrogen. A set of destruction vessels or a multiple Carius-furnace is a convenient basis for routine analysis.

9.5. Radiochemical separation schemes

Separations in (neutron) activation analysis are characterised by at least three features:

1) The distinction between "chemical", "radiochemical" and "radionuclide" purity. The second property governs the success of γ-ray spectrometry.
2) The possibility of adding "carrier" after the irradiation. This facilitates the elimination of losses greatly.
3) The radiation hazards.

Usually separations are standardised and combined into a separation scheme [30,65-67]. Such schemes are applied to achieve two ends at the cost of an acceptable radiation burden and labour investment:

1) The separation of the mixture of radionuclides into groups which can be handled by γ-ray spectrometry.
2) The isolation of one radionuclide to enable a very sensitive measurement.

Separation may be performed (a) prior to the activation or (b) after irradiation. Generally the latter option is preferred. The advantages of early separation are:

- Possible sample deterioration during transport and/or storage may be eliminated.
- The sample may be brought in a form that can stand an intense irradiation.
- The reduction of the radiation levels during the further handling of the sample.

The main disadvantage is the sensitivity towards contamination by the reagents.

Separation before activation is mandatory in cases of rapid deterioration of the sample or when radionuclides with short half-lives are to be measured. An example of the first case is the analysis of water [88]. The determination of Al in blood by ashing, ion-exchange and NAA [89] refers to the second situation. In most other cases separation is performed *after activation*. Since 1957 over a hundred separation procedures have been reported. Until 1974, the number published per year tended to increase; thereafter a marked decrease set in.

Of these systems, more than fifty use ion-exchange chromatography [68]. The relative simplicity of the technique combined with the high capacity and separation factors and the usually good recovery make this choice understandable.

Second comes solvent extraction [68-78]. The extracting agent may be loaded on an inert support to perform extraction chromatography [79].

Precipitation and electrodeposition can be applied after addition of carrier [68]. Here it is essential that carriers are added for all elements of interest and the major interferences to prevent adsorption and occlusion.

The combination of destruction and distillation has been applied frequently [16,25,52,80-84]. Now the main problem is the design of convenient apparatus.

In recent years the application of inorganic adsorbers has become important. Hydrated antimony pentoxide (HAP) was used to remove ^{24}Na and ^{42}K from sample solutions [66,81]. Titanium phosphate (TIP) and zirconyl phosphate can be applied to adsorb ^{42}K and $H^{32}PO_4''$ respectively [85].

The phenomena of adsorption and co-precipitation are primarily discussed in analytical literature as sources of error. Their application to achieve separations was first studied by radiochemists [86,87]. A survey of the use of inorganic co-precipitants is given in ref. [63]. Activated carbon was used for the collection of various trace elements from water [88]. The application of this simple technique to biological samples after wet destruction resulted in a fast procedure for multi-element analysis [95].

The obvious trend in the development of separation schemes is towards standardization and automation. This is caused by the improvement in the resolving power and efficiency of the detectors as well as by the steady increase of the cost of labour. Table 9.I. summarizes the main features of the "automatic" systems which have been applied to biological materials. Although data on the time involved are generally scarce, it is possible to estimate the time spent per element. The values given in table 9.I. are expressed in man minutes.(element)$^{-1}$; they refer to

Table. 9.I. Summary of automated separation systems

Author	Reference	Automated operations	Elements determined or separated	Time needed	Number of samples processed simultaneously	Time per element in min.
Damsgaard	Report RISØ-271 June, 1973	- Extraction	Na, Mg, Al, P, K, Ca, V, Cr, Mn, Cu, Zn, As, Se, Sr, Sb, Ba, La, Hg, U	not specified ≥ 1 day	1	≥ 20
Elek	J. Radioanal. Chem. 16 (1973), 165	- Reagent supply - Extraction - Phase separation - Fraction collection	Cu, As, Ag, Sb, Hg	not specified ≥ 1 day	1	≥ 80
Fourcy	Mod. Trends Act. Anal. 1968, p.160	- Reagent supply - Ion exchange - Fraction collection	N, P, K, Ca, Sc, Mn, Rb, Sr, Cs, Ba, lanthanides	not specified ≥ 1 day	8	≥ 4
Gaudry	J. Radioanal. Chem. 29 (1976), 77	- Reagent supply - Mineralization - Ion exchange	Na, P, K, Sc, Cr, Mn, Fe, Co, Cu, Zn, Ga, As, Se, Br, Rb, Mo, Ag, Cd, In, Sb, Cs, lanthanides, W, Au, Hg	1 day	4	≥ 4

Table 9.I. (Continued)

Author	Reference	Automated operations	Elements determined or separated	Time needed	Number of samples processed simultaneously	Time per element in min.
Guzzi	Report EUR 5282[e] (1974)	- Reagent supply - Ion exchange	Na,P,K,Ca,Sc,Cr,Mn,Fe, Co,Zn,Cu,Ga,As,Se,Sr, Mo,Pd,Cd,Sb,Cs,Ba,W, Au,Hg	not specified ≳ 1 day	6	≥ 3
Goode	Analyst 94 (1969), 728	- Reagent supply - Solvent extraction - Phase separation	Na,Ca,Sc,Cr,Fe,Cu,Rb, Sr,Zr,In,Sb,Cs,Ba, lanthanides,Hf,Ta,Th	not specified	2	≥ 10
Iyengar	Report KFA Jül. 1308 June 1976	- Reagent supply - Ion exchange - Fraction collection	Na,P,Cl,K,Ca,Cs,Cr,Mn, Fe,Co,Cu,Zn,Ga,As,Se, Br,Rb,Sr,Mo,Ag,Cd,In, Sn,Sb,Cs,lanthanides, Hf,W,Au,Hg	1 week	18	≃ 4
Kvčera	Radiochem. Radioanal. Lett. 24 (3),215 (1976)	- Reagent supply - Solvent extraction - Colum chromatogr.	Sc,Fe,Co,Cu,Zn,Ga,As, Se,Br,Mo,Pd,Ag,Cd,Sb, Hf,Ta,W,Au,Hg	not specified ≥ 1 day	1	≥ 25

Table 9.I. (Continued)

Author	Reference	Automated operations	Elements determined or separated	Time needed	Number of samples processed simultaneously	Time per element in min.
Lievens	Anal.Chim. Acta <u>80</u> (1975), 97	- Reagent supply - Ion exchange - Column chromatogr.	Sc,Cr,Mn,Fe,Co,Cu,Zn, As,Se,Rb,Mo,Ag,Sn,Sb, Cs,La,Hg	5 hours for the separation only	1	≃ 18
Nagy	J.Radioanal. Chem. <u>34</u> (1976), 261	- Reagent supply - Mineralization - Distillation - Ion exchange	As,Se,Sn,Sb,Te	2-5hours for the separation only	1	≥ 24
Samsahl	The science of the total environment <u>1</u> (1972), 65	- Reagent supply - Mineralization - Distillation - Ion-exchange	Na,Cl,K,Sc,Cr,Mn,Fe,Co, Cu,Zn,Ga,Ge,As,Se,Br, Rb,Mo,Ag,Cd,In,Sn,Sb, I,Cs,lanthanides,Hf,W, Re,Os,Ir,Au,Hg,Th	3-4 days [Ion-exchange in 5 minutes]	3	≥ 13

Table 9.I. (Continued)

Author	Reference	Automated operations	Elements determined or separated	Time needed	Number of samples processed simultaneously	Time per element in min.
Schelenz	Progress Report BFE 1976/4	- Reagent supply - Distillation - Ion-exchange	Na,P,K,Ca,Cr,Fe,Co,Cu, Zn,Ga,As,Se,Br,Rb,Sr, Mo,Cd,Sb,Cs,Ba, lanthanides,Ta,W,Hg, Th,U	4 days	1	≃ 60
Schuhmacher	Proc. 1976 Conf. Mod. Trends in Act. Anal. p. 322	- Dissolution - Reagent supply - Ion-exchange - Adjustment of p_H	P,Cl,Sc,Cr,Mn,Fe,Co,Cu, Zn,As,Se,Br,Mo,Ag,Cd, Sn,Sb,Te,I,lanthanides, W,Au,Hg	4.5 h	4	≃ 3
Tjioe	Report IRI 133-76-11	- Reagent supply - Mineralization - Distillation - Ion-exchange - Fraction collection	Na,P,K,Cr,Fe,Co,Cu,Zn, As,Se,Br,Mo,Ag,Cd,Sb, Au,Hg	48 samples per week for 3-4 analysts	6-12	≃ 10

the separation only. It can be seen that the lowest value is ≃ 5 minutes. Furthermore, it is obvious that separation techniques are preferred which can be automatized easily, like ion-exchange and solvent extraction. Distillation holds a special position as it may be combined with destruction. The time spent per separation-run is usually somewhere between 4 and 10 hours while the turn-over time of the whole analysis is of the order of 2-4 weeks. This sets a severe limit to the application of these systems in routine analysis.

9.6. A system for multielement analysis of dry biological material

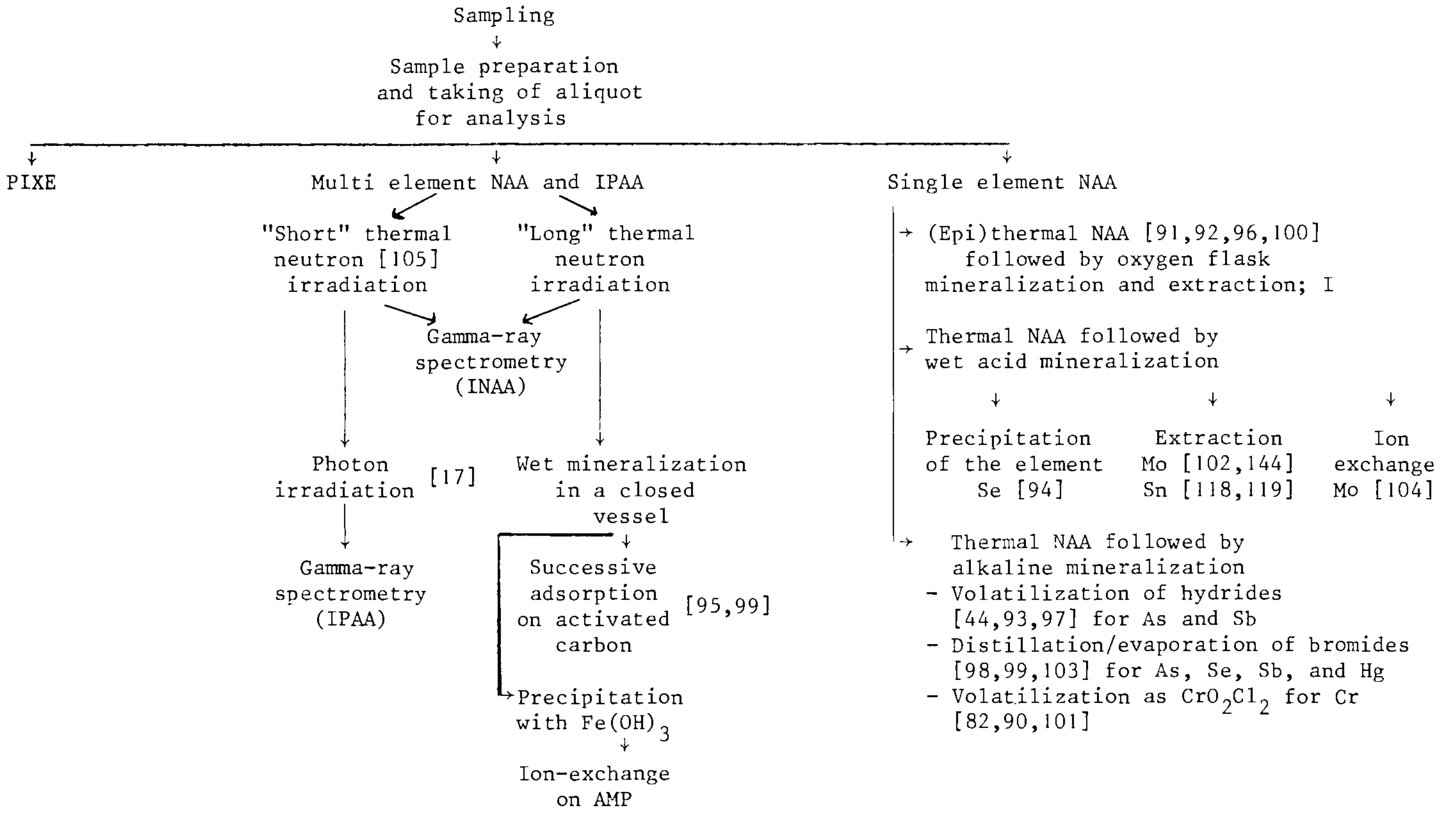
- An up to date system for the determination of many elements by radioanalytical techniques should be based on the criteria mentioned in section 9.1. and on a few additional reflections. These are:
  - a) The system should be adaptable to all possible combinations of minimal representative aliquot and available irradiation facilities.
  - b) Elements which can better be determined by separate runs or by other methods should be kept out rigorously.

  Furthermore, the system should be applicable in case that the aliquot is unique and as much information as possible should be extracted from it. The scheme could be along the lines of that shown in table 9.II. which gives the idea only. For details one should consult the original papers. Excellent reviews have been given by various authors [106,107].

- The following can be remarked on the activation analysis part:
  - All determination are based on counting with a coaxial Ge(Li) detector. Thus the scope of the analysis depends on the size and shape of the crystal.
  - "Short" irradiations refer to irradiation times up to ~ 30 min . In practice a distinction is made according to the half-life.
    - (a) The "very short" lived radionuclides ^{38}Cl, ^{77m}Se and ^{110}Ag. They require a "fast" rabbit system [135]. For the even shorter lived ^{8}Li a super-fast rabbit system is necessary [108].
    - (b) The "short" lived radionuclides ^{27}Mg, ^{28}Al, ^{47}Ca, ^{52}V, ^{56}Mn, ^{66}Cu, ^{80}Br, ^{86m}Rb, ^{101}Mo and ^{128}I.

      They can be used if some "slow" pneumatic rabbit system is available [105].

Table 9.II. Radioanalysis of dry biological material without pre-irradiation separation



(c) The "additional" radionuclides ^{24}Na, ^{38}Cl, ^{42}K and ^{82}Br which are usually measurable after a short activation.

Often only a fraction of all these radionuclides are of any analytical use due to spectral interferences. In most cases however, it is possible to determine Na, Cl, K and Br. For all other radionuclides it depends on the matrix. Pre-irradiation chemistry may often be mandatory.

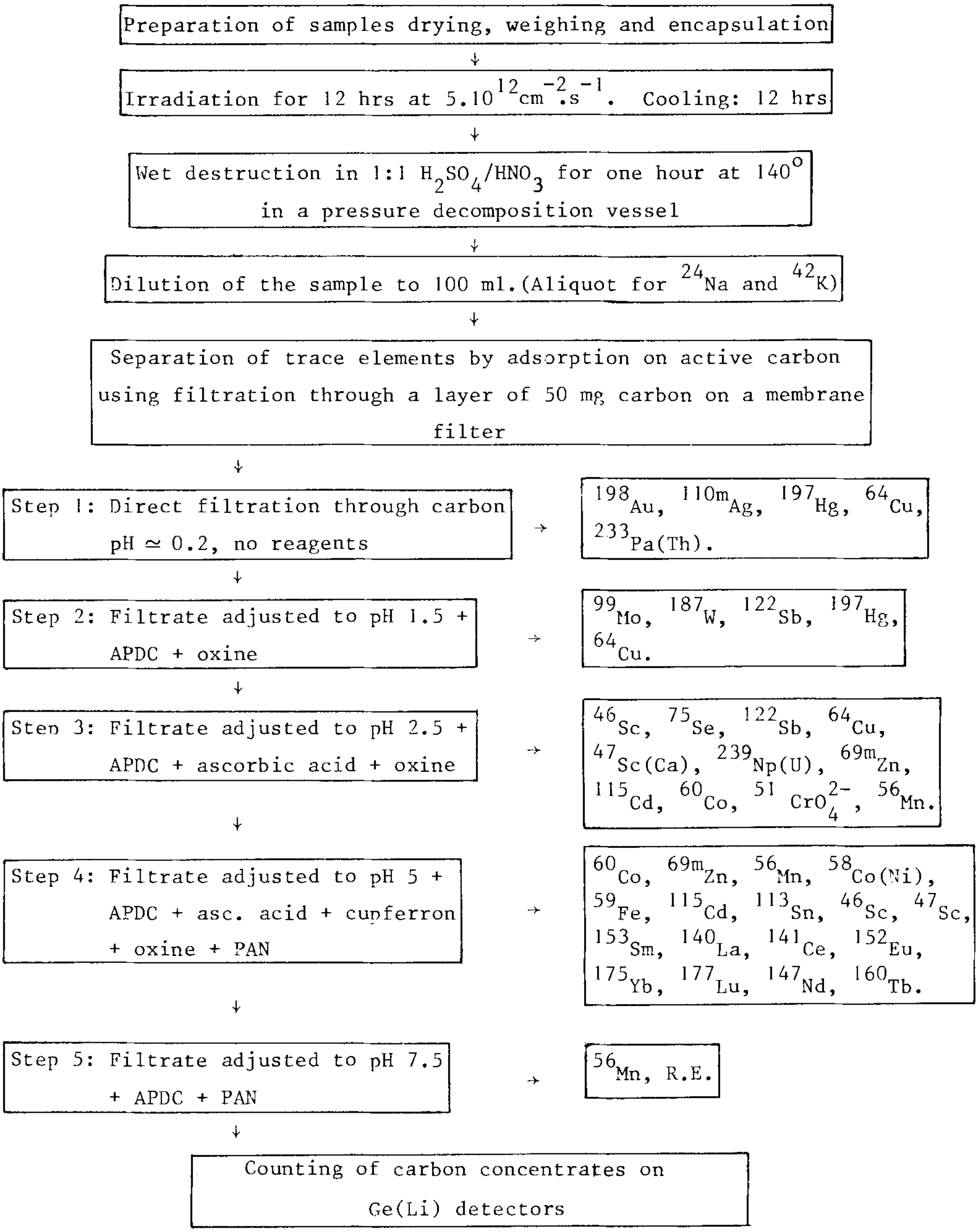
☐ Irradiations with fast neutrons are usually short as well. They may lead to the determination of N, P and K and sometimes to that of F, Mg, Si, Cl, Ca and Fe [109-111]. In general one uses large sample-weights. For small (mg) samples or surface effects charged particle activation is preferable [112,113]. A very high fast neutron flux could increase the possibilities still [134] but such facilities are scarce. The same holds for proton beams of high and variable energy [136].

☐ The sample which served for the short-irradiation may be used for photon activation after sufficient decay of the ^{24}Na. The scope of photon activation analysis is wide [17,114-116]. In the domain of dry biological material the addition to the data obtained by (I)NAA is rather scarce however. The determination of Mg, Ca and Sr is the most reliable application [117].

☐ "Long" irradiations may range from 6 h at a thermal neutron flux of 10^{12} $cm^{-2}.s^{-1}$ to 48 h at 5.10^{13} $cm^{-2}.s^{-1}$. One should look for a facility which enables regular access and the simultaneous irradiation of many samples packed in polythene or perspex, in approximately the same neutron flux and exactly the same neutron spectrum.

☐ The collection of trace elements on active carbon seems to be the most rapid scavenging technique available [95,99]. From 15 to 25 elements may be assayed in this way [99] (cf. table 9.I.).
The co-precipitation with $Fe(OH)_3$ and ion-exchange on ammonium-molybdophosphate (AMP) add another four. Table 9.III^a. gives the flow-sheet of the procedure [99]. The reagents mentioned are aqueous solutions with the concentrations given in table 9.III^b. The procedure is described in table 9.III^c, together with that for co-precipitation with $Fe(OH)_3$ and ion-exchange on AMP. It is

Table 9.III[a]. Flow scheme for the determination of trace elements in biological material



Preparation of samples drying, weighing and encapsulation

Irradiation for 12 hrs at $5.10^{12} cm^{-2}.s^{-1}$. Cooling: 12 hrs

Wet destruction in 1:1 H_2SO_4/HNO_3 for one hour at 140° in a pressure decomposition vessel

Dilution of the sample to 100 ml. (Aliquot for ^{24}Na and ^{42}K)

Separation of trace elements by adsorption on active carbon using filtration through a layer of 50 mg carbon on a membrane filter

Step 1: Direct filtration through carbon pH ≃ 0.2, no reagents → ^{198}Au, ^{110m}Ag, ^{197}Hg, ^{64}Cu, $^{233}Pa(Th)$.

Step 2: Filtrate adjusted to pH 1.5 + APDC + oxine → ^{99}Mo, ^{187}W, ^{122}Sb, ^{197}Hg, ^{64}Cu.

Step 3: Filtrate adjusted to pH 2.5 + APDC + ascorbic acid + oxine → ^{46}Sc, ^{75}Se, ^{122}Sb, ^{64}Cu, $^{47}Sc(Ca)$, $^{239}Np(U)$, ^{69m}Zn, ^{115}Cd, ^{60}Co, $^{51}CrO_4^{2-}$, ^{56}Mn.

Step 4: Filtrate adjusted to pH 5 + APDC + asc. acid + cupferron + oxine + PAN → ^{60}Co, ^{69m}Zn, ^{56}Mn, $^{58}Co(Ni)$, ^{59}Fe, ^{115}Cd, ^{113}Sn, ^{46}Sc, ^{47}Sc, ^{153}Sm, ^{140}La, ^{141}Ce, ^{152}Eu, ^{175}Yb, ^{177}Lu, ^{147}Nd, ^{160}Tb.

Step 5: Filtrate adjusted to pH 7.5 + APDC + PAN → ^{56}Mn, R.E.

Counting of carbon concentrates on Ge(Li) detectors

Table 9.III^b. Solutions needed for the determination of trace elements in biological material

Reagent	Solvent	Concentration in $g.l^{-1}$
APDC *)	double distilled water	15
Ascorbic acid	double distilled water	60
Cupferron	double distilled water/acetone 1:1	10
Oxine	isopropanol	5
PAN *)	isopropanol	2.5

*) APDC = Ammonium pyrrolidine dithiocarbamate

PAN = 1-(2-pyridylazo)-2-naphtol

Table 9.III^c. (continued)

- 100 μl $FeCl_3$ solution containing 4.5 mg Fe^{III} is added.
- The pH is raised to $\simeq$ 9 by addition of conc. NaOH and the solution is heated to boiling.
- The precipitated $Fe(OH)_3$ is filtered over a membrane filter. It contains $^{76}As(T\frac{1}{2}$ = 26.4 h) and $^{51}Cr(T\frac{1}{2}$ = 27.7 d). The filtrate is collected.
- The filtrate is acidified to pH 1.0 with 7.3 N HNO_3 and 2 g AMP is added. The mixture is stirred for 10 minutes. Then the AMP is separated by centrifugation and decantation.
- The last step is repeated. The two AMP fractions are combined. They contain $^{86}Rb(T\frac{1}{2}$ = 18.7 d) and $^{134}Cs(T\frac{1}{2}$ = 2.06 y).
- The $Fe(OH)_3$ and AMP samples are transferred to testtubes and the γ-ray spectra are recorded.

- The time spent on the chemical separation using activated carbon is < 2 minutes per element determination. The separation using $Fe(OH)_3$ and AMP takes about 5 minutes per element.

It should be remarked that for As, Se and Sb the separation as the hydrides [44] is certainly superior to that with active carbon and $Fe(OH)_3$.

Table 9.III^c. Procedure for the determination of trace elements in biological material by multi-element scavenging and Ge(Li) counting

Collection on active carbon

- A carbon suspension of 50 mg per ml is prepared by immersion in isopropanol. It is stirred continuously during sampling.
  Carbon covered filters are prepared by pipetting 1 ml of the suspension on the filters, addition of 5 ml double distilled water and suction.
- The solution which results from the mineralization or the evaporation is transferred to a 200 ml beaker and diluted to 100 ml with double distilled water. The pH will be ≃ 0.2. An aliquot is taken for the measurement of ^{24}Na and ^{42}K.
- The solution is led through a carbon-loaded filter at a rate of 25 ml min^{-1}. The filtrate is collected in a 200 ml beaker.
- The pH is raised to 1.5 by dropwise addition of conc. NH_4OH and 2 ml aliquots of the APDC and oxine solutions are added. Then the sample is passed through a layer of 50 mg activated carbon on a membrane filter at a rate of 25 ml min^{-1}. The liquid is collected in a 200 ml beaker and the carbon is washed with the corresponding solution of the reagents in double distilled water.
- The pH is raised to 2.5 and the filtration step repeated after addition of small aliquots of solutions of the reagents:
  APDC: 2 ml, ascorbic acid: 5 ml, oxine: 2 ml.
- The pH is raised to 5 and the filtration step is repeated after addition of:
  APDC: 2 ml, ascorbic acid: 5 ml, cupferron: 2 ml, oxine: 2 ml, PAN: 2 ml.
- The pH is raised to 7.5 and the filtration step is repeated after addition of 2 ml aliquots of the APDC and PAN solutions.
- The loaded filters are transferred to polythene vials with snap cap. These are put in test tubes and counted.
- The different carbon fractions may be combined to one counting-aliquot for routine purposes.

Determination of Cr, As, Rb and Cs by co-precipitation with $Fe(OH)_3$ and adsorption on AMP and Al_2O_3.

These determinations are performed on a separate aliquot preferably:

- After mineralization, the solution is transferred to a 200 ml beaker and diluted to 100 ml.

obvious that the procedures depend on a reliable computer-programme for spectrum devolution and a good knowledge of the occurring γ-lines (cf. [150]).

□ Of the important trace constituents, mentioned in the beginning of this chapter, some are missed by the presented scheme. Moreover the elements Al, V, Mn and I require preconcentrations sometimes. The trace constituents Cr, Ni, Cu, As, Se, Mo, Cd, Sn and I may impose the necessity of post-irradiation separation. A few proved techniques are mentioned in table 9.II. As radiochemical purity is the most important criterion, the use of substoichiometric amounts of reagent may be of advantage [133].
Furthermore, if an epithermal neutron facility is available, this could enhance the determination of at least As, Cd, I, Mo and U [137,138].

The routine determinations by PIXE can best be done with 2-3 MeV protons at moderate vacuum on thin targets spread out over an inert support [120,121].

The elements which may be determined often are Mn, Fe, Cu, Zn, Br, Rb and Sr [121,125]. In blood and serum Se can be determined [121].

9.7. Pre-irradiation separations

- Sometimes a pre-irradiation decontamination is necessary. Either the element of interest is isolated or the interferences are removed. The most important criteria are the radiation burden and the blank value. It is advisable to make a "radiation-budget" and a "blank-budget" for the procedure which includes all reagents and equipment. If one is not interested in the chemical form of the element, the mineralization and decontamination may be combined. Such is the case for Al [33] V [126,245] and I [127]. Wet acid destruction in a closed vessel and removal of Na by stirring with HAP [105,128] is a procedure of the same type. If possible, only the mineralization is performed prior to the irradiation [129].
- In the analysis of serum it is essential to know to what protein a certain element is bound. Here the analyst has to conform to the separation techniques of the medical laboratory while modifying them

such that the blank-values become acceptable. Gel permeation with saline solution as the eluent is often used [130,131].
It should be noticed that some ionic metal species in the eluent are capable of bond-formation with the proteins on the column or with the gel itself [132]. A reliable pretreatment procedure should be fully standardized and performed in a "dust-free" laboratory [140].

9.8. Analytical conclusions

- To a certain extent the analytical possibilities may be judged from the data published for the Standard Reference Materials. As these papers are often the result of special efforts, one should be cautious in drawing general analytical conclusions from them. Moreover, the situation depends on the matrix very much [141].
- Purely instrumentally one may determine from 5 to 15 elements, depending on the sample by INAA and about 5 by PIXE. In animal tissue one may assay Na, Al, Cl, Mn, Fe, Co and Zn [95] by INAA; for the last three elements chemical separation gives better results [140]. By PIXE one obtains Cu, Fe, Zn and Br [142] and sometimes Se [121]. In dry plant material the elements Na, Mg, Cl, K, Ca, Sc, Cr, Mn, Fe, Co, Zn, Br, Rb, Sr, Sb, Cs, Ba, La, Ce, Sm, Eu, Hf, Au, Hg and Th may be obtained by INAA with thermal neutrons [95,117]; moreover epithermal activation will confirm Na, Mg, Ca and Mn while adding I and U and possibly Mo [138]. Instrumental photon activation (IPAA) may confirm the data for Na, Mg, K, Ca, Mn, Fe and Sr [143]. Here PIXE adds K, Ca, Mn, Fe, Cu and Zn [121,142]. In Bowen's kale more elements were determined [125].
- The scope of the separation schemes may be judged from tables 9.IV. and 9.V. In the first the results of the active carbon separation for the SRM No. 1571 Orchard Leaves are stated [95]. Apart from 7 data obtained by INAA, 25 elements are determined and 3 upper limits are given. Table 9.V. gives the comparison between the separation system of Cornelis et al. [140] and the active carbon technique [95]. Both groups of data are based on two analyses. It can be seen that:
  (a) The agreement is, in general, satisfactory.
  (b) The carbon method adds a group of elements which are of lesser importance but lacks the important trace elements Cr, Mo and Cs.

Table 9.IV Data for SRM 1571 Orchard Leaves obtained purely instrumentally or by the active carbon method.

* = Determined instrumentally

All data in μg.g^{-1}.

Material dried for 4 h at 85 °C.

Element	Concentration found	NBS certified value	Other literature data
Na	85±2 *	82±6	81-88
Mg	6100±400 *	6200±200	6170
Al	824±50 *		
Cl	730±60 *		700-800
K	14500±200 *	14700±300	14000-15000
Ca	20000±800 *	20900±300	20000-21000
Sc	0.058±0.004		0.04-0.2
Cr	1.9±0.2		2.0-2.8
Mn	{ 90±1 91±4 *	91±4	86-95
Fe	285±5	300±20	290-330
Co	0.16±0.02		0.1-0.21
Cu	10.5±1.0	12±1	10-12.6
Zn	24.5±0.6	25±3	23-27
As	9.5±1.0		9.7-12.1
Se	0.11±0.03	0.08±0.01	0.08-0.10
Rb	10.8±0.2		11.3-11.8
Mo	0.32±0.06	0.3±0.1	0.33
Ag	0.013±0.005		
Cd	0.07±0.02	0.11±0.02	0.10-0.12
Sb	2.85±0.06	2.9±0.3	2.7-3.7
Cs	0.033±0.003		0.037
La	0.80±0.05		0.99-1.2
Ce	0.91±0.06		0.9-1
Pr	≤ 0.1		
Nd	≤ 0.65		0.32
Sm	0.105±0.004		0.15

Table 9.IV.(Continued)

Element	Concentration found	NBS Certified value	Other literature data
Eu	0.022±0.008		0.03-0.3
Tb	0.009±0.001		0.0012
Yb	0.011±0.03		0.021
Lu	0.006±0.02		0.006-0.06
W	0.016±0.004		
Au	0.004±0.002		0.001-0.004
Hg	0.14±0.02	0.155±0.015	0.09-0.19
Th	0.05±0.01		
U	≤ 0.02		0.029

Table 9.V. Data for SRM 1577 Bovine Liver obtained purely instrumentally or by the active carbon method [95] and the separation scheme of Cornelis et al [140]

* = Determined instrumentally.

All data in μg.g.$^{-1}$. Materials dried for 4 h at 85 °C [95] or lyophilized [140].

Element	According to [95]	According to [140]	NBS certified value	Other literature data
Na	1949±30 *	2632±29 *	2430±130	2550
Al	15.3±1.1 *			
Cl	2650±100 *			2600
K	11200±200 *	10323±258 *	9700±600	9980
Sc	≤ 0.001	< 0.0005		0.001
Cr	-	0.074±0.005 0.123±0.006	0.088±0.012	0.12-0.16
Mn	10.1±0.2 10.9±0.3 *	11.2±0.5 *	10.3±1.0	10.2-10.3
Fe	293±8	236±5	270±20	240-272
Co	0.23±0.02	0.223±0.011		0.24-0.26
Cu	190	187±8	193±10	177-195
Zn	127±1	135±5	130±10	133-136
As	0.04±0.01	0.056±0.0041		0.058-0.08
Se	1.05±0.12	1.02±0.03	1.1±0.04	1.06-1.14
Rb	17.8	17.97±0.60	18.3±1.0	18.8-19.0
Ag	0.065±0.005	0.051±0.011		0.068
Cd	0.26±0.03	0.288±0.035	0.27±0.04	0.30
Sb	0.004±0.001	0.0048±0.0005		0.007-0.015
Cs	≤ 0.01	0.0149±0.0022		0.013-0.016
La	0.014±0.005	0.0173±0.0004		0.024
Ce	0.018±0.004			0.046
Sm	0.0013±0.0004			0.0019
Hf	0.001			
Au	< 0.0005			0.00023
Hg	0.013±0.004	0.0223±0.00004	0.016±0.002	
Th	0.006±0.003			
Mo	-	3.19±0.14	-	32
Sn	-	< 0.6	-	-

(c) The reported precision of the carbon technique is somewhat less for As, Se and Hg.

The rapidity of the carbon technique (cf. table 9.III.) makes it possible to complete it with simultaneous single-element analyses. If however, only one single sample is available, a system like that described in [140] is of advantage.

- For the important trace elements V, Cr, As, Se, Mo, Sn, Sb, I and Hg separate determinations are often to be preferred.
  These elements are best determined by the following techniques:
  V : Pre-irradiation ion-exchange [145].
  Cr : Evaporation of CrO_2Cl_2 [90].
  As and Sb : Hydride formation and trapping on active carbon [44].
  Mo : Liquid extraction from 1 N H_2SO_4 [102,144].
  Sn : Liquid extraction from > 1 N H_2SO_4 [118,119].
  Se : Precipitation of elemental Se [94] or hydride formation.
  I and Hg : Volatilization and trapping on active carbon [92,146].

  Sometimes the elements Mn and Cu have to be isolated too. This is usually done by liquid extraction; with oxine [26,147] or tetraphenylarsonium chloride [148] for Mn and with neocuproine for Cu [149]. The realization of all this, however, depends on the amount of sample available. Furthermore, radioanalysis is often applied in combination with other techniques, e.g. AAS, which will yield a number of elemental concentrations as well. The drawing of the balance depends on the local conditions.

9.9. A survey of applications

The applications are manyfold. A few trends may be signaled here.

- Dry plant material
  There are four main reasons to analyse (dry) plant materials:
  (a) The distribution of trace elements over plants in relation to the composition of the soil [151-153].
  (b) The trace element content of commercial crops [110,116,154-160].
  (c) Plants as monitors for air-borne environmental pollution [161,162].
  (d) Forensic characterization of drugs [163].

  Apart from the obvious requirements for the sampling procedure, the subjects (a)-(c) require a very good organizational framework.

- Whole blood and serum

  The significance of this branch depends on the sampling procedure entirely [107]. The main environmental reason for the analysis of blood and serum is the search for possible relations between elemental concentrations and the presence or absence of certain diseases, especially malignant growths [129,164-172]. Sometimes acute cases of poisoning are described in which the concentration of the element is followed through time [173].

- Dried animal tissue

  The remarks made for blood and serum hold here as well.
  Much work is devoted to material obtained from the human body by obduction or biopsy [174-186]. These investigations are completed by comparative studies on animals [187-193].
  Links are laid with the intake of man by his diet at one hand [194,195] and the concentration in single cells or parts of it at the other [196]. Much effort is spent on organisms from the aquatic environment to test and use them as indicators of environmental pollution. Plants [197,198], snails [198], mussels [197,199] and fish [197,200-202] were examined. A notable investigation is that on the influence of metal implantations [209] and medication with Pt^{II}-complexes against tumors [189] on the trace concentration levels.
  The general tendency is to combine activation analysis and atomic absorption and to concentrate on the notoriously toxic elements As, Cd, Sb, Hg and Pb as well as on the essential traces Cr, Mn, Fe, Co, Cu, Zn, and Se.

- Bone and teeth

  Most of the determinations are performed by instrumental fast neutron activations [111,203] concentrating on N, F, P, K and Ca. The combination of thermal and fast activation yields a survey of the trace elements in the human skeleton [204,205]. The relative age determination of fossile bones by the N/F-ratio yields acceptable results [206].

- Tartar, bile, kidney and bladder stones

  All the work in this field depends on surgery, either routine or experimental [207-209]. No clear conclusion has been drawn from the observed wide scatter.

- Hair and nails

The use of hair as a monitor for environmental pollution has obtained considerable attention. As in the earlier forensic hair studies, it appears that the trace element contents of hair are subject to many factors, ranging from fashion to environment. A good survey can be found in [210].

Three types of investigations may be distinguished:

a) Determination of a single element to find out possible industrial, food or health influences. Examples are arsenic [211-214], manganese [215], mercury [216,217] and calcium [218].

b) Multielement determinations and the application of some correlation technique may give an insight in variations with age, sex, occupation and habitat [219-225].

Disease or industrial activity are reflected by the data [226-228].

c) Forensic studies, if performed with great care, may be of some practical use [229,230].

The use of nail clippings for environmental investigations is scarce. Average concentrations of healthy people have been reported [231].

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CHAPTER 10.

SILICATES, COAL AND RELATED SOLIDS FROM ENERGY PRODUCTION

SUMMARY

In this chapter the analysis of silicates, particulate matter and (fly-) ash is considered. The fact that these materials are usually of a grain-like structure entails the necessity of further definition by some physical or chemical separation steps. Moreover distinctions have to be made between total and available concentrations and between surface and bulk-phenomena. Radioanalysis of these materials thus comprises elemental analysis and radiotracer experiments.

10.1. Introduction

- The environmental radioanalyst is invariably confronted with large series of solid samples which mainly consist of silicates. They may be divided into three categories:

  ☐ Sediment and soil.
  ☐ Particulate matter, collected from the atmosphere or from water.
  ☐ Ash obtained from various places in a coal-fired plant.

  In addition to these materials and often within the scope of the same investigation, there are a number of matrices which pose similar analytical problems. One may quote fertilizers, wood and plant-ash and (brown-) coal.
  Usually two questions have to be answered by the (radio-)analyst. The first pertains to the (trace-)element contents and the second to the leaching and adsorption-properties.
  From the elemental composition one hopes to deduce the potential hazard of the material or some evidence about its provenance and its relation to other, similar, samples. The leaching and adsorption-properties bear on the actual risks and benefits, caused by the presence of this particular material in nature.

- The materials involved are often grain-sized and almost always visibly inhomogeneous. This presses for a further definition by some pretreatment such as sieving, selective dissolution or separation according to specific gravity differences. Occasionally magnetic separation may be applied. Thus the number of aliquots may increase considerably.
  The distinction between total and available concentration extends the task of the analyst still further. Often the availability is defined in terms of leachability by ground or rain-water. The direct measurement of the leached amounts thus implies the analysis of minor changes in the concentration of water samples. Alternatively, radiotracer experiments with pre-activated solid aliquots may be applied. The leaching and adsorption-properties may be described on the basis of a simple specific mass-transfer function, as discussed in chapter 3.
  By measuring the total dissolved mass as well as the released amounts of trace elements it is possible to define the preferential leaching of individual elements.

- A further difficulty is presented by the fact that particulate matter has to be collected on some support from which it often cannot be retrieved. One has then to analyse a thin layer of material, of the order of 1 $mg.cm^{-2}$, on a much thicker support. The blank has to be controlled sharply and the limit of determination is now chiefly determined by this blank-value.
  This situation may be turned to advantage by combining INAA and PIXE as the thin-layered aliquots are ideally suited for the latter technique.
- As in other domains of environmental analysis, the trend is towards purely instrumental elemental analysis, completed by some determinations based on chemical group separations. Table 10.I. gives a general estimate of the scope of instrumental radioanalysis and its completion by a few chosen radiochemical separations.
- Finally the (radio-)tracer experiments should be mentioned as one of the major contributions of radioanalysis to environmental investigations. Nowadays, the trend is primarily towards activable tracers.
  The spiking of water with bromide or of air with an indium-containing aerosol can be mentioned.

Table 10.I. Survey of the possible application of radioanalysis to silicates, aerosol and coal

Technique	Elements
INAA with thermal and epithermal reactor neutrons	(Li), Na, Al, Cl, K, (Ca), Sc, Cr, Mn, Fe, Co, Cu, Zn, (Ba), Ga, (Sb), (Se), Br, lanthanides, Hf, Th, (Ag), (Au), U.
INAA with 14 MeV neutrons	N, O, (F), Mg, Si, P.
Prompt capture γ-ray measurements (PGAA)	H, B, (N), S, some lanthanides, major constituents.
Proton induced X-ray measurements (PIXE)	S, Cl, K, Ca, V, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Zr, Nb, Pb.
Neutron activation analysis including radiochemical separation	As, Se, Rb, Mo, Ag, Sn, Sb, Te, I, Cs, Ba, Au, noble metals.

- Photon activation analysis has been omitted. For a review see: Chatt, A. and R.E. Jervis, Anal. Chem. 46 (1974), 1630.
- Elements in brackets are marginal or can be measured in small series only.

10.2. Elemental analysis of silicates, coal and related matrices by INAA

- Instrumental neutron activation analysis, mostly based on comparison to standards, is the usual radioanalytical technique for the elemental analysis of silicates. In general, the samples are submitted in a powdered state although eventually chips or slices are available. The implications of the sample-mass and form on the geometry and the radiation-level are obvious.
  As there are excellent techniques for the determination of the major constituents of silicates, INAA is used for the assay of minor and trace elements primarily. There are, however, established exceptions to this rule, if the elements involved are determined with apparent ease. Thus Na, Al, Fe and occasionally K are obtained by thermal neutron activation while Si responds to fast neutrons. In case of photon activation analysis one gets Mg, Ca and Ti as well.

- In general, the emphasis in silicate analysis is on the "long-lived" ($T\frac{1}{2} \geq 10$ h) radionuclides. This enables the analyst to irradiate large series of aliquots simultaneously and to use a sample-changer for the subsequent measurement. Depending on the nature of the material, the computer-programme and the maximal acceptable standard deviation, between 10 and 40 elements are determined. The use of a (pneumatic) rabbit system for the analysis by way of short-lived radionuclides ($T\frac{1}{2} < \sim 1$h) entails two problems: Firstly the capacity is low as only one or a few aliquots are irradiated. Then there is the correction for the residual dead-time losses which may be appreciable for materials rich in Al. Correction is based on the total dead-time fraction at the beginning of the measurement [1] which thus has to be recorded, or on some special electronic device to keep the total dead-time constant over the measurement [2]. As the γ-ray spectrum of the shortly irradiated silicates is dominated by ^{28}Al ($T\frac{1}{2}$ = 2.3 min) application of short activation in environmental activation analysis is useful only in some special cases, e.g. when ^{52}V ($T\frac{1}{2}$ = 3.8 min) or ^{66}Cu ($T\frac{1}{2}$ = 5.1 min) have to be measured. A separate sub-discipline of wider application is the measurement of the medium-lived radionuclides with half-lives between 1 h and 12 h. Elements which can be determined in this way comprise Mn, Ga and Dy.

- The major limitations of the technique are, except in the need for a reactor with a sufficiently high flux and an adequate irradiation facility, mainly found in the spectral interferences and the rather long turnover time of 2-4 weeks, due to the necessary decay of short and medium-lived activities. This classifies INAA of silicates as a typical off-line technique.

  The system used at ECN consists of three branches [3]:

  - o A short irradiation for 1 minute at a thermal neutron flux of $10^{11}cm^{-2}s^{-1}$ in the Low Flux Reactor, using a pneumatic shuttle, followed by Ge(Li) γ-ray spectrometry for Al, V and Mn.
  - o A 2 hours irradiation at $5.10^{11}cm^{-2}.s^{-1}$ in the Low Flux Reactor for the medium-lived radionuclides. The integrated flux is monitored by a fission chamber. Measurement follows after 11-12 hours.
  - o A 2-12 hours irradiation at $5.10^{12}cm^{-2}.s^{-1}$ in a rotating facility for the medium and the long-lived radionuclides. Iron flux monitors are mounted in the cap of the polythene vials which are placed in a 400 ml polythene wide-neck flask with screw cap. Cooling takes 1-2 days if the medium-lived radionuclides are considered and 3-4 weeks for the long-lived. The first measurement is performed at a distance of 10 cm from the surface of a 87.5 cm^3 coaxial Ge(Li) detector with a FWHM of 1.9 keV and an efficiency of 14.5% at 1332 keV. Counting-time is 1000-3000 seconds; the flux-monitors are measured separately with a NaI-detector. The routing of the data is as described in chapter 7.

  Table 10.II gives the γ-ray used and the corresponding decay-times. Comparison with the compilations available in literature [4] reveals that the choice is very restricted; the mentioned 1115.4 keV line of ^{65}Zn ($T_{\frac{1}{2}}$ = 244 d) is interfered by the 1120.3 keV photopeak of ^{46}Sc. The precision obtained for the in-house standard "Gray-shale", obtained from the USGS, is summarized in table 10.III.

- To get a good appraisal of the procedure applied in one's own laboratory, a comparison of both precision and accuracy should be performed. The precision can be checked by repeated analyses and comparison of the experimental data with the predictions obtained as described in chapter 6. Furthermore, a good impression of the current state of the art may be obtained, i.a., from refs. [5-7]. The accuracy is more difficult to control; use has to be made of Standard Reference Materials,

Table 10.II. Dependable gamma-lines for neutron activation analysis of silicates [3].

Isotope	E_γ in keV	Decay-time	Isotope	E_γ in keV	Decay-time
^{28}Al	1778.9	-	^{177}Lu	208.4	2 d
^{59}Fe	1098.6, 1291.5	~ 30 d	^{177m}Lu	208.4	30 d
^{24}Na	1368.4	2 d	^{147}Nd	91.4, 531.0	~ 30 d
^{42}K	1524.7	2 d	^{86}Rb	1076.6	~ 30 d
^{56}Mn	846.9	-	^{122}Sb	564.0	2 d
^{76}As	559.2	2 d	^{124}Sb	1690.7, 602.6	~ 30 d
^{133}Ba	496.3	~ 30 d	^{46}Sc	889.4	~ 30 d
^{141}Ce	145.5	~ 30 d	^{153}Sm	103.2	2 d
^{60}Co	1173.1, 1332.4	~ 30 d	^{182}Ta	1221.6	~ 30 d
^{51}Cr	320.0	~ 30 d	^{160}Tb	298.6, 879.4	~ 30 d
^{134}Cs	795.8	~ 30 d	^{233}Pa (Th)	311.8	~ 30 d
^{165}Dy	94.6	5 h	^{239}Np(U)	228.2	2 d
^{152}Eu	121.8, 1407.5	~ 30 d	^{187}W	685.7	2 d
^{181}Hf	482.2	~ 30 d	^{175}Yb	395.1	2 d
^{140}La	1596.4, 485.8	2 d	^{65}Zn	1115.4	~ 30 d

Table 10.III. Reproducibility of the in house - standard (gray shale 46W 4100, Ward's) [3].

Element	Concentration in μg.g^{-1}	SD (%) (n = 6)	Element	Concentration in μg.g^{-1}	SD (%) (n = 6)
Al	9.56 %	1.2	Ba	440	6.1
Fe	3.66 %	1.1	La	39.6	1.3
Na	0.295 %	1.4	Ce	95	1.0
Sc	18.69	0.8	Sm	7.22	1.2
Cr	105.5	1.0	Eu	1.39	3.6
Co	21.75	1.0	Yb	3.52	3.4
As	32.1	1.0	La	0.77	13
Rb	3.52	3.4	Hf	4.70	3.4
Sb	2.3	10	Th	17.4	2.9
Cs	10.8	2.9			

issued by the US Geological Survey (USGS) at Reston, Virginia; the Centre de Recherche Petrographique et Geologique (CRPG) at Nancy, France and the International Atomic Energy Agency (IAEA) at Vienna. In addition to that, a direct confrontation of different, competing, analytical techniques should be organized. Ref.[8] gives an example of the comparison between atomic absorption spectrophotometry measurements in 18 laboratories.

- Numerous applications of INAA to the problem of classification of silicate samples have been published by many authors for rocks [9,10], pottery [11,12] and marine sediments [13,14]; the present references give a few examples only.
  The usual aim of these applications is to discover differences within one relevant collection. The obvious initial parameters are place of sampling respectively way of production. Often a first separation is effectuated by sorting according to colour, grain-size, specific gravity or magnetic properties.
  Three questions have to be put then:
  - o Should the bulk material be analyzed or should one divide it (further) and analyze the separate fractions?
  - o What is important: The total concentration, the available concentration or both?
  - o Would it make sense to give absolute concentrations or should ratios be obtained, f.i. trace/major constituent?

- A further division of the sampled material is mandatory in the case of sediments [15]. In fact, important conclusions on environmental transport mechanisms have been drawn based upon INAA of fractionated sediments [16,17] and suspended particulate matter [18,19];again the references give a few chosen examples only.
  There are many situations in which the available rather than the total concentrations are of interest. The uptake by plants of trace elements from sewage sludge, used as fertilizer or the leaching of trace elements from the surface of river sediments upon its contact with saline water [20]. The determination of the available concentration implies some standardized leaching procedure. Then, atomic absorption spectrometry (AAS) is the preferred technique. Eventually, INAA may be adapted by performing elution measurements on previously irradiated aliquots, to obtain a multi-element procedure. Care should be taken

to prevent changes due to γ-heating and Szilard-Chalmers effects. It was found at ECN that irradiation in a thermal neutron flux of $5.10^{12}cm^{-2}s^{-1}$ up to an integrated dose of $10^{17}cm^{-2}$ at a γ-heating of < 0.5 $W.g^{-1}$ did not result in significant alteration of the aliquot.

- The analysis of coal and fly-ash by INAA has been practiced intensively in recent years [21-26]. The primary aim of the determinations is either to establish a mass-balance or to draw a comparison between different types of coal and different firing practices. The first step in this procedure is the analysis of coal and to establish a databank [27]. Cluster analysis of these data may be used to set-up a trace-element based classification. Analogous work on fuels is described in ref. [79].

  The obvious parameters are rank, type and grade of the coal, as well as the particle diameter(-distribution) of the fly-ash. Figure 10.1. gives microscopic pictures of fly-ash from the 4 serial electrostatic precipitators of a powder-coal fired power station. The most frequent particle diameter is 1-1.5 μm. Figure 10.2. gives the appearance of some of the representative fly-ash particles. If the concentrations are plotted against the particle-size, the "concentration-profile" is obtained which may serve as a clue to the processes of deposition and distribution [25]. Alternatively, the (mass-) emission-rates in μg per Joule of heat input may be computed and plotted as a function of the particle diameter [26].
  Figure 10.3. summarizes the distribution-ratios precipitator (2-4)/precipitator 1 for the mentioned power-station. It is seen that the "volatile" elements tend to be located at the surface of the finest particles.

- Epithermal neutron activation has become of some importance in recent years. The advantage is the relative suppression of the contribution of ^{24}Na, ^{32}P and ^{42}K [28]. The most obvious applications are the determination of U [29] and Th [30,31]. The construction of a handy Cd or B_4C-cover is essential [29]. Simultaneously, the use of (n,p) reactions can be envisaged [32]. The elements F, Si, Ni and Ti may be determined. Figure 10.4 demonstrates the effect for long-lived radionuclides.

- Fast neutron activation analysis yields a few essential elements: Si in rocks, sediments, fly-ash and coal [33]; O and F in fly-ash and coal [34]; N in coal [35]. The main problem here is the deconvolution

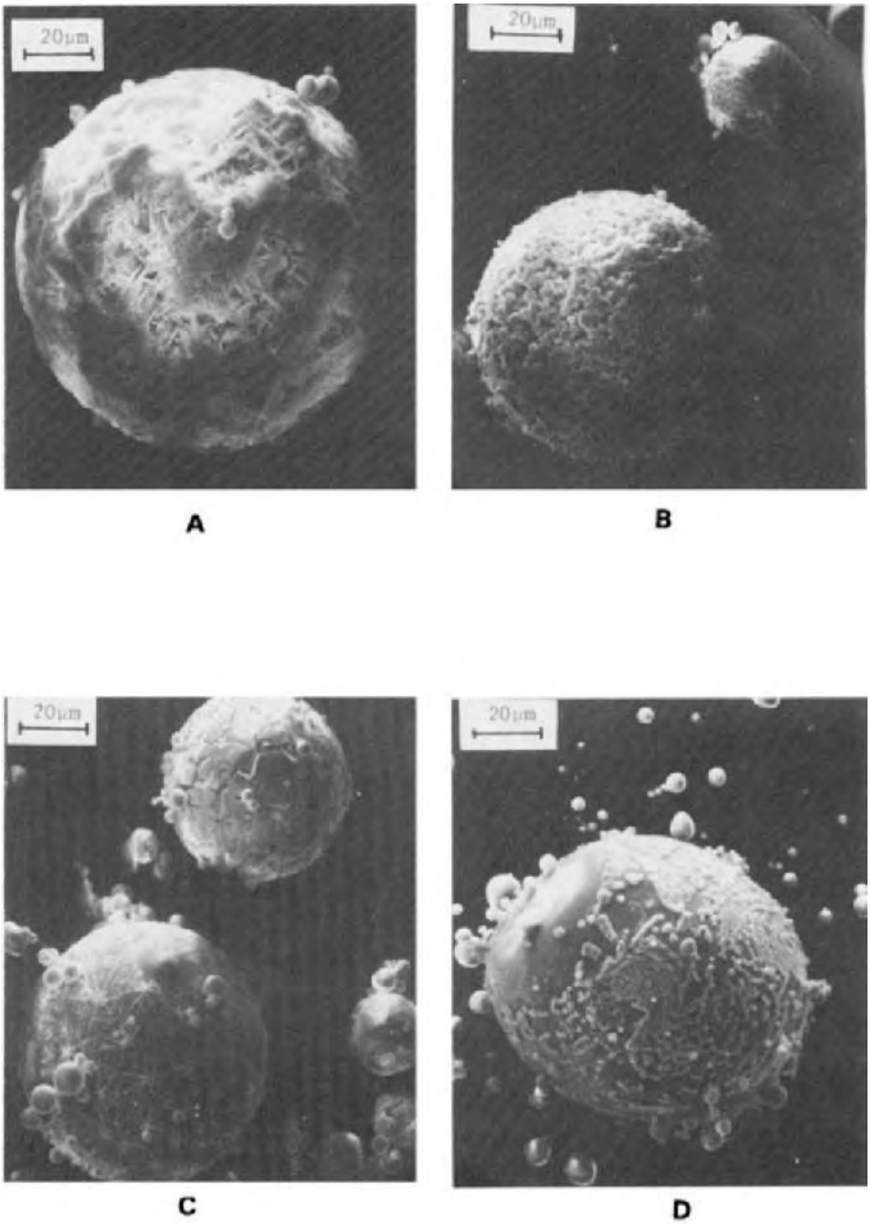


Figure 10.1. (Radiochemical laboratory of ECN, unpublished work).

Ash from the four sequential electrostatic precipitators of a powder-coal power station at 800 x magnification.

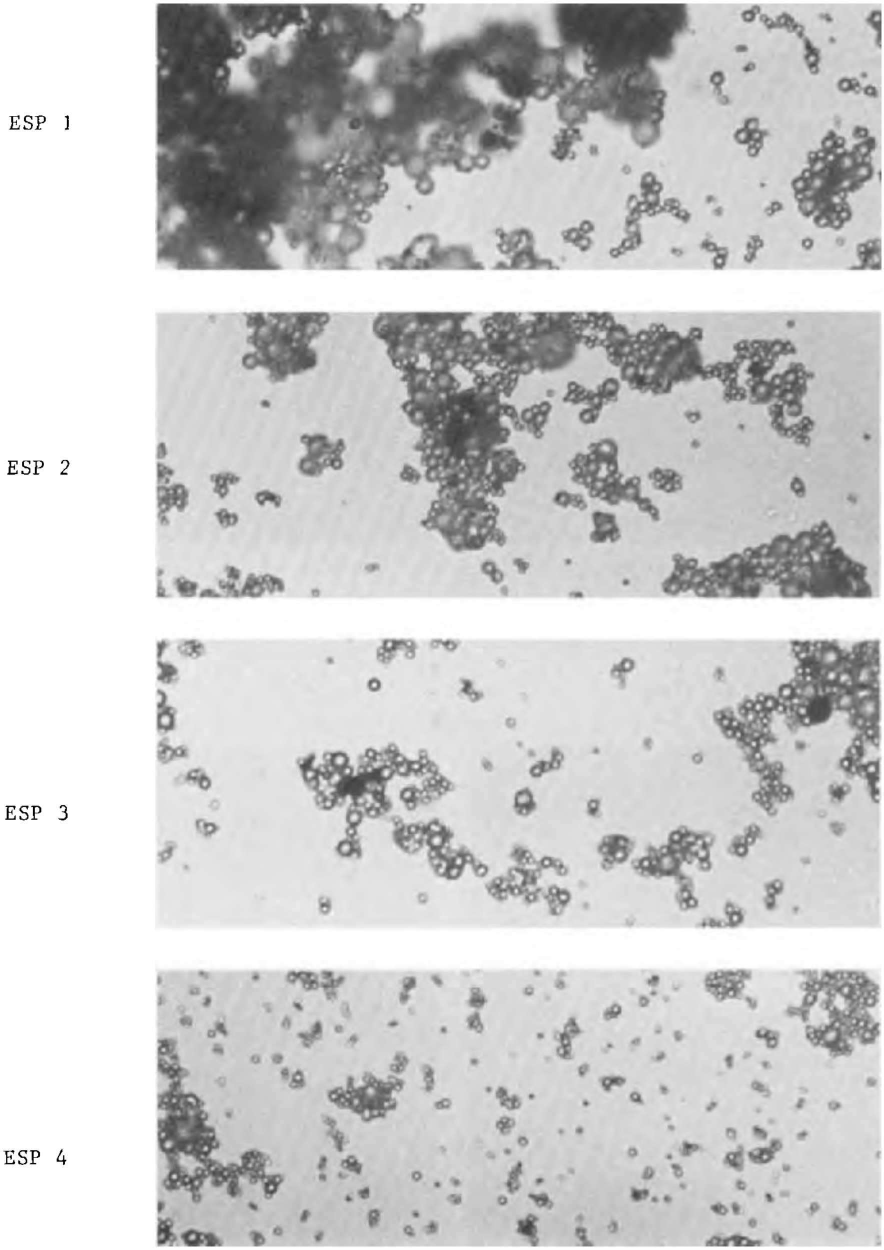
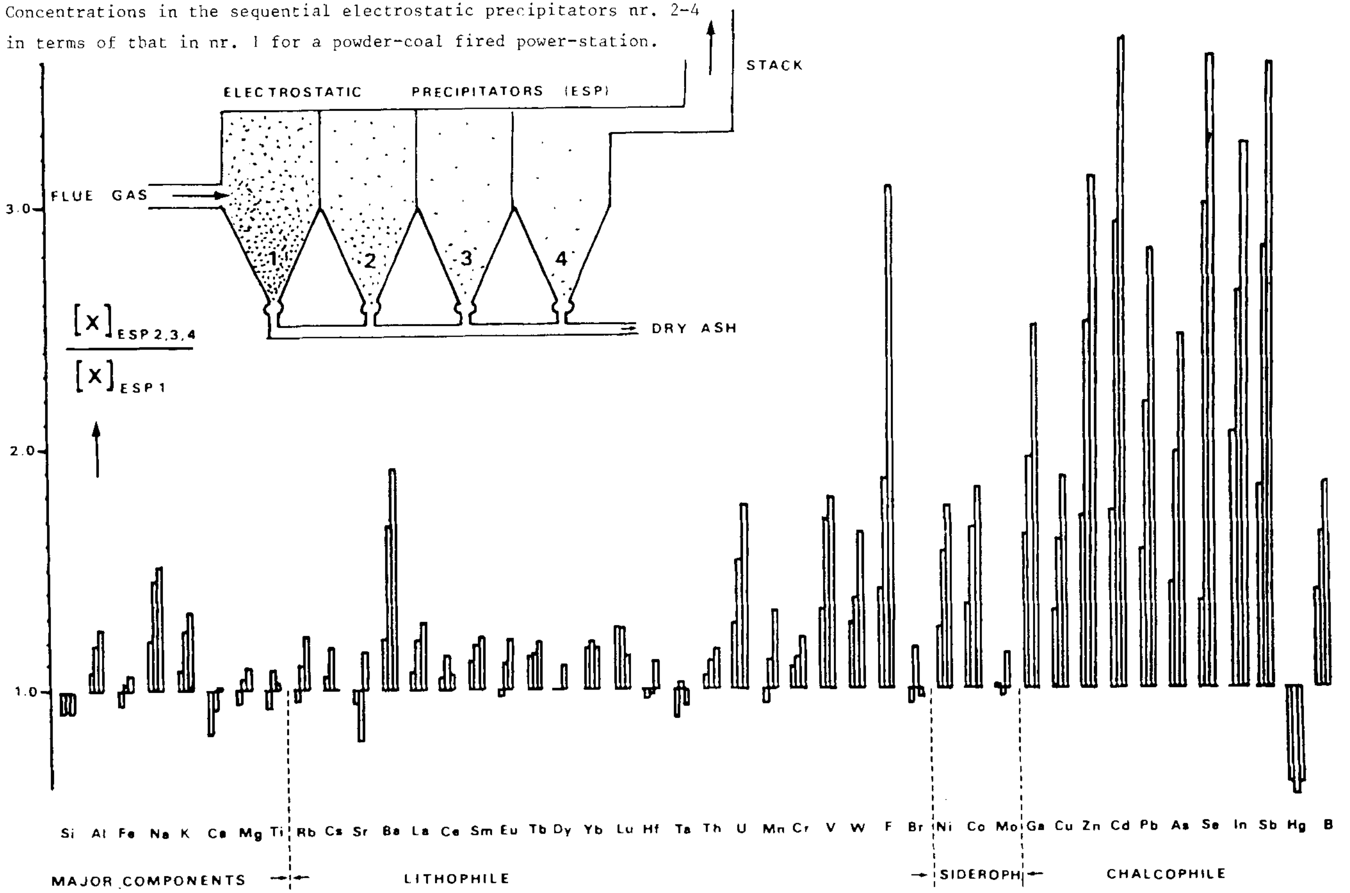


Figure 10.2. (Radiochemical laboratory of ECN, unpublished work). Some typical ash-particles form a powder-coal power-station. ESP = Electrostatic Precipitator.

Figure 10.3. (Radiochemical laboratory of ECN, unpublished work). Concentrations in the sequential electrostatic precipitators nr. 2-4 in terms of that in nr. 1 for a powder-coal fired power-station.



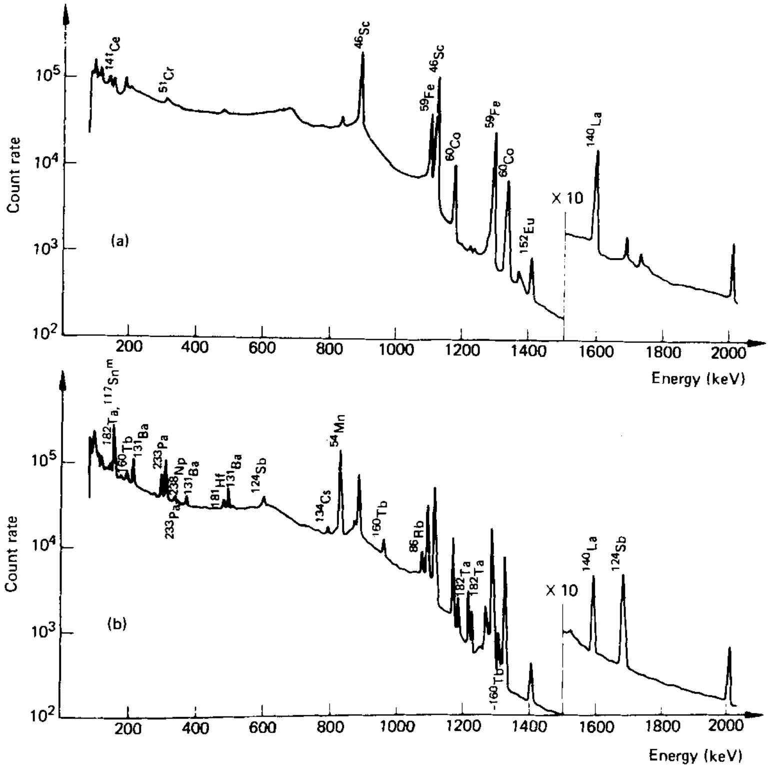


Figure 10.4. (Ref. [77]).

Gamma-ray Ge(Li) spectra of BCR-1: (a) irradiated without a Cd cover; (b) irradiated with a Cd cover.

of the 511 keV decay-curve.

10.3 Elemental analysis of silicates by NAA, including radiochemical separation

- Radiochemistry takes equipment and time and thus costs money. On the other hand one cannot stay away from it completely in some specific cases, as was already indicated in table 10.I. Although dissolution of the sample opens up the way for AAS and other techniques, it may be still advantageous to use activation analysis in view of the blank problems. For environmental studies, the determination of the heavy metals, notably Cr, As, Se, Sb, Hg and eventually Mo and W is of interest. Determinations of Cd and Pb are possible by NAA and photon activation analysis respectively; however AAS is the common practice.
- If radiochemistry is to be performed for long-lived isotopes it should be done on the INAA aliquot in the first case. Thus it may be used for the determination of Cr by evaporation of CrO_2Cl_2 [36] or liquid extraction [34].

  The determination of As, Se and Sb can best be done by isolation as their hydrides [38]. Table 10.IV. gives the results obtained for some USGA Standard Rocks.

  For Mo and W, NAA is definitely the best choice. Both elements are separated by post irradiation-chemistry; Mo by liquid extraction [39] and W by scavenging with active carbon [40].

10.4. Prompt capture γ-measurement of silicates and coal

- The application of prompt capture γ-ray measurements (PGAA) in silicate analysis is usually applied for a few elements with a high cross-section only [41,42]. The widest scope comprises 9 to 17 elements [43,44]. The most comprehensive study was made on NBS Standard Reference Materials [44], notably on fly-ash. Figures 10.5. and 10.6. give the γ-ray spectrum in the low-energy region. The intervals of 70-900 keV and 5800-7700 keV are used for determinations at a thermal neutron flux of $2.10^8 cm^{-2}.s^{-1}$ with ~ 2% contribution from more energetic neutrons.

  Ref. [44] also gives a list of recommended lines which cover the energy-region from 180 to 11000 keV. The conclusions is: "The combination of INAA and prompt capture γ-measurements allows one to measure ~ 45

Table 10.IV. (after ref. [38]).

Results of the hydride-technique for some USGS Standard Rocks

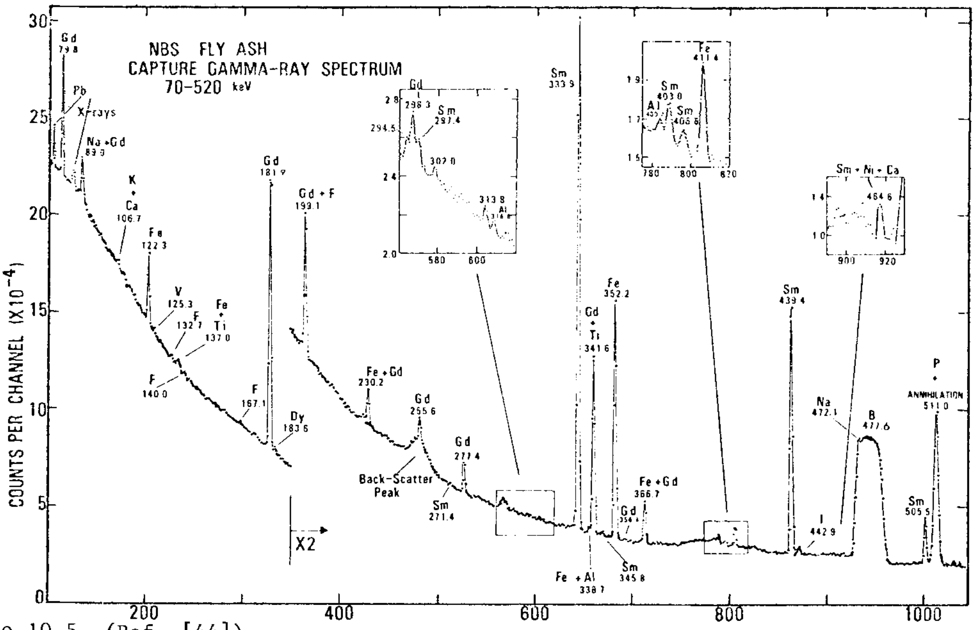
All data in $\mu g.g^{-1}$

Standard	As		Sb		Se	
	Found	Literature values	Found	Literature values	Found	Literature values
QLO-1	2.07 2.14	3.0	1.10 - 1.44	1.76 - 2.84	0.011	0.010
SCO-1	12.4	10.8 13	2.04 - 2.29	2.4 - 2.7	0.93 0.96 1.06	0.80 0.91
BMVO-1	0.45 0.46	1.5 0.57	0.11-0.13	0.5 0.17	0.036 0.063 0.066	0.01 0.067 0.136
SDC-1	0.23 0.22	0.22	0.30 0.42 0.53 0.56	0.53 - 0.56	0.022 0.024 0.026	0.033 0.039
MAG-1	9.6 9.5	6 5	0.90 0.96 1.20	0.82 - 1.00	1.00	1.00 1.13 1.31
STM-1	4.7 5.6	5.0	1.57 1.73	1.6 - 1.8	0.006	0.0087 0.010 0.030
BIR-1	0.04 0.06	0.6	0.33 0.36 0.39	0.15	0.015 0.016 0.016	0.02
DNC-1	0.10 0.08	0.12	0.28 0.35 0.40	0.23	0.15 0.19 0.26	0.20
W-2	0.94 0.87	1.16	0.42 0.47 0.54	0.19	0.084 0.095 0.13	0.10

Single values refer to independent measurements.

Ranges include several independent determinations.

Literature data taken from the USGS compilation and recent publications.



CHANNEL NUMBER

Figure 10.5. (Ref. [44]).

Prompt γ-ray spectrum of NBS Fly Ash (SRM 1633a) in the region of 70 to 520 keV observed by irradiating an 0.82-g sample for 20 h in the external thermal-neutron beam from the NBS reactor. Peaks are labeled by energies in keV and the element of origin

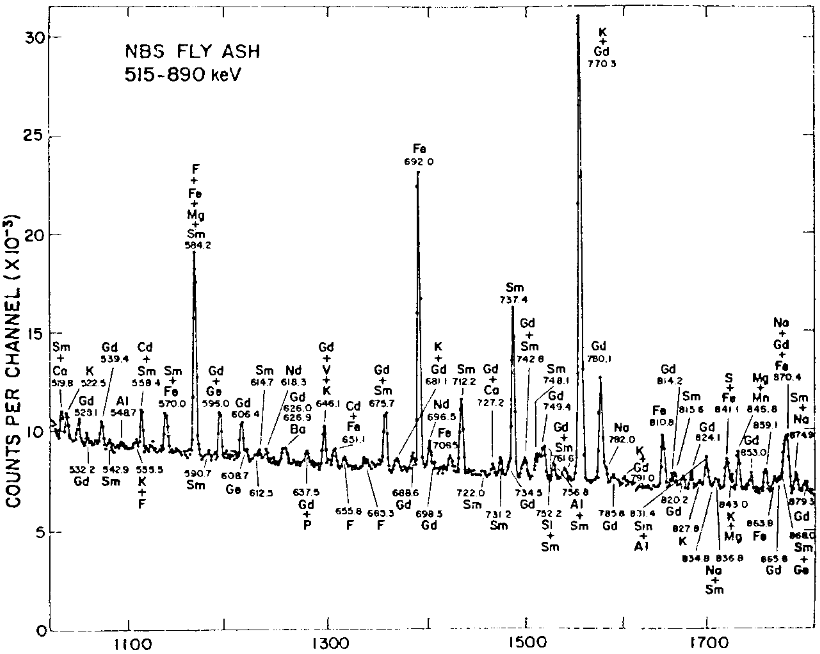


Figure 10.6. (Ref. [44]). CHANNEL NUMBER

Prompt γ-ray spectrum of NBS Fly Ash (SRM 1633a) in the region of 515 to 890 keV elements in "crustal" samples such as rocks, soil, coal, fly-ash". Of these 45, typically ~ 15 are obtained by PGAA.

- The contribution of the technique to the analysis of coal can be visualized by dividing the periodic table between (I)NAA and PGAA. One then gets the result given in table 10.V. Of the 12 elements which may be assayed, 3 are of primordial importance; H, N and S. The complexity of the obtained γ-ray spectra puts a severe limitation to the scope of multi-element PGAA. Even for the apparently best line of S one must be aware of an occasional interference [45].
  The precision of PGAA can be judged from the data given in refs. [44] and [46]. Table 10.VI., taken from [46], gives the comparison for coal-analysis between PGAA and classical techniques like Kjeldahl-combustion. The main restriction remains the parcity of the facilities. Simple constructions are described in refs. [47] and [48].
- The use of a portable ^{252}Cf-source may extend the scope of the prompt technique [49-51]. A 1 mg source yields 2.4 x 10^9 neutrons per second, which have to be thermalized. The main applications are: Determination of S and of the ash-content by way of Fe. Sources of 15 μg up to 1 mg ^{252}Cf have been applied on aliquots of ~ 100 kg coal. Regarding the measurements of the ash-content it should be remarked that simple back-scatter techniques [52] may offer an alternative.
- The "in situ" applications of prompt γ-measurements fall outside the scope of this text. Ref. [53] gives an account of the principles.

10.5. PIXE analysis of air-dust and coal

- The main strength of PIXE lies in the analysis of thin layers, up to ~ 5 mg.cm^{-2}. The requirement of preparing such layers of a uniform thickness and composition restricts the application of PIXE to powdered materials which can be spread out evenly. The most obvious choice is air-dust, collected on cellulose or teflon-filters [54-57]. Aliquots of other materials have to be prepared by gradual dropping on a rotating support [59,60]. Infinite thick target measurements may be applied to materials which may be pressed into pellets [66].

Coal is pulverized in an agate mortar to pass 200 mesh and then pressed at 2.4 x 10^7N.m^{-2} [67]. If possible, the samples are irradiated at

Table 10.V. (after ref. [44]).

Elements observable by INAA and PGAA in NBS Coal

INAA	PGAA
	H
	B
	C
	N
Na	Na
Mg	Mg
Al	Al
	Si
S	S
Cl	Cl
K	K
Ca	Ca
Sc	
Ti	Ti
V	V
Cr	
Mn	Mn
Fe	Fe
Co	
Cu	
Zn	
Ga	
As	
Se	
Br	
Rb	
Zr	
	Cd
In	
Sb	
I	
Cs	
Ba	
La	
Hf	
Ta	
W	
Au	
Ce	
Nd	Nd
Sm	Sm
Eu	
	Gd
Tb	
Yb	
Th	
U	

Table 10.VI. (from ref. [46]).

Carbon and hydrogen concentrations in environmental standards (%)

Standard	Carbon			Hydrogen		
	LASL (This work)	Previous work[a]	Ratio LASL/Previous	LASL (This work)	Previous work	Ratio LASL/Previous
Kodak						
$(C_6H_5O)_3PO$	70 ± 15	66	1.06	4.8 ± 0.02	4.6	1.04
$(C_{20}H_{34}O_2)Ni$	63 ± 3	60	1.05	8.0 ± 0.4	8.6	0.93
$(C_{20}H_{34}O_4)Pb$	41 ± 4	44	0.93	6.5 ± 0.3	6.2	1.05
$(C_{2}H_{27}O_6)Fe$	60 ± 3	60	1.00	5.0 ± 0.3	5.0	1.00
ISGS-Coal						
15263	69 ± 4	73.2	0.94	4.5 ± 0.2	5.3	0.85
16139	69 ± 4	66.2	1.04	4.4 ± 0.2	4.6	0.96
16408	72 ± 4	71.2	1.01	4.5 ± 0.3	4.9	0.92
14630	76 ± 5	73.7	1.03	4.5 ± 0.2	4.8	0.94
15231	68 ± 4	68.1	1.00	5.4 ± 0.3	5.0	1.08
17215	67 ± 4	65.3	1.03	4.7 ± 0.2	5.0	0.94
NBS						
1570	—	—	—	5.6 ± 0.1	None	
1571	47 ± 5	45.8 ± 1.3	1.03	6.1 ± 0.1	None	
1573	—	—	—	5.0 ± 0.1	None	
1575	54 ± 2	50.4 ± 1.5	1.07	6.5 ± 0.1	None	
1577	51 ± 2	49.6 ± 1.5	1.03	7.0 ± 0.1	None	
1632	73 ± 3	69.6 ± 2.1	1.05	4.3 ± 0.1	None	
			$\bar{x} \pm \sigma$ $\overline{1.02} \pm 0.04$			$\bar{x} + \sigma$ $\overline{0.97} \pm 0.07$

[a] Previous work on NBS materials done by combustion.

LASL = Los Alamos Scientific Laboratory.

normal air-pressure [56,67]. The use of a "classical" vacuum scattering chamber has been described [60,61] but limits the capacity of the analysis as sample-changing is time-consuming. The use of the circular tray of a slide-projector within the rectangular target chamber [59] is an efficient solution of this problem. It permits the variation of the pressure to minimize electrical loading of the target (cf. section 7.5).

- Usually, the target is kept under a 45° angle with the beam [59,60, 66,70]; a ~90°-angle is applied in the "classical" scattering-chambers [60,61]. Preferably a large spot-size is used; values quoted are between 4 mm^2 [56] and 1 cm^2 [58]. Microbeams are, as a rule, not applied to these types of samples. To enhance the selectivity, filters of Be [59], Al [67] or perspex [70] are used to eliminate low-energy X-rays. Proton-energy depends on the type of target, the absorbers used and the Z-values of the elements to be determined. The energy-loss in a thin air-dust aliquot of ~ 0.5 $mg.cm^{-2}$ is of the order of 5% while in infinite thick targets the energy comes down to zero.
  The usual choice in thin target irradiations is ~ 2.5 MeV which is appropriate for $Z \geq 20$. For $Z \geq 13$-20 one should use ~ 1.4 MeV [59]. The current-density varies from ~ 100 [58] till ~ 600 $nA.cm^{-2}$ [59]. Irradiation-time is of the order of 100 seconds. A Si(Li)-detector [58,59,61] or a high-purity Ge crystal [60,70] is used for the measurement of the X-ray spectra.

- The obtained spectra have to be evaluated by a sophisticated computer-programme as both the separation for the compton-background and from interfering peaks is difficult. The programmes AUTOFIT [56], PROFANAL [59,62], SPECFIT [60,63] and CUTIPIE [61,64] are current examples. The blank spectrum is used as an approximation of the shape of the background-spectrum. Eventually, this blank is subtracted prior to the peak-evaluation [56,65]. Preferably, the background-fit should be non-linear [59,62].
  The correction for matrix-effects may be omitted in the case of very thin layers (< 100 $\mu g.cm^{-2}$) [61]. Otherwise programmes like described in refs. [59,60] have to be applied. Subsequently, a standardization with respect to the integrated beam-current has to be made. The latter quantity may be obtained form measurements with a Faraday-Cup [56,58,59,68] or by back-scattering from a 80 $\mu g.cm^{-2}$, calibrated gold foil [61]. Attempts have been made to use the bremstrahlungs-

Table 10.VII. Some applications of PIXE to the elemental analysis of silicates, aerosol and coal

Matrix	Aliquot	Energy of protons in MeV	Beam-current in nA	Target spot in mm^2	Irradiation time in minutes	Number of aliquots per run	Calibration	Elements determined	Reference
Glass	Thin layer of powder on "hostaphan" foil	2.5	100	~ 4	30	5	Against Mo in the samples	Ti,V,Cr,Mn,Fe, Ni,Cu,Zn,Rb,Pb, Sr,Zr,Nb	60,69
Aerosol Silicate standard	≤ 300 μg.cm^{-2} on "nuclepore" filter	2	24-109	~ 12	5-15	1	Against thin standards	Ca,Fe,Cu,Zn,Br, Pb	68
Aerosol	Thin layer on "nylon" foil	3.7	100		3	80	"	S,Cl,K,Ca,V, Ti,Mn,Fe,Cu,Zn	58
		2.5			4	1	Against thin standards Control by AAS	Si,S,Cl,K,Ca, Ti,V,Cr,Nu,Fe Ni,Cu,Zn,Pb,Br, Rb	56
Aerosol	0.1-3 mg.cm^{-2} thin layers on "suprathen" foil	$\left.\begin{array}{l}3\\1.4\end{array}\right\}$	20-300	~200	5-6	100	Against thin standards	S,Cl,K,Ca,Ti Mn,Fe,Ni,Cu,Zn, Pb,Br	59
Aerosol	30 μg.cm^{-2} thin layers on cellulose acetate filters	2	2-3	~ 1	25	1	Absolute method	Si,S,Cl,K,Ca, Ti,[V,Cr],Fe,Cu, Zn	61
Aerosol	200 μg on on 12 cm^2	1.5-2.5			1-10	24	Relative	S,Cl,Ca,Fe	78
Coal	Infinite thick pellets	2.5-5.5	5-70			multiple	Comparison to Standard Reference Materials	Fe,Zn,As,Br,Pb, Sr,Zr,Rb,Y,Cd, Sn	67

spectrum to this end [59]. The resulting corrected peak-areas should be free from a Z-dependent systematic bias and, if possible, of all systematic biases. If the second requirement is not fulfilled, the analysis yields concentration-ratios only; absolute data may then be obtained by independent measurements on one or more suitable elements [60].

Absolute results are based on comparison to standards of the same material and thickness [56] or obtained by absolute calculations. The latter imply the knowledge of the excitation-functions involved and of the absolute efficiency of the detector as a function of the X-ray energy. Details are given in refs. [60,61,66].

- Some recent examples of determinations by PIXE in silicates, aerosol and coal are listed in table 10.VII. Most are on thin layers of aerosol. The number of determined elements varies between 8 and 15. The lower limit of determination depends on the specific load, the compton-background, the blank caused by the support and the irradiation-time. The obtained number of counts is proportional to the specific load only in case of thin layers. The net peak-area is affected by the compton-background in the usual way (cf. sections 6.6. and 6.7.). The subtraction of the two net peaks, for loaded filter and blank, increases the statistical error. The signal obtained is proportional to the irradiation-time. If a small beam with a high current-density is used and a small hole is burned through the aliquot and its support, the collection of the signal should start after that.

10.6. (Radio-)tracer applications to the inorganic environment

- Radiotracers and activable tracers may be applied in the study of field-phenomena and under laboratory-conditions. In the field the main reason is the determination of flow-rates and residence-time distributions (cf. section 3.6.).

  In the laboratory mass-transport and isotopic exchange in closed (batch-) and open (column-)systems may be measured by (radio-) tracer experiments.

- For the measurement of atmospheric movements radioactive gases have been used [71,72] but as a rule a non-radioactive tracer is preferred. To this end artificial aerosols of dysprosium [73] and indium [74] have been applied. By burning an ethanol-water solution of $InCl_3$, it is possible to generate particles of 0.01-0.1 μm diameter [74].

- The movement of water through soil and sediment is best measured by way of a tritium-injection. In practice the use of (stable) bromide is much simpler. It appears that, in most cases, both techniques give the same result [75].

  For small scale experiments, labelling of solids with (radio-)tracers may be useful. An example is met in the labelling of fly-ash with ^{99m}Tc [76].

- In the laboratory, dissolution, leaching, and adsorption-processes have to be studied for minerals, sediments and fly-ash.

  The principle of these experiments is described in section 3.4. The leaching of antimony from a basic fly-ash by double distilled water may be quoted as an example:

  ◘ Total Sb-content, determined by INAA: (15 ± 1) $\mu g.g^{-1}$.

  ◘ Leachable concentration, determined from batch experiments with 2-10 grams of fly-ash at water/ash-ratios of 10^{-2} to 10^{-1}: (2.3 ± 1.0) $\mu g.g^{-1}$ or (15 ± 8)%.

  ◘ More than 99% of the leached antimony is readsorbed by the solid.

Corresponding studies on the field situation are, like the laboratory experiments, based on simple mass-conservation laws [80].

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