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TRAINING COURSE SERIES No.4

**Sampling and Analytical Methodologies for
Instrumental Neutron Activation Analysis
of Airborne Particulate Matter**

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INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1992

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FOREWORD

The IAEA supports a number of projects having to do with the analysis of airborne particulate matter by nuclear techniques. Most of this work involves the use of activation analysis in its various forms, particularly instrumental neutron activation analysis (INAA). This technique has been widely used in many different countries for the analysis of airborne particulate matter, and there are already many publications in scientific journals, books and reports describing such work.

The present document represents an attempt to summarize the most important features of INAA as applied to the analysis of airborne particulate matter. It is intended to serve as a set of guidelines for use by participants in the IAEA's own programmes, and other scientists, who are not yet fully experienced in the application of INAA to airborne particulate samples, and who wish either to make a start on using this technique or to improve their existing procedures.

The methodologies for sampling described in this document are of rather general applicability, although they are presented here in a way that takes account of the particular requirements arising from the use of INAA as the analytical technique. The analytical part of the document, however, is presented in a form that is applicable only to INAA. (Subsequent publications in this series are expected to deal specifically with other nuclear related techniques such as energy dispersive X ray fluorescence (ED-XRF) and particle induced X ray emission (PIXE) analysis).

Although the methods and procedures described here have been found through experience to yield acceptable results, they should not be considered mandatory. Any other procedure used should, however, be chosen to be capable of yielding results at least of equal quality to those described.

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EDITORIAL NOTE

In preparing this material for the press, staff of the International Atomic Energy Agency have mounted and paginated the original manuscripts and given some attention to presentation.

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1. INTRODUCTION

There are a variety of reasons to sample and analyze airborne particulate matter. Sampling may be done to determine if the concentrations of total particulate matter are high enough that public health may be adversely affected. Thus, sampling may be part of an exposure assessment in which risk is being assessed, information is being gathered to permit risk management, or monitoring is being conducted to support epidemiological studies. Sampling may be conducted to determine compliance with air quality laws or regulations. Alternatively, studies of atmospheric transport, transformation, and deposition processes may require particle sampling and compositional characterization. Similarly, visibility degradation is in large part due to airborne particle concentrations, particularly in the sub-micron size range and information may be needed regarding particle concentrations to relate to other observed properties of the atmosphere. These various purposes lead to quite different requirements for sampling and analysis and it must be understood that it is not possible to establish a single sampling and analysis protocol that will provide satisfactory results for all of these possible types of studies. There are also a wide variety of options available to buy or build sampling equipment and to utilize a number of different filter media. The choice of a particular combination of sampler, media, and analytical method will depend heavily on the ultimate purposes to which the data are addressed and the resources available to conduct the study.

Neutron activation analysis (NAA) is a very powerful technique for the non-destructive multielemental determination of many trace elements in aerosols, both in the natural environment and the occupational workplace. Due to the differences in nuclear properties of the stable isotopes, sensitivities and hence analytical detection limits vary from element to element with large fluctuations. For instance, elements such as aluminum, arsenic, antimony, indium, manganese, selenium, sodium, vanadium, halogens and many rare earths are easily detected by neutron activation methods with very good precision. On the other hand elements such as cadmium, sulphur and lead are difficult or impossible to determine non-destructively in airborne particulate matter. Typically 30-40 trace elemental concentrations can be determined in the aerosol containing very small amounts (less than one milligram although many samples have much higher quantities depending on the area being investigated) of material. Because neutron activation methods are multielemental, an enormous amount of information can be gathered from a relatively small number of analysed samples. The results can be used either in undertaking background monitoring, to conduct epidemiological studies, to investigate source apportionment methodologies using source-receptor models, to study long range transport phenomena, and to establish a more cost effective plan to control air pollution.

In characterizing airborne particulate matter, both the physical and chemical properties of ambient samples can affect the choice of sampler, collection media, and analysis protocol. For instance, sampling in remote areas requires longer collection times as compared with collections in the urban environment. Because of logistics in remote areas, far more preparation time and cost is involved in

sampling these areas. In addition, more sensitive analytical methods are needed since the elemental concentrations in the atmosphere may be at least one order of magnitude lower. In this report some of the considerations in airborne particle sampling are presented and then specific analytical methodologies for instrumental neutron activation analysis (INAA) are discussed. As an example of the application of these methodologies an outline protocol is presented in Annex 2 for the study of baseline elemental concentrations for airborne particulate matter.

2. SAMPLING

The ability to obtain a sample of material that is, in fact, representative of the ambient environment is an extremely difficult task. In general, there will always be some aspects of the sample that prevent it from being ideal, and in fact, there are mutually incompatible combinations of sampling device, filter media, and analytical methodology. Thus, it is necessary that these defects are understood in the design of the sampling/analysis programme so that the results obtained from the analyses can be placed in proper perspective and possible systematic biases estimated. Careful thought should be given before starting a project as to the ultimate uses of the data for which the sampling and analyses are being performed so that a sampling and analysis protocol can be designed to meet the programme's objectives.

The general concept of sampling airborne particles is to use a pump or pull a known volume of air through a filter so as to collect the particles. The airstream can be processed on its way to the filter so that only particles fulfilling some set of predetermined aerodynamic characteristics are allowed to reach the filter or that, before arriving at the filter, reactive gases have been removed from the flow to prevent them from modifying the collected sample. The possibility of volatility losses of material from the filter must also be considered and appropriate backup filters or traps put into position if such volatile components are of interest (e.g. mercury and selenium). The characteristics of the filter will govern the efficiency of particle collection and the presentation of a sample suitable for a particular analytical technique.

2.1. SAMPLERS

2.1.1. High volume samplers

The most widely used airborne particle sampler is the high volume sampler. In the United States of America it has been designated as the standard method for sampling total suspended particulate (TSP) matter and determining compliance or non-compliance with the old USA National Ambient Air Quality Standard (NAAQS) for particulate matter [1]. This very simple device was first developed and put into wide use in the early 1960s [2]. There is a housing that shelters the filter holder from direct precipitation and that, to some extent, acts to keep very large particles

from reaching the filter. The exact maximum size of particle collected by the sampler depends strongly on the ambient wind speed and direction [3]. Thus, although this sampler has been the 'standard method' for collecting airborne particulate samples, it is not a very desirable sampler in that it does not provide samples with a well defined range of particle sizes. Another problem with the sampler is that it permits windblown dust to accumulate on the filter even when the pump is not running. This 'passive loading' can lead to an overestimation of total airborne particulate levels. Modifications to the samplers are now available that minimize this problem, but it does represent a problem which remains for most of the historical samples collected with this device.

The standard medium for particle collection is the glass fibre filter. Although these filters have a high retention capacity for particles greater than $0.3 \mu\text{m}$, artifact sulphate can be produced on the filter [4], which may distort the TSP measurement. These filters are also not suitable for analysis by instrumental neutron activation analysis (INAA) or energy dispersive X ray fluorescence (ED-XRF). For the analysis by other techniques the particulate matter can be leached and the dissolved material analysed by atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES); however, it is difficult and time consuming to achieve quantitative recovery of the material from the filter. Thus, this combination of sampler and filter material is not well suited to most studies that are aimed to perform multielemental chemical analysis on the collected material. However, the high volume sampler can also be used in conjunction with most of the other filter media discussed in Section 2.2.

An initial approach to improve sampling is to utilize an inlet to provide an upper size cut-off. Initial designs were for 50% efficiency collection at $10 \mu\text{m}$ [5,6]. These samplers eliminate most of the wind speed and direction problems as well as being able to prevent most of the passive loading difficulties. A significant improvement in the collection of a well defined sample is represented by these inlets.

2.1.2. Dichotomous samplers

For many purposes, including the better assessment of exposure to respirable toxic materials or the identification of the sources of particles and quantitative apportionment of the observed mass to those sources, it is useful to recognize that different types of source processes give rise to different size particles. Fine particles ($< 2 \mu\text{m}$) arise primarily from condensation of vapour or chemical conversion of gaseous compounds to low volatility vapours that can subsequently nucleate (Figure 1). These initially very small particles coagulate into relatively stable particles. Coarse particles ($> 2 \mu\text{m}$) are generated principally by mechanical action. Thus, separation of particles into different size categories may provide samples that are affected by fewer sources or which behave differently in the human respiratory tract. A device developed to provide such a separation is the dichotomous sampler.

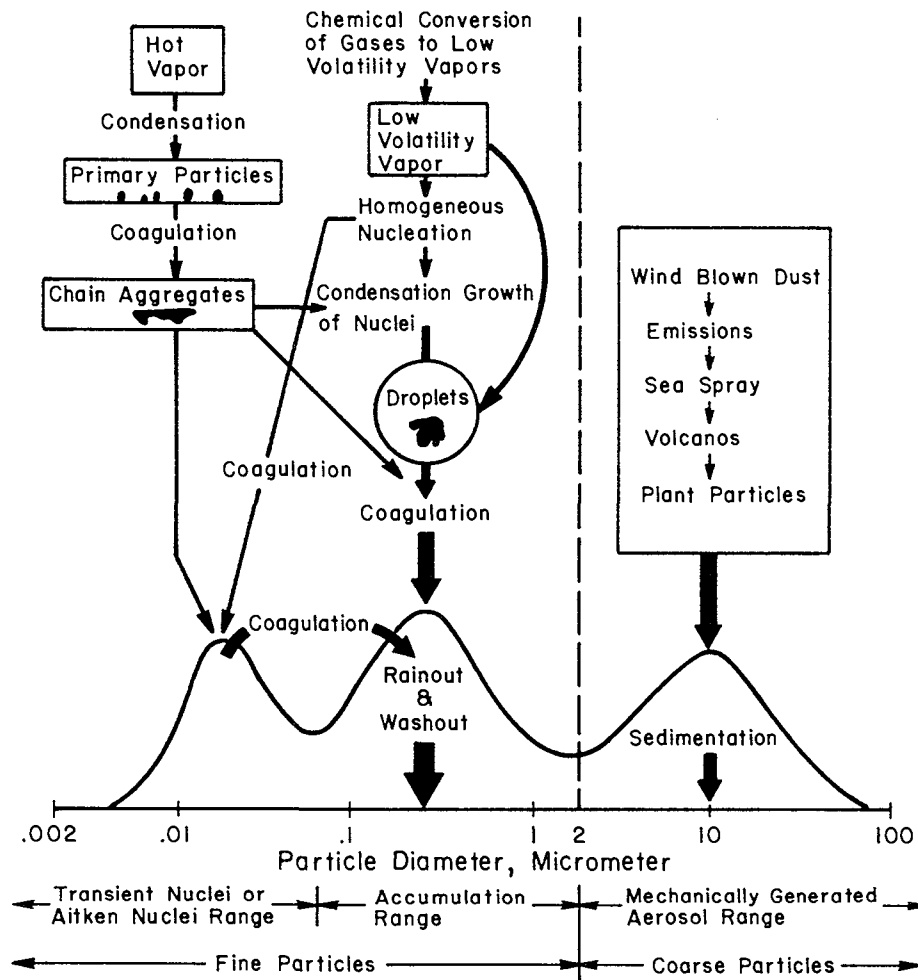


FIG. 1. Idealization of the atmospheric aerosol surface area distribution showing the principal modes, main sources of mass of each mode, and the principal processes involved in ejecting mass in each mode as well as primary removal mechanism (taken from Whitby and Cantrell (1976) and used with permission of IEEE. Copyright 1976 IEEE).

The originally designed dichotomous sampler is shown schematically in Figure 2. It was designed to separate samples at a 50% efficiency for $2.5 \mu\text{m}$ aerodynamic diameter particles and to exclude large particles by having a 50% efficient inlet for $15 \mu\text{m}$ diameter particles. The values of $2.5 \mu\text{m}$ and $15 \mu\text{m}$ were chosen primarily on the basis of trying to match the sizes that are important in understanding the particle transport and deposition that occurs in the human respiratory tract, but they are also useful size ranges for source separation (see Figure 3).

The separation of the fine ($< 2.5 \mu\text{m}$) particles from the coarse fraction is provided by a virtual impactor. For particles above $0.2 \mu\text{m}$ there is sufficient inertia that, when the airstream in which they are being transported is rapidly forced to change direction, the particles will separate from the airstream and generally be collected on the surface used to create the divergence of the flow. However, it is possible to draw sufficient quantities of air from a flow to cause a separation of particles. The fine particles move with the diverted stream while the larger particles

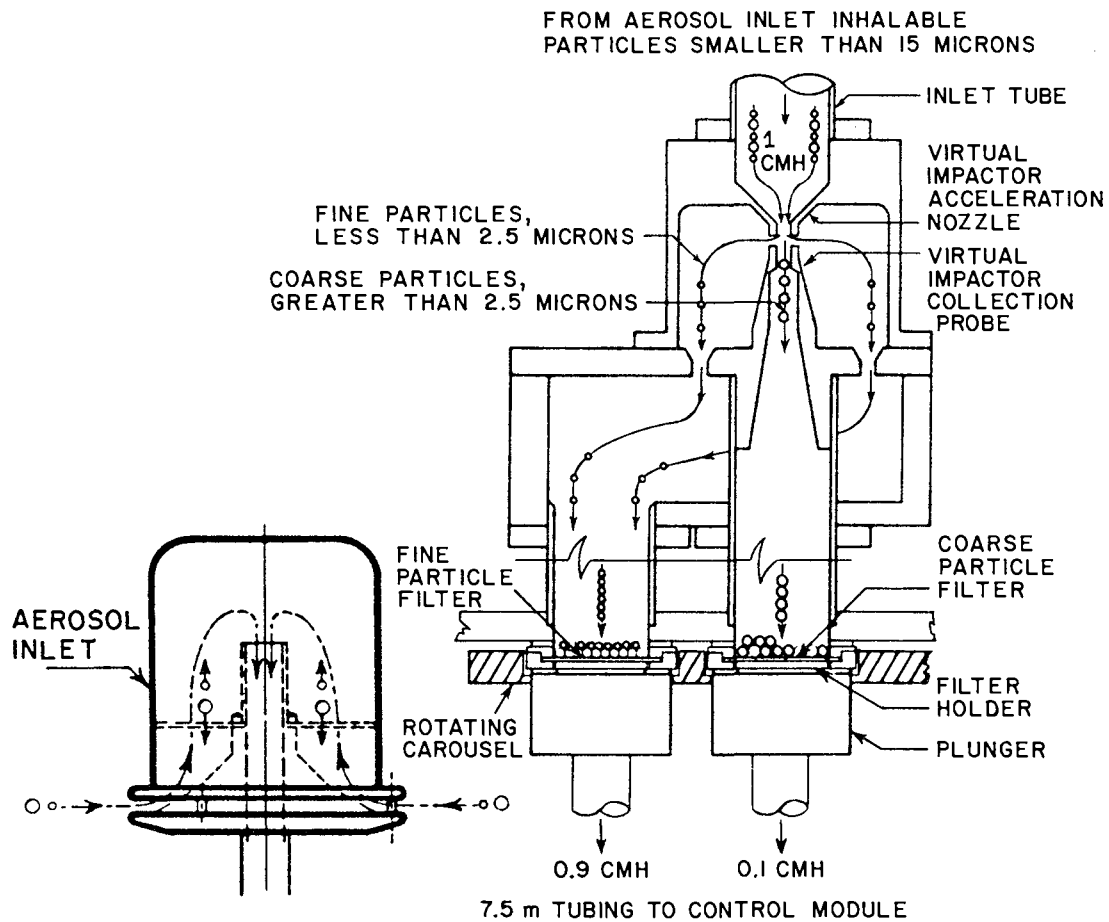


FIG. 2. Design of a dichotomous particle sampler for separating airborne particulate matter into two size fractions (courtesy of Sierra Instruments, Inc., Carmel Valley, California, USA).

move ahead through the virtual impaction surface. Thus, the separation is not caused by the interaction of the collected particles with the impaction surface and the separated particle streams are available for collection by standard filter media (see Section 2.2).

There have been several intensive evaluations of these samplers to investigate the accuracy of their aerodynamic sizing and their sensitivity to wind speed and direction effects. Wedding et al. [7] showed that the inlet size cut-off was strongly dependent on wind speed and that there could be considerable variation in the size of the particle that could penetrate the sampler. John et al. [8] have also shown that nozzle concentricity was a difficult parameter to measure but, when determined, samplers could be found to be significantly out of specified tolerance ranges. This failure of concentricity affects the rate of wall loss for particles of $3 \mu\text{m}$ and larger.

In the early 1980s interest shifted to a sampler with a 50% efficient size cut-off of $10 \mu\text{m}$ as it was decided that this better represents the maximum size of inhalable particles. New inlets were designed to provide the separation and also address the wind speed dependency of the previous designs [9]. The dichotomous

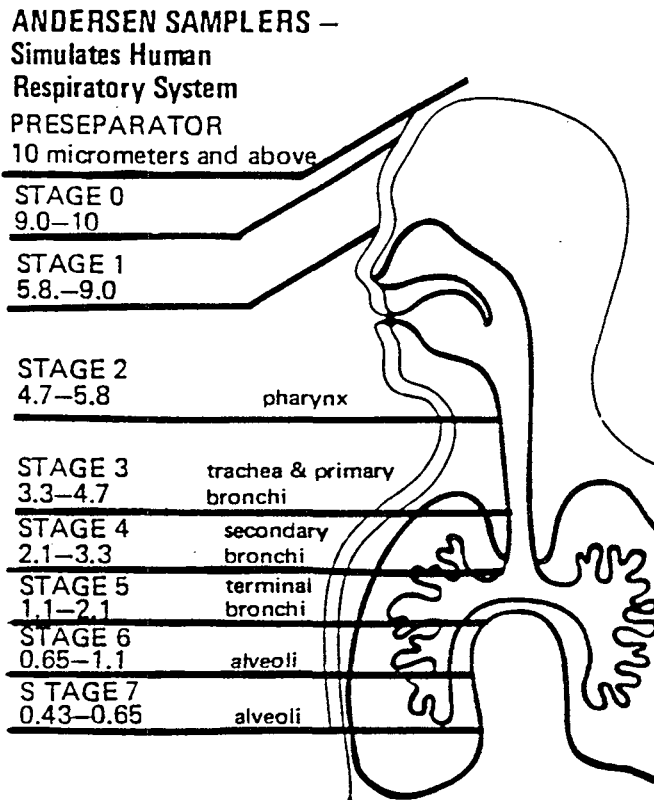


FIG. 3. Diagram depicting the human respiratory system and its various cutoff points.

sampler is thus a very useful device where well characterized size range samples of different ranges are provided.

The particles are collected in the sampler on membrane filters. Currently, the most commonly used are Teflon (PTFE) filters. In the past, polycarbonate Nuclepore and cellulose acetate filters were employed. All of these membrane filters provide samples that are well suited for automated mass measurement using beta gauge techniques [10] and for elemental analysis using ED-XRF and/or INAA. However, the flow rates in these samplers are limited by the ability of membrane filters to pass air and by their tendency to clog as the particles accumulate. Automated dichotomous samplers are available that change filters when the pressure drop across them exceeds a preset limit. However, it has been shown from considerable field experience that there are many difficulties with the dichotomous sampler. It was designed as a research tool and requires too much skilled operator interaction to be useful in routine monitoring.

2.1.3. Stacked filter units

Another comparable system available is the stacked filter unit. Two filters are placed in series, whereupon the coarse particles are collected on the first filter and the fine particles on the second. These particles are usually collected on Nuclepore or Teflon filters. A distinct advantage of this system is that different pairs of pore

sizes can be used. In general the coarse fraction is collected on a filter with an 8 μm pore size and the fine fraction is collected on a filter with a 0.4 μm pore size.

2.1.4. PM-10 samplers

An initial approach to improve high volume sampling is to utilize an inlet to provide size cut-off. Initial designs were for 50% efficiency collection at 10 μm [5,6]. These samplers eliminate most of the wind speed and direction problems as well as being able to prevent most of the passive loading difficulties. A significant improvement in the collection of a well defined sample is represented by these inlets.

With the advent of new air pollution guidelines in the USA [11], samplers were needed to separate the particles with 50% efficiency at 10 μm (PM-10) for the National Ambient Air Quality Standard (NAAQS) for particulate matter. The NAAQS for PM-10 is defined so that any sampler that meets a series of performance criteria can be designated as a reference method and thus can be employed to monitor and enforce the standard [12]. In 1989, there are high volume flow heads built by several companies that meet these requirements and have been certified as reference methods [12]. One device uses a cyclone [5] to provide the 10 μm particle separation while the other uses an impactor [6]. In both cases, as a result of problems with particle bounce from the collection surfaces, the manufacturers now require the use of coatings on the collection surfaces. Thus, more maintenance in the field is required by the samplers if they are to retain their specified separation efficiency. To eliminate this problem, Marple et al. [13] have developed a high volume virtual impactor inlet so that the size separation is made as in the dichotomous sampler, without the use of a physical impaction surface. This device has not yet been certified as a reference method nor has it undergone extensive field use, so its long term utility and reliability are not yet known.

In order to operate these PM-10 samplers at their higher flow rates, fibre type filters (quartz, glass or cellulose) are needed to obtain the necessary low pressure drop that does not increase substantially with particle loading. As a result, the provided samples may not be appropriate for all of the possible analytical methods that could be employed for particle characterization.

2.1.5. Cascade impactors

It is possible to obtain detailed information on the size distribution of the airborne particles and their constituents using a cascade impactor. There has been considerable use of cascade impactors that provide multiple samples in various size ranges with the particles collected in each stage of the impactor. A recently published monograph describes the types and uses of cascade impactors in great detail [14]. These samplers can be single or multiple jet devices that collect air over a wide range of flow rates. The concept of a cascade impactor is shown in Figure 4. The impactor is designed so that the airstream carrying the entrained

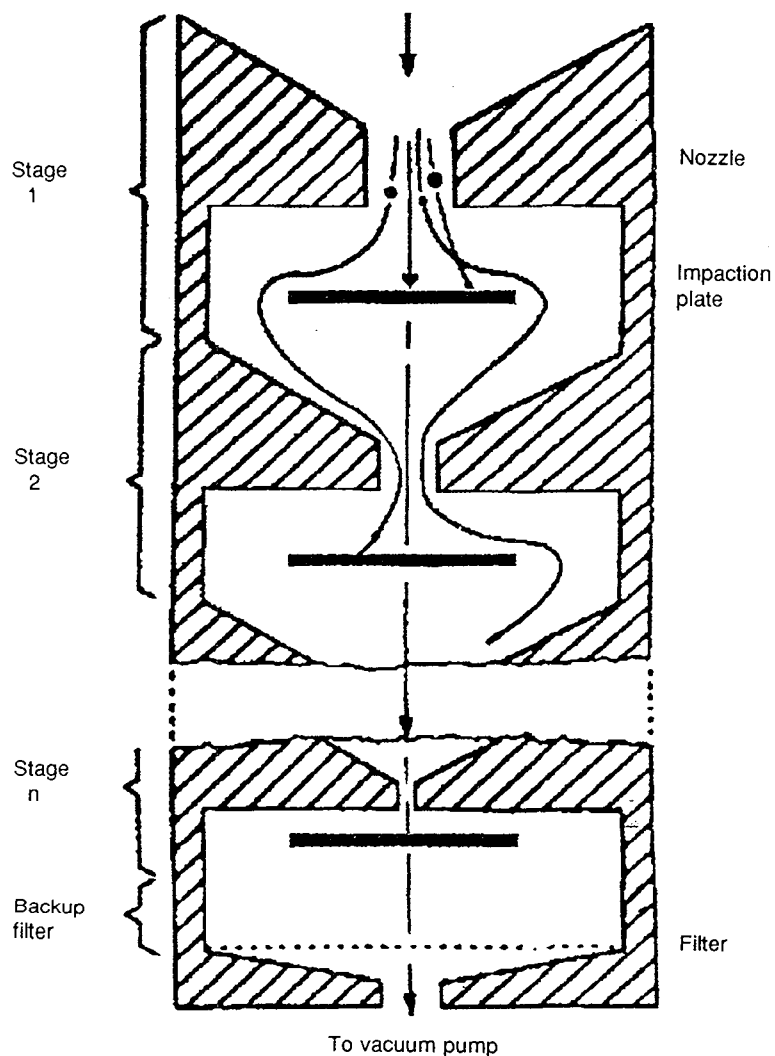


FIG. 4. Design of a cascade impactor.

particles is forced to change direction rapidly. Particles with sufficient inertia detach from the streamline and impact on the collection surface. A major difficulty with impactors is the bounce of particles after collision with the collection surface. Problems of this nature have been reviewed by Esmen and Lee [15]. It is necessary to exert some care and effort toward minimizing this problem in order to yield properly size-segregated samples.

One approach has been the use of a virtual impactation surface as in the dichotomous sampler. However, the virtual impactor concept has not been extended beyond the one stage separation in the dichotomous sampler. Coatings have often been applied to lower bounce in conventional multistage impactors [16]. In some cases with low volume flow systems, the impactor has been used upside down so that particles that bounce are forced back onto the same impactor stage. The individual particle size fractions can then be analysed. They are generally quite suitable for instrumental analysis such as INAA or ED-XRF, although there is usually only a small amount of mass collected. Typical urban size distributions have been

given by Gladney et al. [17], Paciga and Jervis [18], and Kowalczyk et al. [19]. The additional information available on the elemental size distributions has really not yet been employed effectively in receptor models that rely on collected particle composition data.

2.2. FILTERS

Another important consideration in obtaining a useful sample is the material on which it is collected. The filter should be retentive of particles but permit ready air flow through it. It should provide the sample in a manner that makes it easy to quantify both the total mass of collected material and the chemical composition of the sample. Although these conditions seem straightforward, there are several inherent and unresolvable conflicts in these requirements.

There are two general types of filters: fibrous and membrane filters. Fibrous filters include the glass fibre filters already mentioned, quartz fibre filters and cellulose (paper). In effect, particles are captured as the air moves through and around the randomly positioned fibres that have been pressed together into a mat, often with a binding material to help keep the filter together. These filters have relatively low pressure drops across them and are well suited to high volume sampling. The glass and quartz fibre filters have a high retention of particles with sizes above $0.3 \mu\text{m}$.

Neustadter et al. [20] found that cellulose filter materials, e.g. Whatman-41, could be employed in ambient monitoring with insignificantly lower collected mass if proper care were taken in the humidity equilibration that must be conducted before taking exposed or unexposed filter weights. Paper filters have been found to have somewhat lower retention when sampling begins [21] but to improve in their collection capability as the filter begins to develop a loading of particles [22]. They have a high loading capacity and have low blank values [23].

The glass fibre filter also has a high capacity but it also has a well known positive artifact mass due to the in situ conversion of sulphur dioxide to sulphate. It also has very high blank values and is quite unsuitable for trace element analysis. The quartz fibre and paper filters do not show appreciable sulphate artifacts [4]. The use of quartz fibre filters can provide accurate mass values that neither paper nor glass fibre filters can yield although extra care must be taken in handling them because they tend to be fragile. Also the quartz fibre filters, while better than glass for blank values, still have blank values too high to make them suitable for trace element analysis. Because of the unequal penetration of the particles into the filter mat, the fibrous filters are not useful for ED-XRF analysis either.

For trace elemental analysis studies, it is more common to collect the sample membrane filters that provide samples better suited for INAA, ED-XRF or microscopic analysis. The filters commonly used for particle sampling include polycarbonate (e.g. Nuclepore) and polytetrafluoroethylene (PTFE). The latter is

commonly known as Teflon and filters made of this material are now produced by several manufacturers. Other types of filters made from polyester include Millipore and Sartorius. Spurny et al. [24] provided the first review of these relatively uniform sized Nuclepore filters. There have been a number of subsequent tests of the filtration efficiency of these membrane type filters [25,26]. The collection efficiency depends on the pore size, particularly for the Nuclepore filters. For example, John and Reischl [26] found that 0.8 μm Nuclepore filters had only a 72% efficiency for sub-micron particles observable with a condensation nuclei counter. In contrast, 1-3 μm pore Ghia fluorocarbon filters and 1 μm Fluoropore filters are >99.9% efficient under the same experimental conditions.

Two other Teflon filters are manufactured by Gelman Sciences. They are Teflo and Zefluor filters. In general, the problem with Teflon filters is that the thin membrane is hard to handle. The filters are mounted in a polymethylpentane ring; however, it has been found that these rings add substantially to the filter blanks and need to be cut-off before any NAA is done. Thus, if both ED-XRF and NAA are to be performed on the same filter, ED-XRF should be performed first.

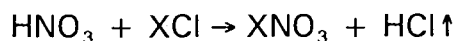
The Zefluor filters are a thin membrane mounted on a porous Teflon mat. It is important for the ED-XRF analysis that the membrane side be used as the particle collection surface. If the mat side is used, there is more total mass per unit area, leading to higher blank values and lower sensitivity. It is difficult to distinguish the membrane and mat sides and field personnel need to be trained in order to mount the filters properly for sampling.

Although there can be some difficulties in handling the fluorocarbon filters when preparing them for INAA, they seem to be the filter of choice for inorganic analysis. They also have proved to be a useful substrate for X ray diffraction analysis of particle samples [27]. One problem that has arisen with the fluorocarbon filters is the loss of coarse particles from the filters in handling and transport from the sampling site to the laboratory. Dzubay and Barbour [28] have suggested the use of an oil coating on the filters to prevent such shake-off effects. It is clear from the experience of a number of investigators that the loss of coarse particles is a common problem and some kind of coating is essential for proper coarse particle sampling. The coating should also be applied to the blank samples that are analysed as part of the analytical process.

2.3. ANNULAR DENUDEERS

A final consideration in sampling is the interaction of gaseous species with the sample as it is collected on the filter. This can be prevented by the use of a denuder - a tube with a reactive surface coating which is installed upstream of the filter to absorb the offending gases before they reach the filter. Increased use of such methods can be expected to occur as more attention is paid to the possible chemical interactions that can occur between the gaseous and particulate species in the sampling process. This is particularly important when trying to attribute

bromine or chlorine to specific sources. For example, during the summer, a substantial portion of the nitric acid is in the gas phase. The interaction of the nitric acid with alkaline coarse particles can lead to collection of the nitric acid on the particle surface and an increase in the sample mass. Gas-phase acids can interact with fine or coarse particles that contain halogens to cause the evolution of the halogen by the reaction:



There is the possibility of neutralization of collected sulphuric acid or ammonium bisulphate by gaseous ammonia, and other gaseous-particle interactions. There are also possibilities of volatile species losses. Thus, to effect a complete collection of a sample, it is necessary to include other components in the sampling train. Such components include denuders to remove gaseous species and impregnated back up filters and/or traps to collect material volatilized from the filter after collection. Denuders with filter packs have been described by Possanzini et al. [29], Vossler et al. [30] and Koutrakis et al. [31,32].

2.4. FLOW MEASUREMENT AND CONTROL

One of the most common problems in measuring airborne concentrations is the accurate quantification of the volume of air sampled. If airborne concentrations are to be expressed as a mass of measured substance (total particle mass, chemical elements, etc.) per unit volume of air, then both the total quantity of that substance and the total volume of air sampled must be carefully determined. Since the desired quantity is a ratio, excellent accuracy and precision in the analysis of the numerator (mass of substance) is meaningless if the volume of air sampled in the denominator is only known to a limited degree of accuracy relative to the accuracy and precision of the numerator. All of these aspects of sampling must be considered in the development of the experimental design of the sampling and analytical programme.

Thermal conduction flow control devices are used in many samplers. Wedding [33] has shown that there can be considerable errors in flows with thermally based mass flow controllers if particular care is not taken in the calibration of the flow controller for the temperature and altitude conditions under which the sampler is to be employed.

An alternative to mass flow control is volumetric flow control with critical orifices. As the cross-sectional area of the tube through which the air flows is reduced, it will reach a point at which the speed of the flow approaches the speed of sound. At that point, the air molecules cannot move faster, and the flow is therefore limited to that value. It is possible to obtain a critical orifice even for very high flows as has been accomplished by Wedding [34]. These devices assure constant volumetric flow and are now available commercially (e.g. Andersen). It is possible to obtain reliable and accurate flow information either by mass flow or

volumetric flow control. It is necessary that control and calibration be an integral part of the quality control/quality assurance programme developed as part of the design of any field sampling campaign.

The thermal mass flow controller and the critical orifice provide flow control. If less precision is required in the total volume of air to be sampled, the flow rates can be measured. Measurements of the flow rate can be achieved with rotameters, wet test meters and dry test meters. A rotameter is a tube with a float in it; the air flow traverses the tube from bottom to top. Thus, the balance of the drag force of the air at a given pressure drop against the force of gravity gives a measure of the flow rate. It is important to remember that the rotameter must be vertical and the pressure drop versus the flow characteristics must be measured for each rotameter. Such calibration can be achieved with wet or dry test meters that depend on displacement of a fluid (air or water) to drive a rotating meter. However, such devices are not as easily transported and thus are better employed to calibrate the rotameters.

It must be also kept in mind that the ambient barometric pressure is not always one atmosphere. In sampling at higher elevations, the diminished atmospheric pressure must be taken into account if proper flow measurement is to be achieved. Normally rotameter measurements are made at the start and end of the sampling interval and the flow rate is assumed to vary linearly between these values over the sampling period. This linear behaviour is unlikely and typical volumetric errors are in the range of ± 10 to $\pm 30\%$.

3. ANALYTICAL LABORATORY FACILITIES

3.1. IRRADIATION FACILITIES

The analytical methods described in this section are not meant to be used in conjunction with neutron generators or isotope sources. It is assumed that with the techniques and methods discussed in these guidelines, access to a nuclear research reactor equipped with neutron activation facilities is available. The reactor should also preferably be equipped with a pneumatic transfer facility for activation analysis with short lived radionuclides. Facilities for irradiating multiple samples are also very beneficial so that high throughput can be achieved.

Access to an on site reactor is not essential to perform all the measurements. However, if the reactor is off site, then information will be unattainable for radionuclides whose half-lives are of the order of half a day or less (see Table I). Typically, the thermal neutron flux density should be of the order of 10^{12} neutrons \cdot cm⁻² \cdot s⁻¹ or more. Although this criterion is not as important for short lived activation analysis it is much more useful to have a higher flux density for activation analysis in the measurement of medium and long lived radionuclides. For instance, to achieve the same detection limits for identical samples irradiated for

the same length of time but at fluxes differing by a factor of ten, the counting time for the samples that received the lower flux will have to increase by a factor of ten. Space for epithermal activation is also beneficial for those elements which have their sensitivities augmented by such irradiations.

TABLE I. PROPERTIES OF REACTIONS PRODUCING SHORT LIVED RADIONUCLIDES

Element	Isotope	Half-life	Gamma ray energies (keV)
Ag	^{110}Ag	24.6 s	657.8
Al	^{28}Al	2.24 min	1778.9
Ba	^{139}Ba	83.2 min	165.9
Br	^{80}Br	17.7 min	616.2
Br	$^{80}\text{Br}^m$	4.42 h	37.1
Ca	^{49}Ca	8.7 min	3084.4
Cl	^{38}Cl	37.3 min	1642.4, 2167.5
Co	$^{60}\text{Co}^m$	10.48 min	58.6
Cu	^{66}Cu	5.1 min	1039.4
Dy	^{165}Dy	2.33 h	94.7
F	^{20}F	11.0 s	1633.8
I	^{128}I	25.0 min	442.3
In	$^{116}\text{In}^m$	54.2 min	416.9, 1097.3
K	^{42}K	12.36 h	1524.7
Mg	^{27}Mg	9.45 min	843.8, 1014.4
Mn	^{56}Mn	2.58 h	846.7, 1810.7
Na	^{24}Na	15.0 h	1368.6, 2754.1
Se	$^{77}\text{Se}^m$	17.4 s	161.7
Sb	$^{122}\text{Sb}^m$	4.15 min	61.5
Si	$^{29}\text{Al}^*$	6.6 min	1273.0
Sr	$^{87}\text{Sr}^m$	2.81 h	388.4
Ti	^{51}Ti	5.8 min	320.1
U	^{239}U	23.5 min	74.6
V	^{52}V	3.76 min	1434.1

* Si is detected by the $^{29}\text{Si}(n,p)^{29}\text{Al}$ reaction

Although the use of very fast pneumatic transfer facilities employing ultra short lived radionuclides can be employed in biological and geological studies, such a facility is probably of limited use in investigations of airborne particulate matter. It has been reported in the literature that lead can be determined using the $^{207}\text{Pb}(n,n')^{207}\text{Pb}^m$ reaction with its characteristic 0.8 second half-life. Since ^{207}Pb is radiogenic (its isotopic composition varies in nature to a significant degree), serious errors can arise in the determination of lead in environmental samples by this method. Furthermore, the cost benefit of such a system is not justified since almost all the elements that can be determined by ultra short lived isotopes can also be determined by conventional neutron activation analysis. A far more cost effective approach would be the installation of a dedicated cyclic activation facility to improve the sensitivity for the determination of a variety of radionuclides with half-lives between several seconds and a couple of minutes.

3.2. LABORATORY DESIGN AND STAFFING

Separate working areas are required (preferably as separate rooms) for the following operations:

- (1) Sample preparation prior to analysis. This is an inactive area and should preferably be as clean as possible with respect to trace element contamination. A so-called 'clean room' is not absolutely essential, but it is useful to have a clean workbench (e.g. laminar flow hood). It is also useful to have a chemical-type fumehood for operations that lead to acid fumes, e.g. during cleaning of tools and sample vials. If quartz encapsulation of the samples is being used, then a suitable facility for sealing the ampoules will be needed.
- (2) Sample preparation following activation. This working area should include a chemical-type fumehood for operations (e.g. opening of vials) that may lead to the escape of radioactive gases or particles. An area for storage of radioactive samples is also required; this should be of adequate floor loading strength so that lead bricks can be placed there for shielding. This working area will also contain the terminus of the pneumatic transfer - if such is available - for analyses with short lived activation products.
- (3) Gamma ray spectrometry. This working area should be suitably equipped (see Section 3.3) and should also be equipped with whatever means may be necessary for control of the temperature, humidity and power supply so as to ensure the stable and uninterrupted functioning of the electronic equipment.

Although neutron activation analysis can be performed by a single person, it is usual to have a least one full time technician to oversee the day to day operations. These functions include procurement of equipment and chemicals, sample preparation and counting, daily, weekly and monthly health physics

monitoring, report writing and procedure documentation, liaison with reactor operators and other users and, in some cases, INAA method development and upgrading of computer software. All personnel should be required to take an introductory health physics course as well as an initial training period in handling radioactive materials.

3.3. GAMMA RAY SPECTROMETRY

Most of the measurements in INAA are performed using high resolution (about 2.0 keV or less FWHM for the 1332 keV ^{60}Co peak) gamma ray spectrometers with a high purity germanium coaxial detector. It is very advantageous to have a high efficiency (25% or greater) detector for counting. In particular, counting times can thereby be reduced significantly for the longer lived radionuclides. To maximize the amount of information obtainable from radioactive samples, detectors are now available that are capable of processing both low and high energy gamma rays. Hence an additional low energy photon detector is not necessary. The detector is usually surrounded by a cadmium and copper lined lead shielding with a sample holder for easily reproducible positioning of the samples. An automatic sample changer is very useful for many types of routine measurements.

4. ANALYTICAL PROCEDURES

A complete description of the theory and application of thermal and epithermal NAA of airborne particulate matter is beyond the scope of this review. Several general and specific papers have appeared on this subject [35-50]. The subjects discussed in these papers also include short lived activation analysis, cyclic activation analysis, epithermal NAA of airborne particulate matter, the use of low energy photons and uranium fission interferences.

4.1. PREWEIGHING AND TRANSPORTATION OF FIELD SAMPLES

It is often very useful in studies of airborne particulate matter to know the total mass collected during a sampling period. Depending on the air environment, duration of sampling, size of filter and amount of air collected, the particulate matter collected may vary from less than one to tens of milligrams on a filter that may weigh several grams (e.g. Whatman-41; membrane filters weigh much less). Therefore precise and accurate weighing is crucial. It is preferable to have a balance with at least four to five decimal places for milligram weighing and six decimal places for microgram weighing. If the total mass is needed, then the filters should be weighed in a temperature controlled, low humidity area, preferably a designated 'clean' or 'semi-clean' room. Before weighing, filters should be acclimatized to the room conditions for at least 24-48 hours. All filters must be handled with

acid-washed plastic tongs. After weighing, the filters should be placed in clean or acid-washed polyethylene bags or plastic containers and transported to the sampling sites. After sampling the filters should be immediately placed in the identical bag or container labelled clearly with non-vanishing ink, and sampling conditions should be logged in a book. These parameters include meteorological conditions such as temperature, humidity and precipitation events. Filter field blanks should be handled identically, i.e. a blank filter should be placed in the collection unit for the same collection time as the sample, but the pump should be turned off. If the sample is to be pre analysed by X ray fluorescence, then consideration must be given to the total mass collected so that attenuation of X rays can be minimized.

4.2. SAMPLE BLANKS AND CONTAMINATION

Both accuracy and sensitivity can be severely compromised as a result of inherent trace element contamination from filters and counting vials. Before any sampling is undertaken, a detailed analysis of the chosen filter type must be done. At least five to ten filters should be analysed to determine not only the trace concentrations but also the reproducibility of the results. A large standard deviation may be unacceptable if the element of environmental interest has concentrations in the same range as the blank element. Another consideration in choosing filters is the presence of elements in high amounts and those which have large activation cross-sections. For instance, high Compton backgrounds in short lived activation analysis can be attributed to aluminum ($^{27}\text{Al}(n,\gamma)^{28}\text{Al}$), chlorine ($^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$), manganese ($^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$) and sodium ($^{23}\text{Na}(n,\gamma)^{24}\text{Na}$) reactions resulting in poor analytical detection limits for elements such as vanadium and copper. Bromine ($^{81}\text{Br}(n,\gamma)^{82}\text{Br}$) and sodium ($^{23}\text{Na}(n,\gamma)^{24}\text{Na}$) photopeaks have the same effects in long irradiations on the determination of some of the radionuclides of medium half-life (e.g. ^{76}As , ^{122}Sb , ^{72}Ga and ^{42}K). In fact, many ^{82}Br peaks usually seen in such spectra contribute to the high background resulting from the Compton effect. It is important that, for each new set of filters acquired, blank determinations be made since variability in trace elements and concentrations are not uncommon for different filter batches produced.

Trace contaminants can also arise in field blanks as a result of improper handling, unclean bags or containers used in transportation and the sampling apparatus itself. Field blanks and real samples should also include filter samples taken upwind and downwind from major and minor pollution sources. This is especially true for samples taken from pristine environments where contributions from specific local pollution sources may give rise to abnormally high elemental concentration levels.

Analytical problems may also arise from trace constituents in vials. Trace elements such as Al, Br, Cl, Mn, Na, Se, V, Zn, are present in many types of irradiation containers. Several papers have appeared regarding trace contaminants in vials [35]. These concentrations are usually negligible when analyzing geological

material, but are important when analyzing air filters. Other possibilities include placing filters in ultra thin precleaned polyethylene bags. However, it is advisable, that for short lived activation studies, the filters be removed from their irradiation containers and be placed into inert vials for counting. This procedure also hold true for medium and long lived neutron activation analysis. Each inert vial must be clearly labelled. This transferring procedure is not practical or feasible in determining short lived radionuclides such as ^{20}F , $^{77}\text{Se}^m$ and $^{110}\text{Ag}^m$. During longer irradiations, several types of filters (e.g. Whatman) become very flaky. Their transfer to inert vials is not only difficult but it may result in losses of sample material.

One way of overcoming this difficulty is pressing the Whatman filters into a pellet. However, great care must be taken so that no external contamination arises from either handling the filter or the presser itself. Other types of filters (e.g. Nuclepore) may be much more resistant to irradiation damage so that transfer to inert vials is possible.

As with filters, an evaluation of the trace contamination in irradiation containers must also be done. Sample contamination caused by the irradiation vials themselves can be reduced by subjecting the vials to a minimum 24 hour soak in diluted concentrated HNO_3 , followed by three rinses with distilled and/or deionized water, and thorough air or oven drying. Cleaned vials should be stored in a sealed polyethylene bag or container until use. For long lived irradiations, ultrapure quartz may also be utilized, but precaution is needed when torches are used to heat seal the vials, both for safety reasons and so as not to ignite the sample or add to the contamination. Often torches are kept in workshop areas where contamination of the samples is quite likely; this should be avoided, if possible. One additional procedure to reduce surface contamination of quartz is to etch them in hydrofluoric acid. However, special precautions should be observed in working with such chemicals.

4.3. CALIBRATION

There are essentially two different ways to calibrate the NAA system for elemental analysis.

One is the comparator technique. In this method liquid standards are prepared either from commercially available solutions or preparation from basic chemicals. If basic chemicals are chosen, extreme care should be given to the stoichiometry of the chemical including any hydrated forms. Inorganic chemicals recommended for use in calibration have recently been reviewed [51]. All chemicals used should be oven dried to remove the moisture content. Both polyethylene and quartz vials can be used for the encapsulation of liquid samples. Liquid standards are pipetted into acid-washed vials and heat-sealed. If polyethylene vials are used, the liquid samples should be doubly encapsulated for irradiation due to inherent leakage. The heat-sealed vial should be placed in a larger vial which is then also heat-sealed. If a larger vial cannot be used, the heat-sealed smaller vial should be

wrapped and taped in polyethylene sheeting or heat sealed in small polyethylene bags. After irradiation, all liquid standards should be transferred to labelled inert vials for counting. In some reactors either facilities are not made available for liquid irradiations or the neutron flux is so high that evaporation and extensive leaking is a problem due to thermal heating.

In the comparator method, calibration can also be done by pipetting a known amount of one or more elements onto a filter paper. This method is commonly used but several factors must be taken into consideration. The filter paper used should contain only negligible concentrations of contaminants when compared to the amount pipetted onto the filter paper (hence the need for a trace element characterization of the filter paper before use). When combining two or more elemental quantities it should be ascertained that the elements do not contain trace or minor contaminants which are the same as the elements to be added. For instance, it is quite conceivable that commercially bought or laboratory prepared arsenical compounds may contain unspecified quantities of other elements such as antimony. Filters should be placed in acid-washed vials for irradiation, then transferred to labelled inert vials prior to counting. However, some types of filter paper may not be transferable due to their condition following irradiation. Filter papers can also be prepared in the form a pellet but care must be given to contamination from the apparatus used for the procedure. The advantage of pelletization is that an exact geometry can be reproduced for irradiation and counting procedures.

The third means of calibration in the comparator method is through the use of reference materials. In general, reference materials should not be used for the calibration procedure but rather for testing the analytical accuracy and precision of the system. Many geological or biological reference materials have trace and minor elements either not certified with known concentrations or are only certified with accuracy errors of up to $\pm 20\%$ (and in some cases even more). This means that the final derived elemental concentrations in the actual air filters will not have accuracies better than the reported errors of the individual elemental concentration. The existence of spectral interferences may also limit the application of certified reference material made from geological material. For instance, the 136.0 keV and 264.7 keV gamma rays coming from to the $^{74}\text{Se}(n,\gamma)^{75}\text{Se}$ activation product are susceptible to substantial interferences from the same photopeaks arising from the $^{180}\text{Hf}(n,\gamma)^{181}\text{Hf}$ and $^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}$ reactions, respectively. Other elements, such as nickel, exhibit poor sensitivities in thermal activation analysis of geological material and should not be used in the calibration procedure.

The second method is the k_0 method. Essentially, it is an absolute technique in which uncertain nuclear constants have been replaced by factors which characterize the nuclides [52].

The last method is the absolute method, the use of no calibration standard. However, this technique is based on knowing the cross-section, the detector

efficiency and neutron flux. In general, this method is not extensively used since the above parameters are difficult to calculate with the accuracy needed for activation analysis.

4.4. REFERENCE MATERIALS

Reference materials should be used to test the accuracy and precision of the analytical system and generally not as calibration standards (see Section 4.3). An ongoing protocol to ensure reliability of analytical data must be established in each NAA laboratory. This includes: (1) the analysis of certified reference materials;

TABLE II. SOME SUITABLE CERTIFIED REFERENCE MATERIALS

CODE	PRODUCER	MATRIX
SRM-1632b	NIST	Coal
SRM-1633a	NIST	Coal fly ash
SRM-1634	NIST	Fuel oil
SRM-1635	NIST	Coal
SRM-1648	NIST	Coal
SRM-2676c	NIST	Metals Cd, Pb, Mn, Zn on filter media
SRM-2677a	NIST	Be and As on filter media
SRM-2678	NIST	Various trace elements on cellulose
SRM-2680	NIST	Various trace elements on cellulose acetate membrane
SRM-2681	NIST	Various trace elements on ashless blank filter
SRM-2689	NIST	Coal fly ash
SRM-2690	NIST	Coal fly ash
SRM-2691	NIST	Coal fly ash
CRM-038	BCR	Coal fly ash
EOP	IRANT	Coal fly ash
ECH	IRANT	Coal fly ash
ENO	IRANT	Coal fly ash

NIST - National Institute of Standards and Technology, formerly NBS (USA)

BCR - European Community Bureau of Reference (Belgium)

IRANT - Institute of Radioecology and Applications of Nuclear Techniques (Czechoslovakia)

(2) re-irradiation of selected samples to determine short lived radionuclides so as to ascertain analytical reproducibility of the methods used; (3) a careful evaluation of each individual spectrum to see if any potential interferences exist (e.g. uranium fission); (4) the analysis of at least two gamma rays from the same nuclide to determine if any spectral or nuclear interferences exist; and (5) the participation in interlaboratory comparison studies. Several reference materials are available from international organizations. Not all of them are perfectly suited to this kind of application considered here, since they represent coal, fly ash, bulk particulate matter, or artificially prepared filters, but in general they are adequate for NAA work. A list of some suitable certified reference materials is shown in Table II.

4.5. PREPARING FILTERS FOR IRRADIATION

Air filters generally come in strips, sheets, or circular formations (e.g. 47 mm diameter) and they may also be attached to plastic rings. All tools used to prepare these filters for irradiation should be acid-washed with diluted HNO_3 , rinsed with distilled and/or deionized water and then air or oven dried. Each tool should also be rinsed with distilled and/or deionized water and air dried between use with each filter. When not in use, cleaned tools should be stored in a sealed polyethylene bag or container. Filters should never be touched with one's fingers as this may result in sample contamination.

Using cleaned tools, filters should be carefully folded with the sample side facing in. The amount of folding needed to fit the filters into the acid-washed irradiation containers should be predetermined using blank filters in practice runs. Filters should be carefully removed from plastic rings by using tweezers to hold the ring stable and a scalpel to cut the filter from the ring at its junction. The filter should roll onto itself, with the sample material inside. It is important to retain a nearly identical geometry between samples and standards, requiring that each sample be folded or rolled to the same size and be encapsulated with the same configuration. The use of very small vials is suggested for the irradiation of the small air filters as this maintains a tighter sample geometry. An alternative approach, as discussed earlier, is to pelletize the sample. This will ensure much better counting geometry. However, in this case all standards must also be placed on filters and be pelletized.

4.6. IRRADIATION AND COUNTING PROCEDURES

Depending on neutron flux density, mass of airborne particulate matter and efficiency of the germanium detector, irradiation times may vary, but generalized schemes can be adhered to. Typically there are two irradiations which are performed; one to determine short lived radionuclides (several minutes) and one to determine medium and long lived radionuclides (several hours to one day). These neutron irradiations are done for the same sample. If any epithermal INAA is

required (particularly to augment the sensitivities of some radionuclides with short lived half lives) then an additional irradiation is necessary. For activation analysis to produce short lived radionuclides, irradiation times from one to ten minutes are employed. The radionuclides produced are shown in Table II. A decay period of at least five minutes is needed to let the usually high ^{28}Al activity decrease by two half-lives. High backgrounds due to the Compton effect are caused by this high activity. Counting periods from 5-15 minutes are usually employed to determine the rest of the elements. To improve detection limits for barium, iodine, indium, potassium and strontium, longer (30-60 minutes) decay and counting (30-60 minutes) periods may be employed. Detection limits for these elements and silicon are significantly improved by using epithermal neutrons.

For the determination of medium and long lived activities, irradiations of several hours are needed to activate sufficiently the samples for achieving good counting statistics. The other main limiting factor for good detection limits is the high background resulting from ^{24}Na and ^{82}Br . Improved detection limits for arsenic, antimony, gallium, molybdenum and tungsten can be achieved by epithermal INAA since the Compton background due to ^{24}Na is significantly decreased. However, this procedure would be at the expense of not having enough activity for the long lived isotopes (since the epithermal flux density can be one order of magnitude less than thermal flux density). If filters can be cut in half, with one portion being used for the medium lived nuclides and one for the long lived activation products, then epithermal INAA may be advantageous. Elements that can be determined by medium lived radionuclides are shown in Table III.

Spectrum evaluation can be performed by peak fitting and NAA routines available from commercial companies or other laboratories. Many types of software presently available are compatible with PC computers. In general, there are few nuclear or spectral interferences in the analysis of aerosols and those few can easily be accounted for. In fact, the vast majority of the photopeaks can be evaluated manually by taking backgrounds on both sides of the peak. Simple computer programs can be written to do this automatically.

A list of long lived radionuclides is presented in Table IV. In general, several hours of counting time are needed to achieve the required statistics. Since no high activity radionuclides are usually present in air filters, the background continuum is much lower than in the measurement of medium lived radionuclides following long activation times. For the measurement of long lived radionuclides, shielding of the detector with cadmium- and copper-lined lead bricks is a highly advantageous means to reduce the effect of background radiation from the counting room which can otherwise deteriorate the detection limits. Furthermore, 'cross-talking' with other samples counted on other detectors and radiation from stored sources is thereby significantly or totally reduced.

Sample positioning is crucial in air filter analysis and every effort should be made to retain a nearly identical geometry for the samples and standards. The vertical germanium detectors are usually more susceptible to effects of small

changes in the counting position than are the horizontal ones. Automatic turning of the sample in front of the detector can also be used to ensure better reproducibility of the counting. Due to their size and structure, most air filters must be folded or pelletized to fit into counting vials. Once encapsulated, some of the filter's particulate material may be off-centre. This is particularly crucial when counting at close distances from the detector. A quality control check can be performed by turning the sample 180° and seeing if the new calculated concentrations are significantly different. With the use of pelletized samples either vertical or horizontal oriented detectors can be used. A list of the salient features of the elements that can be determined in air filters, including their spectral and nuclear interferences is presented in the following sections. It should be noted that for the determination of very short lived radionuclides such as $^{77}\text{Se}^m$, ^{110}Ag and ^{20}F the use of Teflon filters is not possible since fluorine is a major component of the

TABLE III. PROPERTIES OF REACTIONS PRODUCING MEDIUM LIVED RADIONUCLIDES

Element	Isotope	Half-life	Gamma ray energies (keV)
As	^{76}As	26.3 h	559.1
Au	^{198}Au	2.7 d	411.8
Br	^{82}Br	35.3 h	554.3, 776.5
Cd	$^{115m}\text{In}^*$	53.5 h	336.3
Ga	^{72}Ga	14.1 h	834.0, 629.9
Ge	^{77}Ge	11.3 h	264.4
Hg	^{197}Hg	64.1 h	77.4
Ho	^{166}Ho	26.8 h	80.6
K	^{42}K	12.36 h	1524.7
La	^{140}La	40.23 h	1596.2, 328.8, 487.0
Mo	^{99}Mo	66.02 h	140.5
Na	^{24}Na	15.02 h	1368.6, 2754.1
Pd	^{109}Pd	13.7 h	88.0
Sb	^{122}Sb	2.72 d	564.0
Sm	^{153}Sm	46.7 h	103.2
U	$^{239}\text{Np}^{**}$	2.35 d	277.7
W	^{187}W	23.9 h	85.8
Zn	$^{69}\text{Zn}^m$	13.8 h	438.6

* Cd is determined from the $^{114}\text{Cd}(n,\gamma\beta)^{115}\text{Cd} \rightarrow ^{115}\text{In}$ reaction

** U is determined from the $^{238}\text{U}(n,\gamma\beta)^{239}\text{U} \rightarrow ^{239}\text{Np}$ reaction

substrate. This results in a very radioactive sample for a period of about one minute until the short lived ^{19}F decays away. Counting of other short lived radionuclides during this time is impossible due to the very high deadtime of the system.

TABLE IV. PROPERTIES OF REACTIONS PRODUCING LONG LIVED RADIONUCLIDES

Element	Isotope	Half-life	Gamma ray energies (keV)
Ag	$^{110}\text{Ag}^m$	249.8 d	657.8
Ce	^{141}Ce	32.5 d	145.4
Cr	^{51}Cr	27.72 d	320.0
Cs	^{134}Cs	2.06 a	795.8
Co	^{60}Co	5.27 a	1173.2, 1332.4
Eu	^{152}Eu	13.4 a	1408.0
Fe	^{59}Fe	44.5 d	1099.2, 1291.6
Hf	^{181}Hf	42.4 d	482.2
Hg	^{203}Hg	46.6 d	279.2
Lu	$^{177}\text{Lu}^m$	160 d	378.5
Nd	^{147}Nd	10.99 d	91.1
Ni	$^{58}\text{Co}^*$	70.9 d	810.8
Rb	^{86}Rb	18.7 d	1076.6
Sb	^{124}Sb	60.2 d	1691.0
Sc	^{46}Sc	83.8 d	889.3, 1120.5
Se	^{75}Se	119.8 d	136.0, 264.7, 400.7
Sn	^{113}Sn	114.4 d	391.7
Sr	^{85}Sr	64.84 d	514.0
Ta	^{182}Ta	115.0 d	1221.4
Tb	^{160}Tb	72.1 d	879.4
Th	$^{233}\text{Pa}^{**}$	27.0 d	311.9
Tm	^{170}Tm	129 d	84.3
Yb	^{175}Yb	4.19 d	396.3
Zn	^{65}Zn	243.8 d	1115.5
Zr	^{95}Zr	64.0 d	756.7

* Ni is determined using the $^{58}\text{Ni}(n,p)^{58}\text{Co}$ reaction

** Th is determined using the $^{232}\text{Th}(n,\gamma)^{233}\text{Th} \rightarrow ^{233}\text{Pa}$ reaction

4.6.1. Short lived activation products

- Ag A fast pneumatic facility is required to detect ^{110}Ag , which has a 24.3 second half-life. Typical irradiation times are between 5 and 20 seconds. Sensitivities are significantly enhanced using epithermal neutrons [42]. Because of the rapidly decaying short lived products, a good control of the varying deadtime is needed (e.g. pulser or deadtime stabilizer).
- Al The detection of aluminum in airborne particulate matter is very sensitive. However, the interfering $^{28}\text{Si}(n,p)^{28}\text{Al}$ reaction must also be taken into account when using the $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ reaction.
- Ba There are normally no spectral or nuclear problems associated with the determination of ^{139}Ba using the 165.9 keV gamma ray. Sensitivity may be increased by employing either longer decay times and counting times and/or epithermal neutrons.
- Br The analytical accuracy and sensitivity of ^{80}Br using the 616.2 keV photopeak is dependent on several factors. Good spectral resolution is needed from the 620.4 keV gamma ray arising from the double escape peak belonging to the 1642.4 keV photopeak of ^{38}Cl and the possible 619.0 keV photopeak coming from the medium lived radionuclide, ^{82}Br (see Section 4.6.2). The 616.2 keV photopeak is also situated on a high background with possibly detection limits. There is also an internal transition of $^{80}\text{Br}^m$ which has a half-life of 4.42 h and 'feeds' the 616.2 keV photopeak. If identical irradiation and counting times are not applied to the samples and standards, then incorrect calculations may occur. The very sensitive 37.1 keV photopeak of the internal transition may be used but care must be taken for overlapping peaks and self attenuation of the low energy gamma ray.
- Ca No interferences exist for ^{49}Ca although a high efficiency detector is usually needed for this isotope which is activated from the low abundant (0.187%) ^{48}Ca isotope.
- Cl Normally no interferences exist. The use of the 2167.8 keV photopeak usually results in a better detection limit since it is usually situated on a lower background.
- Co The 58.6 keV photopeak of the metastable $^{60}\text{Co}^m$ can be used with no known interferences. Sensitivities are not as good as for ^{60}Co following a long irradiation.
- Cu Analytical sensitivities for ^{66}Cu are only moderate excellent and very low levels can not usually be detected due to the high background under the 1039.0 keV photopeak.

- Dy There is a possible interference from a 94.7 keV gamma ray belonging to ^{233}Th isotope (half-life 23.3 minutes). Contribution of this gamma ray should be done by taking its to the 359.9 keV gamma ray of ^{233}Th . Analytical sensitivities for the detection of ^{165}Dy can improve using both epithermal NAA and/or longer decay and counting times.
- F Fluorine is best determined by epithermal neutron activation. As with silver, a fast pneumatic system delivering the sample to the detector within a few seconds is essential. The detection of ^{20}F is subject to interference from the $^{23}\text{Na}(n,\alpha)^{20}\text{F}$ reaction [45]. A careful evaluation of the interference factor must be taken into account. Sodium may be high in concentration both in the particulate matter and in some cases in the filter paper itself. The determination of fluorine in the samples collected on teflon filters should not be attempted, since fluorine is in the filter matrix.
- I Iodine is determined with good results using the ^{129}I isotope. Excellent sensitivities are achieved using epithermal neutrons. Some potential may exist for loss of iodine during irradiation due its volatility.
- In Indium is usually difficult to detect using either the 416.9 keV or 1097.3 keV photopeaks. Detection limits are dramatically improved by employing epithermal neutrons [46]. The 1097.3 keV photopeak should be used since it is usually on a lower background.
- K No spectral or nuclear interferences are associated with the detection of ^{42}K . This isotope can also be detected following a long lived irradiation and decay period of 1 to 3 days.
- Mg Sensitivities are usually adequate for the detection of 843.8 keV photopeak of ^{27}Mg . Rather serious errors can be introduced either due to the competing $^{27}\text{Al}(n,p)^{27}\text{Mg}$ nuclear interference reaction (for reactors which do not have well thermalized neutrons) or to the possible strong overlapping peak of 846.7 keV from the $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$ reaction. If good resolution is not achieved between these two photopeaks, the less sensitive 1014.4 keV photopeak, also belonging to ^{27}Mg , must be used.
- Mn Manganese can be determined using the 846.7 keV or 1810.7 keV photopeaks. As previously stated, a good spectral resolution is required to remove the overlapping 843.7 keV gamma ray of ^{27}Mg . If time permits one can wait 1 to 2 hours to let the ^{27}Mg gamma rays decay with its 9.45 minutes half-life.
- Sb Antimony can be determined using epithermal neutrons and the 61.6 keV gamma ray [43] although this method of analysis is not often used. Care must be taken to account for any overlapping X or gamma rays in the vicinity, and possible self absorption effects.

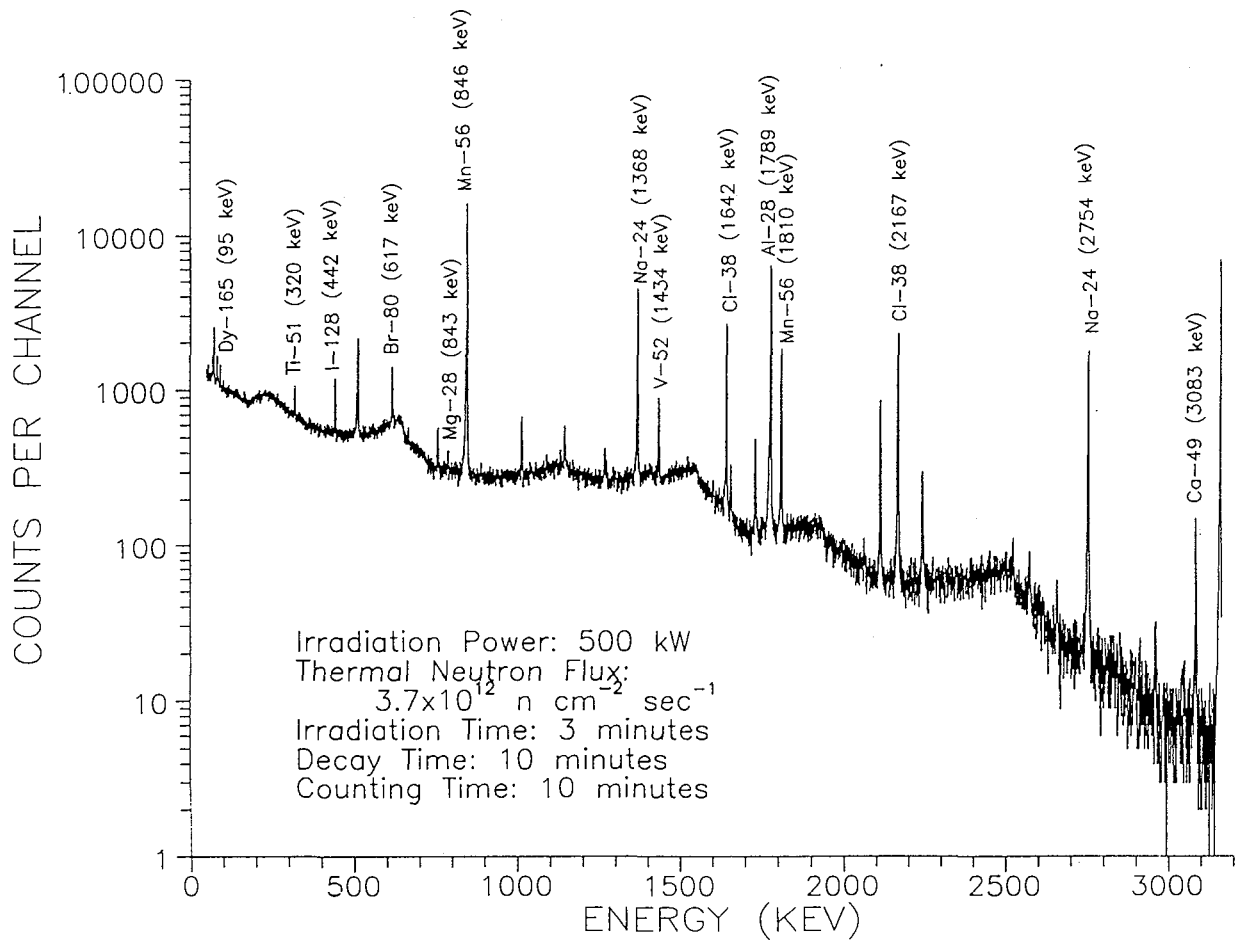


FIG. 5. Short lived NAA spectrum of airborne particulate matter.

- Se This element can be detected using the $^{77}\text{Se}^m$ metastable isotope. As with silver and fluorine, a fast delivery system is required. If the aluminum concentration is high in the sample, this may result in a high deadtime in the counting system. The use of epithermal NAA may increase sensitivities.
- Si The determination of silicon is very difficult in air filters using conventional NAA methods. Silicon is best detected by the $^{29}\text{Si}(n,p)^{29}\text{Al}$ reaction and the analytical sensitivity for the determination of ^{29}Al is greatly improved by using epithermal neutrons.
- Sr No nuclear or spectral interferences are normally associated with the detection of $^{87}\text{Sr}^m$. The use of epithermal NAA and/or longer decay and counting times may result in improved detection limits.
- Ti No nuclear or spectral interferences are normally associated with the detection of ^{51}Ti .

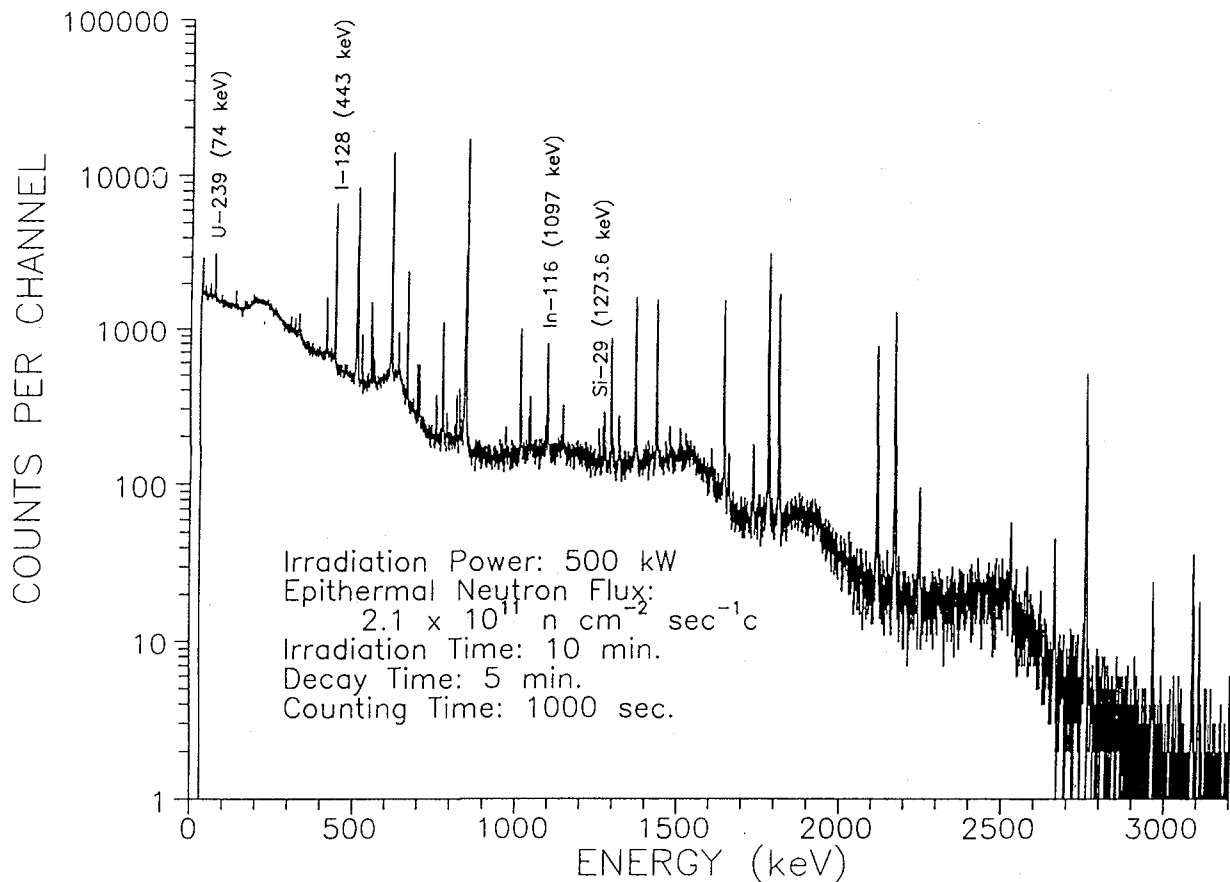


FIG. 6. Short lived epithermal NAA spectrum of airborne particulate matter.

- U Uranium can be detected using the 74.6 keV peak belonging to ^{239}U . However, excitation of lead bricks (used for shielding) by gamma rays interacting as a result of the photoelectric effect will produce photopeaks corresponding to the lead K X rays at 72.8 keV and 74.9 keV. Even the use of and cadmium- and copper- lined lead bricks may not totally eliminate the problem. Sensitivity is enhanced using epithermal neutrons. Another preferred method of analysis is based on the $^{238}\text{U}(n, \gamma) ^{239}\text{U} \rightarrow ^{239}\text{Np}$ reaction followed by measurement of the 277.7 keV photopeak (see Section 4.6.2).
- V The sensitivity of vanadium in air filters is excellent with no known spectral or nuclear interferences.

Typical spectra for short lived thermal and epithermal INAA for airborne particulate matter are shown in Figures 5 and 6, respectively.

4.6.2. Medium lived activation products

- As Arsenic is detected with good precision using the 559.1 keV gamma ray. Spectral resolution of the 554.3 keV and 564.0 keV gamma rays belonging to ^{82}Br and ^{122}Sb is essential. Otherwise the less sensitive 657.0 keV photopeak also belonging to ^{76}As can be used. Increased sensitivity can be achieved using epithermal neutrons.
- Au Gold can be detected using the 411.8 keV photopeak. Since gold exhibits resonances in the epithermal region, sensitivity is increased using epithermal neutrons. There is a 411.1 keV gamma ray arising from ^{152}Eu and it must be taken into account by comparing the net counts of the 411.1 keV peak to the 1408.0 keV peak of ^{152}Eu .
- Br The detection of bromine is very sensitive using the 554.3 keV photopeak of ^{82}Br . Typically, good spectral resolution is needed to resolve the 554.3 keV, 559.1 keV, and 564.0 keV peaks of ^{82}Br , ^{76}As and ^{122}Sb , respectively. Sensitivities are also improved using epithermal neutrons. Bromine can also be determined using the 776.5 keV gamma ray.
- Cd Cadmium is best determined using the $^{114}\text{Cd}(n,\gamma)^{115}\text{Cd} \rightarrow ^{115}\text{In}^m$ reaction with the 336.3 keV gamma ray characteristic of $^{115}\text{In}^m$. A decay time of at least 35 hours is required so that equilibrium can be achieved between ^{115}Cd and $^{115}\text{In}^m$ and that the $^{115}\text{In}^m$ (half-life 4.49 hours), which may have come originally from any indium in the sample, will have decayed to negligible amounts. The 336.3 keV gamma ray then is representative of the 53.5 h half-life of ^{115}Cd .
- Ga Gallium is best determined using epithermal neutrons. The 834.0 keV gamma ray is subject to spectral interference from the $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ reaction. This results in an 834.8 keV photopeak. Since iron is in much higher concentrations the less sensitive 629.9 keV gallium peak should be used. Gallium can also be detected following a 10 to 15 minute short epithermal irradiation.
- Ge The detection of germanium is not very sensitive by NAA and is usually not reported in atmospheric studies. A possible spectral interference exists from the 264.7 keV gamma ray of ^{75}Se .
- Hg Mercury can be detected using the low energy 77.4 keV photopeak. It is well known that mercury can volatilize under normal reactor irradiation conditions. Sealing of the samples in high purity quartz tubing is essential if accurate quantitative results are to be obtained. Spectral interferences may also arise from the many other low energy gamma rays or high energy X rays in the vicinity of the 77.4 keV photopeak. Therefore mercury is usually determined using a long lived radionuclide (see Table IV).

- K Potassium is easily detected using the 1524.7 keV photopeak. There are normally no spectral or nuclear interferences associated with this photopeak.
- La Lanthanum is easily detected using the 1595.2 keV photopeak with very good detection limits. Other usable photopeaks include the 328.8 keV and 487.0 keV photopeaks. The nuclear reaction arising from the fission of uranium, $^{238}\text{U}(n,f)$, may result in potential inference of ^{140}La [44].
- Mo Molybdenum is determined using the 140.5 keV photopeak. Usually a decay time of 4 to 6 days is needed to optimize the sensitivity for measurement of ^{99}Mo . The uranium fission reaction $^{238}\text{U}(n,f)$ strongly interferes with this determination and a very careful evaluation of uranium in the blank filter and sample must be done. There is a significant decrease in the fission interference and improvement of detection limits using epithermal neutrons [44].
- Na The measurement of sodium is excellently suited for neutron activation measurements. In general there are no spectral or nuclear interferences. However, ^{124}Sb also decays with a characteristic gamma ray at 1368.2. If there are high concentrations of antimony, this could potentially interfere with the sodium analysis. Then both photopeaks of ^{24}Na , 1368.4 keV and 2754.1 keV belonging to ^{24}Na should be analysed as an internal check of the potential antimony interference.
- Pd Palladium, usually not reported in air filters, can be determined using 88.0 keV gamma ray. There is a potential interference from the 88.0 Kev photopeak of ^{109}Cd .
- Sb Antimony is usually determined by the 564.0 keV gamma ray of ^{122}Sb . However, there is a small but significant spectral interference arising from ^{76}As ; a gamma ray of energy 562.8 keV is characteristic of the ^{76}As decay scheme. It is approximately 2.5% of the abundance of the dominant 559.1 keV photopeak. If the arsenic concentration is much higher than that of antimony, the interference may be very important. The interference factor should be calculated using single elemental standards. Since ^{122}Sb has a half-life almost three times longer than that of ^{122}Sb one can also wait sufficiently long for the ^{76}As to decay away to negligible amounts. Detection of antimony can also be improved using epithermal neutrons. Spectral resolution from the 559.1 keV gamma ray of ^{76}As is important.
- Sm The determination of Sm is extremely sensitive by neutron activation methods. Several potential interferences exist from uranium and thorium reaction products [45].

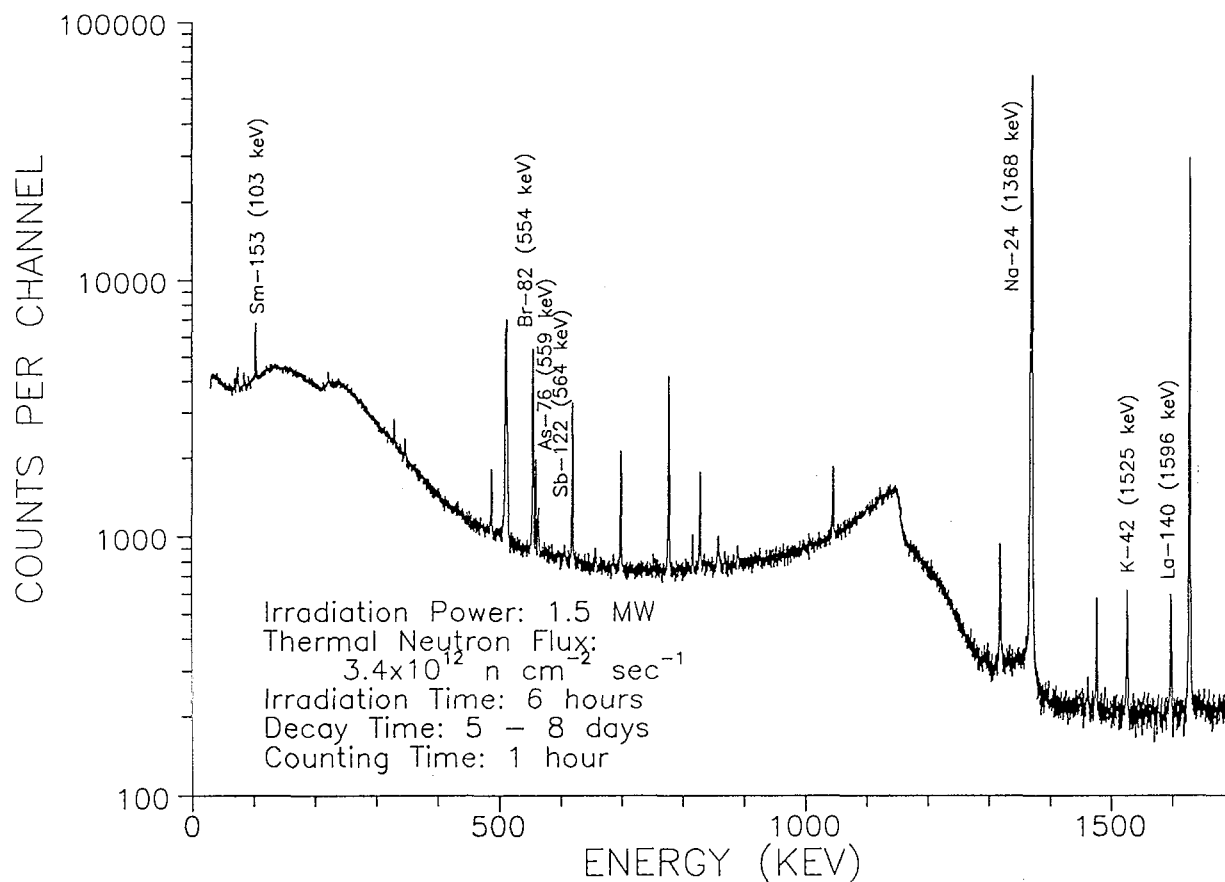


FIG. 7. Medium lived NAA spectrum of airborne particulate matter.

- U Uranium is best determined using the $^{238}\text{U}(n, \gamma\beta)^{239}\text{U} \rightarrow ^{239}\text{Np}$ reaction. There are normally no spectral or nuclear interferences using the 277.7 keV gamma ray. Analytical sensitivities are significantly improved using epithermal neutrons.
- W Tungsten is best determined using epithermal neutron activation analysis. No spectral or nuclear interferences normally exist in using the 685.8 keV gamma ray.
- Zn Zinc, which is usually determined by means of the long lived ^{65}Zn isotope, can also be determined by the $^{69}\text{Zn}^m$ isotope. The sensitivity is usually not adequate enough in thermal NAA. Improvement can be achieved using epithermal NAA.

A typical spectrum for medium lived INAA for airborne particulate matter is shown in Figure 7.

4.6.3. Long lived activation products

- Ag Silver can be determined using the 658.8 keV photopeak of $^{110}\text{Ag}^m$. No spectral or nuclear interferences are normally present.
- Ce Cerium is detected with the 145.4 keV of ^{141}Ce . Nuclear spectral interference from uranium fission must be taken into account [44]. There is also a potential spectral interference from the 142.6 keV photopeak belonging to ^{59}Fe .
- Cr Chromium is detected with good sensitivity using the 320.0 keV gamma ray. The interference from the $^{54}\text{Fe}(n,\alpha)^{51}\text{Cr}$ is usually negligible.
- Cs Cesium is readily determined using the 795.6 keV photopeak of ^{134}Cs . Usually no spectral or nuclear interferences exist.
- Co Neutron activation analysis is well suited to determine cobalt in airborne particulate matter. There are normally no nuclear or spectral interferences.
- Eu Europium can be readily determined using the 1408.0 keV gamma ray characteristic of ^{152}Eu . The 121.8 keV gamma should not be used since there are other spectral interferences at that energy.
- Fe Iron is detected with good precision using both the 1098.2 and 1291.6 keV photopeaks.
- Hf Hafnium is detected with good precision using the 482.2 keV gamma ray. Normally there are no spectral or nuclear interferences.
- Hg For the reliable determination of mercury, the samples must be encapsulated and heat sealed in quartz. There is a serious spectral interference from the 279.6 keV gamma ray of ^{75}Se which completely overlaps the 279.2 keV photopeak of ^{203}Hg . A subtraction of the interferences can be made by normalizing to the 400.7 keV photopeak of ^{75}Se . Normalization to the 136.0 keV or the 264.1 keV gamma rays should not be done since spectral interferences already exist from other gamma rays (see Se).
- Lu Lutetium is best determined using the 378.5 keV gamma ray of $^{177}\text{Lu}^m$. However, there is a possibility of a uranium spectral interference.
- Nd Neodymium is determined using the 91.1 keV gamma line belonging to ^{147}Nd . Uranium fission corrections have to be taken into account [44].
- Ni Nickel is determined using the $^{58}\text{Ni}(n,p)^{58}\text{Co}$ reaction using the 810.8 keV gamma ray line. The analytical detection limit for nickel is improved using epithermal NAA. However, the long lived background continuum is usually

low enough so that thermal activation is suitable. There is a potential spectral interference from ^{152}Eu which also decays with a 810.8 keV gamma ray. As with gold, normalization should be with the 1408.0 keV gamma ray of ^{152}Eu .

- Rb Rubidium is determined using the 1076.6 keV gamma ray of ^{86}Rb . There are no nuclear or spectral interferences.
- Sb Antimony can also be determined using the 1691.0 keV gamma line belonging to ^{124}Sb . Although the activation cross-section is not as high as for ^{122}Sb , the 1691.0 keV peak is situated on a much lower background than the 564.0 keV photopeak of ^{122}Sb .
- Sc The sensitivity for scandium is excellent using NAA. The 889.3 keV photopeak from ^{46}Sc should be used instead of the 1120.3 keV photopeak since there is a 1120.0 keV background gamma ray from the ^{226}Ra series.
- Se Selenium is detected by using both the 136.0 keV and 264.7 keV photopeaks of ^{75}Se . Both peaks are associated with spectral interferences from ^{181}Hf and ^{182}Ta , which have gamma rays of 136.2 keV and 264.1 keV, respectively. The 264.7 gamma ray is preferred since the tantalum interference is less important, the concentrations of tantalum being usually lower than those of hafnium and the photopeak is on a lower background. The interference free 400.7 keV photopeak can be used.
- Sn Tin is detected using the 391.7 keV gamma ray. There is a possible spectral interference from ^{160}Tb which also decays with a 392.5 keV gamma ray. Normalization is done with the 897.4 keV gamma ray of ^{160}Tb .
- Sr Strontium can also be detected using the 514.0 keV gamma ray belonging to ^{85}Sr . Normally there are no nuclear interferences. However, the 511.0 annihilation photopeak must be spectrally resolved.
- Ta Tantalum is detected using the 1221.4 keV gamma ray of ^{182}Ta . There are normally no spectral or nuclear interferences.
- Tb The 879.9 keV gamma ray of ^{160}Tb is preferred since it is interference free.
- Th Thorium is determined via the $^{232}\text{Th}(n,\gamma\beta)^{233}\text{Th} \rightarrow ^{233}\text{Pa}$ reaction using the 311.9 keV gamma ray line. There are no spectral or nuclear interferences.
- Tm Thulium is determined by the 84.3 keV photopeak of ^{170}Tm . There are normally no spectral or nuclear interferences. Care should be taken that there are no background photopeaks in this energy region from any shielding material.

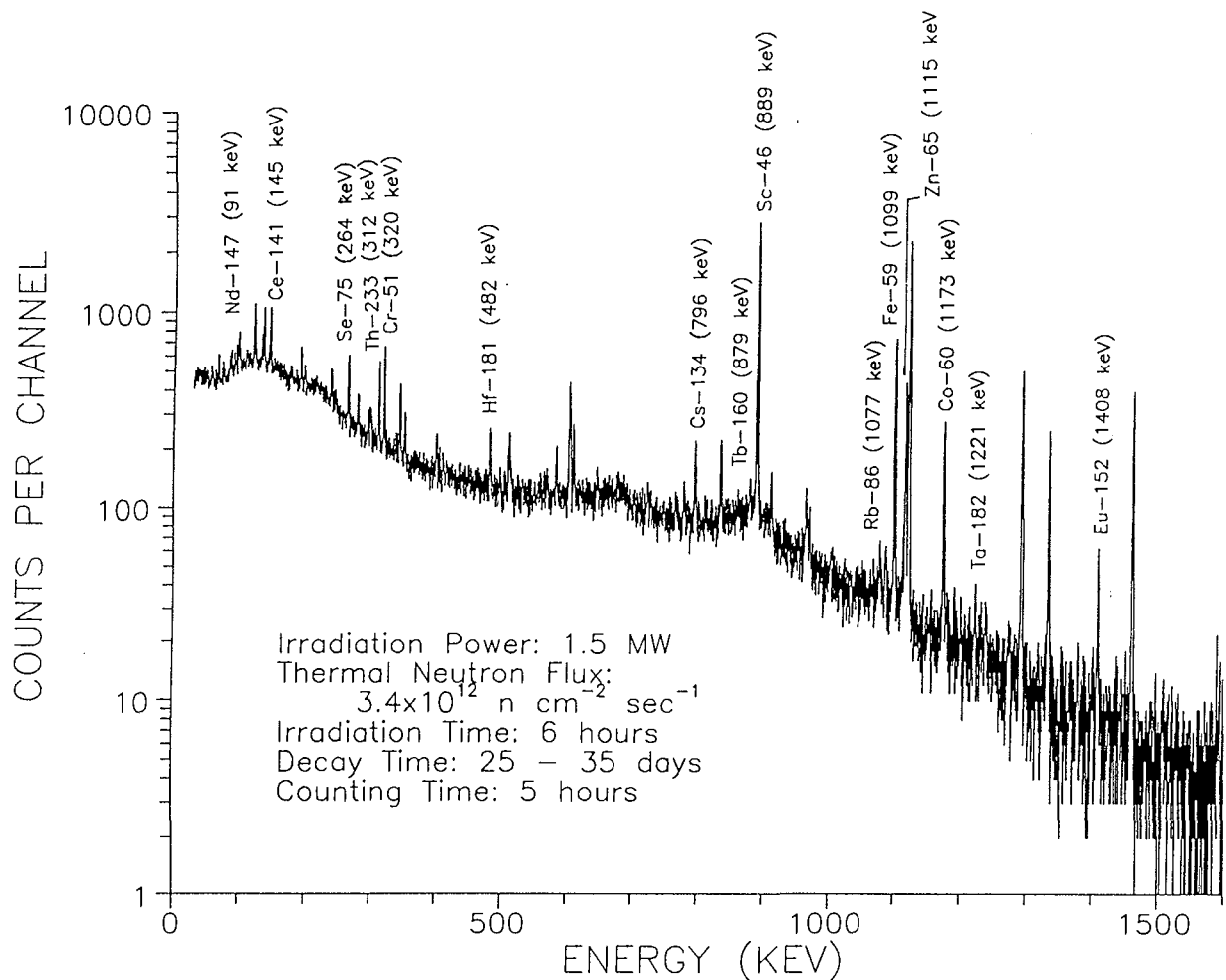


FIG. 8. Long lived NAA spectrum of airborne particulate matter.

- Yb Ytterbium is best determined using the 396.3 keV gamma ray of ^{175}Yb . There are normally no spectral or nuclear interferences but the 398.2 keV photopeak from ^{233}Pa must be spectrally resolved.
- Zn Zinc is determined using the 1115.5 keV gamma ray of ^{65}Zn . There are two overlapping peaks at 1120.3 keV from ^{46}Sc and at 1112.3 keV from ^{152}Eu . Good spectral resolution is required. The potential spectral interference from the 1115.3 keV gamma ray from ^{160}Tb is usually negligible. (See Zn in Section 4.6.2).
- Zr Zirconium is determined using the 756.7 keV photopeak of ^{90}Zr . A very large uranium fission correction exists and should be taken into consideration [44].

A typical spectrum for long lived INAA for airborne particulate matter is shown in Figure 8.

4.7. DATA REPORTING AND EVALUATION

Results for the concentrations of the particulate matter can either be expressed in ng, μg or mg per cubic meter of air. These are by far the most common ways of expressing the results. In addition, the amount can be calculated in weight per mass of solid (e.g. parts per million). However, in this case the exact weight of the material collected must be known. This means that proper weighing procedures should be followed (see Section 4.1).

It is not essential to try and determine every element listed in Tables II-IV. The trace constituents needed to be determined will be greatly influenced by the scientific objectives of the sampling protocol. However, since so much information can be obtained from only three different types of measurements (short, medium and long lived radionuclides), it does not take all that much more time to evaluate all the photopeaks that appear in the spectra. Once a calibration procedure is done, all that is needed for future calculations, besides the usual information on irradiation, decay and counting times, is to take into account any variation of neutron flux. This can be easily monitored by the use of prepared standards or flux monitors.

Limits of detection should be calculated by previously defined criteria [53]. For many sets of samples there will always be some elemental concentrations that are below the analytical detection limit. Certain statistical programs will only operate with a completely filled data set. One way to overcome this deficiency is to assign a value between zero and the detection limit as calculated by a random number generator.

It is advisable that the output data be put in a format that can be easily read by any statistical data handling program (e.g. Lotus, Statgraphics, SPSS, BMDP) to create large multivariate databases. Several methods are available to present the data for subsequent geophysical and environmental interpretation. As a first step the type of frequency distribution of the data should be determined. The results can also be reported as individual values and the associated confidence intervals as interquartile ranges. The arithmetic mean, median, range and rank order statistics should also be calculated.

A first exploratory step in the interpretation of the data is the use of enrichment factor (EF) calculations which are used in conjunction with Tables V and VI. An EF of an element is defined as the double ratio of the element of interest in the sample to a reference element in the sample divided by the ratio of the same elements found in a reference material (e.g. rock, soil, seawater). This expression can be written as follows:

$$EF = \frac{\left(\frac{X}{C}\right)_{aerosol}}{\left(\frac{X}{C}\right)_{reference}}$$

TABLE V. ABUNDANCES OF TRACE ELEMENTS IN THE EARTH CRUST ACCORDING TO FIVE DIFFERENT REFERENCES (ppm)

Element	Mason (crustal) [54]	Vinogradov (sed. rocks) [55]	Vinogradov (soils) [55]	Wedepohl (crustal) [56]	Taylor (crustal) [57]
Li	20	60	30	30	20
Na	28300	6600	6300	24500	23600
K	25900	22800	13600	28200	20900
Rb	90	400	100	120	90
Cs	3	12	(5)	2.7	3
Be	2.8	7	6	2	2.8
Mg	20900	13400	6300	13900	23300
Ca	36300	25300	13700	28700	41500
Sr	375	450	300	290	375
Ba	425	800	500	590	425
F	625	500	200	720	625
Cl	130	160	100	320	130
Br	2.5	6	5	2.9	2.5
I	0.5	1	5	0.5	0.5
Al	81300	104500	71300	78300	82300
Si	277200	248000	330000	305400	281500
S	260	3000	850	310	260
Sc	22	10	7	14	22
Ti	4400	4500	4600	4700	5700
V	135	130	100	95	135
Cr	100	160	200	70	100
Mn	950	670	850	690	950
Fe	50000	33300	38000	35400	56300
Co	25	23	8	12	25

TABLE V. (cont.)

Element	Mason (crustal) [54]	Vinogradov (sed. rocks) [55]	Vinogradov (soils) [55]	Wedepohl (crustal) [56]	Taylor (crustal) [57]
Ni	75	95	40	44	75
Cu	55	57	20	30	55
Zn	70	80	50	60	70
Ga	15	40	30	17	15
Ge	1.5	7	(1)	1.3	1.5
As	1.8	6.6	5	1.7	1.8
Se	0.05	0.6	0	0.09	0.05
Zr	165	200	300	160	165
Nb	20	20	--	20	20
Mo	1.5	2	2	1	1.5
Ag	0.07	(0.9)	(0.1)	0.06	0.07
Cd	0.2	0.3	(0.5)	0.1	0.2
In	0.1	--	--	0.07	0.1
Sn	2	30	(10)	3	2
Sb	0.2	1	--	0.2	0.2
Te	0.01	--	--	0.002	--
Y	33	33	50	34	33
La	30	40	(40)	44	30
Ce	60	30	(50)	75	60
Nd	28	1.8	--	>30	28
Sm	6.0	5	--	>6.6	6.0
Eu	1.2	1	--	1.4	1.2
Yb	3.4	2.2	--	3.4	3.0
Lu	0.5	(0.2)	--	0.6	0.5

TABLE V. (cont.)

Element	Mason (crustal) [54]	Vinogradov (sed. rocks) [55]	Vinogradov (soils) [55]	Wedepohl (crustal) [56]	Taylor (crustal) [57]
Th	7.2	11	6	11	9.6
U	1.8	3.2	1	3.5	2.7
Hf	3	(4)	(6)	3	3
Ta	2	3.5	--	3.4	2
W	1.5	--	--	1.3	1.5
Au	0.004	--	--	0.004	0.004
Hg	0.08	0.4	0.01	0.03	0.08
Pb	13	20	10	15	12.5

In general for EF calculations in aerosols, aluminum or scandium is taken as the reference element both in the sample and reference material (rock or soil). An enrichment factor of ten or greater is indicative that the source of the element is anthropogenic in nature, that is, its source is not from the natural environment. An EF value close to one is indicative that the main source of the trace element is of crustal origin. For trace elements which are of marine origin (e.g. bromine, chlorine and iodine) the reference element is usually sodium and the reference material is seawater. The global averages of various trace elements for rock and soil is presented in Table V while the global averages for elemental composition of seawater are shown in Table VI.

Specific elements may also be indicative markers for particular source emissions, e.g. Br/Pb (automotive), Cl/Na (seawater), V/Ni and La/Sm (residual oil burning), Se/S (fossil fuel burning), etc. Airborne contributions of certain marker species which can be used in these elemental ratios is shown in Table VII. To investigate the interdependence of variables such as elemental concentration, mass and meteorological conditions, factor analysis can be used. After determining the number of factors to be retained, VARIMAX rotation can be performed. The resulting loadings, which represent correlation coefficients between the variables and the factors, help one to identify the emission sources (e.g. soil dust, incinerators, fossil fuel power plants, smelters, etc.).

It is recommended to use an additional step, namely by the application of an 'absolute' factor analysis receptor model. This involves converting the loadings into source profiles and then calculating the absolute factor scores, thus providing estimates of source apportionment. Other receptor models include target

TABLE VI. ELEMENTAL AVERAGE CONCENTRATION OF SEAWATER AND RATIOS TO SODIUM [58]

Element	Conc. (ppm)	X/Na
Li	0.17	1.6×10^{-5}
Be	6×10^{-7}	5.7×10^{-11}
F	1.3	1.2×10^{-4}
Na	10500	1.00
Mg	1350	0.128
Al	0.01	9.5×10^{-7}
Si	3	2.8×10^{-4}
S	885	0.084
Cl	19000	1.81
K	380	0.036
Ca	400	0.038
Sc	4×10^{-5}	3.8×10^{-9}
Ti	0.001	9.5×10^{-8}
V	0.002	1.9×10^{-7}
Cr	5×10^{-5}	4.7×10^{-9}
Mn	0.002	1.9×10^{-7}
Fe	0.01	9.5×10^{-7}
Co	5×10^{-4}	4.8×10^{-8}
Ni	0.002	1.9×10^{-7}
Cu	0.003	2.8×10^{-7}
Zn	0.001	9.5×10^{-8}
Ga	3×10^{-5}	2.8×10^{-9}

Element	Conc. (ppm)	X/Na
Ge	7×10^{-5}	6.7×10^{-9}
As	0.003	2.8×10^{-7}
Se	0.004	3.8×10^{-7}
Br	65	0.0062
Rb	0.12	1.1×10^{-5}
Sr	8	7.6×10^{-4}
Y	3×10^{-4}	2.8×10^{-8}
Nb	1×10^{-5}	9.5×10^{-10}
Mo	0.01	9.5×10^{-7}
Ag	3×10^{-4}	2.8×10^{-8}
Cd	1.1×10^{-4}	1.0×10^{-8}
Sn	0.003	2.8×10^{-7}
Sb	5×10^{-4}	4.8×10^{-8}
I	0.06	5.7×10^{-6}
Cs	5×10^{-4}	4.8×10^{-8}
Ba	0.03	2.8×10^{-6}
La	3×10^{-4}	2.8×10^{-8}
Ce	4×10^{-4}	3.8×10^{-8}
W	1×10^{-4}	9.5×10^{-9}
Au	4×10^{-6}	3.8×10^{-10}
Hg	3×10^{-5}	2.8×10^{-9}
Pb	3×10^{-5}	2.8×10^{-9}
Th	5×10^{-5}	4.8×10^{-9}

transformation analysis, multiple linear regression techniques and chemical mass balance methods. Chemical mass balance methods require a prior knowledge of the contributing sources and source profiles. In an urban airshed the source profiles have to be measured locally whenever possible (otherwise published source profile libraries may be used, but with caution). Computer software for chemical mass

TABLE VII. AIRBORNE CONTRIBUTIONS OF CERTAIN MARKER SPECIES

Source	Elements
Coal-fired plants	As, Se, S
Oil-fired plants	V, Ni, rare earths
Motor vehicles	Br, Pb
Refuse incineration	Ag, Zn, Sb, Cd, Sn, Pb
Limestone/concrete	Ca, Mg
Soil	Mn, Al, Sc, Si, Fe, Ti
Wood burning	K, volatile C, elemental C
Mobile sources	Pb, Br, volatile C, elemental C
Refineries	Rare earths
Sulfide smelters	In, Cd, As, Se, S

balance calculations is available from the US Environmental Protection Agency. For the multivariate receptor models, commercial statistical packages are available for use on PC based computers. Still further sophisticated methods may be obtained from individual laboratories. Finally, measured concentrations of air pollutants should be compared with national and international air quality guidelines.

4.8. FUTURE ANALYTICAL DEVELOPMENTS

There are several areas in which further analytical method development can be expected. One is a comprehensive study using epithermal neutron activation analysis to categorize the distinct advantages for certain trace elements in airborne particulate matter. Some previous work has been done in this area [43,46,58]. However, much more detailed investigation is needed including the use of both cadmium and boron filters. Recent advances in NAA have been reviewed [38] and the authors have referenced a number of papers in which epithermal NAA has been employed; however, none have included the analysis of airborne particulate matter. A re-evaluation of the use of low energy gamma rays should also be studied. Very little work has been performed in this area for airborne particulate matter [43,60,70]. In principle, this method should not be nearly as complicated for the analysis of air filters as for geological samples. The self-attenuation of the gamma rays is minimized since the mass of the sample is usually small and close matrix matching with standards is possible. The use of well type germanium detectors is also very advantageous since its efficiency is dramatically improved [62], thus decreasing the counting time, but little work has been reported on airborne particulate matter.

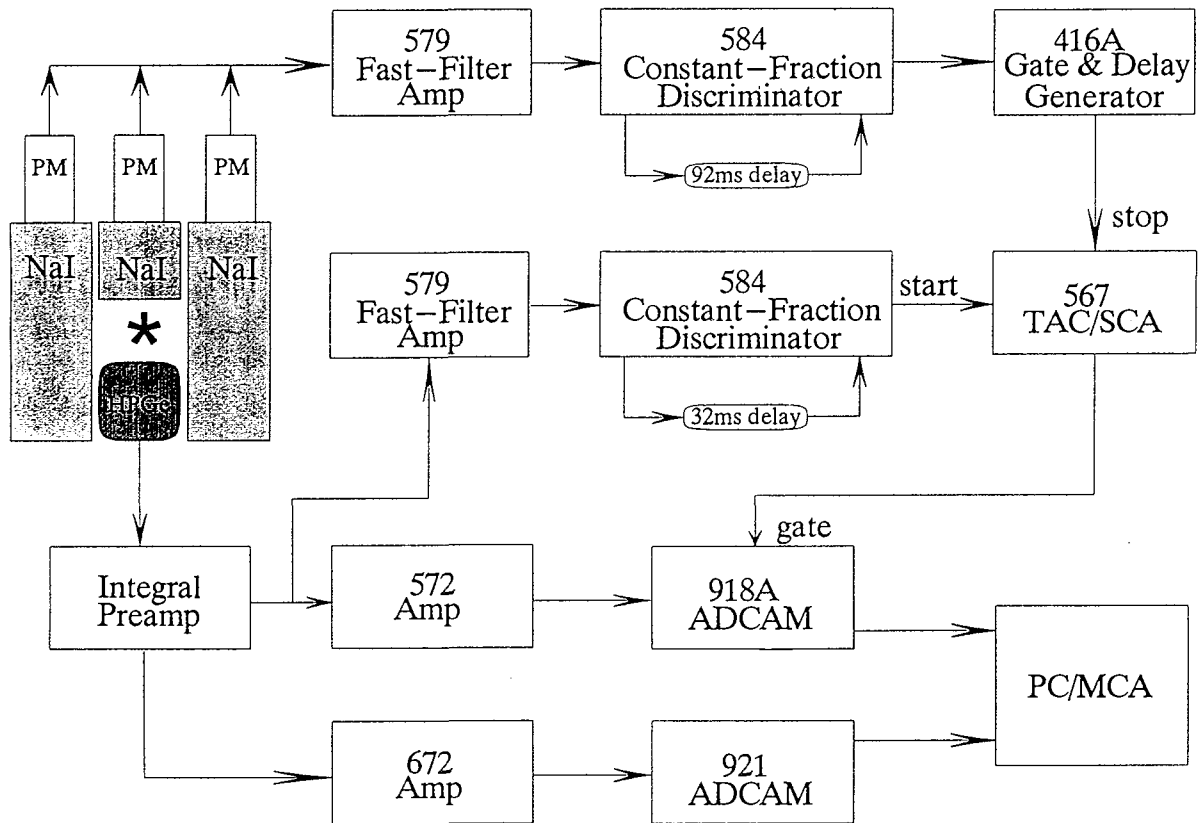


FIG. 9. Typical Compton suppression setup.

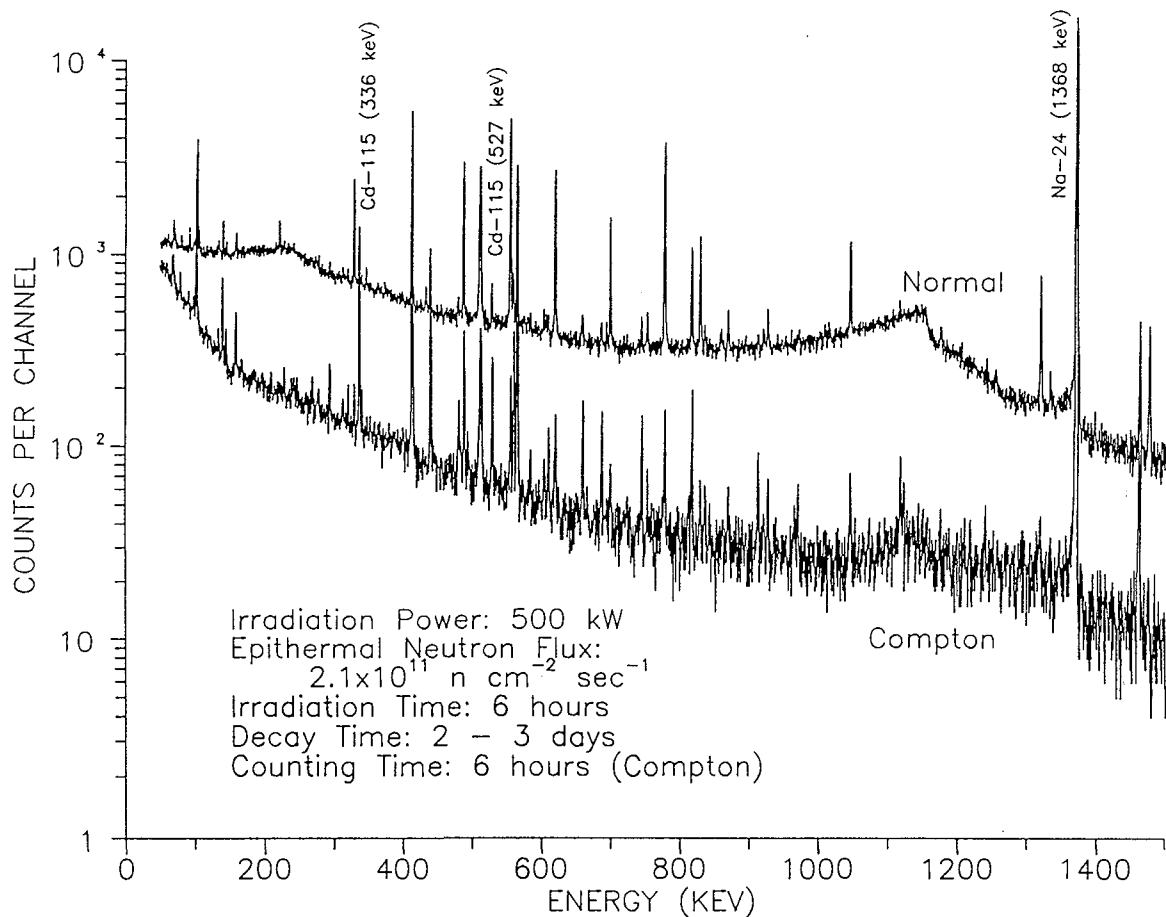


FIG. 10. NAA spectrum of environmental tobacco smoke using Compton suppression.

Other techniques including prompt gamma NAA and 'cold neutron' activation analysis are possible. Few such facilities exist, and they should be considered to be more research oriented and not suitable for routine environmental analysis. These two methods have been reviewed by Ehmann and Vance [38]. The methods of Compton suppression and gamma-gamma coincidence counting are promising, but their application to airborne particulate samples should also be considered in the research development phase. A typical Compton suppression setup is seen in Figure 9 while a comparison of normal and Compton suppressed spectra is shown in Figure 10.

ANNEX 1

SAFETY IN THE WORKPLACE

SAFETY is the first rule for working in a neutron activation laboratory. The following list provides basic safety rules for such work:

- laboratory room should be accessible **only** to trained or qualified personnel
- the eating of food, drinking of beverages and application of make up should be strongly discouraged in the sections of the laboratory used for sample preparation and radioactive counting
- always wear a dosimeter (ring and/or badge) when working with irradiated materials - the badge should be at chest or neck level - the ring must be on the dominant hand
- **never** handle irradiated material with your hands; use tongs or tweezers
- transport irradiated samples in lead pots
- tools designated specifically for the handling of radioactive material should be handled only when wearing disposable gloves, and such tools should not be removed from the 'contaminated' areas of the work place
- do all unpacking/transferring of irradiated materials in a fumehood
- place all contaminated waste in a trash bin labelled 'Radioactive Waste Only'
- do not carry loose contaminated material (e.g. emptied vials or wrappers) from the fumehood to the trash bins - take the appropriate trash bin to the fumehood with you then return it to the storage area when done
- ensure that sample vials are not leaking when removing them from the fumehood to the storage area or detector
- always clean up after yourself when working with irradiated materials and check your body for contamination by using a GM counter
- familiarize yourself with emergency safety rules and know whom to call in emergencies
- abide by all regulations posted in the laboratory
- **never** leave the laboratory unattended with the door open
- be safety-conscious and be considerate of fellow workers - their safety also depends on you.

ANNEX 2

OUTLINE PROTOCOL FOR THE STUDY OF 'BASELINE' CONCENTRATIONS OF AIRBORNE PARTICULATE MATTER USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

The following is a suggested protocol for the study of 'baseline' levels of atmospheric pollution. This kind of application is similar to studies recommended by the World Meteorological Organization (WMO) within the framework of the Background Air Pollution Monitoring Network (BAPMoN) [63]. The following protocol draws extensively on the WMO report just referenced, modified, however, by a careful selection of the topics, and by additional comments, based on the choice of analytical technique - in this case NAA.

Although 'baseline' has not been defined exactly by WMO, it may reasonably be regarded as being the lowest observed value in a pristine region, i.e. a region devoid of anthropogenic or special natural pollutants. For the purpose of establishing a baseline, monitoring stations must be placed with consideration to meteorological information and geographical conditions. Densely populated and anthropogenically polluted areas should, however, also be included in the sampling network since the inventories of pollution sources and the measurement of pollutant concentrations near them are useful in the estimation of future baselines.

SAMPLING

- (1) A large particle size cut-off inlet should be used with all airborne particulate matter samplers. The inlet should be designed with a cut-off point for 50% collection efficiency at a lower particle size rather than with a cut-off point for 100% collection efficiency at a larger particle size, since the latter may cause severe discrimination against smaller sizes. Sampler inlets with a 50% cut-off at 15 μm aerodynamic diameter are recommended to ensure that only particles smaller than about 30 μm are sampled.
- (2) Sampling by high volume samplers without particle size fractionation should be used for studying daily average concentrations of airborne particulate matter. Between 1500 and 2000 m^3 air per day is drawn through the sampler. Several daily samples are needed for the establishment of an accurate baseline for each month. In very remote areas it may be necessary to sample for perhaps 2-3 days in order to collect enough material for analysis by INAA. Membrane filters (Teflon, polycarbonate, cellulose ester) are preferred for elemental analysis since they can be also used for ED-XRF analysis. However, cellulose filters (Whatman-41) may also be used. The costs of cellulose filters are significantly lower than of membrane filters.

- (3) In addition, a low volume air sampler is recommended for the collection of monthly average samples. The amount of air that is drawn is 900-1300 m³ per month. Size fractions of airborne particulate matter can also be collected using polycarbonate membrane filters (Nuclepore) stacked in series. Separation into two fractions, coarse and fine, is desired. For routine use, a 50% efficiency cut-off at 1-2 μm between the two fractions is practical.
- (4) A multistage cascade impactor is also very useful for detailed determinations of particle size distribution. Successful sampling with cascade impactors for particle size fractionation requires close control of air flow rates and a knowledge of the particle efficiency for each stage. Typical cascade impactors are equipped with stages for 4-8 fractions in the 0.1 to 10 μm range. Due to the low mass collected by cascade impactors for the individual stages, long sampling times may be necessary. The samples should be collected on membrane filters (teflon, polycarbonate, cellulose ester), but Whatman filters can also be used. Several trial runs of the analysis by INAA methods should be performed in order to establish optimum collection parameters.

ANALYSIS

For analysis by INAA, the procedures described in Section 4 should be followed, using a combination of different irradiation and counting procedures (Section 4.6). As many elements as can be detected should be reported (Section 4.7).

SPECIAL CONSIDERATIONS FOR INAA

The use of INAA to determine short lived radionuclides is extremely cost effective in comparison with other analytical techniques. Furthermore several key elements including halogens (Br, Cl and I) can be determined. The determination of bromine is now very important in ozone studies. These elements can easily volatilize during analysis by proton induced X ray emission methods. Other key elements of interest in anthropogenic emission studies, which may be readily determined by INAA, include vanadium and manganese. The analytical sensitivity for aluminum is excellent by INAA and this element is very important in calculations of enrichment factors.

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