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PARTICLE INDUCED X-RAY EMISSION ELEMENTAL ANALYSIS: SAMPLE PREPARATION FOR A VERSATILE INSTRUMENTAL METHOD

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Abstract

Particle induced X-ray emission (PIXE) has found extensive application as a multi-element analysis tool. The energetic nature of both the incident particle beam and the emitted characteristic X-rays has lead to considerable versatility in regard to samples which may be analyzed by the PIXE technique. This paper does not deal with the theory, equipment, or data analysis for PIXE, but it should bring to the reader a broad perspective of methods for sample preparation and should point the way into the literature where more complete details are given. Both physical and chemical processes for sample preparation are outlined. Preparation often requires a combination of methods. Characteristics of the PIXE method should be given careful consideration when preparing samples for analysis and these are briefly noted.

KEY WORDS: Particle Induced X-ray Emission, ion beam, X-ray emission, elemental analysis, sample preparation, biological material, inorganic material, aerosol.

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Introduction

In 1970 Johansson et al., (1970) hung a carbon foil (40 $\mu g/cm^2$) in the open air for a day, allowing air dust to adhere to the foil. The foil was bombarded with 1.5 MeV protons and the spectrum of characteristic X-rays from elements in the air dust was collected using a Si(Li) detector of the type successfully used in X-ray fluorescence analysis. This first report of modern PIXE analysis clearly demonstrated the ease of sample preparation and the practicality of simple sample preparation methods in ion-beam analysis.

Building upon this beginning many workers have optimized and used to good advantage simple, physical methods of sample preparation while others have developed specialized sample preparation methods employing both chemical and physical operations in order to achieve their diverse purposes for element determinations. This paper will suggest a number of considerations that must be kept in mind when preparing samples for PIXE analysis. Then an introduction will be given to an interesting variety of preparation procedures. The discussion will relate to PIXE using standard particle accelerator beams, but many of the techniques and most of the considerations will apply to microbeam analysis as well.

In the following discussion "sample" will refer to material presented to the PIXE analyst and carried through a procedure in preparation for analysis. Once the sample is in the form for particle beam irradiation it will be referred to as a target.

Reviews of the PIXE analysis method by Johansson and Johansson (1976), Campbell (1977), Mangelson et al., (1977), Cahill (1980) and Mangelson and Hill (1981) provide references and discussion of sample preparation techniques as they developed during the first ten years of PIXE analysis. Proceedings of the four international conferences on PIXE analysis will also provide valuable information (Johansson, 1977; Johansson, 1981; Martin, 1984; Van Rinsvelt et al., 1987). Recently the first book devoted entirely to PIXE analysis was published (Johansson and Campbell, 1988) and it contains much in relation to sample preparation and the factors that influence the choice of preparation technique. Maenhaut (1988) has published a review on ion beam analysis in biology and medicine.

Fundamental Principles for Sample Preparation

A discussion of sample preparation needs to be introduced with a consideration of general principles that apply to all techniques of analysis. There are also some specific characteristics of the PIXE method that must be considered to avoid pitfalls and to take full advantage of PIXE with its unique strengths.

Sample Parameters

Sample validity in trace-element studies of biological materials has been discussed by Iyengar (1987a, 1987b). The principles he suggests are equally valid for analysis in other fields as well. Trace-element analysis is a multidisciplinary science requiring combined insight from experts in the field of specific study and experts in performing the specific analytical methods used. Cooperative planning by the experts is essential before the samples are taken. Objectives of the study must be clearly agreed upon and every step in the procedure from sampling protocol to interpretation of results must be scrutinized to see that there is no procedural compromise that will invalidate the conclusions to be drawn from the sample analyses.

The sample (or samples) collected in the field should be representative of the structure to be studied. In some cases the structure of interest may be extensive in mass or time while in the other extreme a micro structure may be of interest. Materials and containers used for sample collection and storage must be carefully selected to prevent contamination or selective loss of elements. Storage conditions such as temperature and humidity need to be given consideration.

Preparation of the sample for PIXE analysis must also be carefully designed to retain a representative target. Selection of the subsample and separation of phases or particle sizes must be carefully considered. Every container and every device that comes in contact with the sample is a potential source of contamination. Of even greater concern is the addition of any reagent, including water, for each of these is also a potential source of contamination.

Iyengar (1987a) also points out the necessity of validating the analytical procedures through the use of reference standards and standard reference materials. The matrix and the preparation of samples and standards should be matched as closely as possible. It is of value to have available a large variety of reference standards. Perhaps it is safe to suggest that ten per cent or more of the analysis time and effort should be spent on quality control to ensure system calibration and freedom from contamination.

Characteristics of PIXE Analysis

Some characteristics of PIXE analysis should be kept in mind when designing sample preparation methods. Truly thin samples, which will not attenuate proton energy (for $E_p > 1.50$ MeV) or require X-ray attenuation corrections for the elements aluminum and heavier have areal densities on the order of 50 micrograms/cm^2 or less. By contrast, thick samples, with areal densities greater than 10 milligrams/cm^2 for many materials, have enough material to stop the particle beam within the sample. Corrections for decreasing particle energy and X-ray attenuation are usually required for thick samples in order to relate X-ray intensity to element content using the system calibration. Samples betweem these limits are of intermediate thickness and corrections to the X-ray intensities must be applied. The extent of corrections depends on system parameters, such as particle energy and detector angle, and on sample parameters, such as matrix and X-ray energy.

The low-energy, bremsstrahlung background in a PIXE spectrum will be kept to a minimum by keeping the PIXE target as thin as possible. Keeping the target thin will also reduce the amount of heating in the target which helps to minimize target damage. Electronics used for PIXE analysis are designed to process incoming data at 10kHz or higher; however at these high data rates spectral resolution must be sacrificed and sum peaks begin to interfere with element emission lines. Target thickness, the mass of elements on the target for which PIXE is sensitive, and the beam current determine the data collection rate.

Targets may be analyzed in the vacuum of the particle beam line. As an alternative, the particle beam may pass through a foil from the vacuum into an atmosphere of ambient air or helium (Johansson and Campbell, 1988) where the target is mounted. The latter arrangement is surely advantageous for direct analysis of large, irregular objects. The external beam arrangement will aid in cooling targets and in preventing the build up of static charge on target material.

This paper will identify a variety of preparation methods in order to provide a perspective on the adaptability of PIXE analysis. There will be little opportunity in the space here to provide an evaluation of the relative merits of the methods, but that will be left to papers and reviews which have been published. The book by Johansson and Campbell (1988) would be an excellent resource in this regard.

Sample Support Materials For Thin Targets

Most samples that are analyzed as thin targets or targets of intermediate thickness require a thin supporting film or backing.

Thin Membranes

Table 1 lists several common films which have been used for sample support. Included in the table are areal densities indicating the thinnest material usually used. There are also qualitative indications for the trace element impurities present and for strength of the films in relation to handling and irradiation by particle beams. The use of these backings have

Table 1. Support Materials for Sample Deposit or Impaction Surfaces

Trade Name	Materials	Density (gm/cm^3)	(Nominal) Areal (mg/cm^2)	Impurity Rating	Strength Rating
	Carbon foil	2.0	≥0.02	excellent	good
Formvar	(C,H,O)	1.2	0.04	excellent	poor
Kapton (H)	Polyamide	1.24	≥1.2	good	excellent
Kimfol[a]	Polycarbonate	1.2	≥0.25	excellent	good
Mylar	Polyester	1.39	≥0.5	good	good
	Polypropylene (stretched)		≥0.06	excellent	fair
	Polystyrene	1.0	≥0.04	excellent	poor

[a] No longer manufactured under this trade name.

been reviewed by Herman et al., (1973), Johansson and Johansson (1976), Campbell (1977) and Russell et al., (1981).

The ideal backing would be very thin to minimize bremsstrahlung, have a low level of impurity atoms and be strong enough to be handled easily. Formvar has been used to some extent as it meets some of the criteria just noted, but it is easily broken and will not withstand acid solutions. Carbon foils withstand high beam currents. They are, however, expensive and are easily broken while handling. The thin Kimfol polycarbonate has generally proven to be the most satisfactory. Unfortunately this particular brand of polycarbonate is no longer being manufactured and a new source of clean material must be found. The polypropylene is also a good foil but requires effort to stretch it thin.

Thin Filter Media

Thin filter membranes or mats have been used extensively for sample preparation by filtration and they have also served as the backing or substrate upon which to dry liquid samples or to place thin sections as will be noted below. **Table 2** lists several filter media, their thickness and an impurity rating. Millipore and Selectron have the disadvantage of being much thicker than is ideal. In addition, sample material becomes embedded nonuniformly in the mat. Perhaps the most widely used filter material is Nuclepore. It is relatively thin and easy to handle with an acceptable trace-element level. Teflo is about three times as thick as Nuclepore, has about the same trace element level, and has better flow characteristics. It contains no hydrogen which has dictated its choice when forward particle scattering is used with PIXE for the determination of hydrogen in a sample. There are two disadvantages to Teflo. Protons interact readily with the fluorine leading to prompt gamma decay which adds to the high-energy background in a PIXE spectrum. The fluorine in Teflo has also been found to contaminate the vacuum system which interferes with the subsequent determination of fluorine by particle induced gamma-ray emission.

Air Particulate Collection and Analysis

From the time of the first published spectrum (Johansson et al., 1970) it was evident that PIXE analysis was ideally suited to air particulate analysis. A multi-element analysis could be obtained directly from a filter or membrane with a particulate deposit of 10 to 200 $\mu g/cm^2$ or more. Many studies of air particulate material are reported in the proceedings of PIXE conferences referred to above. The small sample requirement led naturally to analysis of size-fractionated air particulates (Hardy et al., 1976). It was soon found, however, that in order to take full advantage of PIXE, sampling systems should be modified of specifically designed.

A group at Florida State University (Bauman and Nelson, 1985) developed several samplers that collected air particulate material in a time sequence by moving a Nuclepore filter surface over a vacuum inlet. They also modified the design of a cascade impactor for more detailed particle size information (Bauman et al., 1981). Jupe et al., (1981) have studied the particle deposition characteristics of such cascade impactors.

A group from the University of California at Davis developed a dichotomous sampler, designated as a stacked filter sampler, which collects two size fractions at remote sites (Cahill et al., 1977). This group also developed a drum sampler which collects size fractions in time sequence (Cahill et al., 1987). In the drum and cascade samplers air particulates impact on membranes of Kimfol or Mylar which have been coated with Vaseline, paraffin or Apiezon grease

Table 2. Filter Media Suitable for PIXE Analysis

Trade Name	Materials	Areal Density (Nominal) (mg/cm^2)	Impurity Rating
Teflo (Gelman)	Teflon (PTFE)	≈2.8	fair
Nuclepore	Polycarbonate	≥0.6	fair
Millipore	Cellulose Acetate and Nitrate	≥3	fair
Selectron	Cellulose Acetate	≈5	fair

to prevent the particles from bouncing off the surface. The first filter in the stacked filter sampler is treated in a similar way.

Researchers at the Lund Institute of Technology, in addition to ambient aerosol measurement, have adapted air particulate samplers and developed aerosol collection systems for analysis of emission sources and of indoor living and work environments. In one study (Ahlberg et al., 1984) bulk power-plant, size-fractionated particulate emissions were collected and thick samples were used to characterize the element content of the emissions. In another study (Malmqvist et al., 1981) an air collection bonnet was fashioned to ensure reproducible samples of aerosol during welding and metal spray operations. A cascade impactor was used to collect size-fractionated samples. The last two collection stages were modified from the normal impactor design. Off-axis rotation of the collection stages prevented these stages from becoming overloaded with aerosol. The Lund PAM (Lund personal aerosol monitor) has been designed and tested (Malmqvist, 1984) for assessment of personnel exposure to aerosol in the work environment. This monitor allows time sequence samples in two size fractions, >5 μm and <5 μm, to be collected and characterized by PIXE analysis.

Internal Standards

In general, the quantitative determination of element concentrations in a sample will be improved if an internal standard is included. This can be done most easily with liquid samples and in some cases a spike can be added to a well divided powder sample. **Table 3** contains a list of some elements that have been used as internal standards. Note that all are in the high energy region of the spectrum where background is least intense and where there is the least likelihood of interference with another element. Listed in the table are the elements which will have interference from the L X-ray lines of the spike.

The method of standard additions has been successfully used by Van Rinsvelt et al., (1974) and more recently by Yagi et al., (1987). This method is particularly useful when there is not a complete calibration of the PIXE system and when there is not a systematic correction for matrix effects.

Physical Methods of Sample Preparation

There are a number of purely physical methods that have been used for sample preparation and some of them are discussed here.

Filtering

In the discussion above, filtration of air as a method of sample collection and support was described. Filtration may be used for separation in many cases where a solid is suspended in a fluid. Aqueous samples may contain particulate material which can be collected on a filter. Procedures for water analysis often specify filtration with a filter of 0.4 μm pore size, on the assumption that the filtrate which passes through the filter is in the aqueous phase. The solid material retained on the filter may be suitable for PIXE analysis when care is taken to control the thickness and uniformity of the particulate on the filter and if the particle size is small. The authors of this paper have used filtration for analysis of suspended material in scrubber water collected at an incinerator. (Material is being prepared for publication.) Tanaka et al., (1981) analyzed filtered samples from rain water and run-off water. Nuclepore filter media are ideally suited for this purpose. Suspensions in any fluid could be sampled by this filter method.

Evaporation

Any liquid sample is a candidate for simple evaporation of a small drop on a support membrane such as those listed in Table 1 or on a filter such as those listed in Table 2. Most such membranes, however, are hydrophobic causing the drop to shrink as it dries forming a small, solid residue that is thick and unpredictable. Nuclepore filters have been pretreated to make the surface more hydrophilic so that in some cases that liquid spreads out too much. The liquid on a filter is drawn into and dries in the filter pores which helps to keep the sample uniform. Filters are, however, relatively thick which results in bremsstrahlung and the

Table 3. Some Elements Used As Internal Standards

Element	X-ray Line Type	X-ray Line (keV)	Likely to Interfere With:[a]	Reference
Strontium (Sr)	K_α	14.142	Si,P	Campbell et al., 1975
Yttrium (Y)	K_α	14.933	(Si),P	Campbell et al., 1975 Boerma et al., 1989 Mangelson et al., 1979
Ruthenium (Ru)	K_α	19.235	(S),Cl,(Ar)	Boerma et al., 1989
Palladium (Pd)	K_α	21.123	Cl,Ar	Navarrete-Dominguez et al., 1982
Silver (Ag)	K_α	22.104	Ar,K	Yagi et al., 1987 Navarrette et al., 1978
Cadmium (Cd)	K_α	23.109	(Ar),K	Campbell et al., 1975

[a] Elements in parentheses will have less severe interference than those without parentheses.

requirement for thickness corrections. Membranes may be treated with sodium hydroxide and a dilute solution of PVP (polyvinyl pyrrolidone--a surfactant) which renders the surface somewhat hydrophilic (Mangelson et al., 1977) so that many solutions, including those resulting from chemical treatment as discussed below, may be directly evaporated. Barrette et al., (1976) have prepared targets using single drops of blood serum and Tanaka et al., (1981) used single drops of runoff water.

When single-drop samples are slowly air dried the residue may form unacceptable, large and non-uniform crystals. Barrette et al., (1976) placed the samples in a vacuum which approached freeze-drying conditions and found that only small crystallites form. Chemical methods of dealing with crystallization will be given in a later section. Targets made by drying fluid drops must be considered nonuniform and the whole spot must be irradiated with a beam of uniform particle distribution.

The above single-drop evaporation is not suitable for analysis of dilute samples because much more volume than one drop must be evaporated to provide a residue containing enough of some elements to fall within the PIXE detection limits. Tanaka et al., (1981) added an yttrium spike to 200 mL of filtered rain water and evaporated to less than one mL before evaporating one drop on Mylar. Hansson et al., (1984) have developed a device for preconcentration of water using a spray-drying method. An internal standard was used and about 30% of the material from a 10 mL sample was collected on a PIXE target.

Freezing Drying, Homogenizing and Pulverizing

These methods may be used individually and sometimes are used together or as steps in a preparation procedure. Freezing drying reduces the sample mass by removing water and may make the sample easier to pulverize. The latter two methods reduce particle size and at the same time blend a more homogeneous and, perhaps, a more representative sample. Maenhaut et al., (1984) have freeze dried human and animal tissue and then pulverized at liquid nitrogen temperatures. A small amount of the powder was fixed to a thin membrane with a solution of 1% polystyrene in benzene, making a target of intermediate thickness.

Carlsson (1984) made pellets of pulverized geological material and geological reference material which were subsequently used as PIXE targets. Lessard and Houdayer (1983) have pulverized small samples of pottery shards and bound the pulverized material in collodion to make relatively thin PIXE targets. NBS Bovine Liver (SRM 1577), which was prepared by freeze drying and pulverizing, was pressed by Clayton (1987) into an aluminum cup for PIXE analysis.

Thin Sections

This sections of material may be cut with a microtome, placed on a support backing and analyzed by PIXE. If the sections are biological material they may be freeze dried before analysis. Campbell (1977) reviewed the early work using the method. He noted that samples prepared in this manner may not be representative of the bulk sample. For the particle beam microprobe analysis, where microscopic structures are to be studied, samples prepared by thin section methods present the ideal sample in many cases. Cichocki et al., (1987) reported the study of thin sections of human arteries.

Self-Supporting Targets of Moderate Thickness

Some workers have taken advantage of the polymeric and adhesive characteristics of natural, biological materials in order to make self-supporting targets. Such targets of cerebrospinal fluid have been developed by Lapatto et al., (1988). Yagi et al., (1987) have prepared plant material by working a small, dried sample and water to a paste in a quartz homogenizer and spreading the paste to form a self-supporting target.

Unaltered Materials

Unaltered materials, often of archaeological importance, have been analyzed directly. Duerden et al., (1984) placed obsidian chips in the vacuum chamber of PIXE and PIGE ?? analysis. Recently Swann and Fleming (1988) have reviewed PIXE applied to unaltered artifacts of copper-based alloys, iron, gold and glass matrices. Most of the work was carried out with external beam systems. Deconninck (1977) has reported on the use of an external beam for the direct analysis of a small liquid stream and Wolfe (1979) has reported on direct PIXE analysis of gases contained in a gas target of the type common in nuclear physics.

Chemical Methods of Sample Preparation

Chemical methods of sample preparation have the potential for providing at least three beneficial effects: matrix reduction, homogeneity, and component separation. The disadvantages are: consumption of time, potential contamination from reagents and uncontrolled, selective loss of trace elements. However, when care is taken, the disadvantages may be minimized and the advantages often provide considerable benefit.

High Temperature Ashing

One of the earliest reports on the use of PIXE analysis was that of Kliwer et al., (1972, and Rudolph et al., 1972) who dried or freeze dried organic samples which were then ashed at about 600°C. The ash was pulverized and secured to a thin foil with a 1% solution of polystyrene in toluene. The major disadvantage of this method is the loss of volatile elements which may be minimized by the addition of an ashing aid such as a sulfate.

Low Temperature Ashing

This procedure, using a stream of excited oxygen molecules, effects ashing at much lower temperatures than the above procedure and thus reduces the loss of volatile elements. Pallon and Malmqvist (1981) pressed thick pellets of the ash from biological samples while Maenhaut et al., (1984) secured a small amount of ash to target backing foils. Both of these workers and Mangelson and Hill, (1981) dissolved ash in nitric acid and then placed a few μL of the solution on target backing foils to be dried and analyzed. It has been shown that even with low temperature ashing, selenium and bromine were lost and cadmium was partially lost (Maenhaut et al., 1984).

Acid Digestion

A few microliters of the solution resulting from acid digestion are usually deposited on thin target backings and allowed to dry in preparation for analysis. For this reason hygroscopic acids, i.e., sulfuric, perchloric and phosphoric, may not be used in preparing PIXE samples. Drying acids such as nitric, hydrofluoric and hydrochloric have proven to be useful. Some chemical species containing chloride or fluoride ions are volatile and may be lost from the sample when there is an excess of these ions.

Campbell et al., (1975) have reported biological sample digestion with nitric acid in open vessels. Lytle et al., (1987) reported the use of nitric acid in a vigorous digestion method for organic materials. Samples have also been digested with nitric acid in Teflon lined pressure bombs (Campbell et al., 1975; Maenhaut et al., 1984). Pinheiro, et al., (1989) digested tissue samples with nitric acid in a Teflon container heated in a microwave oven. Obsidian samples have been successfully digested with hydrofluoric acid (Nielson et al., 1976).

Table 4 indicates the approximate degree of matrix reduction achieved with various digestion procedures. The high and low temperature ashing procedures achieve the greatest degree of matrix reduction, but reduction depends upon sample composition and digestion method. The alkaline reagent (TMAH) digestion brought human autopsy tissues into homogeneous solution; however, it did not reduce, but rather added to, the matrix.

Chemical Separations

A number of the preparation methods discussed above involved physical separations. It is also possible to use chemical means for separating chemical components of a sample. Mangelson and Hill, (1981) reviewed the PIXE analysis of separated blood components, including various cellular and non-cellular fractions. Some subcellular components have been separated using the accepted procedures of biochemistry and analyzed by PIXE (Weber et al., 1980; Jahnke et al., 1981). The iron content of proteins separated by gel electrophoresis has been determined by PIXE (Szokefalvi-Nagy et al., 1987).

Chelating agents and ion exchange resins have been used to selectively concentrate trace elements from water. It has been shown by Lochmüller et al. (1974) that part-per-billion levels of elements in water may be determined by PIXE analysis of ion-exchange membranes that were equilibrated with the water. Ground-water trace elements have been selectively concentrated by Hall et al., (1984) using sodium dibenzyldithiocarbamate. They reported detection limits of 40 parts per trillion. Johansson and Johansson (1984) have reported the concentration of elements in sea water by chelation, absorption on graphite and extraction into acid. Analysis of sub-parts-per-trillion concentrations were achieved.

Williams and Finston (1981) have reported the removal of selected elements (those in high concentration) from solution by precipitation reactions, thus facilitating PIXE analysis of less concentrated elements. In a study of aerosol chemistry in a copper smelter plume, the soluble portion of air particulates was extracted into a dilute HCl solution (Mangelson et al., 1974). PIXE analysis was used to identify the soluble elements.

Uniform Targets From Liquid Drops

When the PIXE target is made by evaporation of a few microliters of solution on a thin foil

Table 4. Matrix Change for Several Sample Preparation Procedures-Biological Material

Procedure	Matrix Reduction Factor	Reference
High temperature ash	0.1	Rudolph (1972)
Low temperature ash	0.2 to 0.05 0.05	Maenhaut et al., (1984) Mangelson and Hill (1981)
HNO_3-H_2O_2 digest	0.6	Mangelson and Hill (1981)
HNO_3-Bomb digest	0.5 to 0.4	Maenhaut et al., (1984)
HNO_3-Microwave digest	0.5	Pinheiro et al., (1989)
Tetramethylammonium Hydroxide (TMAH) digest	1.5	Mangelson and Hill (1981)

the sample is usually not uniform, as has been discussed above. In some cases the sample dries with relatively large crystals or thick deposits. The addition of insulin (Johansson and Johansson, 1976), of a mixture of liposomes (Robaye et al., 1980) or of sonicated lecithin (Campbell et al., 1985) have been shown to reduce this problem. EDTA has been added to solutions of cerebrospinal fluid to prevent crystallization of elements during the drying process (Lapatto et al., 1988).

Summary

This paper give an accounting of many types of sample preparation methods. Both physical and chemical procedures have been used. These may find use singly, as a one step procedure, or they may be used together in a more complicated procedure. Some procedures are designed to combine parts of the sample into a homogeneous target which is representative of a whole sample. Some procedures are designed to separate a sample into its physical or chemical components. While almost all samples have been prepared for presentation to the particle beam in solid form, it has been shown that liquids and gases may also be analyzed by PIXE.

As targets for PIXE analysis are being prepared, allowance must be made for the characteristics of this analytical method in order to have an accurate analysis and to take best advantage of the capability of PIXE. It is hoped that the above will provide some initial direction to workers with a particular analytical requirement who may be considering analysis by PIXE-a powerful and flexible method.

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Discussion With Reviewers

W. Maenhaut: In the section Thin Filter Media it is stated that Teflo has better flow characteristics than Nuclepore. What is ment by this?

Authors: The Teflo filter has a higher porosity (effective percent open area) than Nuclepore which means that for a given pressure differential accross the filter the volume flow per square centimeter through the filter is greater for the Teflo filter. Filter pores in the Nuclepore filter also begin to plug and restrict air flow at much lower filter loadings than for the Teflo. Of course these improved flow characteristics for Teflo must be considered in light of the smaller areal density for Nuclepore which results in a reduced spectral background.

W. Maenhaut: In reference to the section Filtering: How small should the particle size be?

Authors: The answer to this question is not easly given. "Small" is relative to the parameters of the experiment, the matrix of the particles, the elements to be determined, and the extent of matrix corrections to be made. A recent paper (Jex et al., 1989) has explored some of these relationships. For example, consider aluminosilicate particles of 2.0 μm diameter and a 2.0 MeV proton beam. For analysis of calcium and all heaver elements, matrix corrections are 10 % or less. Matrix corrections for lighter elements gradually increase to a value of 30 % for aluminum. As particles become larger, corrections increase for light elements because of X-ray absorption, but corrections also increase for heavy elements because of reduced X-ray emission cross sections due to proton energy loss in the thicker particles.

W. Maenhaut: In the section High Temperature Ashing it is stated that loss of volatile elements during ashing may be minimized by the addition of sulfate. How does this ashing aid work and for what elements would it be beneficial? Could you provide some examples and/or literature references?

Authors: Iyengar and Sansoni (1980) have listed Ag, As, Co, Cr, Hg, I, K, Na, Pb, Sb, Se, Sn and Te as examples of elements that may be lost by volatilization. To this list should be added Mn, Zn and Cu. Loss is dependent upon the nature of the sample being analyzed. Sulfate forms sulfates of low volatility with many elements and is added to form these compounds. High temperature ashing methods have been discussed by Gorsuch (1976).

W. Maenhaut: In reference to the section Acid Digestion: What elements that one can measure by PIXE form volatile chloride and/or fluoride compounds? Could you give some examples?

Authors: Glass and some silicate minerals may be digested using hydrofluoric acid or a mixture of acids including HF. These procedures are based on the property that SiF_4 is a gas and is removed from the sample leaving other elements in solution. As, Ge, Se and W are examples of elements forming fluoride compounds that are gases or low boiling liquids and may also be lost from a digestion solution or during PIXE analysis. Si, Ge, Pb and As form some chloride compounds which are liquids at room temperature and have relatively low boiling points at standard pressure. These may be lost during sample preparation or during proton bombardment in a vacuum. For example, we have found that germanium ion in a weak hydrochloric acid solution is paritally lost in the process of preparing and analyzing the solution by PIXE.

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