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SAMPLING, STORAGE AND SAMPLE PREPARATION PROCEDURES FOR X RAY FLUORESCENCE ANALYSIS OF ENVIRONMENTAL MATERIALS

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FOREWORD

In the frame of the regular programme, the IAEA provides extensive assistance to the Member States in the field of nuclear instrumentation. One specific area of the assistance is nuclear spectroscopy which includes i.a. establishing/upgrading infrastructure and transfer of methodologies for effective applications of nuclear analytical techniques in environmental pollution monitoring, geology, mineral prospecting, etc. Within the nuclear analytical techniques being supported by the IAEA, the X ray fluorescence (XRF) method is one of the most commonly used because of its multielement and non-destructive character, speed, economy and ease of operation. From the point of view of quality assurance practices, sampling and sample preparation procedures are the most crucial steps in all analytical techniques (including also X ray fluorescence), applied for the analysis of heterogeneous materials. About 15 years ago, the IAEA published IAEA-TECDOC-300 on Sample Preparation Techniques in Trace Element Analysis by X-ray Emission Spectroscopy. This publication did not cover the recent modes of the X ray fluorescence method and recent developments in sample preparation techniques. Therefore, under the IAEA's 1995–1996 programme it was foreseen to prepare a technical document (manual) on sampling and sample preparation procedures for XRF analysis of environmental materials.

The draft manual of the present report was prepared during a consultants meeting held in Vienna, 9–12 October 1995. The IAEA is grateful to the following persons for their contribution to the manual and to certain chapters in particular: R. Van Grieken (Chapters 2 and 5), B. Holynska (Chapters 3 and 4, and Appendix 4), R.D. Vis (Chapter 6), S. Bamford (Chapter 7), E. Greaves (Appendices 3 and 4). The IAEA officers responsible for this publication were A. Markowicz and M. Dargie of the Agency's Laboratories at Seibersdorf and R.L. Walsh of the Physics Section, Division of Physical and Chemical Sciences.

EDITORIAL NOTE

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CONTENTS

1. INTRODUCTION

Methodological and technological advances in X ray fluorescence (XRF) analysis, observed in recent years, have made it possible to perform elemental analysis of virtually all types of materials, including those of environmental origin. The tremendous growth of environmental analysis in the last decade is primarily due to a necessity to assess the quality of our environment — which requires the availability of reliable analytical data.

Key elements in all analytical measurements from the point of view of quality assurance practices are sampling and sample preparation procedures, which are frequently the most time-consuming steps of the whole analysis. Although the literature on these two topics is rather extensive, e.g. [1–7], it is difficult to identify only one source which covers all aspects related to sampling and sample preparation procedures thoroughly. Moreover, it is rather impossible to find a complete description of the procedures which could be followed without looking for some additional details. This manual covers sampling and sample preparation procedures for environmental materials prior to X ray fluorescence measurements in a comprehensive way and provides complete instructions for selected procedures which reflect the state-of-the-art in this area.

Representative sampling which relies on the principles that (i) "the sample taken from the system should have exactly the same chemical composition as the original material" and (ii) "the probability of being selected from a total population must be equal for each individual", is extremely difficult (or practically impossible), especially for environmental materials.

In order to come as close as possible to the two principles, some basic practical rules have to be followed carefully [2]. These are:

- avoid contamination of the sample
- avoid any volatilization of chemical compounds and other losses of the elements during transportation and storage
- take reasonably large samples
- take account of seasonal fluctuations in the composition of the original material and of other parameters influencing its composition (temperature, humidity, etc.)

As a rule, sample preparation should be avoided as much as possible or kept to a necessary minimum. Moreover, simple physical sample preparation procedures, like drying, freeze-drying, homogenizing, pulverizing, and cutting of thin sections are recommended and, if possible, should be used before any chemical method [3]. Any sample preparation method always requires a careful control of contamination and losses of analyte elements, as well as simultaneous preparation of a blank sample.

Although most of the sampling and sample preparation procedures presented in this manual are in principle adequate for both the wavelength-dispersive (WD) and energy-dispersive (ED) modes of X ray fluorescence, they have been tested and used successfully in the field of EDXRF only.

Throughout the text the meaning of the following acronyms is: XRF (a conventional EDXRF technique with either radioisotope or X ray tube excitation); TXRF (total reflection XRF).

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2. ANALYSIS OF AIRBORNE PARTICULATE MATTER

2.1. INTRODUCTION

The analysis of airborne particulate matter or aerosols is one of the major applications of X ray spectrometry and it has been in extensive use for two decades, also for official monitoring programs like in the USA. There are hundreds of publications on this topic; every year another 50 or so still appear in the literature and several extensive reviews have been published [1, 2]. XRF measurements of aerosols are usually done in the context of monitoring of toxic heavy metals. Although it has been estimated that the human uptake of heavy metals is appr. 70% through food, 25% through drinking water and only 5% through air, the absorption factors (fraction retained in the human body) are appr. 0.05, 0.15 and 0.50 for food, water and air, respectively, so that the eventual contributions are roughly equal. One should also realize that a substantial fraction of the heavy metals in soil, hence in food and drinking water, is derived from deposited airborne heavy metals. All this is sufficient justification for the monitoring of aerosols, a task for which XRF is truly excellent and superior, as will be shown below. Moreover certain trace elements in aerosols can serve as a tracer for air pollution; e.g., Pb is derived from leaded gasoline or metallurgical activities, V and Ni are due to diesel oil combustion, Fe, Ti and Si are related to soil or fly ash, Na and Cl point to seasalt, S is generally indicative for combustion sources, etc.

The determination of the content of heavy metals in airborne particulate matter does, of course, involve different steps: first the particles are sampled by filters or impactor collection plates (see below), then the collected particles are preferably measured directly. The fact that e.g., loaded aerosol filters can be presented directly to an XRF instrument, often as an ideal thin target, constitutes a major advantage of XRF over nearly all other trace analysis techniques like AAS, ICP-AES, ICP-MS, etc. The representative sampling of atmospheric particulate matter requires attention to meteorological parameters, physical and chemical properties of atmospheric constituents and physical characteristics of the sampling equipment. Knowledge about the behaviour of gases and aerosols in the atmosphere is required in any study of air pollution. Finally, the conditions of sampling are dictated by the purpose of sampling itself.

2.2. AEROSOL SAMPLING

2.2.1. Sampling strategy

In the air, the heavy metals are almost exclusively in the particulate phase, which is typically present at concentrations of 50–500 micrograms per m^3 and very large preconcentration factors are achieved straightforwardly by simply drawing a large air volume through a filter by using a pump, to retain the aerosols on the filter for XRF analysis. Even such common and obvious filter sampling is, however, easily affected by various sources of errors.

A successful sampling campaign depends in the first place on an optimized strategical positioning of the samplers and the timing, frequency and duration of sampling, which will depend on the purpose of the sampling campaign and on the capabilities of the XRF unit. The sampling should be done at a representative location, not too close to walls or other obstacles for the air flow which might cause local anomalies.

Preferably the inlet of the sampling unit is placed about 1.5 m (breathing level) from the ground, it is facing downwards (when cascade impactors are used) or upwards (when simple filter holders are used) and, in the latter case, it is covered with a Plexiglas hat, at ca. 10 cm distance (to prevent rain and dustfall to enter the filter directly). When the inlet is horizontal, the collection of large particles may vary with the wind speed or direction.

Of course, the air volume that has been drawn through a filter should be assessed. For the determination of the sampled air volume there are two basic types of equipment: the flow rate meter or rotameter and the dry gas meter, which records the volume of the gas. A flow rate meter or rotameter is a slightly conical glass tube in which a sphere (plastic or stainless) steel floats higher when the upward air flow through the rotameter is higher. However a rotameter is quite expensive, it requires calibration and it gives an instantaneous reading of the air flow, e.g. at the beginning and end of a sampling period. When a power failure has occurred during the period, this will lead to errors. Therefore it is recommended to use a simple integrating dry gas meter, such as is used for domestic natural gas metering. Its price is in the order of 100 USD; various sizes exist depending on the volume to be measured. A scheme of a sampling equipment is given in Fig. 2.1. If a vacuum gauge and a rotameter are not available, sampling can go on without them.

Three very common and *very major sources of error* should be emphasized:

- the gas meter (or rotameter) should always be placed behind the pump, and neither between the filter and the pump (because there is normally a pressure drop over the filter and the gas meter has been calibrated to work at atmospheric pressure) nor before the filter (because the gas meter will interfere with the aerosol sampling on the filter).

- leaks in the plastic tubing (preferably reinforced plastic which does not collapse at lower pressure) and especially in the connections of the tubing with the filter holder, the pump and the gas meter should absolutely be avoided since they provide erroneous volume readings. To check this, it is recommended to have two identical filter holder-pump-gas meter systems operating simultaneously; the volume reading should not differ by more than 5%.

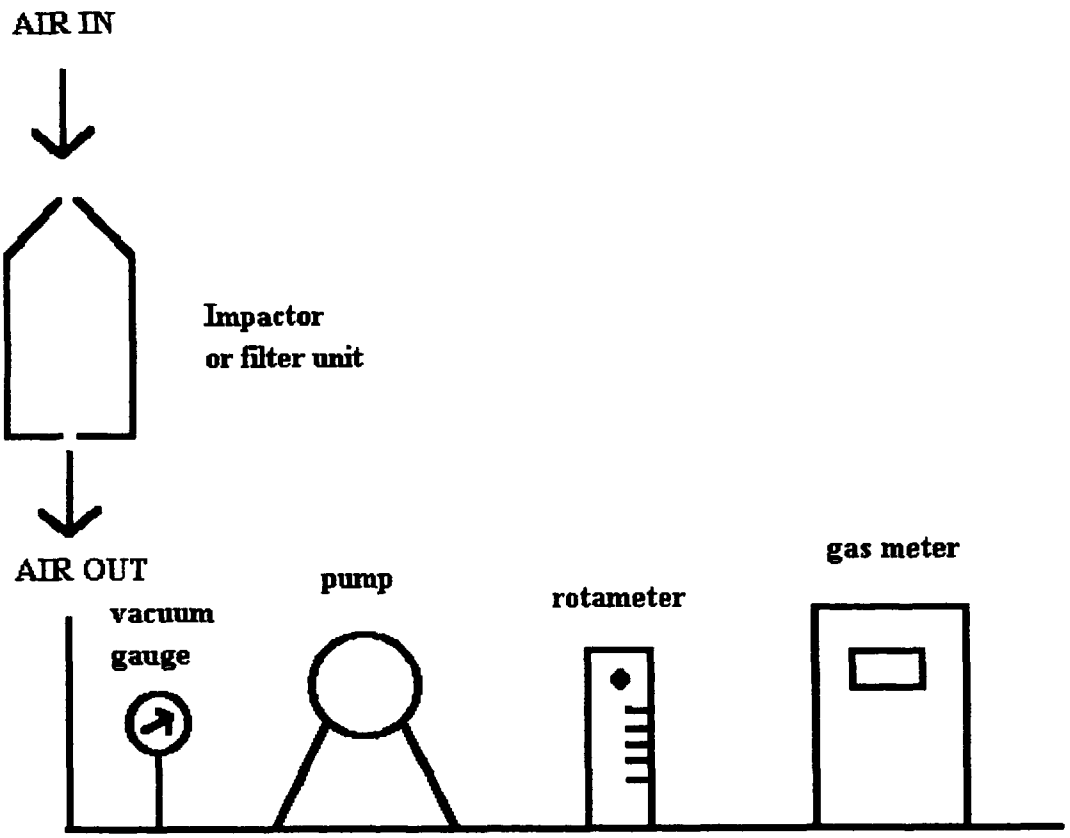

FIG. 2.1. Scheme of sampling equipment.

- the exhaust of the pump should be brought with a long plastic tube as far as possible away from the sampling site and downwind from it (passing of pump exhaust gases through the filter may lead to totally erroneous measured concentration of Cu, Fe, etc.).

Of course, blank samples should also be taken regularly; the collection substrate is then brought into the sampling device without sucking air through it to check for contamination during sample transport, etc.

Finally one should realize that, ideally, so-called isokinetic sampling (i.e. where care is taken that the air is drawn into the sampling unit with the same linear velocity as that of the air flow by the wind at that moment) should be used, since otherwise very large particles (especially those larger than 10 μm) might escape sampling. However, isokinetic sampling is difficult to realize in practice and such giant aerosol particles, although very important with respect to atmospheric deposition, are not very relevant for health considerations, since they normally cannot penetrate into our lungs.

2.2.2. Filter type

The selection of a particular filter type is the result of a compromise among many factors that include the requirements of the analytical procedures, cost, availability, collection efficiency, the ability of the filter to retain its filtering properties and physical integrity under ambient sampling conditions, etc. Before selecting a filter for a particular application, the blank count of the filter background level of the material to be analyzed must obviously be determined, since all the filters contain various elements as major, minor and trace constituents.

Although they are very suitable for organic analysis, glass fibre filters should never be used for XRF because of their very high inorganic blanks.

Very suitable for aerosol sampling in combination with XRF analysis are commercial polycarbonate (PC) membranes, e.g. Nuclepore. They are very thin (ca. 1 mg cm^{-2}) and thus produce little X ray scatter background in XRF. They are pure and essentially collect aerosols at the surface only, what is very important for XRF, since no X ray absorption of the incident radiation and of the generated characteristic X rays in the filter material has to be taken into account. Standard Nuclepore polycarbonate membranes are available with pore sizes ranging from 0.015 μm to 12 μm; 0.4 μm is most common for aerosol work. Such filters are almost ideal for optical or electron microscopic analysis. Disadvantages are that e.g. Nuclepore filters tend to be expensive, that they are sometimes difficult to handle because they become electrostatic and, mostly, that they allow only a low air-flow rate so that the aerosol sampling might have to be long, or the detection limits (expressed in ng m^{-3}) might be unfavourable for XRF setups with poor sensitivity and the elemental range of the XRF analysis might be limited to relatively abundant elements, like Fe, Ca, etc. only, particularly in relatively clean air. Although polycarbonate membranes are not prone to water absorption, clogging with mist droplets occurs in high humidity conditions. All this has to be checked experimentally before a sampling campaign.

For trace element analysis in air pollution studies, particularly suitable are polycarbonate filters of the so-called aerosol-type, due to their very low trace metal concentration. Aerosols membranes are produced in the following pore sizes: 8.0, 0.4 and 0.2 μm. They are lightly coated with Apiezon (AP) type L grease for increased particulate adhesion.

Useful for aerosol sampling are also Teflon or polytetrafluoroethylene (PTFE) membrane filters. They can be used with any standard membrane holder for filtration. E.g. Sartorius membrane PTFE filters SM 118 are available in the pore size 0.2, 0.45, 1.2 and 5 μm. They are inert to practically all chemicals.

Cellulose fibre filters, such as Whatman-41 are a suitable alternative for Nuclepore membranes. They are very cheap, strong and easy to handle. Grades 4 and 5 are commonly in use for air filtering. Grade 4 has a high flow rate with good retention of larger particles while grade 5 has a low flow rate and it is the most efficient qualitative paper for collecting small particles. Very importantly, such loosely woven filters allow much higher flow rates than e.g. polycarbonate membranes, hence much more aerosol material can be collected per cm^2 in a given time. On the other hand, such filters are thicker (8.5 mg cm^{-2}) and hence they produce a larger X ray scatter background, resulting in higher XRF detection limits. Another complication is that cellulose filters do not only collect particles at their surface but also in depth (because of collection by impaction on the cellulose fibers), particularly for small particles (submicrometer size). Hence a correction must be carried out for the absorption of impinging and especially characteristic X rays by the filter material itself. Since the distribution of the elements within the filter depends on the particle size and is unknown, a convenient approximation is to fold the filters during XRF-analysis as a sandwich with the loaded side inwards, to assume that all elements are present at the centre of this sandwich (which is true for the elements on large particles that have been collected at the surface of the filter and is, on the average, true for elements on small particles which have partially been collected in the depth of the filter) and to correct for the X-absorption by 8.5 mg cm^{-2} of cellulose [3]. For high-energy X rays, this sandwich geometry will also lead to doubled sensitivities.

2.2.3. Storage of filters

Aerosol filter samples often are transported a long way from the sampling site to the laboratory and therefore have to be adequately stored before analysis. Material losses due to due to transport and storage could often occur. A cheap and easy way of storing filters is to put them into paper envelopes. Gravimetrical determination showed average material losses of 8 ± 3 % for cellulose paper filters when exposed filters were stored in normal laboratory conditions for 1 month. A more expensive and less-space saving method is to store the sampled filters in Petri dishes in a way that their sampled side does not come in contact with solid material. This method provides satisfactory results, with less than 1% of the material lost. For aerosol samples, some elements, e.g. halogens, may be volatilized as a result of chemical reactions which take place on the collection substrate during sample storage; such losses may be minimized by storing the samples in a cool, dark place, in a freezer, and by keeping the storage time as short as possible.

2.2.4. Weighing of filters

Filters must be weighed before and after the sampling to determine the total air particulate matter. Cellulose filters are hygroscopic and weight differences of 3% can easily result in e.g. differences of 25 mg on a filter paper of 800 mg. These weighing errors are severe because usually only a few hundred mg of material are collected. A solution for this problem is to leave the filters for 24 hours in an atmosphere of a constant humidity and to weigh them subsequently. Nuclepore filters produce negligible weighing errors of 0.04 ± 0.03 %.

2.2.5. Overall filtration sampling devices

The choice of the sampling device is determined by the research objectives, the costs and the sensitivity of the XRF setup. Usually, a small and convenient filter system can be used, e.g., Sartorius SM 16598 which is supplied with a stainless steel inlet tube. The filter holder accepts the standard 47 mm diameter Nuclepore or Whatman-45 filter. The operational flow rate is 27 l min^{-1}. It does not make sense to use much larger filters since the irradiation area in XRF systems is only one or two cm^2.

The following are typical airborne concentrations, in an urban environment and in a cleaner environment:

Urban area (ng m^{-3}):
S 10,.000; Fe 300; Ni 20; Cu 20; Zn 80; As 3; Pb 130

Remote area (ng m^{-3}):
S 100; Fe 50; Ni 1; Cu 1.5; Zn 10; As 0.5; Pb 2.

Hence, if the XRF instrument used has a detection limit of 10 ng cm^{-2}, if the filters have a diameter of 4.7 cm and hence an active area around 10 cm^2, and if one wants to see at least a factor of two above this level, then about 30 m^3 of air should be collected in clean air and about 3 m^3 in urban air to be able to see for e.g. Zn in a given concentration range. These numbers should be taken into account when designing the overall sampling setup.

When aerosol sampling involves one of the filter units described above, a small volume flow rate pump is needed. If the operational flow rate of the filter is about 27 l min^{-1} (1.62 m^3 h^{-1}),

then a single stage pump with a nominal flow rate of 30 l min^{-1} (1.8 m^3 h^{-1}) is requested. Such pump is also suitable for size fractioned aerosol collection with stacked filter units or cascade impactors. The technical data of e.g. the rotary vane vacuum pump UNO 1.5 are: max. pressure (1.5 bar), speed at 50 Hz (2760 min^{-1}), motor rating (0.13 kW), weight (8 kg).

2.2.6. Sampling aerosol particles as a function of their particle size

If the interest is to collect the coarse and fine particulates separately, a simple, non-expensive sampling device is so-called stacked filter unit. It consists of two filters placed in series. The first, coarse filter is a Nuclepore filter, with the pore-size in the range of 5–8 μm, and the second one is a Nuclepore filter with much smaller pore-size, like 0.4 μm.

More sophisticated and powerful size-fractionating devices are called "cascade-impactors". For TXRF analysis, single-jet cascade impactors, based on the Battelle design are to be preferred [4]. They consist of e.g. 7 impaction stages (cut-off diameters 0.25, 0.5, 1, 2, 4, 8 and 16 μm) and a back-up filter. This impactor operates at flow rate of 1.2 l min^{-1}. Its price is around 2000 USD. For TXRF analysis, impactor stages are loaded as impaction substrates with quartz or plexi discs, that are also used for the standard TXRF technique. The discs are only specially cut in order to allow appropriate mounting above the stage orifice. A steel spring presses them firmly against the disc holders. At the end of each sampling interval, the cascade impactor has to be taken to the laminar flow hood where the impaction slides are transferred to Petri dishes. The sample nozzle should be washed with 1% HNO_3 prior to the next sampling program.

To avoid bounce off of the aerosols from the quartz substrates during the impaction step, the quartz or Plexiglas impaction discs are siliconized with a silicone solution, as is usually done for TXRF anyway. Plexiglas discs are greased with Vaseline, apiezon or paraffin.

2.3. AEROSOL ANALYSIS BY XRF

After e.g. the Nuclepore or Sartorius membranes or the Whatman-41 cellulose filters (see Section 2.2.2) have been adequately loaded with air particulate matter (see Sections 2.2.1 and 2.2.5) and stored (see Section 2.2.3), the recommended way is to present them directly to the XRF unit, with the loaded side towards the XRF instrument in case of Nuclepore filters, or preferably in the "sandwich-geometry" (see Section 2.2.2) in case of Whatman-41 cellulose filters. Unless the filters are extremely loaded, no correction for the X ray absorption in the aerosol material is usually necessary, but absorption through 8.5 $mg.cm^{-2}$ must be considered for Whatman-41 sandwiches (see Section 2.2.2). Calibration is preferentially done by using thin film standards (see below), or standard reference filters loaded with glass powder. The analysis results, in $ng.cm^{-2}$, are easily converted into $ng.m^{-3}$, using the volume of air that the sample represents, as it has been measured with a rotameter or preferably a gas meter (see Section 2.2.1).

2.4. AEROSOL ANALYSIS BY TXRF

2.4.1. Aerosol analysis using filter digestion

Aerosol loaded filters can be dissolved prior to TXRF analysis with supra pure concentrated (70%) HNO_3 and HF acids in a high-pressure digestion vessel (see Chapter 4). Then, the sample residue is supplied up with 1 ml ultrapure water and ultrasonically treated for 10 min and finally

an aliquot of 5 ml is transferred to the quartz carrier, vacuum dried and measured. A standard is added prior to the digestion procedure. The recovery can be quantitative within the usual standard deviation of 10 to 15%. Of course, digestion under microwave radiation is also possible. However, filter digestion is certainly more troublesome and complicated and less sensitive than the method discussed hereafter (see Section 2.4.2).

2.4.2. Direct aerosol analysis by TXRF

A direct and new method [4] is based on the aerosol deposition on the TXRF reflector quartz discs (see Section 2.2.6). Prior to the sampling, siliconizing of the quartz disks is achieved by dispersing a 5 µl drop of silicone solution. Then, the discs are positioned in a single orifice impactor (see Section 2.2.6) and loaded with aerosols. Either all stages of the impactor are used, and then separate information will be obtained on the composition of the aerosols as a function of the particle size. Or only the last stage of the impactor (with a cutoff size of 0.25 µm) is used alone; then all aerosols will be collected on this stage, and information is obtained on the bulk aerosol, as with filter sampling. The collected airborne particle spot on the quartz reflector is subsequently supplied with Ga or Co as an internal standard, by pipetting a 5 µl drop of 5 µg ml^{-1} standard solution upon the spot, and the sample is allowed to dry in a desiccator under reduced pressure and then analyzed immediately. All handling has to be done in a laminar flow clean bench; no rubber gloves are to be used because they lead to remarkable Zn contaminations. Obviously, this method is very simple. The limits of detection are in the order of 0.2 ng for most heavy metals. Contrary to aerosol sampling by filters followed by XRF, the gain in sensitivity is several orders of magnitude so that the aerosol sampling time can be in the order of a few minutes only. Moreover no tedious filter digestion step is needed. Unfortunately one needs a (one stage) impactor sampling device, and the quantitative character of the results has not been proven very extensively in the literature since the method is very new.

2.5. CONCLUSION

XRF is an excellent method for the analysis of atmospheric particles. Except for e.g., neutron activation analysis (which measures a very different suit of elements), hardly any other analysis method can measure directly on loaded filter; nearly always a tedious digestion step is required in which some refractory elements may not be dissolved. Therefore the use of XRF should be encouraged in this field, even if other analysis methods are available.

The novel direct way of TXRF analysis after aerosols have been collected directly on the common quartz or plexiglass reflectors seems quite promising.

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3. ANALYSIS OF GEOLOGICAL MATERIALS

3.1. INTRODUCTION

The major concern in sampling has to be that the sample is representative, which means that the sample taken must reflect the overall composition of the entire material to be evaluated [1–4]. If possible, the analyst himself should take part in the sampling procedure to be sure that no changes in sample composition occur during transport and storage. If it is not possible, at least a knowledge of the origin and history of the sample is necessary. In general, only a small part of the total material is used to provide the analytical signal from which the concentrations of the elements of interest are calculated. A method of representative sampling depends on the kind of material to be analyzed. The smallest sample size that still possesses the essential characteristics of the bulk material depends on differences of specific gravity of the various components, size, number and shape of grains (for granulated materials), the average content of the element to be determined, the magnitude of the acceptable error. Geochemists have found, for example, that a few grams of glassy lava may be representative while hundreds of kilograms of granite are needed for certain elements (Mo, Nb) determination, which are concentrated in inclusions. A random sampling can easily be used for truly homogeneous substances such as liquids. When random sampling is applied for inhomogeneous material several samples need to be taken and standard deviations due to sampling need to be calculated. The overall error largely depends on the degree of inhomogeneity. It is important that the error introduced during the entire sampling

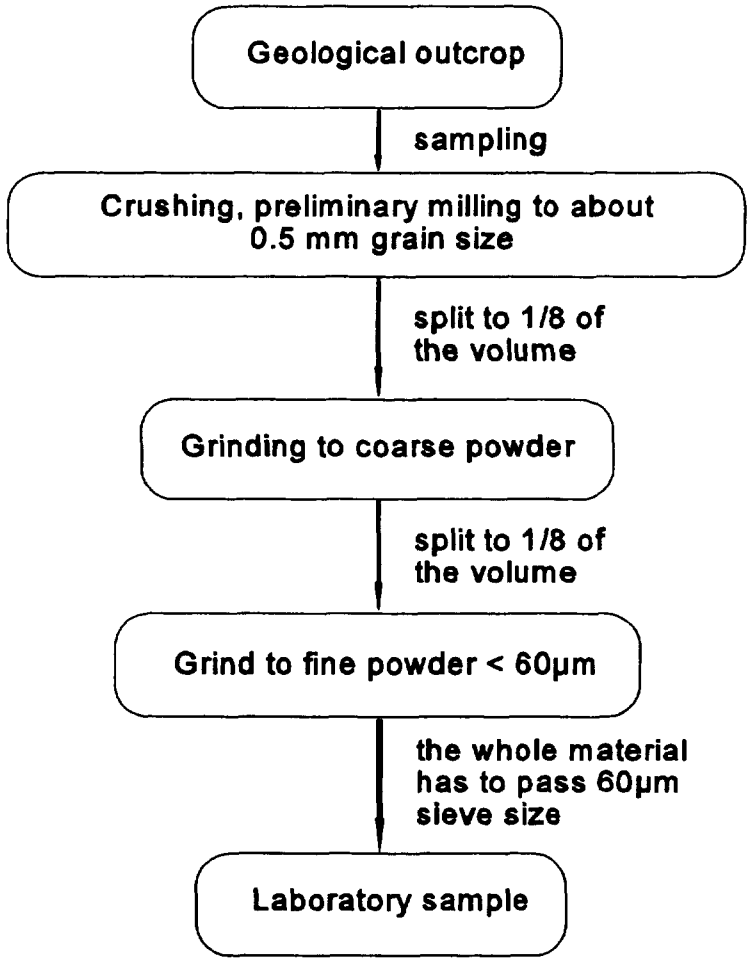

FIG. 3.1. Comminution of geological materials prior to sample preparation.

operations should be at most of the same order of magnitude as the error of the subsequent analytical procedure.

3.2. SAMPLING [5, 6]

Collection from a large outcrop area can be done on a grid basis or a random pattern, providing that sampling is statistically valid. After collecting a rock sample, subsequent crushing and splitting the crushed material have to be performed as seen in Fig. 3.1. A method of coning and quartering is usually used. One should bear in mind that using crushers and mills made of steel can introduce W, Cr, Mn, V, Co, and Zr contamination.

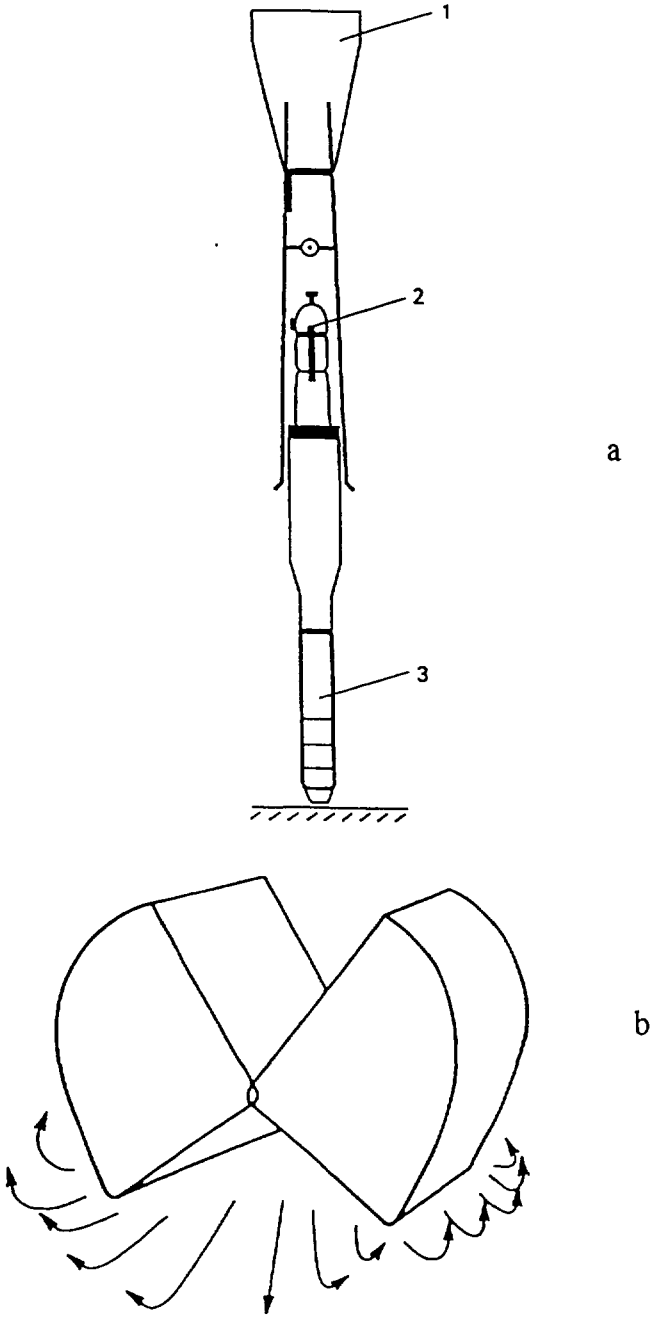

FIG. 3.2. (a) Niemistö sampler: 1-ruder blade, 2-catch, 3-tube made of polyvinyl chloride with metal shielding. (b) Van Veen scoop.

Soil has a heterogeneous structure and different composition with depth. Often the distribution of some trace elements in depth down to 50 cm is of interest for studies of e.g. mobility of trace essential and hazardous elements and their deposition. This is especially the case when soil is suspected to be polluted. Manual excavation is suitable for nearly all soil types. When digging the pit all soil removed must be piled on one side, so that the wall is preserved for sampling purposes. After sampling all vegetation and debris should be discarded. The samples are collected to clean glass jars or plastic bags and stored at 4°C, if necessary, to retard compositional changes due to biological activity. Analysis of sediments has become very important since a relation between chemical and mineralogical composition of sediments and air and water pollution has been observed. Sediment cores are often taken by driving a sharpened polyvinyl chloride tube vertically into a suitable place in river sediment, shallow sea sediment or wetland. A scheme of such a sampler is presented in Fig. 3.2.a. When sampling from a boat, often a Van Veen scoop shown in Fig. 3.2.b can be used. The sediment cores are usually sectioned into 1 or 2 cm thick layers, weighed, dried at 70–80°C and homogenized upon arrival in the laboratory. Aliquots of each layer are taken for the various chemical and elemental analyses.

3.3. SAMPLE PREPARATION [7, 8]

The samples can firstly be air-dried in a clean place, then ground, to break down aggregates. Preliminary ground sample is then subdivided by using quartering. The sample obtained in such a way is ground again into fine powder to yield an acceptable number of particles of each component of the heterogeneous material. An example for soil comminution is shown in Fig. 3.3. The sample is sieved through a sieve of 60 μm size and the oversize is ground again until no grains larger than 60 μm are left. Sieves made of nylon are recommended to avoid contamination by metals. A few samples should be taken from the laboratory sample for measurement, to evaluate the homogeneity, which should be better than 5% relative. Geological samples and soils after grinding can be further prepared in various ways prior to XRF or TXRF measurement (Fig. 3.4).

3.3.1. XRF

For XRF measurements a sample has to be additionally pulverized, homogenized and pressed into pellet with or without a binder. Usually chromatographic cellulose, boric acid or starch are used as a binder in a proportion 1:10 by weight (in some cases a liquid binder might be used). For the emission–transmission method usually a 150 or 200 mg pellet is prepared (25 mm diameter). Although XRF is mostly used for minor and trace element analysis, major elements can be determined after proper dilution with cellulose or starch (in a proportion 1:1 by weight). Even simple sample preparation needs to be done carefully and with the use of proper devices to prevent contamination. Therefore the devices such as mills, mortars and pulverizers should be made of agate, silicon carbide or tungsten carbide. They should be washed thoroughly with tap water, then distilled water and dried. For more complete cleaning, grinding with pure quartz sand, followed by careful washing with tap and distilled water should be applied.

When dealing with samples containing heavy elements in a light (low density) matrix, which is often the case in geological samples analysis, the grain size effect can be an additional source of error in XRF analysis [9, 10]. The way of minimizing this effect is reduction of particle size by grinding. However, different particle size reduction occurs in most grinding procedures because the various constituents are reduced in size at different rates due to their differences in

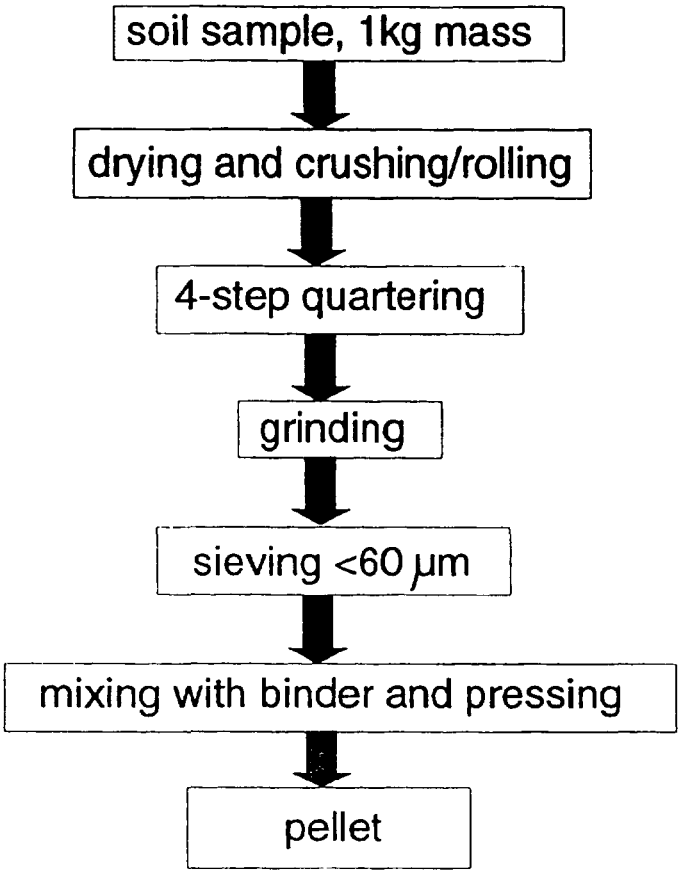

FIG. 3.3. Comminution of soil prior to sample pelletizing.

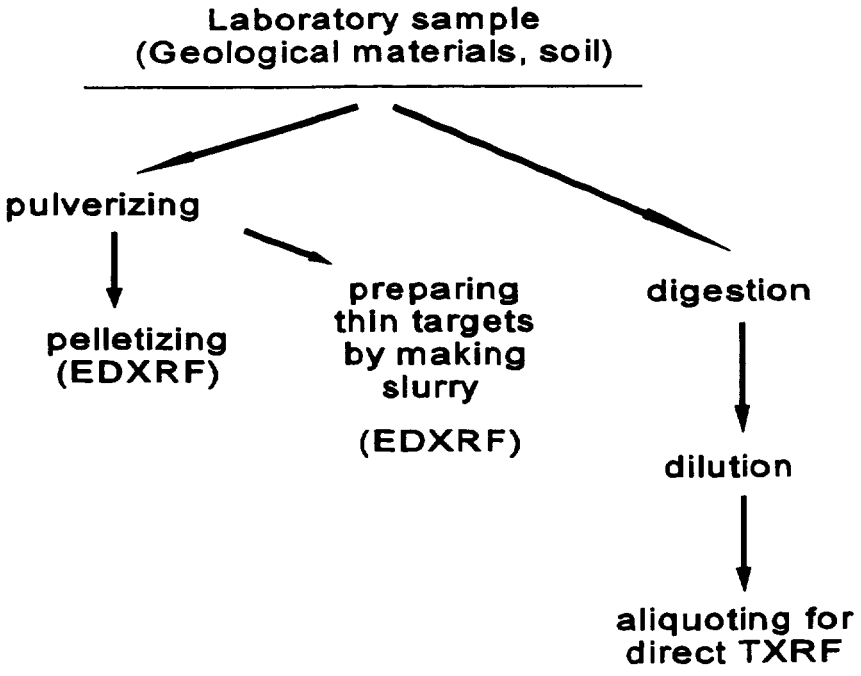

FIG. 3.4. Solid sample preparation techniques for XRF and TXRF.

hardness, which may result in segregation. When diluents are added prior to pressing, a sample has to be mixed carefully to avoid segregation. A number of Teflon or Teflon-coated devices for homogenization are commercially available. In analysis of powdered materials, usually thick or intermediate samples are used. Thin samples are sometimes applied with the use of so-called "slurry " technique, for very fine powder (below 10 micrometer size). This technique works for water insoluble materials. A water slurry is prepared out of a few miligrams of powder and a few mililiters of water. A turbulent suspension is made followed by rapid filtration through a Nuclepore filter [11]. This method results in fairly uniform thin layers and is applied in XRF.

In the analysis of particular geological materials, and soil when concentrations of trace elements are to be determined, wet digestion might be applied.

3.3.2. TXRF

Geological materials and soils have to be digested prior to TXRF measurement for trace elements analysis. Digestion, should be preferably performed in a Teflon bomb in order to avoid use of $HClO_4$ and H_2SO_4 acids, as well as to prevent losses of volatile elements.

Example : Digestion procedure for geological samples in Teflon bomb

Weigh the sample (0.2–0.4 g) on a glossy paper and transfer it to the Teflon bomb. Add appropriate mixture of acids (see Table 3.1), seal the bomb and heat it in an oven for 5–6 hours at 165 °C. After digestion, allow the bomb to cool to room temperature for a few hours or overnight. Open the bomb and add 100 µg of selenium as an internal standard (from 1000 mg/l standard solution). Mix well and transfer the sample solution to 25 ml calibration flask. Then dilute the sample to 25 ml with 4% boric acid to dissolve CaF_2 precipitate and to remove HF acid (at room temperature complete dissolution of CaF_2 is obtained within 2 hours). Pipet an aliquot of 5 µl on a quartz carrier, and dry it under infrared lamp or in vacuum.

TABLE 3.1

Type of sample	Acid combination (conc.)	Result after addition of H_3BO_3
Sediment	1 ml HNO_3 + 3 ml HCl + 1 ml HF	Colourless solution
Rock	1 ml HNO_3 + 3 ml HCl + 2 ml HF	Colourless solution
Soil	1 ml HNO_3 + 3 ml HCl + 1 ml HF	Colourless solution

Note

1. Always prepare a blank sample and subtract the blank values.
2. For safety reasons, before using a Teflon bomb, read carefully the instructions given by the supplier and strictly follow them.
3. Before use, clean the Teflon bomb using the following procedure: After digestion, rinse the bomb thoroughly with analytical grade acetone, then soak it in 10% nitric acid for 2 days, and rinse it again three times with double distilled water.

3.4. REFERENCE MATERIALS

Many standard reference materials (SRM) and reference materials (RM) are available which should be used by an analyst to verify the analytical procedure which is to be routinely applied. Many institutions and agencies, e.g. National Institute of Standards and Technology (former NBS) in the USA or the International Atomic Energy Agency in Vienna, are involved in manufacturing such materials in several countries. The use of a SRM enables the analyst to test the accuracy of a method, devised especially, when a multi-stage sample preparation including trace elements preconcentrations is used. A SRM of similar qualitative and quantitative composition should be analyzed using the same procedure. Such practice is helpful in finding and eliminating systematic errors of methods even if they are characterized as high-precision methods.

Generally, SRMs are not recommended to be used for calibration, because they are not primary standards. However, a large array of SRM's of similar matrix material (e.g. geological materials) can be used for calibration [12,13].

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4. ANALYSIS OF BIOLOGICAL MATERIALS

4.1. INTRODUCTION

In recent years there has been a considerable growth of interest in trace element analysis of food and various biological materials such as plants, animal and human tissues, bones and fluids [1, 2]. Since most of the elements of interest are in μg/g and ng/g concentrations, sampling of these materials should be carried out with special care to avoid contamination. Contamination of the sample by trace and other elements during sampling may occur from the environment and sampling operation itself, from dust in the air and from tools used for sampling. Types of contamination which may be derived from the laboratory atmosphere are presented in a summarized form in Table 4.1. The minimum requirement to prevent contamination by air dust is that a clean working area should be available for handling the sample. This can be provided by a laminar flow clean air bench, or at least by a clean glove box. (The laminar flow clean bench should never be switched off). Non-metallic tools and laboratory-ware materials should be used and they are shown in Table 4.2.

Leaching of elements from container walls by reagents can be another source of contamination of which examples are given in Table 4.3 [3, 4]. Special precautions should be taken to avoid changes in mean sample composition due to loss of water. This is a difficulty often experienced with small tissue samples, e.g. biopsy samples. The necessary precautions for this type of samples are storage in a closed system or freezing immediately after sampling. Also, chemical processes such as hydrolysis, redox reactions, fermentation or photochemical reactions may result in changes in mean composition.

During transport to the laboratory, the samples should be kept cool (4°C), if transport takes only a few hours. Otherwise they should be frozen. For long-term storage deep-freezing (down to -18 °C) is necessary. Containers made of non-wettable material such as Teflon, high pressure polyethylene, polypropylene, synthetic quartz are commonly used and are recommended. Surface preconditioning, for beakers and containers can be carried out by chelating reagents such as EDTA (1% solution) followed by mineral acids (ultra pure HNO_3), and then thorough rinsing with double distilled water.

4.2. SAMPLE PREPARATION [5]

Biological materials are generally heterogeneous. When dealing with solid samples, drying, powdering, homogenizing and homogeneity testing may be necessary before preparing the samples for measurement. Samples of body fluids form suspension or emulsion. For these, a separation or homogenization have to be considered.

Various treatments of biological materials include drying, lyophilization, ashing and wet digestion [6–9].

Drying in an oven or freeze-drying are commonly applied as means of preconcentrating the sample before measurement. During oven drying it is important to control the temperature. Some plant materials (e.g. cabbage) decompose at temperatures above 85 °C. The biological materials should not be dried at temperatures above 100 °C. After drying or freeze-drying, the material is next ground and homogenized before pelletizing or taking the aliquots for wet digestion (NOTE: biological and geological materials should not be dried at the same time in an oven). Before drying biological materials the oven should be carefully cleaned.

TABLE 4.1.ENVIRONMENAL CONTAMINATION OF SAMPLE BY SOME ELEMENTS (after Sansoni and Iyengar [1])

Element	Non-filtered air dust (μg/g)	Filtered air dust (μg/g)	Tabacco smoke condensate (μg/g)	Hair (μg/g)
Al	3000	6		4–29
As	55	< 0.01	2.85	0.2–3.7
Ca	2690	< 0.004		300–3190
Cd	2.8	0.1		0.24–2.7
Cr	39	< 0.006	0.39	0.1–3.6
Cu	213	< 0.02		11–32
Fe	3230	< 0.006	7.3	5–68
K	7920	< 0.004		150–860
Mn	116	< 0.006		0.3–5.7
Ni	70	< 0.50		0.6–6.5
Pb	2150	< 0.04		3–70
Sn	10	< 0.05		?
Sr	13.5	< 0.01		0.05–0.9
Ti	258	3		0.05–14
Zn	1640	< 0.02		99–450

TABLE 4.2. SOME TRACE ELEMENT IMPURITIES WHICH CAN BE FOUND IN LABORATORY-WARE MATERIALS (after Sansoni and Iyengar [1])

Element	Glass (pyrex) μg/g	Polyethylene High pressure μg/g	Plexiglass μg/g	Synthetic quartz μg/g	Teflon μg/g
Ca	1000	20–20000			
Co	0.08	5	0.05	0.3	0.3–1.7
Cr		15–300	10	1.6	ND–30
Fe	3000	600–2100	140	160	ND–35
Mn	1000	10	10		
Pb		200	200		
Sb	2.9	5	5	0.4–3.8	ND
Zn	0.73	90	90		8

TABLE 4.3. CONTAMINATION OF SOME MINERAL ACIDS BY LEACHING OF CONTAINER WALL DURING EVAPORATION [3, 4]

Element leached	HNO_3			HF	
	Polyethylene ng/g	Teflon ng/g	Quartz ng/ml	Polypropylene ng/ml	Teflon ng/g
Al		2	20	0.54	3
Ca		4	60		1
V		0.76			
Cr		7			0.4
Mn	50	0.2	0.6		0.1
Fe		14	20	0.3	3
Ni		1.0	ND	0.02	0.4
Cu	160	0.01		0.2	0.4
Zn		0.04		0.1	
Br	38				
Cd				0.0007	
Pb		ND	1	0.03	0.1

Ashing is used for removing the organic matrix. Ashing methods include dry ashing with air in a muffle furnace (at a temperature of 450–500°C), and wet ashing with oxidizing acids mixtures. Ashing in a furnace at a temperature of 450–500°C is not recommended because of loss of volatile elements. Wet ashing, with a mixture of acids (e.g. HNO_3 + $HClO_4$), is generally preferred to dry ashing because it results in lower losses of trace elements as well as faster and often more complete removal of organic substances. Wet ashing can be carried out in an "open way" using an electric heater and a round bottom flask with or without air cooled reflux. Numerous systematic errors in the decomposition of organic materials are reduced when dissolution is carried out in a PTFE pressure bomb. Pressure decomposition requires a small acid volume and prevents losses of volatile elements (e.g. Hg, As, Se, Br, I). The disadvantage of the pressure bomb is that the sample weight is strictly limited to 0.5g for the reason of safety (NOTE: Before using a PTFE bomb, read carefully the operating manual and follow the instructions). In recent years wet digestion has been facilitated by introducing laboratory microwave digestion heaters. The microwave energy is directly absorbed by the acid and biological material, which results in faster sample decomposition [10, 11]. A scheme of biological sample preparation is shown in Fig. 4.1.

The digestion method should be optimized, and the recovery of the elements and precision of the procedure should be thoroughly tested. After wet digestion, preconcentration of trace metals can be carried out.

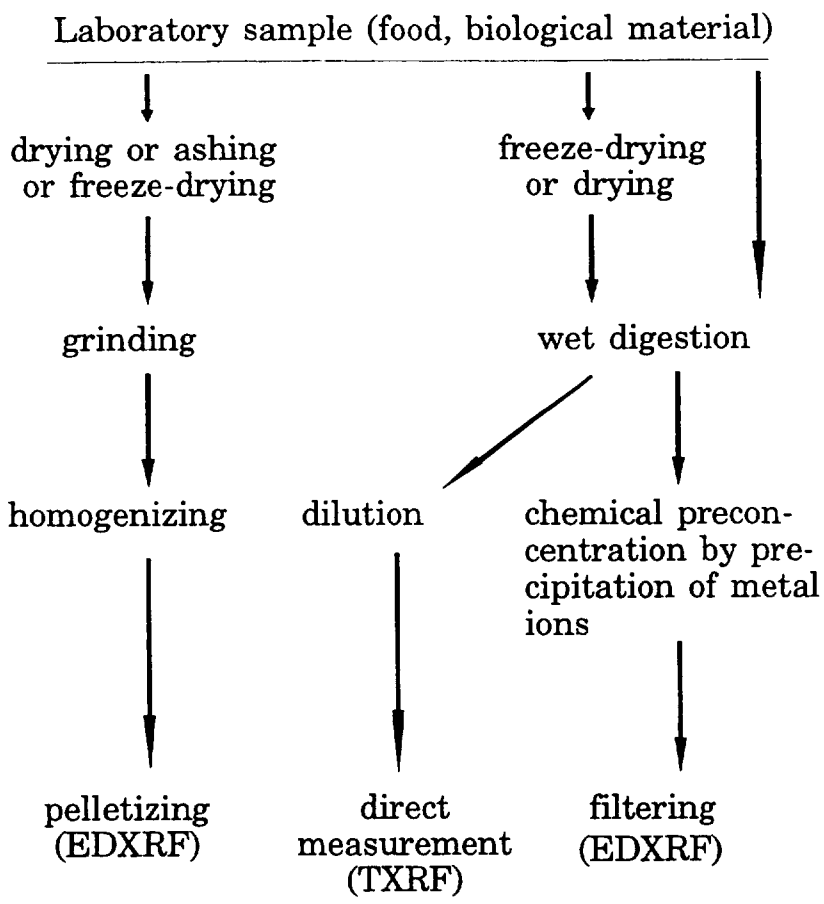

FIG. 4.1. A scheme of biological sample preparation.

4.2.1. XRF

The simplest way of preparing biological samples for XRF is pelletizing the dried and pulverized material. However the detection limits are not low enough to determine the elements in concentrations below a few ppm. In such a case wet digestion is preferable followed by preconcentration. Preconcentration techniques that have been mostly used for water analysis can also be applied for biological samples, such as ion exchange using Chelex 100 resin in the form of granulated beads, precipitation with organic reagents such as NaDDTC, APDC, DBDTC, PAN which form strong insoluble chelates with many transition metal ions. The precipitate is filtered through a membrane or Nuclepore filter, dried and measured.

Below are examples of wet digestion procedures for plant materials and tissues. The properties of the acids are given in Appendix 2.

Examples

Wet digestion of plant material (on electric heater)

One gram of dried plant material (or about 5 g of fresh material) is taken for analysis together with 25 ml of high purity concentrated nitric acid and heated until brown fumes of nitrogen oxides disappeared (≈ 40 min). AFTER COOLING (never pour perchloric acid to warm

acidic solution) 10 ml of 70% perchloric acid is added and the solution is heated again until it becomes colourless and clear (≈ 40 min). After cooling, and diluting by adding 25 ml of double distilled water, the pH is adjusted to about 5 with gaseous NH_3. This is done by placing a beaker with a solution in desiccator filled in the bottom with concentrated ammonium hydroxide. If fresh ammonia is used in the dessicator the pH adjustment takes about 1 hour. In the process, check every 15 minutes the pH with pH paper in the range of 3.5–6.0. For preconcentration of trace metals to be determined (Fe, Zn, Cu, Pb, Ni) precipitation of metal ions with NaDDTC solution is used. Cadmium carrier can be added (10 ml of 10 ppm solution) to facilitate quantitative precipitation. Usually 10–15 ml of 2% NaDDTC water solution (freshly prepared) is added and the resulting precipitate allowed to stand for about 20 min. The precipitate formed is filtered through Nuclepore filter, dried and directly measured [12].

Digestion procedure for animal and human tissue

The digestion mixture contains 10 g of sodium molybdenate (as catalyst) dissolved in 150 ml of double distilled water and 150 ml of H_2SO_4 (conc.). After cooling, 200 ml of 70% perchloric acid is added.

One gram of lyophilized or 5 g of fresh blood or tissue is put in a round bottom flask (150 ml volume) together with 40 ml of digestion mixture. Then the mixture and sample is heated about 1 h at a temperature of 160°C. The obtained solution should be clear. After cooling (NEVER pour perchloric acid to warm acidic solution) and diluting sixfold with water, the solution should be boiled in order to remove chlorine. After cooling the pH is adjusted by gaseous NH_3 to about 5 (see method above). For preconcentration of trace metals to be determined (Fe, Zn, Cu, Pb, Ni) precipitation of metal ions with NaDDTC solution is used. Cadmium carrier can be added (10 ml of 10 ppm solution) to facilitate quantitative precipitation. Usually 10–15 ml of 2% NaDDTC water solution (freshly prepared) is added and the resulting precipitate allowed to stand for about 20 min. The precipitate formed is filtered through Nuclepore filter, dried and directly measured [13].

4.2.2. TXRF

The advantage of applying the TXRF technique is that sample after digestion and dilution can be directly measured. Biological material can be digested after freeze drying or in a fresh form. The digestion in an open system using nitric and perchloric acid can be applied but is not recommended. Evaporation on a quartz carrier takes longer time, the residue is thicker due to the presence of chlorides, which results in higher background and higher detection limit. For the above presented reasons, the digestion in Teflon bomb is highly recommended.

Example

Digestion procedure for biological samples in Teflon bomb

Weigh the freeze dried sample (0.2–0.5 g) on a glossy paper and transfer it to the Teflon bomb. Add 3 ml of concentrated HNO_3 and 1 ml of H_2O_2. Seal the bomb and heat it in an oven for 3–5 hours at 165°C. After digestion, allow the bomb to cool to room temperature for a few hours or overnight. Open the bomb and add 10 µg of cobalt as an internal standard (from 1000 mg/l standard solution). Mix well, and without further dilution, pipet 10 µl of sample solution onto a quartz carrier and dry it under infrared lamp or in vacuum.

NOTE:

1. The concentration of the internal standard used for determination of concentration of elements present in the sample is calculated as follows: in the case when 0.4 g of sample is taken and after digestion 10 µg of cobalt standard solution is added to the sample, the concentration of internal standard is 25 ppm (10 µg/0.4 g ppm).
2. DO NOT use the same Teflon bomb for biological and geological materials.
3. All the acids used for digestion should be ultrapure grade.
4. NEVER use perchloric acid for digestion in Teflon bomb.

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5. ANALYSIS OF WATER SAMPLES

5.1. INTRODUCTION

The relevance of measuring toxic elements in drinking water is obvious. The composition of river water, ground water, lake and sea water may be reflected in the biosphere and affect the composition of our food. Rain water is an indicator for air pollution. Therefore intensive monitoring of the quality of different water types is considered a necessity in many countries.

XRF is, by its nature, preferentially used for solid samples and is not very suitable for the assessment of dissolved components in aqueous samples; some preconcentration is often necessary and other trace analysis techniques as AAS, ICP-AES and ICP-MS will generally perform better than XRF in this field. However XRF is superior to analyze the suspended fraction in aqueous samples. It is also excellent to analyze sediments (see Chapter 3); sediments are very good integrating indicators of water quality; they are easy to sample and their heavy metal concentrations are usually sufficiently enriched to allow high quality and simple routine XRF measurements.

TXRF, on the other hand, is by its nature uniquely suited for multi-element trace analysis of aqueous samples; especially for those that contain little salinity and hardness, as e.g., rain water. In such cases it outperforms most other methods.

5.2. SAMPLING, SAMPLING STRATEGY AND SAMPLE STORAGE

5.2.1. Rain water

The rain water collector, officially adopted by the American Society for Testing and Materials [1] consists of a 633 cm^2 PVC funnel with 60° slopes, which is well fitted to the 2 l polyethylene (PE) collection bottle. It is supported by a stainless steel framework. The funnel is protected from dry deposition with a well fitting plastic bag. At the beginning of each rain shower the funnel is manually (or automatically) uncovered. Immediately after the shower the collection bottle is emptied in a 250 ml acid cleaned PE bottle and the funnel is rinsed with ultra pure water.

For sampling the suspension from the rain, the following procedure is recommended: immediately after rain sampling, the suspended matter is filtered off on a 25 mm diameter Nuclepore 0.4 μm aerosol-grade polycarbonate filter by using, for example, a Millipore 25 mm glass vacuum filter holder or similar with 30 ml funnel and with glass frit filter support. These small filters are used because the collected quantity of rain and the number of suspended particles in rain water are small in comparison with e.g., sea water. Blanks are taken by placing a filter in the filter holder and adding 50 ml of ultra pure water. Before use the funnels and collection bottles are acid cleaned with the following procedure:

1. Rinse in ultra pure water
2. Soak 3 nights in 10% HNO_3 (pro analysis)
3. Rinse in ultra pure water
4. Soak 3 nights in 10% HNO_3 (pro analysis)
5. Rinse in ultra pure water
6. Soak 3 nights in ultra pure water
7. Rinse in ultra pure water
8. For storage the bottles are kept closed, the filter holder is closed and wrapped in protective paper.

All necessary lab ware should be cleaned in the same way.

Generally all water samples are preserved for storage by either acidification to pH1.7 with ultra pure HNO_3 or freezing or both. When the samples are frozen, they should never be filled up for more than about 80%; otherwise expansion due to freezing can drive out the last millilitres from the bottle, and because of fractional crystallization, these are enriched in many trace elements. The filters loaded with suspended matter from rain are air dried in Millipore Petri dishes and stored in a deep-freezer.

5.2.2. River water

River water sampling is commonly done with the use of PE bottles cleaned in the same way as it is described in Section 5.2.1. The samples are commonly taken at half depth of the river and at the point where total mixing with the carrier stream occurs. The problem of the representativeness of measurements from a single sampling station at a river section is well known. Thorough mixing of water-bodies may be completed only at a large distance.

Immediately after the sample is taken, 1 l of it is filtered through a weighed 0.4 μm Nuclepore filter (pressure filtration). The filtrate is acidified, immediately after the separation with HNO_3 (to pH1.7; often 4 ml l^{-1}) and stored in a precleaned PE bottle in a refrigerator until analysis. The particulate matter loaded filter is stored in a precleaned plastic dish and is dried and weighed before analysis. Separation of the phases could be also done by centrifugation at 3000 units of g, with a sample volume of about 5 l (g is the gravitational acceleration).

5.2.3. Tap water

To collect a representative tap water sample, one should take care to have the water running for at least 30 min., after stagnation of the water has occurred in the tubing system, e.g., overnight.

5.2.4. Sea and lake water

Many recipes exist to collect deep waters. One is to take sea water samples with a 10 l PTFE so-called Niskin bottle on a stainless steel wire which is free from rust [2]. A messenger, made of bronze, is allow to fall down along the wire; via a special mechanism, it closes the Niskin bottle at a certain depth. Other sampling devices are so-called Mercos-samplers. Such systems tend to be expensive (about 2000 USD) but are normally present on all oceanic or limnological research vessels. The unfiltered sub-samples are tapped in 1 l PE bottles which have been washed with acid (see Section 5.2.1) and rinsed with sample water.

Surface water samples can directly be taken into a cleaned PE bottle from a rubber dinghy at a distance of about 350 m from the ship to avoid contamination from the hull [3].

Since it is important to minimize the time between sampling and filtration, as interaction between the dissolved and particulate phases may occur, filtration is done immediately after sampling. The suspended matter is filtered off on e.g. 47 mm diameter 0.4 μm pore-size aerosol-grade polycarbonate filters by using a Sartorius SM 16510 polycarbonate filter holder. Before use, the filter holder and all glass lab ware are cleaned with the same procedure used for storage bottles. To remove the freshly crystallized sea salt, the filters are washed three times with 50 ml of ultra pure water. A blank is obtained by putting a filter in the filter holder and adding three times 50 ml of ultra pure water.

Samples are preserved for storage by either acidification with ultra pure HCl (for 0.5 l of sea water, add 1 ml 30% HCl) or freezing or both. The filters loaded with suspended matter from sea water are dried in Petri dishes, and stored in a deep-freezer. For the case something should go wrong with the filters, some of the unfiltered water is also stored in 250 ml PE bottles.

To avoid any contamination at the extremely low trace metal concentrations present in sea water, all handling and chemical operations of the samples should be done under clean room conditions.

5.3. SAMPLE PREPARATION FOR XRF

The major problems with liquids, when analyzed directly by XRF in a cup with a thin Mylar bottom foil, are:

- high X ray scatter background resulting in poor limits of detection
- evaporation of the solvent
- bubble formation during the analysis what changes the analyte line intensity
- poor sensitivity for low atomic number elements whose radiation must pass through the window of the sample cup
- unsuitable for vacuum irradiation
- heating during irradiation may cause chemical reactions or ionization of liquid due to the interaction with radiation
- spilling of water sample during the measurement might severely damage the detector window.

Typical detection limits with 30 min counting times are in the ppm range and this is absolutely not sufficient for environmental applications (although it may be sufficient for some industrial problems).

Indeed, the dissolved trace element concentrations in natural waters are often so low, that a preconcentration step is needed. In principle, any preconcentration and separation method developed for any analytical technique could be used in combination with XRF, but multielement preconcentration leading to solid thin targets is ideal. In an exhaustive overview, dating back to 1982 [4], over 150 references were already given and numerous additional recipes have appeared since then, both for multielement and single element water analysis by XRF. The most relevant of these will be outlined below. It should be borne in mind, however, that preconcentration can be labour- and time-consuming, that it does imply additional risks for sample contamination and may be inaccurate because of the possibly different behaviour of the different chemical species of an element. On the other hand, the detection limits can sometimes be lowered spectacularly, interelement effects may be reduced and the sample may be converted into the most convenient form for XRF analysis, i.e. a thin homogeneous solid target.

For suspended matter, the ideal preconcentration step is very simple; filtration through e.g. Nuclepore membranes with 0.4 μm pore-size (this is the conventional limit between "dissolved" and "particulate" matter in environmental water samples), much as has been discussed for aerosol analysis (see Section 2.2.2).

5.3.1. Physical preconcentration

Direct physical removal of the water matrix is interesting for rain water, which leads to little residue, and especially for waste and sewage waters, which are so complex and so much loaded with organic material, that they are difficult to analyze in any other way. In the residue, all elements are collected quantitatively.

A large water sample can be directly evaporated or freeze-dried, and the residue can be pelletized, possibly after mixing with an organic binder to reduce matrix effect variations. Freeze-drying of 250 ml of waste water on 100 mg graphite followed by grinding and pelletizing of the residue can lead to XRF detection limits of 5 $\mu g\ l^{-1}$.

5.3.2. Chemical preconcentration

Many different approaches have been proposed. Electrochemical preconcentration, use of ion exchange columns and solvent extraction are not very interesting because they lead to targets

that are not ideal for XRF or because the resulting enrichment factors are poor. Preconcentration by filtration through ion exchange or chelating membranes seemed promising at some time, but at present it is not to be recommended because such filters are not readily available commercially and because of their limitations for environmental water which are often rich in alkali and alkaline earth ions. Chelation and subsequent sorption immobilization performs well, even in waters with a high natural organic load, but it involves a time-consuming two step procedure.

(Co-)precipation seems to be the method of choice for multielement trace analysis of aqueous samples by XRF. An enormous array of (co)-precipitation reagents has been proposed in the literature and also various ones have been proposed for XRF [4]. The most appropriate ones are: sodium diethyldithio-carbamates (DDTC) and especially ammonium pyrrolidine-dithiocarbamate (APDC) or a combination of both. The carbamates are particularly attractive because of the low solubility of their metal chelates.

In one recommended procedure, the pH of a 100–500 ml of the water sample is adjusted to 3.5. Then 2 ml of a 1% aqueous solution of APDC is added. After 40–60 min. stirring, the precipitate is filtered of on a 0.22 or 0.4 μm pore-size Nuclepore membrane and the loaded filter is analyzed after drying. The detection limits can be below 1 $\mu g\ l^{-1}$ for a suit of cations.

It should be recognized that chemical preconcentration inherently holds some risks. Naturally occurring organic material might interfere with the (co)-precipitation reaction; bringing the sample to pH3.5 constitutes a compromise in this respect: much of the organic material will be destroyed already and adjusting the sample to a lower pH does imply more contamination by the acid. (In some waters, the organic matter content is so high that a prior acid digestion step is needed). Many elements are not collected in the proposed way, e.g., alkali and alkaline earth ions (but they are usually abundant and not of very much interest with respect to environmental contamination) and Mn^{2+} (except at very high pH). And some species of elements might escape precipitation; e.g., Cr^{3+} will be collected but not CrO_4^{2-} . Such problems are inherent to all chemical preconcentration methods.

5.4. SAMPLE PREPARATION FOR TXRF

5.4.1. Rain water

Direct analysis on the carrier

For rain water, an ideal matrix for TXRF, direct analysis may be done. About 100 ml are collected in beakers. To an aliquot of 1 ml, a few drops of HNO_3 are added (acidifying to pH1.7) and a standard solution (a single-element standard, e.g. Co or Ga, at the $\mu g\ ml^{-1}$ level). Standards are prepared by the use of standard solutions and ultrapure water. The standard is homogeneously mixed and aliquots of 5 to 50 μl of the final solution are pipetted on the clean TXRF reflector holders (quartz or plexi). The drop is evaporated under reduced pressure, e.g., in an exsiccator. Drying the samples in an oven is more risky with respect to contamination and should be avoided. The residue of less than 1 μg is further on analyzed by TXRF.

Freeze drying

The freeze drying technique for element concentration is especially recommended for samples without matrix effects and with very low element contents. A volume of 20 ml of rain

water is transferred to a 30 ml PTFE bottle and an internal standard is added (e.g. 50 μg ml^{-1} Co or Ga standard solution). Then, the sample is freeze dried and afterwards, the residue is dissolved in 0.3 ml HNO_3 and diluted with 0.6 ml ultrapure water. After leaching for 2 hours at 85°C, an aliquot of 25 μl is pipetted on the sample carrier, dried and measured. In this way, trace elements in rain water are preconcentrated by a factor of 20, and more elements will be detectable.

5.4.2. River, lake and tap water

Direct analysis

Direct analysis of river water is possible but it can suffer from the high content of suspended matter [5] and the limits of detection are not below 10 ng ml^{-1}. The choice of the sample preparation procedure depends on whether the sample originates from the limnic or brackish region of a river. Direct measurements are feasible when the filtrates are from the limnic region only [6]. In that case, the sample is shaken for 30 s, and 1 ml of sample is pipetted into a small PTFE vessel and mixed with the solution containing 1 μg of Co or Ga as internal standard (1 μg ml^{-1}). An aliquot of 50 or 100 μl of standardized sample is transferred onto a quartz disc, dried and measured. Elements from P to U could be detected in a concentration range from 66 mg l^{-1} for Ca to 3 μg l^{-1} for U [7].

Freeze drying

The filtrate of some 10 ml can be freeze-dried and the residue can be digested with 2 ml HNO_3. The procedure is the same as it is described in Section 5.4.1.

Suspended particulate matter

The suspended particulate matter (SPM), collected on e.g. a Nuclepore filter, is weighed and digested in a small bottle (30 ml) with 1 ml HNO_3 (65%) and 1 ml HF (40%) at 110°C for 3 h. The solution is diluted to about 5 ml and 40 μg of Co or Ga is added as internal standard. Then 20 μl of the standardized sample solution is transferred onto the sample support, dried and measured [7]. Detection limits reach down to 5 μg g^{-1}.

Another simple and convenient method involves the use of microwave power for digestion. The SPM loaded Nuclepore filters are weighed, and then digested with concentrated HNO_3 (4 ml) in a closed Teflon vessel. Heating is done in several steps, each for two minutes, at 300 W. After each heating step, the vessel is cooled. The total digestion time, including time for cooling the vessel, is around 30 minutes. An internal standard is added prior to digestion. After digestion is completed, the sample is diluted with ultrapure water, ultrasonically treated and an aliquot of 10–25 μl is ready for measurement.

5.4.3. Sea water

Direct method

For sea water, direct analysis by TXRF will suffer from the interference by the salt matrix and the generally very low trace metal concentrations. By applying direct measurements, only uninteresting elements like S, K, Ca, Rb, Sr and Ba are determinable.

Preconcentration procedure with the use of APDC (ammoniumpyrrolidinedithiocarbamate)

About 600 µl of NH_3 solution is added to 100 ml of an acidified sea water to obtain a pH between 3–4. Then, 2 ml of freshly prepared 1% APDC solution is added, mixed and allowed to stand for 40 min at room temperature. Then the suspension is filtered through a Nuclepore filter (0.2 µm pore size). The precipitate on the filter is dissolved in 1 ml of concentrated HNO_3 and 10 µl of Co or Ga standard solution is added. An aliquot of 5 µl is pipetted on the reflector and dried before measurement.

Suspended particulate matter

The procedure is the same as for river water (see under Section 5.4.2).

5.5. CONCLUSIONS

While XRF is ideal for suspended matter and sediments from the aqueous environment, for dissolved trace ions it is not as appealing as some alternative analysis methods, since some sample pretreatment is always necessary in view of the usually low levels of e.g. heavy metals. This preconcentration can be simple evaporation or freeze drying for samples of low salinity or hardness, but very often a more tedious and error-prone chemical preconcentration is necessary. Still, with sufficient care and experience, good results can be obtained even for dissolved heavy metal ions. Often, however, for natural waters, the number of relevant ions that is seen simultaneously by XRF, even after a preconcentration step, will be disappointing and limited to five or less.

TXRF, on the other hand, is very well suited for the multi-element analysis of rain water and other dilute samples, and superior to many other trace analysis techniques. Yet, for e.g. sea water with high salt content, a tedious sample pretreatment should be carried out.

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6. SAMPLE PREPARATION FOR X RAY MICRO-ANALYSIS

6.1. INTRODUCTION

Micro-analysis refers to a method in which analytical information is extracted from a small sample or a small sample volume. Although there are no sharp boundaries between the various sample quantities, sample masses of less than 10 mg are considered as sufficiently small to allow the use of the term micro-analysis (see also Fig. 6.1). A well known example in the realm of environmental materials is single particle analysis of aerosols.

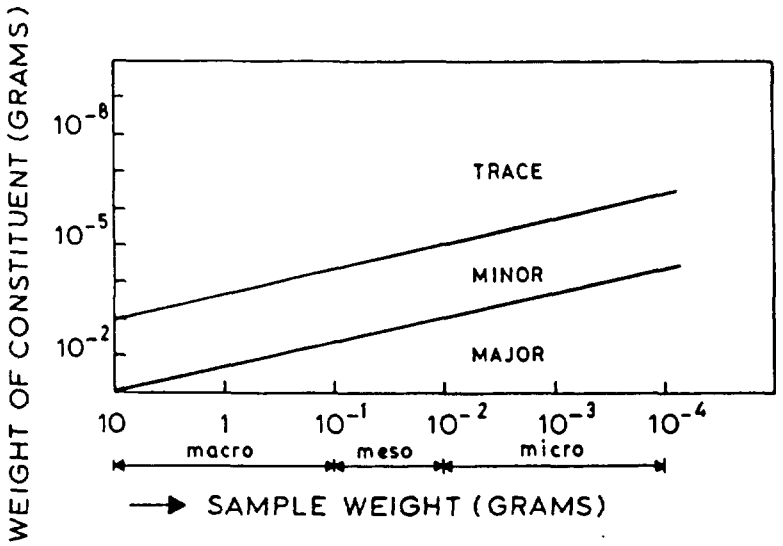

FIG. 6.1. A working definition of micro-analysis.

The other type of micro-analysis is the procedure in which one measures the distribution of the elemental composition on a micro-meter scale. For that purpose, micro-beams incident on the sample are used in the scanning mode. The sample is then divided into volume elements (sometimes called voxels) that are sufficiently small to justify to be referred to as micro-samples. For both types of methods, sample preparation procedures are different and will be discussed separately.

6.2. THE PROBE

It is assumed that the probe is a well collimated and/or focussed beam of X rays. This assumption is important for 2 reasons.

(i) The X ray beam penetrates deeply into the sample. As most samples are inhomogeneous in 3 dimensions, one should be aware of this fact. Measurements aiming at a good spatial resolution have to be performed on samples that are not thicker than the required resolution to avoid information from deeper layers reaching the detecting system.

(ii) X rays do not carry charge and therefore evaporation of a conducting layer on top of samples is not necessary.

6.3. SMALL SAMPLE MASS

In environmental work, the amount of sample is rarely a limiting factor. For detailed studies, however, of the transport mechanism of pollutants, knowledge of the distribution of elements over various types of particles (aerosols, fly-ash) can be very crucial indeed. If one has a large number of particles available and if one is interested in the analysis of a number of single particles, spin rotation of a suspension is attractive. With a diluted solution and a relatively high rotational speed of the substrate one can produce a specimen on which the individual particles are well separated. As a substrate for spin rotation, glass is the obvious choice, but not recommended due to its trace element rich composition. An elegant way out is to spin rotate a suspension of particles in a solution of 1% formvar in chloroform or dioxan. After rotation, one can float off a thin layer of formvar in which particles are embedded and mount the film on a sample holder (see also Fig. 6.2).

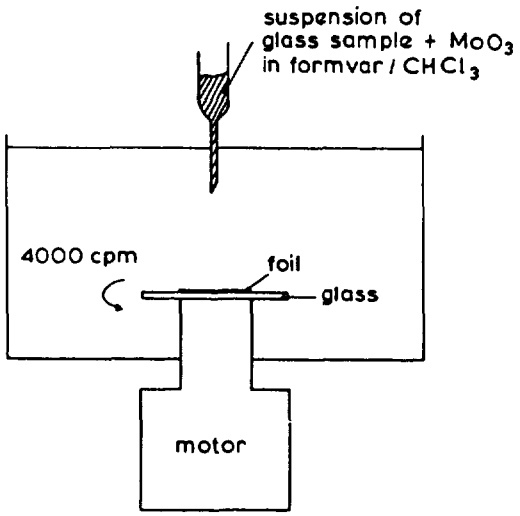

FIG. 6.2. A simple apparatus for spin rotation.

If one has only a few particles available, spin rotation is not an option. Embedding is still possible, although the manipulation of such minute amounts is cumbersome and requires experience. The easiest way out is just mounting of a few particles on a backing using a drop of a diluted formvar solution in chloroform or dioxan. As a backing foil, various plastics are used with trade names as mylar, hostaphane, kimfol, etc.

Sometimes, one can sample aerosols on Nuclepore filter material in such a way that individual particles are distinguishable. These samples can be analysed without further sample pre-treatment.

6.4. SPATIALLY RESOLVED MEASUREMENTS

For successful operation of an X ray microprobe system to obtain elemental maps, sample preparation procedures are very crucial. Apart from the normal requirements for clean operation, dust free sample preparation and, if applicable, pure backing foils, conservation of the trace element distribution is a must. This obviously excludes dissolving, homogenization, adding an internal standard and comparable procedures. Extra requirements are:

(i) The normal structural relationships of the specimen should be adequately preserved. The morphological spatial resolution should be better than the X ray spatial resolution one expects.

(ii) The amount of material lost from or gained by the sample must be known. Also the chemical identity of material lost from or gained by the sample must be known. Losses of KCl or NaCl are reported during freeze-drying. The use of metal-containing fixation agents is an example of selective weight gain.

(iii) The amount of elemental redistribution and translocation within the sample must be known. Although a given procedure may not change the total concentration of an element, it may well have caused gross redistribution of the elements in the sample. Artificial movement of material in the sample is probably the most difficult phenomenon to access.

6.5. PREPARATION OF THIN SLICES OF BIOLOGICAL MATERIAL

6.5.1. Sampling

The selected organ, part of an organ, part of a plant etc. must first be dissected from the organism. Care should be taken to avoid any obvious sources of contamination. The pieces for sectioning should be cut to shape under clean conditions before fixation and embedding.

6.5.2. Fixation and embedding

The samples should be fixated immediately after dissection. In order to minimize chemical contamination, cryo-fixation is the recommended technique, but this requires cryogenic sectioning and handling facilities. Chemical fixation may be used, provided that the method is carried out with a view to minimizing contamination.

6.5.3. Sectioning

Thin sections are cut using a (cryo-)microtome. The selection of the section thickness is influenced by a number of considerations. Thin sections are normally thought of as less than 1 μm.

6.5.4. Mounting

The sections must be collected on a suitable substrate. For soft tissue this is usually a thin plastic foil or a copper grid. The mounting method depends on the type of section. Resin embedded sections may be floated on a water bath and collected onto grids. Cryo-sections must be picked up directly onto a self-supporting foil.

6.5.5. Drying

Finally, if the section is still frozen it must be dried. The simplest method is to allow the sample to dry naturally in air at room temperature. Some samples require freeze sublimation to avoid sample distortion by rapid evaporation of water.

6.6. HAIR SAMPLES

It is worthwhile to pay attention to sample procedures for hair. The value of hair analysis as a monitor for body burden of the various elements is evaluated by the IAEA (IAEA report on the significance of hair mineral analysis as a means for assessing internal body burdens of environmental pollutants; NAHRES-18, Vienna, 1993). Microprobe studies do have the advantage of possibilities to discriminate against influences of external contamination by measuring the part of hair that was still inside the skin.

6.6.1. Sampling

For proper use of hair as sample material it is important to select hairs in the anagen phase. It has been recommended by the IAEA to apply a washing procedure that involves an acetone, several water and finally another acetone wash. For microprobe studies, however, it is recommended not to wash at all. Wiping with a dry and clean tissue to remove dust is appropriate.

6.6.2. Sample preparation

Selected hair is stretched on a sheet of paper and cut using a scalpel blade into segments of 10 mm. This 10 mm hair segment is put into a little hole in the centre of a cylindrical shaped piece of plastic and fixed with a little stabilite. Subsequently, the cylindrical block is covered with a PVC mantle and filled with an araldite resin mixture AY103 with hardener HY956. This resin contains between 1000 and 2000 ppm Cl and a trace of Br, but no other detectable concentrations. The resin is hardened overnight at 315 K. The hardened araldite can easily be stripped of the PVC mantle. The cylindrical piece of araldite, containing the hair sample can be cut in the desired shape. For thin sections a microtome is necessary, preferably equipped with a tungsten-carbide knife. The so obtained araldite sections are stretched with a drop of aqua bidest on a warm glass plate, air dried and glued with a glucose solution on a sample holder.

6.7. MINERAL SAMPLES

Also in the earth sciences, araldite is quite often used to embed small pieces of sample. Problems may arise during polishing of the surface due to differences in hardness of the sample material and araldite. In such cases, waterglass is recommended. It is customary to perform the embedding procedure on a backing, such as a microscopic glass plate. At some laboratories, pure quartz backings are used; these backings allow optical observation in transmitted light and enable to polish thin sections for XRF analysis without being disturbed by the trace elements in ordinary glass.

6.8. SAMPLE STORAGE

All samples prepared for microanalysis should be stored in closed containers and kept dry. For biological sections, it is recommended to store the containers below 0°C.

6.9. MILLI-BEAMS

It is worthwhile to to mention that interesting environmental research can be done with a mm-sized X ray beam. Examples of such studies are the distribution of trace elements over

leaves, cross-sections of roots of trees to measure uptake of trace elements, tree rings to assess seasonal variations and variations over the years etc. In these cases sample preparation is less critical. Again embedding in araldite can be very useful for fixation of the sample. A clean and reasonably flat sample surface is adequate for such analyses as the thickness of the sample is less critical due to the moderate lateral resolution.

7. QUALITY ASSURANCE AND GOOD LABORATORY PRACTICES IN X RAY FLUORESCENCE ANALYSIS

7.1. INTRODUCTION

In analytical chemistry, the term "quality assurance" is the name given to a set of experimental and statistical procedures used to ensure that a measurement process produces data of sufficient quality enough for their intended purposes.

7.1.1. The importance of quality assurance

Quality assurance is necessary for the following reasons:

- to establish the necessary technical and organizational framework to assure quality analytical services
- to prevent and detect departure from technical specification and requirements
- to ensure that results are obtained with predictable uncertainties.

7.1.2. Quality parameters

The major quality parameters (i.e. factors that will affect the quality of results significantly) in XRF analysis are:

(a) Sampling and sample preparation
(b) Instrumentation (physical calibration)
(c) Calibrations (analytical)
(d) Data recording, evaluation, and reporting
(e) Staff competence.

For an effective quality assurance programme, the tolerable limits for the measurement process at each of the recognizable and significant stages of analysis must be established considering the technical and economical factors.

Quality assurance is carried out at two distinct but related levels [1]:

(i) Quality control and
(ii) Quality assessment.

These quality assurance procedures assist in the introduction of principles of Good Laboratory Practices (GLP) in XRF analytical laboratories, for the purposes of obtaining reliable, accurate, comparable and traceable results.

7.2. QUALITY CONTROL

Quality control is the mechanism established to control errors [1]. A quality control programme therefore comprises actions (activities) which provide a means to measure and control the characteristics of an item, process, or facility in accordance with established requirements.

Consequently, quality control programmes must be designed and established for each major quality parameter identified in XRF analysis.

7.2.1. Quality control programmes

7.2.1.1. Sample control programme

This programme should include:

(a) a sampling programme
(b) homogenization and homogeneity test
(c) sample preparation procedures.

(a) Sampling programme

In any sampling programme or plan, the following items must be considered:

1. Reason for taking the samples
   - objectives for the study must be clearly spelt out;
   - clear and concise questions about the problem, for which answers are being sought, must be formulated.

2. Types of sample to be taken
   - choice and nature of the samples is dependent essentially on 1. above, and the XRF facility available.

3. Location of sampling points
   - dependent on the nature, and degree of homogeneity of sample.

4. Size and number of samples
   - influenced by sample homogeneity, number of replicate measurements, and analytical technique available;
   - consideration must be given to the relative amounts of sample to be taken for, (a) field samples, (b) laboratory samples, and (c) analytical samples.

5. Frequency and duration of sampling
   - dependent on sample homogeneity, manpower availability, and equipment limitations.

6. Sampling equipment and techniques
   - The nature of the sample, and sample homogeneity will influence the decision to use either random or systematic sampling. Besides, the sampling technique must not be preferential or cause alterations in the sample.

7. Sample containers
   - Consideration must be given to the elimination of contamination from the containers to the sample.

8. Sample preservation storage
   - This becomes necessary when the sample cannot be analyzed immediately.

9. Transportation and holding times
   - consideration must be given to the nature of the analyte, loss of material, and cross-contamination.

10. Documentation
   - clear and meaningful labeling of samples collected;
   - adequate information about the samples must be documented to assist in the interpretation of results obtained.

(b) Homogenization

Homogenization becomes important in the following samples:

(i) most solid (rocks, minerals, etc.),
(ii) powders (coarse grains), and
(iii) some biological materials (blood, leaf, etc.).

For (i) and (ii) homogenization can be done through grinding or milling to pass a 100-mesh sieve before carrying out a homogeneity test. Grinding beyond 100-mesh can cause absorption or loss of H_2O, CO_2, and S. Excessive grinding may oxidize ferrous iron to ferric [3]. For biological materials homogenization is achieved by means of ashing, oven-drying, or freeze-drying followed by grinding/milling [4,5]. Since the control of particle size is critical, greater control of both sample weight (1–10g, ball mill) and grinding time (5–10 min) is necessary for quantitative analysis [6–8].

Homogeneity test

Test portion of about 50–100 mg (depending on which XRF analytical systems) should have an uncertainty of 3%. The test portions may be from portion to portion of a sample, or from sample to sample.

The degree of inhomogeneity can be expressed as:

$$S_{INH} = (S_a^2 + S_h^2)^{1/2}$$

S_a^2 = variance due to random errors of analysis (i.e. repeatable measurements of one identical sample under identical conditions)
S_h^2 = variance due to random sample inhomogeneity

In addition,

$$S_h^2 = (S_b^2 + S_w^2)^{1/2}$$

where S_b^2 is variance related to inhomogeneity between batches, while S_w^2 is variance within batch. The homogeneity test is performed by counting X ray intensities of some identifiable elements in the sample (refer IAEA homogeneity test procedures for the AQCS programme).

(c) Sample preparation procedures

Refer to Chapters 2–6 of this TECDOC.

7.2.1.2. Equipment control programme

Improper performance of XRF instrumentation may be attributed to:

(a) malfunctioning of equipment due to [9]:
- adverse environmental conditions
- ageing
- incorrect component replacement;

(b) maladjustment of instrument settings
- due to improper training and inexperience of analyst.

The major tools available to the X ray analyst for equipment control is physical calibration by signal analysis, and optimum adjustment of instrumental settings.

Physical calibration

Calibration of preamplifiers, amplifiers, and multichannel analyzers must be carried out occasionally, and after any major repairs. The facilities essential for signal analysis are:

- pulse, and ramp generators
- dual channel oscilloscope
- probes.

The principle in signal analysis is to send appropriate signals to an input and observe whether an output signal is obtained, and has the expected shape and amplitude. Some of the features used in controlling equipment performance are [9, 10]:

(a) For preamplifiers
- ramp signal (sawtooth shape) output
- inhibit signal output.

(b) For amplifiers
- amplitude of output pulse (not exceeding 10 V)
- well-shaped signal (gaussian).

(c) For multichannel analyzers
- linearity test (using integral non-linearity (INL), and differential non-linearity (DNL))
- the ratio FWHM/FWTM.

Optimum settings

Factors considered in adjustment of XRF equipment for optimum performance include:

(i) baseline restoration
(ii) dead time and pile-up rejection
(iii) pole zero cancellation.

For (i) and (ii) it is necessary to monitor equipment response (effects) when switched on, and then when switched off.

7.2.1.3. Analytical calibrations

Analytical calibrations are required to relate instrument response to chemical quantification [1]. In XRF analysis this may be categorized as:

(a) energy calibration
(b) efficiency calibration
(c) sensitivity calibration
(d) spectrum analysis.

(a) Energy calibration

A useful range for carrying out energy calibration is 2.3–17.4 keV, involving the use of standard samples ranging from sulphur (S) to molybdenum (Mo). Once an energy calibration has been done for an XRF spectrometer, it must be verified prior to the commencement of analysis everyday. Another energy calibration must be carried out each time some equipment settings like amplification, shaping time, etc. are changed. Nevertheless, the equipment settings should be such that it gives an energy calibration equation having a gradient of about 20 eV/channel.

(b) Efficiency calibration

Efficiency calibration must be done within the same energy range as that used for system energy calibration. Critical parameters that control accuracy in estimation of efficiency values include:

* Detector physical parameters
  - beryllium window thickness
  - gold layer thickness
  - dead layer thickness
  - detector sensitive volume
* Sample- source-detector geometry.

These values must be accurately specified as inputs to the "system sensitivity and efficiency calibration" portion of the software program (QXAS).

In the QXAS programme, an acceptable efficiency calibration is achieved when the efficiency values reported in the calibration report under EFF-EXP and EFF-CAL have a reasonably good agreement

(c) Sensitivity calibration

System sensitivity calibration must be done in the same energy range as in (a) and (b) using standard samples in any of the following forms (in order of preference):

- pure metal foils
- pure powder
- high purity oxides
- other non-hydrated or non-hygroscopic chemical compounds.

The chemical compounds used should be of analar grade quality and the standard samples must be properly stored (in sheets and appropriate containers for metal foils, and in a desiccator for pelletized standard samples).

The goodness of the sensitivity calibration can be verified by:
(i) visual inspection of a plot of the sensitivity curve;
(ii) variation coefficient of the geometrical factor G, calculated using the sensitivity values obtained. A variation coefficient of $\leq 10\%$ is an indication of a good sensitivity calibration.

(d) Spectrum analysis

Every single peak in an X ray spectra must be identified and accounted for. To this effect care must be given to the possibility of:

- escape peaks
- sum peaks
- spurious signal from electronic effect.

In addition the quality of the spectrum fitting can be controlled using the following features:
- χ^2 difference
- residual plot.

7.2.1.4. Data recording, evaluation, and reporting

The evaluation, review and reporting of analytical data and results is an important aspect of quality control. Guidelines for data evaluation have been developed by ACS Committee on Environmental Improvement [1, 11].

Raw data must be properly stored in an easily retrievable manner (e.g. computer storage on 3.5" diskettes with hard copy printouts filed as back-up). In addition, laboratory records should be kept in note books on issues such as:

- description of samples
- instrumental settings
- calibrations
- experimental procedures.

The records for each analysis must contain sufficient information to permit satisfactory repetition of the analysis [12]. Care must also be given to the format of presentation of evaluated analytical results, considering ease of assimilation by the reader. Some recommended format has been attached as Appendix 5.

7.2.1.5. Staff competence

Factors to be considered include:

- educational background
- training
- experience.

These can be improved by:

- participation of analyst in international, regional and national training courses, workshops, seminars and conferences;
- attachment to experienced laboratories;
- local on-the-job training.

Furthermore, for XRF laboratories with access to later versions of the QXAS program, each analyst in the laboratory must perform the various calibrations using the accompanying set of standard and sample spectra.

7.3. QUALITY ASSESSMENT

This is a mechanism (procedure) used to verify that the analytical process is operating within acceptable limits. It therefore evaluates the effectiveness of the quality control programmes, and ascertains that the uncertainty of results reported are within defined limits. Quality assessment can be done internally or externally [13].

7.3.1. Internal quality assessment

Internal quality assessment, also referred to as statistical quality control, deals with precision. These internal procedures include the use of replicate measurements to verify repeatability and reproducibility [14] of both sampling and measurement processes.

The precision of individual results is determined from a combination of independent random errors associated with different stages of the measurement process [15]:

$$\sigma^2 = \sigma_a^2 + \sigma_b^2 + ... \sigma_n^2$$

The contributions to the overall uncertainty may be due to:

- variations in blank value
- variations in calibration factors
- counting statistics.

In the analysis of precision, agreement between measured standard deviation and derived (using Poisson Statistics) standard deviation is an indication that the analytical method is in statistical control [16], and that random sources of variability have been accounted for. Significant deviations (disagreements) points to the presence of non-random sources of error (systematic errors).

7.3.2. External quality assessment

This assessment enables the validation of the accuracy of the analytical results. Accuracy is influenced predominantly by:

- faulty standards or calibrations
- use of erroneous physical constants
- matrix effects
- calculation errors
- unknown sources of error.

Accuracy can be assessed by:

7.3.2.1. Analysis of reference materials

Certified reference materials (CRM) and standard reference materials (SRM) must be analyzed under similar conditions as in routine analysis. At least, about three different reference materials must be analyzed prior to analysis of unknown samples.

7.3.2.2. Use of different analytical techniques

Whenever possible, where there is access to other analytical techniques using different physicochemical principles (e.g. NAA, AAS, etc.), the sample can be analyzed with these different methods. The results will reveal the biases in the analytical method of interest.

7.3.2.3. Interlaboratory comparisons

Another quality assessment technique is to participate in properly organized interlaboratory comparison programmes, such as the IAEA's AQCS programme.

7.4. GOOD LABORATORY PRACTICE (GLP)

Good laboratory practice (GLP) is concerned with the organizational process and the conditions under which laboratory studies are planned, performed, monitored and reported [17, 18].

GLP principles are established taking the following factors into consideration:

1. Laboratory facilities
   - appropriate facilities, equipment, reagents, and materials must be made available.

2. Staff
   - training, proficiency tests, and responsibilities need to be spelt out and documented.

3. Operating principles
   - Standard operating procedures (SOPs)
   - Sampling and tested practices in the laboratory.

7.5. CONCLUSIONS

The above discussions provide only a framework for producing quality analytical services in XRF laboratories. The design, development, and implementation of a GLP for a particular laboratory remains the responsibility of the entire team of an XRF analytical group.

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Appendix 1

SAFETY PRECAUTIONS IN THE LABORATORY

General rules of safety while handling acids

- When working with acids, always wear eye goggles, gloves and a laboratory coat.
- Carry out as much work as possible in an efficient fume hood or in a well ventilated area.
- Always transfer acids over a sink in order to catch any spills and afford a ready means of disposal.

Additional precautions while using 73% $HClO_4$ acid

- In wet combustion with perchloric acid, treat the sample first with nitric acid to destroy easily oxidizable matter and allow the solution to cool down before adding $HClO_4$.
- Any procedure involving heating of perchloric acid must be conducted in a perchloric acid fume hood with the sash down.
- No organic materials should be stored in the perchloric acid hood.
- Do not allow perchloric acid to come into contact with strong dehydrating agents (concentrated sulfuric acid, anhydrous phosphorous pentoxide, etc.).
- Perchloric acid should be used only in standard analytical procedures from well-recognized analytical texts. This does not apply to analytical research workers.
- Keep the quantities of perchloric acid handled at the bare minimum for safety.

First aid in case of an accident

- Acid splashes should be immediately removed from the skin with plenty of cold water. Continue the treatment for at least 5–10 minutes to avoid burns. Skin that has been in contact with concentrated HF acid should be washed with plenty of water and then 2.5% calcium-gluconate gel should be applied and rubbed into the skin. Application of this gel should be continued for 3 to 4 days.
- Acids entering the eye should be rapidly and thoroughly rinsed out using a special eye wash bottle. If the acid is HF this immediate rinsing should be followed by application of an ice-pack. The ice-pack should remain in place until medical treatment is available.
- If acids enter the mouth during pipetting, plenty of water and milk of magnesia solution should be used to wash the mouth thoroughly.
- In all cases of accidents, after applying first aid, medical check-up or treatment is required.

Appendix 2

PROPERTIES OF DIFFERENT ACIDS

Nitric acid
HNO_3

- strong oxidizing agent
- forms highly soluble nitrate salts
- efficient for decomposition of biological matrix
- boiling point 121°C (open system)
- boiling point 176°C (closed system)

Hydrochloric acid
HCl

- excellent solvent for certain metal oxides, sulphates, silicates and fluorides
- forms soluble chlorides salts
- boiling point 91.8°C
- used in combination with HNO_3 (aqua regia HNO_3:HCl (1:3))

Hydrofluoric acid
HF

- excellent reagent for silica based material
- forms volatile SiF_4
- boiling point 106°C (open system)
- boiling point 180°C (closed system)
- used in combination with other acids

Sulphuric acid
H_2SO_4

- strong oxidizing agent (in conc. form)
- effective solvent for all organic compounds, some inorganic oxides, hydroxides, alloys, carbonates
- ***forms insoluble sulphates with Sr, Ba, Pb and Ca***
- boiling point 339°C
- used in combination with other acids

Perchloric acid
$HClO_4$

- very strong oxidizing agent (in hot conc. form)
- thoroughly decomposes organic material
- places elements in their highest oxidation state
- ***potentially explosive in contact with organic material, should not be used in closed system***
- boiling point 203°C
- ***should never be used on its own*** (always in combination with other acids)

Appendix 3

SAMPLE IDENTIFICATION

Sample identification is very important and should be decided before the sampling or before leaving the lab in the sample collection trip. Identification materials should be collected: labels, if to be used, stickers or paper slips, permanent ink pens capable of writing directly on containers, log books, etc. Codes should be decided beforehand and entered in the Collection Log Book. The use of computers restricts identification to 8-character words. Use common first 1–3 digits for a family of samples. Then your computer sorts them out automatically.

Labels may be lost or deteriorated with time or humidity and the sample identification lost. Use a double bag for sample protection and identification preservation. Use graphite pencil on paper rather than ink as it better withstands humid conditions.

Upon entrance to Laboratorium samples are recorded in the Lab Log Book. The following information is recorded:

1. Name or number of sample
2. Date of collection
3. Person who collected
4. Description of place of collection (see below)
5. Date brought into lab.
6. Date of sample process (for analysis)
7. Comments.

Sampling location identification

In many cases the location of the sampling point is very important such as in studies of pollution distribution, toxic element source location, etc. For this it is necessary to be able to locate the sampling point in a map and eventually in the report of the study. For this a GPS receptor is recommended (Geo Positioning System satellite receptor). This instrument provides accurate and efficient location of the sample collection point. The instrument provides geographical coordinates: latitude, longitude and height above sea level. A sampling point can be located with an accuracy which depends on the cost of the instrument (down to ±one meter in the very expensive instruments). With moderate-priced instruments (ca. $500) the accuracy or repeatability is ± 200 meters. Hence it is easy to place concentration distribution (maps used: Scales of 1:500 000 (national level); 1:250 000 (regional level); 1:200 000 (local level) and 1:25 000 (very local level)). The GPS may not be used to relocate the precise point of sample collection due to positioning error. This has to be done with location description from the Log Book.

Appendix 4

CLEANING OF SAMPLE REFLECTORS, PTFE BOMBS AND GLASSWARE

A number of procedures have been published. It is appropriate for cleaning a few reflectors (1 to 15) in a manual way. Whatever procedure is used, one or more control reflectors should always be tested to assure cleanliness. The following procedures for cleaning of sample reflectors have shown to produce good results.

Procedure I

1. Mechanical cleaning with soap of previous deposit using fingers or soft tissue to rub the surface.

2. Rinsing with distilled water and transfer to a clean beaker.

3. Boil in 10 volume % of analytical grade nitric acid for 15 min. Reflectors are left in this solution, by covering the beaker or they are transferred, with Teflon pincers (or with Teflon tape-covered metal pincers) to a covered beaker containing ultrapure water. This beaker is taken to the clean room or to the laminar flow cabinet for the next step.

4. Each reflector is taken out with the Teflon protected pincers and is rinsed twice with a washing bottle: The first time with deionized ultrapure water and immediately, the second time, with distilled ethanol or acetone.

5. The reflector is immediately dried by rubbing lightly with tissue paper and placed in a covered box (Petry dish is recommended).

6. The reflector should be used soon after cleaning. Storage produces contamination unless the environment is absolutely clean.

Procedure II

1. Clean the reflectors with a paper tissue (ordinary Kleenex paper) under running double distilled water from a wash-bottle to remove any previous sample or dust particles.

2. Rinse the reflectors thoroughly with double distilled water.

3. The reflectors should be kept for 2 h in about 1% EDTA basic solution (in pH about 10) at temperature just under boiling point (use water bath). The EDTA solution should be made out of double distilled water and be freshly prepared, pH should be adjusted by adding ammonia solution.

4. After 2 h take out the reflectors from ***hot solution***.

5. Rinse the reflectors with double distilled water until you get the water after rinsing — pH6.0 –7.0.

6. Then the reflectors should be kept for 1 hr in nitric acid (5–10%) solution (use supra pure acid or subboiled acid). The temperature just under boiling point (use water bath).

7. After 1 hr take the reflectors from ***hot solution***.

8. Rinse the reflectors thoroughly with double distilled water until pH is about 6.

9*. Finally rinse the reflectors with acetone (Analytical Grade) and dry them in a clean place under dust free environment at 30°C.

10. Keep reflector in covered containers to avoid contamination.

* optional – if you notice Ca and K peak in a spectrum of double distilled water, then rinse the reflector with acetone.

NOTES

a. Mechanical cleaning must be very gentle. It is easy to scratch the reflector surface. Avoid cloths, sponges or materials used for domestic cleaning as they often contain abrasives. A scratched reflector increases background and is very difficult or impossible to clean. Repolishing of the reflector surface is possible and is about half the price of new reflectors.

b. About soaps. Soaps and household domestic detergents can be a source of contamination. Simple pure soap (often sold for hand washing of clothing) is best. Locally available soaps should be tested by hand-washing a reflector rinsing and drying, then test in the TXRF to select the best soap.

c. Tissue paper. Locally available tissue paper has to be selected by trial and error. Very clean results are often obtained with cheap, light brown coloured toilet paper. This is better than white Kleenex, soft facial tissue or white toilet paper all of which have traces of bleaching agents and often contaminate with chlorine.

d. Analytical grade ethanol, propanol or acetone may be substituted by commercial grade, denatured ethanol or rubbing alcohol which is distilled for best results in a laboratory glass still.

e. Conditioning of the reflector surface. The surface of reflectors may be made hydrophobic to prevent aqueous drops from spreading out. This is accomplished by siliconizing the surface. For this a commercial silicone oil spray can may be used (normally sold for furniture or for car maintenance): Hold the reflector at 30 cm away from the can and spray for one second. Then lightly rub the surface with tissue paper. To make the surface lipophilic, in order to spread out the drop in direct oil analysis, rub the surface with polyvinyl alcohol. In alternative method for the surface conditioning, 10 µl of silicone solution in isopropanol (Serva 35130) is put at the center of the reflector (the spot should be of diameter of at least 10 mm). After heating the reflector in oven for 1–2 h at a temperature of 80°C, and then cooling, the reflector is ready for use.

f. Very often, a reflector may be re-used with a shortened cleaning procedure just after use, particularly if vacuum dried. Then in Procedure I, skip steps 1 to 3 and go straight to step

4 with softly rubbing of the old sample with tissue paper while rinsing with deionized water. Check the cleaned surface in this case.

Cleaning of PTFE bombs

1. Fill a bomb with hot 1% EDTA basic solution (pH10 adjusted by ammonia) and keep it for 2–3 h in the oven in a temperature about 80°C.

2. Rinse the bomb with double distilled water until you get pH of about 6–7.

3. Pour (depending on the size of the bomb) 2, 4 or 6 ml of suprapure or subboiled HNO_3, tighten the metallic part of the bomb properly and put the bomb to oven for 3 h at 170°C.

4. After digestion wait until the bomb cools down to room temperature.

5. Unscrew the bomb holder, take 10 µl and place on the reflector, dry it and measure. If the spectrum of acid shows the presence of contamination – repeat the cleaning. This should be repeated until no contamination is observed (measuring time 1000s).

Cleaning of glassware

1. Beakers* should be filled with hot 1% EDTA basic solution and kept for 1 hr in water batch.

2. Next rinse the beakers with double distilled water until you get pH about 6–7.

3. Fill a beaker with 5–10% nitric acid (ultra pure) and keep for 1 hr in water bath, then rinse with double distilled water thoroughly until pH of about 6–7.

*Use only polypropylene or polyethylene beakers.

Appendix 5

SAMPLE FORMAT FOR "REPORT OF ANALYSIS"

REPORT OF ANALYSIS

No. ...

1. Analytical Laboratory:

2. Client:

3. Type of analysis requested:

4. Sample description:

5. Analytical methods:

6. Sample preparation:

7. Instrumental setup and measurement conditions:

8. Results:

9. Quality control test(s):

10. References:

11. Analyst(s):

_____ _____

Date Analyst Signature

12. Approved by:

_____ _____

Name Signature and Date

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