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FOREWORD

The IAEA has programme the utilisation of nuclear analytical techniques (NATs), in particular for industrial and environmental applications. A major purpose is to help the developing Member States apply their analytical capabilities optimally for socio-economic progress and development. A large number of institutions in Europe, Africa, Latin America and Asia have established X ray fluorescence (XRF) and gamma ray measurement techniques and facilities for neutron activation analysis (NAA) have been initiated in institutions in these regions. Moreover, there is a growing interest among many institutes in applying more advanced analytical techniques, such as particle induced X ray emission (PIXE) and microanalytical techniques based on X ray emission induced by conventional sources or synchrotron radiation to the analysis of environmental and biological materials and industrial products.

In order to define new areas of application of NATs and to extend the range of these techniques, a number of initiatives have recently been taken. It includes a workshop on industrial and environmental applications of nuclear analytical techniques, organized by the IAEA in Vienna, 7–11 September 1998.

The main objectives of the workshop were as follows: (1) to review recent applications of NATs in industrial and environmental studies; (2) to identify emerging trends in methodologies and applications of NATs; (3) to demonstrate analytical capabilities of selected NATs.

The following topics were reviewed during the workshop: (1) XRF and accelerator based analytical techniques; (2) portable XRF systems and their applications in industry, mineral prospecting and processing, (3) portable gamma ray spectrometers; and (4) NAA and its applications in industry and environmental studies. Micro-XRF and micro-PIXE methods and their applications in the above fields were also discussed, including aspects of synchrotron radiation induced X ray emission.

The major part of the drafting of the final version of the reviews was done by J. Kučera. The IAEA officers responsible for this publication were A. Tajani, Agency's Laboratories, Seibersdorf, and U. Rosengard, Division of Physical and Chemical Sciences.

EDITORIAL NOTE

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ANNEX — PAPERS PRESENTED AT THE WORKSHOP

1. INTRODUCTION

What are nuclear analytical techniques (NATs)?

In principle, NATs may be considered to be based on the utilisation of certain properties of the nucleus itself, in contrast to non-nuclear techniques which utilise the properties of the atom as a whole, primarily governed by the properties of electron shells. This feature of NATs might be taken as a basis for the very narrow definition. It should be pointed out, however, that a contradictory "narrow definition" was recently given by de Goeij and Bode [1.1]. On the other hand, the term NAT is frequently associated with the phenomena of ionising radiation and isotopes. Thus, besides nuclear excitations, nuclear reactions and/or radioactive decay, the utilisation of the processes involved in electron inner shell excitations is also regarded as pertinent to NATs. Moreover, some of the NATs of the latter category, such as synchrotron radiation-induced X ray emission and PIXE can only be performed using nuclear instrumentation, namely various accelerators. According to the above "narrow" definitions, there also are techniques which certainly fall into the category of NATs but sometimes are not considered in this context. Examples are mass spectrometry, nuclear magnetic resonance (NMR) and the use of stable isotopes, because in these techniques ionising radiation is neither produced nor utilised.

Whereas in non-nuclear techniques isotopes of the same element generally cannot be distinguished, in some NATs specific isotopes are measured instead of elements. However, since the naturally occurring poly-isotopic elements have constant isotope ratios, direct quantitative information on the particular elements is obtained. Since isotopes of a given element may be discriminated, analytical information may be obtained by using element enriched in a particular stable isotope or labelled with a radioisotope, e.g. in isotope dilution analysis. Thus, both nuclear and isotope techniques should be considered under the common term NAT.

It appears from the above discussion that fundamentally as well as practically no sharp borderline is useful between nuclear and non-nuclear analytical techniques. Mass spectrometry deals with ionised atoms, and rarely with the bare nucleus; however, the signal is determined by the mass differences of the nucleus. Some NATs are based not only on nuclear properties, but on a combination of nuclear and electronic properties, either within a single technique or within two techniques. Examples of the first category are NMR and Mössbauer spectrometry, where the nuclear signal is fine tuned by the electron energy levels, also giving information on the chemical state. Examples of the second category are modern chemical separation methods coupled to radioactivity detection or mass spectrometry. PIXE as one of the varieties of ion beam analysis, deals with electron shell ionisation and thus is formally a non-nuclear technique. However, since PIXE requires almost the same equipment as other ion beam techniques, it is mostly incorporated in the domain of nuclear physics and most frequently is considered as a NAT. To a lesser extent this is also the trend for the various new modes of XRF [1.1].

The various possible definitions of NATs and their discussion justify the selection of NATs that are included in the present publication. During the workshop, both the invited experts and the IAEA staff members presented reviews of the selected NATs concerning mainly recent developments, advantages and limitations, and present and emerging applications in industry and the environment. The reviews were edited to achieve a similar format of the individual parts in order to express that the participants agreed on the issues discussed. In Annexes, presentations of the individual experts are given. They describe in more detail typical or illustrative applications of NATs or such applications that can be considered typical for a certain country or region. No editorial work has been performed in this part of the publication.

REFERENCE

[1.1] DE GOEIJ, J.J.M., BODE, P., "Nuclear analytical techniques: Strong and weak points, obstacles and opportunities", Harmonization of Health Related Environmental Measurements Using Nuclear and Isotopic Techniques (Proc. Symp. Hyderabad, India, 1996), IAEA, Vienna (1997) 3–15.

2. X RAY FLUORESCENCE ANALYSIS

2.1. WAVELENGTH-DISPERSIVE X RAY FLUORESCENCE ANALYSIS

X ray spectrometry is based on the generation of characteristic X rays from a sample by an energetic beam of photons or ions. When X ray photons are used as the excitation source, the technique is called X ray fluorescence (XRF) analysis. In XRF, fluorescence spectra can essentially be measured in two ways. In wavelength dispersive XRF (WD-XRF), the collimated characteristic X rays are spatially resolved by Bragg diffraction from suitable crystals or multilayer devices and the intensity is then measured with gas proportional counters or scintillation detectors. The critical part of a WD-XRF instrument is the requirement for highly precise repositioning of the crystal and detector, which is routinely done with a repeatability of one thousandth of a degree [2.1-2.7]. In the alternative energy dispersive XRF (ED-XRF), the characteristic X ray spectrum is measured directly with a solid state detector. In many ways, the ED-XRF detector technology is directly related to similar developments in nuclear technology.

The first WD-XRF instrument of modern design was described in 1948, and incorporated a high-intensity, sealed X ray tube, and a Bragg spectrometer with a Geiger counter detector. Since then, WD-XRF has become the real working horse in industry for the analysis of solid materials, such as metals, cement, chemicals, glass, ores and geological materials in general. Usually, solid samples are analysed in the form of metal discs, pelletised powders or fused glass discs. There are now some 15 000 WD-XRF units in operation worldwide, in comparison with only 2000 ED units including instruments incorporated in electron microscopes. Enormous numbers of element determinations are undertaken daily by WD-XRF. In contrast, some 60% of the present XRF literature deals with ED-XRF, reflecting the fact that WD-XRF is widely used for routine and established applications in industry, rather than in research.

WD-XRF has some advantages over ED-XRF: the spectral resolution of WD spectrometers is better for low-Z elements and commercial systems are generally fully automated, and offer better precision in analytical measurements. There have been some gradual but significant improvements in WD-XRF instrumentation over the years; however, no radical and fundamental changes have been noted recently, contrary to what is the case for ED-XRF. Also, the price of WD-XRF instruments can be prohibitive for small to medium enterprises and can vary from some US $ 300 000 for sequential instruments (in which measurements are made by scanning the characteristic lines of selected elements one after another) to US $ 500 000 or more for dedicated simultaneous systems. In view of the current status of XRF and the fact that the IAEA has to date focused mostly on the ED-XRF mode, WD-XRF will not be considered in detail in this review.

2.2. ENERGY-DISPERSIVE X RAY FLUORESCENCE

ED-XRF emerged around 1965 with the development of Si(Li) semiconductor detectors capable of spectrally resolving X ray fluorescence lines of neighbouring elements. In most of the developing countries, the use of ED-XRF was started with the implementation of IAEA technical co-operation (TC) projects, accompanied by the provision of equipment and expert services. Although it has never been as widely accepted in industry as WD-XRF, the technique is now being utilised in the determination of major and trace elements in solid and liquid samples, both of organic and inorganic origin, pertaining especially to industry, agriculture, geological, water and particulate matter, but mainly in research and university laboratories worldwide. This is reflected in the relatively large fraction of the literature dedicated to developments in ED-XRF.

2.2.1. Conventional energy-dispersive X ray fluorescence

Although ED detectors were originally used in X ray tube excitation XRF instruments (using both direct tube and secondary target excitation configurations) and in electron beam instruments, they are now also widely used in combination with excitation by radioisotopes (including in portable instruments), charged particle and synchrotron radiation beams, and in special geometries such as total-reflection XRF (TXRF) and microbeam XRF. Specific sections below will be dedicated to these configurations.

2.2.1.1. Recent developments in conventional ED-XRF

There has recently been significant progress in the instrumentation for ED-XRF. Polarised beam excitation, allowing lower detection limits, has recently become commercially available as well as pen-size X ray tubes for use in portable instruments [2.8]. Major progress has, however, been made in detector technology. The conventional liquid-nitrogen cooled Si(Li) detector has a best spectral resolution of around 135 eV (FWHM @ 5.9 keV). Si(Li) detectors with ultra-thin entrance windows have become available; which allow the detection of the soft X rays from low-Z elements like carbon, nitrogen and oxygen. Thermo-electrically cooled HgI_2 detectors have been available for a while, mostly for use in portable instruments, and their resolution seems difficult to improve below 280 eV [2.9].

The new Si PIN diodes for low-Z elements and the CdZnTe detectors for higher energies, operating slightly below room temperatures, are emerging and exhibit a resolution around 200 eV [2.10–2.12]. A potential important development, however, has been the introduction of experimental superconducting tunnel junction (STJ) [2.13–2.14] and microcalorimeter detectors [2.15–2.16], which have a spectacular resolution of 30 and 10 eV, respectively. However, these devices must operate below 1 K and rely on superconductor technology. If these detectors were to become commercially available, they would revolutionise ED-XRF and supplant WD spectrometer systems. One can only say that, at present, the development in the field of ED-detectors is so fast, that one cannot reliably predict their future role and advantages.

2.2.1.2. Advantages and limitations of conventional ED-XRF

For qualitative analysis, modern ED-XRF can cover a wide range of elements, between boron and uranium. In typical environmental samples, some dozen elements can be assessed simultaneously [2.17]; this is only superseded by neutron activation analysis (NAA), which is inherently much slower, and by inductively coupled atomic emission (ICP-AES) or mass spectrometry (ICP-MS). The latter technique is, however, often prohibitively expensive. For quantitative analysis, ED-XRF offers a large dynamic range, from the mg kg^{-1}-level to 100% m/m, and when preconcentration of samples is incorporated, this range can be extended down to the μg kg^{-1}-level [2.18]. In principle, ED-XRF can analyse a wide variety of samples, but, by its nature, it is more suitable for solid samples, while more common techniques like atomic absorption spectrometry (AAS) and ICP-AES work preferably on liquid samples.

Conventional ED-XRF is not optimal for very low-Z and high-Z elements. The commonly-used Si(Li) detectors have relatively poor spectral resolution usually necessitating the use of sophisticated computer programs for spectrum evaluation (but powerful and accurate procedures have been developed). These detectors need to be cooled by liquid nitrogen. Also, the methodology for accurate analysis of samples of variable thickness, with significant matrix effects, requires rather complicated methodologies, both for ED-XRF and WD-XRF, but these procedures were developed a long time ago.

2.2.1.3. Present and emerging industrial and environmental applications

a) *Industry*

In contrast to WD-XRF, ED-XRF has not been extensively adopted by many industrial laboratories for routine everyday analysis. This is related to the somewhat inferior precision of ED-XRF measurements in comparison with WD-EXRF and absence of complete automation on most commercial ED-XRF instrumentation. However, the successful advent of benchtop ED-XRF units, dedicated to specific applications or elements, e.g. sulphur in oil, has been noted in the past years. Where conventional ED-XRF is widely used in industry, it is nowadays mostly in combination with WD-XRF, for example in instruments with dedicated applications in some cement and petrochemical industrial laboratories. Furthermore many special analyses are done every day by IAEA sponsored laboratories, using ED-XRF, for local industries and small to medium enterprises.

b) *Atmospheric aerosols*

During the last couple of years, there has been a significant re-emergence of interest in atmospheric aerosols. This is due to:

(i) the role that aerosols (might) play in climate change by scattering incoming sunlight and by enhancing cloud formation, in compensating for the heating of the Earth by the well-known greenhouse gases.

(ii) the recently proven detrimental health effects of micrometer-sized particles

(iii) the role of aerosols in depositing micropollutants and nutrients on land and in the ocean.

ED-XRF remains the method of choice for the monitoring of aerosols, mostly for heavy metals. Not surprisingly, there is a huge and expanding literature on this field. No other technique is capable of analysing directly loaded aerosol filters. The popular AAS and ICP-AES techniques require dissolution of particle loaded filters, implying dilution and the risk of incomplete decomposition of refractory phases. ED-XRF is, therefore, extensively used e.g.

by the US Environmental Protection Agency for monitoring air quality. Suitable filter types for ED-XRF are cellulose filters, Teflon filters and polycarbonate membranes, but not glass fibre filters (in view of their inorganic impurities). WD-XRF is now also used increasingly for air pollution monitoring, because it can determine important elements which are difficult by ED-XRF, such as cadmium and mercury. Because of the higher exciting beam intensities available in WD-XRF, the choice of the filter material capable of resisting the exciting beam, is somewhat more critical. For very low concentrations (e.g. for aerosols from remote areas) and for size-fractionated aerosols, particle induced X ray emission (PIXE) and TXRF might be more suitable X ray analysis techniques.

c) *Liquid samples*

Like WD-XRF, ED-XRF can be used for the direct analysis of liquid samples, prepared in special cups with very thin bottom, which must be analysed in air or under helium atmosphere. The detection limits are then mostly in the mg kg^{-1} range. This technique is valuable for a number of industrial applications, including the analysis of brines, and process and waste waters and for the determination of elements such as Cl and S. However, for environmental waters and for monitoring heavy metals, the detection limits are some three orders of magnitude too high. Therefore, a range of chemical preconcentration methods have been proposed over the years, for the analysis, e.g. of natural waters in combination with ED-XRF. These include extraction methods, use of ion exchange columns and ion exchange membranes, chelation followed by immobilisation, precipitation and co-precipitation. There are quite a few complications, though, in each of these approaches and apparently no panacea exists for the simultaneous determination of many elements and their possibly different chemical species, with high sensitivity, simplicity and low-cost. Nevertheless, there is clearly renewed interest in applying ED-XRF to e.g. dilute industrial water samples and for water pollution monitoring. Physical preconcentration can simply involve the evaporation a water volume on to a thin carrier and measuring the residue. For water samples with a low salt content, a high enrichment can, of course, be achieved, but higher salt loads and the formation of finite crystals can lead to unpredictable matrix effects so complicating this approach. Yet, there seems to be a considerable interest at present in applying evaporation preconcentration in combination with micro-XRF, for the analysis of clean reagents, reactor cooling water, industrial process waters and environmental waters.

d) *Biological material*

Although conventional ED-XRF is able to determine directly a number of elements in some biological materials, e.g. human hair and teeth (and has been used much in this context), the concentrations of the environmentally or toxicologically relevant elements in soft tissues are usually too low so that some prior preconcentration step is needed. This implies an added risk of contamination, so that TXRF, but also other techniques such as ICP-AES and -MS have distinct advantages.

e) *Geological material*

In nearly all geochemical and environmental relevant materials, such as minerals and ores, soils and sediments, many elements are present at levels that can directly be assessed with conventional ED-XRF (although WD-XRF might be superior in low-Z element detection and in achieving higher precision, as was discussed above). The only sample preparation required is usually grinding followed by pelletising or fusion with a suitable flux, in order to reduce mineralogical effects and improve the accuracy. Sediments are very interesting as integrating monitors of water pollution by heavy metals, and this field continues to be an ideal application for ED-XRF.

2.2.2. Total reflection X ray fluorescence

2.2.2.1. Recent developments in methodology and instrumentation

TXRF is a specialised excitation mode for ED-XRF analysis. In TXRF, the exciting beam is highly collimated in the vertical plane, and it impinges at a very small angle on a flat, polished sample or support (usually quartz or Plexiglas) carrying a minute amount of sample. If the angle of incidence, of this incident beam, is below the critical angle (a few minutes of a degree), the beam will practically not penetrate into the flat sample or support but be totally reflected. In this way, practically no scattered X rays are generated, and the background measured by a Si(Li) detector (positioned at right angles to the sample) will be extremely low, so that very advantageous detection limits can be achieved. Although TXRF was originally developed in the 70s, its importance has grown much in the 90s, mainly because of the wide availability of commercial TXRF instruments and the growth of applications in the electronic industry [2.19].

The TXRF module that has been provided by the IAEA to laboratories in developing countries is manually calibrated, with some practical inconvenience but with a very low cost. The IAEA's laboratory has now developed a complete computerised instrument capable of providing more reliable results [2.20]. Compact instruments are also commercially available from several manufacturers [2.21], commonly using a line-focus X ray tube. A rotating anode source can also be used to provide higher excitation intensities [2.22].

Various laboratories have investigated improvements in excitation optics for conventional TXRF instruments but one of the most significant recent improvements in TXRF is the use of synchrotron radiation (SR) X ray beams as the excitation source. As an example, this technique has the capability of determining elements from Fe to Zn down to 10^8 atoms cm^{-2} on silicon wafers [2.23]. A further important development is the introduction of windowless Si(Li) detectors, which permit the determination of low-Z elements, such as C, N, O, F [2.24].

Some related techniques have recently been developed. In Grazing emission X ray fluorescence (GEXRF) spectrometry, the sample is irradiated at approximately right angles with an uncollimated polychromatic beam and only the part of the fluorescence radiation emitted at grazing angles about the flat carrier or sample, is detected by a WD spectrometer [2.25–2.26]. Performance should be comparable to TXRF, but the WD-detection system should allow measurement of low-Z elements with better resolution and sensitivity than can be done with a conventional Si(Li) detector in TXRF.

2.2.2.2. Advantages and limitations of TXRF

TXRF allows the direct analysis of liquid samples by simply spotting an aliquot onto a polished carrier. Since the detection limits for the analysis of dilute liquids can be as low as the ng/L-level, ultratrace elements can be assessed simultaneously. In this way, TXRF is comparable to ICP-AES and ICP-MS. In view of the extreme detection limits in TXRF, the risk of significant contamination is, of course, relatively high, and all manipulations must be carried out in a clean hood.

Solid samples can also be analysed, either after microgram of material amounts have been deposited on a polished carrier (e.g. air particulate or minute amounts of paint) or, more commonly, after a suitable dissolution step. In the latter way, again, TXRF has a similar capability to AAS, ICP-AES and ICP-MS. The residue of a dissolved solid sample, deposited on carrier, should be of more than microgram quantities so that the detection limits of TXRF are not jeopardised.

In view of the small amounts of sample involved, matrix effects are minimal and quantification in TXRF is simply carried out by adding an internal standard and by the use of relative sensitivity factors.

The possibility of performing surface analysis of flat samples, such as wafers, near-surface depth profile mapping (by scanning around the critical angle), and assessment of the density, thickness and composition of surface microlayers is an important advantage of TXRF particularly for applications in the electronics industry.

2.2.2.3. Present and emerging industrial and environmental applications

In the environmental field, TXRF has successfully been applied to the analysis of different waters, such as rainwater, drinking water, river water, seawater and even wastewater [2.27]. If the total dissolved content of water sample is relatively high, the sample preparation cannot consist of simply spotting a droplet of water on a carrier. It is then necessary to apply specific preparation methods to remove the salt content. This is a significant complication for the versatile analysis of waters.

TXRF is also suitable for the analysis of airborne particulate matter, where the collection of air dust is carried out by filtration (and subsequent filter dissolution) or by direct impacting of the aerosol on the quartz or Plexiglas carrier [2.28]. TXRF is capable of determining numerous elements down to detection limits of 0.2 ng m^{-3}, even when a simple and low-cost TXRF module is used.

Some inorganic materials, like soils, sediments, sewage sludge and incinerator slag have been analysed by TXRF after digestion and preferably after matrix removal.

Pollution monitoring can be done through the analysis of plants and vegetables, where nitric acid digestion or cold plasma ashing of the freeze-dried and pulverised components are preferred. Tissue samples can be analysed after ashing or digestion, but often it is more convenient to analyse directly thin sections obtained by microtome cutting.

In the semiconductor industry, the method is booming; it has already achieved importance for the surface contamination control of wafers, where the analysis is done with no chemical preparation, to detection limits of around 10^8 atoms cm^{-2}. Multielement determinations of about 20–25 elements can be performed simultaneously with commercially available second generation instruments. The unique capabilities of TXRF for depth profiling (e.g. of ion implants) and measuring the composition, density and thickness of surface microlayers, as mentioned above, are becoming of high importance in the electronics industry. This interest will certainly increase further, now that TXRF is increasingly used in combination with SR-sources to achieve even greater sensitivities, and windowless Si(Li) detectors are used so that also low-Z elements can be determined.

2.2.3. Micro X ray fluorescence technique

2.2.3.1. Recent developments in methodology and instrumentation

The recent evolution and production of new sophisticated X ray optics have given a big stimulus to the development of microanalytical techniques. In particular, laboratory tube-excited XRF microprobes are now becoming widely used due to the low cost of the systems compared to those based on SR-XRF or PIXE. Because of the much higher X ray beam intensities and the possibility of tuning the energy of the beam exciting the sample, SR-XRF microprobes have much greater potential for high sensitivity trace element determinations as well as chemical state analysis using X ray absorption techniques.

In microanalytical systems, the incoming beam is collimated and/or focused down to dimensions in the range of few micrometres by means of optical elements which can comprise glass capillaries, lenses or, in case of SR-XRF sources, sometimes, mirrors. Glass capillary optical elements produce a very fine focused photon beam through repeated total reflection on the inner walls of the tube [2.29]. Glass capillaries can also be used for SR- XRF and since the initial beam is much more intense, it will be possible to produce very small foci with very high photon flux. At the present there are four different types of X ray capillaries available: monocapillary concentrators which can be parallel-bore, conical, or ellipsoidal and monolithic polycapillary lenses (also known as Khumakov lenses).

Parallel bore capillaries are used to transport X rays from a suitable X ray source out to the sample, eliminating the $1/r^2$ losses that occur when X rays are propagated away from an isotropic point source. Conical capillaries work in a similar way but when transporting the radiation from the source to the sample they also 'squeeze' the X ray beam down to the capillary output diameter. Ellipsoidal capillaries are a recent innovation. In case of an ideal ellipsoidal capillary, an X ray originating from one of the two focal points will be transmitted to the other focal point. To achieve best resolution in the transmitted beam, in the case of parallel-bore and conical capillaries, the sample must be placed as close to the end of the capillary as possible, and at the point of focus in the case of ellipsoidal capillaries.

Monolithic polycapillary X ray lenses consist of a very large number of parallel-bore capillaries bundled together so that each transmits X ray photons from the source to the same 'focal point'. The main advantage of the polycapillary lens in comparison with monocapillaries is that a much larger solid angle of X ray photons is transmitted from the source, substantially increasing the intensity available for excitation on the sample. Polycapillary devices are compact and very sophisticated and for this reason, only very few laboratories in the world can produce them.

A typical micro-XRF system consists of an X ray source, a focusing or collimating device, a motorised sample stage with a microscope and an X ray detector. Most micro-XRF systems incorporate a conventional Si(Li) detector. Several manufacturers offer micro-XRF instrumentation based on capillary optics with spatial resolutions of between 10–250 μm.

The SR-XRF microprobes can presently use a probe size down to at least a few micrometers and produce sub-mg/kg detection limits for many elements. One added advantage of the very high available intensity from SR sources is the possibility to perform simultaneous X ray crystallography (micro-XRD). In addition, the SR facilities offer several other techniques for obtaining chemical and structural information, such as EXAFS (extended X ray absorption fine structure) and XANES (X ray absorption near edge structure) [2.30].

2.2.3.2. Advantages and limitations of micro-analytical techniques

Since micro-XRF is based on the excitation of the characteristic X rays by electromagnetic radiation, the scattered X ray background contribution to spectra is considerably lower than the Bremsstrahlung contribution to electron probe X ray microanalysis (EPXMA) spectra. This feature combined with relatively high total X ray yields for excitation by photons results in extremely advantageous detection limits, in the order of 10^{-14} g.

Another advantage of micro-XRF based on X ray tube excitation is the possibility of performing measurements in air so permitting the analysis of biological materials without sophisticated sample preparation procedures. Another important advantage of micro-XRF in comparison with EPXMA and PIXE is the considerably lower energy dissipation by the exciting beam, which results in reduced thermal damages and often negligible losses of the volatile elements. The much larger penetration power of photons, relative to charged particles in particular in light matrix, enables one to analyse thicker layers which might improve representativeness of results from the material under investigation. Finally, the simplicity and relatively low cost of micro- XRF systems can be another advantage compared to EPXMA and PIXE. In contrast, a major disadvantage of the technique is the lower degree of automation and the poorer spatial resolution that is not the case for SR-XRF where the focused photon beam is used for the analysis at a lateral resolution of a few micrometers [2.31]. Because of the restricted access to facilities offering these analytical characteristics, micro-SR-XRF can only be used for carefully selected samples. There is also a more general limitation of XRF in accurately quantifying analytical results in unknown matrices. This is because the correction for attenuation of the primary photons as well as of the characteristic X rays produced in the specimen will be uncertain. This is true also for SR-XRF. However, since relatively thin specimens are normally used for micro-SR-XRF this is less of a problem.

2.2.3.3. Present and emerging industrial and environmental applications

There is a strong interest from industry in the application of micro-analytical techniques. Many analytical problems can be solved with a lateral spatial resolution of between 10 and 100 µm. Demonstrated applications to date include control of film thickness and composition in the plating and microelectronics industries, control of elemental segregation in the metallurgical industry, evaluation of micro-corrosion and other process control problems affecting material production.

Environmental applications of micro-XRF mainly involve the characterisation of individual particles. EPXMA and micro-PIXE as well as micro-SR-XRF are also used in this application for the determination of elemental composition. It has also been shown possible to perform micro-XRD for structural information on the material present in these single particles. Another example is the study of variations in the trace element composition of wood by analysing individual tree rings by micro-XRF.

A recent trend is to apply micro-XRF to the analysis of water after evaporation of a small aliquot of the sample onto a foil. Compared to all older work involving the evaporation of water samples on a filter or a thin film for conventional ED-XRF, three innovations are involved here: (1) the new carrier foils, on which a few microlitres are spotted, are much thinner now (0.15–0.3 μm versus 3–7 μm in earlier work, so that less scattered X ray background is produced) but still sufficiently strong, (2) the foils are provided with dimples or a surface texture so that the residue water residue is collected in a very small spot only, and (3) a micro X ray beam is used so that supporting foil material outside the sample deposit does not contribute to the scatter background. Some quantification problems remain, particularly for lighter elements, but detection limits in the μg/L-range have been claimed for both environmental and industrial waters.

As well as these applications, it is worth mentioning art and archaeometry, where instruments using capillary optics have been used for local and non-destructive analysis of fragile and precious artistic objects.

Regarding micro-SR-XRF, high-resolution measurements lend themselves towards analysis of very small structures. Micro-SR-XRF has been used for archaeological studies to analyse corrosion in ancient glass objects [2.32]. These results have also been compared with those obtained by nuclear microprobe-based micro-PIXE analysis on the same specimen. The fact that PIXE is a better choice for low-Z elements and SR-XRF for high-Z was confirmed.

Geochemistry is another field where micro-SR-XRF has important potential. The possibility of tuning the photon energy to optimise the excitation of specific elements and suppress the excitation of others can be very useful, for instance, for the detection of noble metals in minerals. The non-destructive character and high penetration power of both the excitation and the fluorescence X rays makes micro-SR-XRF ideal for analysing unopened fluid inclusions in minerals. The composition of the fluid inclusion can reveal information on conditions during mineral genesis, of basic geological interest, but also on the conditions for the formation of economically important ores.

In investigation of heavy metal uptake using a microprobe at mm resolution facilitates a detailed study of the distribution. Micro-SR-XRF has been used to investigate lead distributions in human tibia and deciduous teeth [2.33].

2.2.4. Portable X ray fluorescence

2.2.4.1. Recent developments in methodology and instrumentation

Portable XRF is a category of instrumentation that can be carried into the field and used to analyse samples directly in a non-destructive manner. The technique is unusual in that it is not necessary to remove samples to the laboratory; furthermore, after quantification, results can be displayed immediately after acquiring a spectrum. Instrumentation normally comprises a hand-held analyser unit incorporating up to three radioactive excitation sources and an ED X ray detector. The analytical reference face of this unit is placed on or held against the object to be analysed. Spectrum counting times are normally between 50 and 200 s and spectral data is acquired and analysed in a portable data acquisition and analysis unit. Nominally, all the elements above K in the periodic table can be measured, taking account of the detection limit performance of the instrument. However, to achieve full elemental coverage, three excitation sources are usually required (almost always ^{55}Fe, ^{109}Cd and ^{241}Am). A recent innovation has been the development of miniaturised X ray tubes, which are likely to have an important role as an alternative excitation source in this category of instrument. Three types of detector are commonly used in portable XRF instrumentation. The Si(Li) detector (which represents the 'industry standard' in terms of energy resolution, but requires cryogenic cooling), the simple proportional counter detector (which is simple, robust and relatively cheap, but offers poor energy resolution such that care is required in assessing its applicability to an analytical problem), and the relatively new HgI_2 detector [2.34] (which offers slightly inferior resolution to the Si(Li) detector, but does not require cryogenic cooling). However, ED X ray detector technology is a rapidly developing field and several other semiconductor materials and configurations are likely to make a significant impact on future generations of portable instrumentation, including Si PIN [2.35], CdZnTe and possibly Ge detectors.

2.2.4.2. Advantages and limitations of portable XRF

Portable XRF has some unique analytical capabilities that are unmatched by other analytical techniques. It is one of the few techniques that is capable of the direct elemental analysis of samples in situ without the need to remove samples to the laboratory. The only rival in this respect is portable spark-source optical emission spectroscopy, which has been developed primarily for alloy identification and sorting, and is in any case inappropriate for non-conducting materials. Portable XRF has, therefore, some important advantages. The first is that decisions can be made interactively in the course of a sampling programme. That is, selection of the next sample to be analysed can be made on the basis of the analytical results just acquired. This capability is important in assessing contaminated sites, for example, where the objective might be to locate 'hot-spots' to characterise the source of contamination. Another example is in directing underground mining operations in locating ore veins. A second important advantage is that because samples can be analysed in situ and non-destructively, it is possible to analyse rare and valuable objects that cannot be removed from their storage or display location, in particular for reasons of security. Examples include gold and precious metal bullion, unique museum artefacts, paintings and other works of art, illuminated manuscripts etc. A third advantage is in the direct analysis of objects in the field that cannot be sampled or where there are logistical difficulties in returning samples to the laboratory for analysis. Examples would be:

(a) Archaeological or architectural samples that can neither be removed to the laboratory, nor have material removed from them.

(b) Artefacts contaminated with toxic material, where it is judged too hazardous to move or disturb the sample.

(c) The analysis of remote samples where it is judged better to take the instrument to the sample rather than the other way round.

No alternative analytical technique can satisfy these requirements.

Having outlined the unique advantages of the portable XRF technique, it is also appropriate to summarise its limitations. Most of the limitations relate to sample presentation and the relatively small mass of material on the surface of the sample from which the XRF signal originates. When samples are analysed directly by portable XRF (as in the applications summarised above), it is usually not possible to undertake any sample preparation. In some circumstances, the accuracy of analytical results will be affected by the nature of the surface being analysed. Quantitative results can only be obtained directly if the analyser is placed on a flat (polished) surface. Measurements made on samples with irregular or broken surfaces will suffer discrepancies because the irregular surface will not lie exactly in the analytical plain of the instrument. Discrepancies that arise from surface irregularity effects can be corrected using an empirical correction based on measuring scatter peak intensities [2.36]. As in all

XRF applications, the detected analytical signal originates from a depth within the sample of between a few tens of µm to several mm (depending on the energy of the fluorescence photon). Where portable XRF measurements are used to infer information about the bulk composition of the sample, care must be taken to avoid surface effects (e.g. unwanted weathering or corrosion products or surface deposits) which might affect the interpretation of results. Furthermore, it will normally be important to undertake replicate determinations so that sampling effects (e.g. statistical variations in the minerals present in the excited volume) can be quantified. Unless replicate determinations are made, sampling precision cannot be detected.

2.2.4.3. Present and emerging industrial and environmental applications

The most popular current applications of portable XRF instrumentation is in assessing the environmental impact of lead contamination associated with both contaminated soil [2.37] and paint. In the case of contaminated land, the main reason for use of the instrumentation is that portable XRF detection limits are 5 to 10 times lower than 'action' limits for lead in soil. For many of the other toxic metals of environmental interest, the portable XRF detection limits are too high to permit adequate determination down to the action level, although instrumentation may be of value in characterising gross contamination. In the case of paint, portable XRF can provide a rapid assessment of the presence of lead-bearing paint and can also detect lead paint that is covered by more recent coats. Given the considerable contemporary interest in environmental issues, not the least resulting from the US Superfund programme which has stimulated research into the remediation of highly contaminated site, there is likely to be a continuing expansion in the application of portable XRF to environmental studies, particularly of lead contamination.

A number of studies have also been published describing the portable XRF analysis of archaeological samples, museum artefacts, works of art etc. Traditional analytical methods normally involve the removal of small amounts of material from the artefact for analysis by high sensitivity techniques. Where such an approach can be justified because of the quality of results (better detection limits, capability of determining specific elements) traditional techniques are likely to continue to be used. However, it seems probable that in a majority of future studies, the removal of material for analysis will become unnecessary because of the non-destructive capabilities of the portable XRF technique and the fact that in situ analysis by portable XRF is likely to facilitate easier access to a wide variety of valuable objects.

However, arguably the most important area of application that has not yet been fully exploited is industrial applications. It is not simple to generalise, but typical investigations are likely to be in the raw materials industry in:

(i) Trouble-shooting and optimising plant operation

(ii) Checking the composition of waste materials.

(iii) Detecting contamination resulting from plant malfunction.

In the mining and mineral exploration industries, there is also a clear role for the portable XRF technique in characterising mineralisation as a contribution to both exploration projects and in directing mining operations.

The final area of application to which the portable XRF technique is likely to make a significant application is health and safety. Instrumentation has the capability of identifying work place dusts and contaminants, as well as the site analysis of air filters. All these capabilities are likely to be of interest to regulatory authorities and industrial health and safety consultants.

REFERENCES

[2.1] COMPTON, A.H., ALLISON S.K., X-rays in Theory and Experiment, Van Nostrand, New York (1935).

[2.2] BIRKS, L.S., X-ray Spectrochemical Analysis, 2nd edn, Interscience, New York, (1969).

[2.3] DYSON, N.A., x-rays in Atomic and Nuclear Physics, Longman, London, (1973).

[2.4] JENKINS, R., An introduction to X-Ray Spectrometry, Heyden, London (1974).

[2.5] BERTIN, E.P., Principles and Practice of X-Ray Spectromic Analysis, 2nd edn, Plenum Press, New York (1975).

[2.6] JENKINS, R., DE VRIES, J.L., Practical X-Ray Spectrometry, 2nd edn, Springer-Verlag, New York (1967).

[2.7] TERTIAN, R., CLAISSE, F., Principles of Quantitative X-Ray Fluorescence Analysis, Heyden, London (1982).

[2.8] Swedish Patent 95018111-5; US Patent 5,633,908.

[2.9] PONPON, J.P., SIESKIND, M., Nucl. Instr. Methods Phys. Res., **380** A (1996) 173.

[2.10] HUBER, A.C., PANTAZIS, J.A., JORDANOV, V., Nucl. Instrum. Methods **B99** (1995) 665–668.

[2.11] CESAREO, R., et al., J. Trace Microprobe Technol. **14** (1996) 711–725.

[2.12] JORDANOV, V., PANTAZIS, J.A., HUBER, A.C., Nucl. Instrum. Methods **A 380** (1996) 353–357.

[2.13] KISHIMOTO, M., et al., Nucl. Instrum. Methods Phys. Res. **A 370** 1 (1996) 126.

[2.14] UKIBE, M., et al., KEK Proc. **96** 4 (1996) 114.

[2.15] SILVER, E., X-Ray Spectrom. **25** 3 (1996) 115.

[2.16] LABOV, S.E., et al., Nucl. Instrum. Methods Phys. Res. **A 370** 1 (1996) 65.

[2.17] NGUYEN, T.H., BOMAN, J., LEERMAKERS, M., X-Ray Spectrometry **27** (1998) 265–276.

[2.18] DRISCOLL, J.N., FIELD, Int. Environmental Technol. **8/5** (1998) 10–12.

[2.19] SCHWENKE, H., KNOTH, J., in Handbook of X-ray Spectrometry — Methods and Techniques (VAN GRIEKEN, R. MARKOWICZ, A., eds), Marcell Dekker, New York (1992) 453–490.

[2.20] BERNASCONI, G., DARGIE, M., JAIB, M.M., TAJANI, A., X-Ray Spectrometry **26** 4 (1997) 203–210.

[2.21] TORBOLI, A., Lab. 2000 **9** 7 (1995) 48.

[2.22] PETTERSON, R.P., BOMAN, J., Nucl. Instrum. Methods Phys. Res. **A 371** 3 (1996) 553.

[2.23] PIANETTA, P., paper presented 45th Annual Denver X-ray Conf., Denver (1996).

[2.24] STRELI, et al., paper presented at Eur. Conf. on Energy Dispersive X-ray Spectrometry, Lisbon (1996).

[2.25] CLAES, M., VAN GRIEKEN, R., paper presented at Eur. Conf. on Energy Dispersive X-ray Spectrometry, Lisbon (1996).

[2.26] de BOKX, P.K., et al., paper presented at 6th Conference on TXRF, Eindhoven and Dortmund (1996).

[2.27] KLOCKENKAEMPER, R., von BOHLEN, A., X-Ray Spectrom. **25** (1996) 156.

[2.28] VALKOVIC, V., et al., Nucl. Instrum. Meth. Phys. Res. **B 113** (1996) 363–367.

[2.29] JANSSEN, K.H., ADAMS, F., JONES, K.W., Anal. Chim. Acta **283** (1993) 98.

[2.30] JONES, K.W., in Handbook Of X-Ray Spectrometry – Methods And Techniques (Van Grieken, R., Markowicz, A., eds), Marcell Decker, NY (1992) 411–452.

[2.31] JANSSEN, K., et al., Microchim. Acta (Suppl.) **13** (1996) 87.

[2.32] AERTS, A., JANSSEN, K., ADAMS, F., WOUTERS, H., Proc. 24th Microbeam Analysis Society (J. Friel, ed.), NY (1994) 45.

[2.33] JONES, K.W., et al., X-ray Microscopy III, Springer-Verlag (1992).

[2.34] POTTS, P., et al., Analyst **120** (1995) 1273–1278.

[2.35] YOKHIN, B., paper presented at Pittsburgh Conference (PITTCON '96), Chicago (1997).

[2.36] POTTS, P., et al., J. Anal. Atomic Spectrom. **12** (1997) 768–776.

[2.37] ARGYRAKI, A., et al., Analyst **122** (1997) 743–749.

3. PORTABLE GAMMA RAY SPECTROMETERS

3.1. RECENT DEVELOPMENTS IN INSTRUMENTATION

The development of commercially available portable gamma ray spectrometers over the past decade can be summarised in terms of five basic approaches: (1) stand alone or integrated spectrometers linked to a notebook or lap-top computer via parallel or serial interface employing either HPGe or NaI(Tl) detectors; (2) Add-on cards inserted in a lap-top computer employing either HPGe or NaI(Tl) detectors; (3) NaI (Tl) detector dedicated PMT base systems combined with a MCA add-on card or with a portable MCA unit; (4) a CdZnTe (CZT) detector in combination with a stand alone unit consisting of pre-amplifier, amplifier, ADC and MCA; (5) Fully integrated system with a dedicated detector

Due to the rapid development of miniaturised nuclear instrumentation, fully integrated systems with a dedicated detector will appear more frequently. This means that all the electronics including display and battery pack will be contained in a single light-weight unit. However, it appears that such instruments are being designed for specific applications and therefore they cannot be applied for research. Concerning detectors, efforts are continuing to fabricate CZT crystals with large active volumes (>10 cm^3). However, it is unlikely that these devices will ever be able to match the efficiency of either HPGe or NaI(Tl) detectors.

3.2. ADVANTAGES AND LIMITATIONS OF PORTABLE GAMMA RAY SPECTROMETERS

The advantage of portable spectrometers is the ability to bring existing techniques for gamma ray analysis to the field, as well as providing the opportunity to develop specialised techniques exclusively for field applications. Moreover, the quality of currently available portable systems is such that these units can also be used for research in the laboratory.

3.3. PRESENT AND EMERGING APPLICATIONS

Portable gamma ray systems are primarily used for in situ measurements. Typical applications include cargo inspection, non-destructive testing, environmental, industrial, security, and surveillance applications.

TABLE I. ADVANTAGES AND DISADVANTAGES OF PORTABLE SPECTROMETERS UTILISING THE VARIOUS DETECTORS

Advantages	Disadvantages
HPGe	
• excellent resolution (~2 keV @ 1332 keV)	• need for cooling
• broad energy range (5 keV to 10 MeV)	• systems can be large and cumbersome
• large active volumes (up to 400 cm^3)	
• portable systems can be used for laboratory applications	
NaI(Tl)	
• room temperature operation	• moderate resolution (8% @ 662 keV)
• broad energy range (5 keV to 10 MeV)	• PMT and scintillators are fragile
• can be machined in a variety of size and shapes	
CZT	
• room temperature operation	• small active volumes (~0.05 cm^3)
• good resolution (1.5 keV @ 122 keV)	• limited energy range (<1 MeV)

3.3.1. Environmental measurements and decommissioning operations

In situ measurements are playing a vital role in many environmental surveillance and site decommissioning operations. They usually involve measurements at a site for extended periods, often from a vehicle or other temporary shelters. They also involve low level measurements for environmental surveillance, or relatively hot samples in the case of decommissioning operations

3.3.1.1. In situ spectrometry of soil using portable gamma ray spectroscopy systems (Beck method).

A common technique for assessing soil contamination involves use of a "downward-looking" uncollimated HPGe detector positioned 1 m above the ground. The activity per unit mass for a given radionuclide can be derived from the peak count rate using parameters that describe the soil characteristics (moisture, composition, and density) and the depth profile of the radionuclide distribution. In general, the calibration of HPGe or NaI(Tl) spectrometers for the assessment of the radionuclide concentration in soil is done in two steps: (1) the spectrometer is calibrated for fluence rate using certified point sources, and (2) the fluence rate from the source geometry is calculated using the assumed soil and source distribution parameters. A comprehensive discussion of this technique may be found in Refs [3.1, 3.2].

3.3.2. Nuclear safeguards

Portable spectrometers are being used for nuclear safeguards applications. Regulatory agencies routinely make in situ measurements using portable spectrometers during inspection at nuclear sites. Data collection times are often short, and sometimes must be conducted in hostile environments. A spectrometer utilising a CZT detector can be useful for cargo inspections looking for enriched uranium and plutonium. Both U and Pu emit low energy photons, and therefore the excellent resolution and compact size of a CZT make it a sensible choice for such applications.

3.3.3. New indoor and field applications

Future applications for portable systems will include indoor spectrometry as well as extending current field techniques to a greater variety of objects (drums, boxes, and waste containers) and field geometries (limited half spaces, pits, and trenches). New analysis techniques are being developed which will improve the overall accuracy and extend the applicability of in situ measurements. A few such techniques are briefly described below.

3.3.3.1. In situ measurements using an unfolding method for estimation of depth distribution

An unfolding technique for an estimation of the depth distribution has been developed that involves a combination of two methods: peak to valley method and change of track length distribution of photons in soil, registered by a collimated and uncollimated detector. The depth distribution is obtained by unfolding four various responses of in situ measurements. This approach, however, has only been applied to measurement of ^{137}Cs.

3.3.3.2. In situ measurements of radionuclide activity in soil with areas of elevated activity (hotspots).

A method is being developed that utilises a collimator to measure small sections of ground to facilitate a selective searching procedure for hotspot detection. Since scanning a contaminated area looking for hotspots is time consuming and expensive, it is essential that a measurement strategy be developed to determine the optimal grid size for a given hotspot diameter.

3.3.3.3. In situ measurements for dosimetry

The determination of ambient dose requires knowledge of the photon energy spectrum. There are two ways of estimating the energy spectrum: the calculation of the angular distribution of the gamma ray energy spectrum by considering the source and shielding geometry (only the gamma dose from the radionuclide of interest is determined), and the deconvolution of the spectrometer's pulse height spectrum. In this case the total gamma dose from radionuclides and cosmic radiation are determined.

REFERENCES

[3.1] INTERNATIONAL COMMISSION ON RADIATION UNITS AND MEASUREMENTS, Gamma-ray Spectrometry in the Environment, Technical Report ICRU 53, ICRU, Bethesda, MD (1994).

[3.2] BECK, H.L., DECAMPO, J., GOGOLAK, C., In Situ Ge(Li) and NaI(Tl) Gamma-Ray Spectrometry, Rep. HASL-258, USDOE Environmental Measurements Laboratory, NY (1972).

4. NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis (NAA) is based on irradiation of a sample with neutrons, preferably in a nuclear reactor, and subsequent counting of the induced radioactivity, most frequently employing a gamma ray spectrometer with a HPGe detector. For irradiation the whole reactor neutron spectrum can be used or thermal neutrons can be eliminated, using Cd or B filters to achieve selective activation with epithermal and/or fast neutrons (the so called epithermal NAA - ENAA and fast NAA - FNAA, respectively). FNAA can also be performed using 14 MeV neutrons produced by the (d,t) reaction in neutron generators, or with fast neutrons produced in several nuclear reactions of deuterons or protons accelerated in a cyclotron. For a limited number of applications isotopic neutron sources based on either the spontaneous fission of ^{252}Cf or nuclear reactions, such as the (α,n) reactions (e.g. ^{241}Am-Be) or the (γ,n) reaction (e.g.^{124}Sb-Be) may be sufficient, although they provide a neutron fluence rate which is of several orders of magnitude lower than that obtained in nuclear reactors.

In many cases NAA can be performed nondestructively, this analysis mode being termed instrumental NAA (INAA). In the cases where the induced radionuclides of trace elements are masked by matrix activity, a radiochemical separation (i.e. a post-irradiation procedure) is mostly used to eliminate matrix activity or to separate the radionuclides of interest in the so called radiochemical NAA (RNAA).

For the determination of element concentrations in NAA three types of standardisation (calibration) can be used:

- relative (using synthetic, mostly multi-element standards)
- single-comparator, most frequently employing the so called k_0-standardisation
- absolute (parametric).

Since unacceptable uncertainties are still associated with the values of nuclear parameters, namely activation cross sections σ_0, resonance integrals I_0, γ *ray* emission probabilities γ, and isotope abundances θ (in order of decreasing importance), the absolute standardisation is used only rarely and will not be dealt with in the present report.

In the relative standardisation method, a chemical standard with a known mass of the element is co-irradiated with the sample of a known mass and both are counted, usually in the same geometrical arrangements with respect to the HPGe detector, so that the absolute efficiency of the detector need not be determined. When short-lived radionuclides are to be measured both the standard and sample may be irradiated separately using the same reactor conditions, usually with a monitor of the neutron fluence rate.

In the case of relative standardisation, the analysis results are traceable to the materials used in the preparation of standards. Depending on the purity and stoichiometry of the compounds used, traceability to the mole can be established.

The concept of the k_0-standardisation in NAA, one of the most frequently used single-comparator (monostandard) methods, is based on co-irradiation of the sample and a neutron fluence rate monitor and the use of an experimentally determined composite nuclear constant k_0. Details of the k_0-standardisation have extensively been described in the literature [4.1].

In the case of k_0-standardisation, the analytical results are linked to the k_0-factors, absolute detector efficiency and neutron spectrum characteristics. The k_0-factors have been reliably determined in two independent measurements which were related to purity and stoichiometry of various materials. The absolute detector efficiency calibration is routinely performed using internationally recognised radioisotope standards. For determining the neutron spectrum characteristics, internationally recognised certified reference materials for neutron dosimetry are available.(high purity metals or Al alloys containing certified amounts of Au, Co, In, U etc.)

4.1. RECENT DEVELOPMENTS IN METHODOLOGY AND INSTRUMENTATION

Although NAA is sometimes considered as a mature NAT without any dramatic improvements during the last decade, new developments were recently achieved along several lines: reactor-based irradiation facilities of a new type, enhancement of the INAA capabilities by a combination of selective activation and special counting procedures. In RNAA the tendency is to achieve greater simplicity and to develop methods for the determination of individual chemical yields for each separation to attain a very high reliability of determination even at the ultratrace element level. New, INAA and RNAA procedures have also been developed for the determination of not only elements, but also selected radionuclides that are difficult to measure by other methods. Advances have been made in pre-irradiation separation in NAA for speciation analysis, and also continuous improvements in NAA hardware (counting devices) and software.

Since some types of samples, including geological and waste material, can be inhomogeneous by nature so that representative direct subsampling is difficult without extensive grinding to an acceptable particle size and homogenisation [4.2], a special irradiation facility was put into operation allowing analysis of large (up to 50-kg size) samples [4.3]. Prompt gamma neutron activation analysis (PGNAA — i.e. on-line measurement of gamma rays emitted by compound nuclei) appears to be increasingly important for the determination of the low Z elements, especially in biological materials. Since the use of cold neutrons increases sensitivity of this technique, the number of cold neutron sources in experimental reactors is growing. Moreover, PGNAA takes much less time than classical NAA.

It has been shown that in cases where irradiation in the whole-reactor neutron spectrum followed by conventional gamma ray spectrometry does not provide sufficiently low detection limits, a combination of selective activation with epithermal neutrons (ENAA) and selective counting techniques, namely Compton suppression spectrometry, may considerably improve the detection limits and thus extend the multi-elemental capability of INAA. Using this approach, low detection limits similar to those that can be achieved by RNAA were obtained for some elements [4.4].

Traditional alpha spectrometry of the radioisotopes of uranium and thorium (used in many fields involving dating, disequilibrium studies, geological and marine tracing, radioecology etc.) can be advantageously combined with the INAA determination of U and Th (as ^{238}U and ^{232}Th) so as to allow those two nuclides to function as internal standards. Alternatively, if INAA is combined with traditional tracer-added alpha-spectrometry, an independent data set can be obtained for quality control purposes [4.5]. Another methodological development concerns the determination of a number of radionuclides, namely ^{235}U, ^{238}U, ^{230}Th, ^{232}Th, ^{237}Np, ^{231}Pa, ^{129}I and ^{99}Tc [4.6].

The use of NAA after pre-separation of particular chemical forms before irradiation, sometimes termed "chemical or molecular NAA" is growing, because it allows the utilisation of NAA in the field of speciation. Since facilities, techniques, apparatus and reagents have all been greatly improved with respect to minimising contamination, pre separation can often be carried out without prejudicing the results [4.7].

A growth in the range of NAA capabilities and accuracy has also been facilitated by recent improvements in both hardware and software. In terms of hardware we note the availability of bigger, higher efficiency detectors, increased usage of well-type detectors and improvements in the data-handling capacity of electronics, e.g. "loss-free" systems. Software is becoming to be more powerful and there has also been a growing awareness of the need to validate results and undertake inter-comparison of different software programs.

The use of k_0-NAA continues to spread [4.8] and it has been shown how k_0 factors can be used to validate and check relative standards in NAA [4.9].

4.2. ADVANTAGES AND LIMITATIONS OF NAA

The advantageous features of neutron activation analysis have recently been summarised [4.10]. Therefore, only the most important issues are given here as follows:

- sensitivity and applicability for minor and trace elements in a wide range of matrices
- the virtual absence of an analytical blank, if no contamination occurs during sample handling (which usually only involves inserting a sample in an irradiation vial) prior to irradiation
- the relative freedom from matrix and interference effects
- the possibility to perform analysis in many cases nondestructively - by INAA
- the capability of INAA for multi-element determination, often allowing 30 to 40 elements to be determined in many matrices
- an inherent potential for accuracy compared to most of the other analytical techniques. Since the theoretical basis of NAA is simple and well understood, the sources of uncertainty can be modelled and well estimated
- the totally independent principle as a nuclear-based property in contrast to the electronic nature of many other analytical techniques
- the isotopic basis which often offers a choice of analytically independent routes for element determination
- in the cases where the induced radionuclides of trace elements are masked by matrix activity RNAA can provide interference-free detection limits close to the theoretical ones
- trace and ultra-trace (radio) chemistry can be performed under controlled conditions by inactive carrier additions
- the chemical yield of the separation can be obtained simply using carrier budgeting or the radiotracer method.

It is worthwhile elaborating upon some of the above listed advantages of NAA, especially in relation to other analytical methods. No other analytical technique has the capability to provide multielement data non-destructively, often with good detection limits and in a virtually matrix-independent manner. This is largely due to: (i) neutron being a non-charged particle easily penetrates the sample and reacts with nuclei; (ii) the gamma rays emitted by the induced nuclides with energies above 100 keV have also a high penetrating power. Both its inherent potential for accuracy and totally independent principle as a nuclear-based property make NAA invaluable as a reference or referee method. The possibility of determining a particular element using various isotopes, together with the possibility to perform the analysis by INAA and RNAA and to perform other additional checks on the consistency of the results, form the basis for a unique ability to verify the analytical data produced by the technique (the so called self-verification principle of NAA) [4.10–4.11]. It should be pointed out that although the isotopic basis is also employed by a few other analytical techniques, particularly in mass spectrometry, only in NAA a particular isotope can be selected to provide independent analytical data. It is also worthwhile noting that RNAA is the only destructive analytical technique in which the separation yield can easily be monitored.
Limitations of NAA can be summarised as follows:

- As stated above, NAA needs a neutron source. The nuclear reactor is the best neutron source, however its maintenance is an economical constraint. For various reasons, many experimental reactors have been shut down worldwide during last ten years and often have not been replaced. Use of isotope and other neutron sources does not often provide the sensitivity required.
- Determination of elements forming long-lived isotopes is time consuming and results in a low throughput of samples
- INAA is insensitive to the nature of chemical species present unless pre-irradiation separation is carried out. However, this is advantageous when the total concentration has to be measured irrespective of the chemical state
- For certain elements like Pb, and many elements with low Z, NAA does not provide sufficient sensitivity
- Work with samples irradiated in a nuclear reactor requires adherence to radioprotection measures and for these purposes dosimetry services are also needed
- It is prohibited to irradiate liquid samples in some experimental reactors, because an excessive pressure may be created in irradiation vials.

4.3. PRESENT AND EMERGING INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS

There are several application fields in which NAA has a superior, and in some cases even indispensable position compared to the other analytical methods. The nondestructive INAA is especially useful if materials to be analysed are difficult to take into a solution for analyses using some other techniques. A large number of elements determined may result in the so called panoramic analysis in which data for over 60 elements can be obtained, i.e. both values of elements determined and element upper limits. This is frequently required in analysing high purity materials. In such cases, use of the k_0-standardisation method which does not require irradiation of element standards is extremely useful as was demonstrated by panoramic analysis of silicon, silicon wafers and other materials used in the manufacturing of electronics components [4.12–4.13]. Panoramic analysis is also in demand for determination of impurities in the raw materials and solvents used in the production of polymers and for analysis of industrial slurries [4.14]. Other advantageous applications of INAA are in the chemical industry for analysis of catalysts (solids and slurries), and for the determination of halogens and other elements in plastics and photographic materials.

Besides high purity materials, the determination of extremely low element levels by RNAA is frequently required for example in the analysis of biological samples. Normal reference concentrations of many essential or toxic elements, such as As, Co, Cr, Hg, Mn, and V in various human and animal tissues and body fluids, especially in blood and its derivatives and in urine, are below the µg/kg level (dry weight). Using RNAA, it is much easier to prevent sample contamination prior to irradiation than in other analytical techniques involving sample dissolution and a further chemical treatment. This has been demonstrated, for instance, in determining normal values of vanadium in human blood, serum and urine [4.15]. Another important environmental application of INAA is the multielemental analysis of atmospheric, combustion and indoor aerosols, especially in the case of atmospheric aerosols collected in remote (unpolluted) regions.

The inherent potential of NAA for both accuracy and precision, and its totally independent principle compared to other analytical techniques plays a very important role in quality control of chemical analysis, namely in the certification of reference materials of chemical composition, including homogeneity testing. It appears that the share of NAA in the certification of element contents, and especially in homogeneity testing, exceeds that of any other analytical techniques.

In view of the above features, NAA has found extensive applications in many other science and technology fields within the last decade (Cf. Annex X). The trends in various fields can be summarised as follows. A decline is apparent in NAA applications in geochemistry, mineral exploration, and in the material science, especially in the developed countries, due to a strong competition with other more productive trace analytical techniques, namely ICP-MS. The role of NAA biomedical, environmental and health-related studies, including nutritional studies seems to be firmly established. The role of NAA as a reference (or referee) methods in quality control of chemical analysis and in the preparation of certified reference materials is one of its most important and also cost-effective uses, because inaccurate analyses are the most expensive.

REFERENCES

[4.1] DE CORTE, F., The k_0-standardization method: A move to the optimization of neutron activation analysis, PhDThesis, University of Gent (1987).

[4.2] ACHARYA, R.N., BURTE, P.P., NAIR, A.G.C., REDDY, A.V.R., MANOHAR, S.B., J. Radioanal. Nucl. Chem. **220** (1997) 223.

[4.3] OVERWATER, R.M.W., BODE, P., DE GOEIJ, J.J.M., HOOGENBOOM, J.E., Anal. Chem. **68** (1996) 341–348.

[4.4] LANDSBERGER, S., PESHEV, S., J. Radioanal. Nucl. Chem. Art. **202** (1996) 201–224.

[4.5] BYRNE, A.R., BENEDIK, L., Anal. Chem. **69** (1997) 996–999.

[4.6] BYRNE, A.R., Proc. 13th Radiochemical Conf. Marianske Lazne, Czech Republic, 1998; Czech J. Phys. (in press).

[4.7] INTERNATIONAL ATOMIC ENERGY AGENCY, Enhancement of Research Reactor Utilization for Neutron Activation Analysis, IAEA, Vienna (in press).

[4.8] Proc. 2nd Workshop on k_0-INAA, Ljubljana, 1996, J. Stefan Institute, Ljubljana (1997).

[4.9] HEYDORN, K., DAMSGAARD, J., J. Radioanal. Nucl. Chem. **179** (1991) 8791.

[4.10] BYRNE, A.R., Fresenius J., Anal. Chem. **345** (1993) 144–151.

[4.11] BYRNE, A.R., KUČERA, J., "Role of the self-validation principle of NAA in the quality assurance of bioenvironmental studies and in the certification of reference materials", Harmonization of Health-Related Environmental Measurements Using Nuclear and Isotopic Techniques (Proc. Int. Symp. Hyderabad, 1996), IAEA Vienna (1997) 223–238.

[4.12] DE CORTE, F., DE WISPELAERE, A., VAN DEN BOER, M., BOSSUS, D., VAN SLUIJS, R., Anal. Chim. Acta **254** (1991) 127–143.

[4.13] VERHEIKE, M.L., JASPERS, H.J.J., HANSSEN, J.M.G., THEUNISSEN, M.J.J., J. Radioanal. Nucl. Chem. **113** (1987) 397–404.

[4.14] BOSSUS, D., VAN SLUIJS, R., Proc. 13th Radiochemical Conf. Marianske Lazne, Czech Republic, 1998; Czech J. Phys. (in press).

[4.15] KUČERA, J., BYRNE, A.R., "Quality assurance of neutron activation analysis of traces of vanadium in workplace air, the environment and human tissues" Harmonization of Health-Related Environmental Measurements Using Nuclear and Isotopic Techniques (Proc. Int. Symp. Hyderabad, 1996), IAEA Vienna (1997) 349-359.

5. ION BEAM ANALYSIS (IBA)

By bombarding a specimen by light ions (protons, deuterons, alpha particles) of a few MeV/amu, normally produced by a small particle accelerator, close ion-nucleus encounters occur. By detecting the various signals produced during these interactions with atoms and nuclei in the specimen, the elemental/isotopic composition can be revealed. Ion penetration in solid matrices is normally tens of micrometers and depending on the radiation detected, the analytically depth probed can vary from sub micrometer to tens of micrometers. The most common techniques are Particle-Induced X ray Emission (PIXE) [5.1], Rutherford Backscattering Spectrometry (RBS) [5.2] and nuclear reaction analysis (NRA) [5.3]. The analytical characteristics vary from trace element analysis to depth profiling of near surface layers.

5.1. RECENT DEVELOPMENTS IN INSTRUMENTATION AND METHODOLOGY

Since these techniques rely almost entirely on the use of accelerators and relatively complex equipment, the crucial development lies in instrumentation. A few clear trends can be identified regarding instrumentation during the last decade.

Firstly, the equipment used for production of ions is gradually shifting towards dedicated compact tandem accelerators, attained more or less entirely for applied physics studies, including Ion Beam Analysis, accelerator-based mass spectrometry and ion beam modification of materials. The previously common larger accelerators, originally designed for low-energy nuclear physics, are being phased out due to age and high running and maintenance costs. The availability of these new accelerators has made it more feasible to set up new IBA facilities also in environments with less advanced infrastructure. Such a facility now only requires a small staff of a few technicians and with proper training, for instance, students and external users can perform experiments with little guidance, leaving the researchers responsible time to develop new techniques and procedures. The more user-friendly systems also make these techniques easier to implement in an industrial environment where specialist experience is not available.

Secondly, it is possible to purchase almost turnkey systems, including a combined accelerator and analytical set-up. These systems clearly represent a step in the direction towards commercially available self-contained instruments, similar to electron microscopes or wave-length dispersive X ray spectrometers for example.

Finally, there has been a strong interest in the development of micro-analytical systems. The first nuclear microprobe was developed in the early seventies but during the last decade the technique has matured with a proliferation of such systems (>80 systems worldwide). The systems needed for collimating, focusing and manipulating the beam are now commercially available from several sources and also turnkey "desktop" versions can be delivered including a very compact accelerator.

The methods involved in IBA depend heavily on the technical specification of the available equipment as discussed above. The particle energy range and the ion species available will determine which IBA techniques can be used. The most common techniques both in environmental and industrial applications are still PIXE and RBS, due to the high cross-section and high accuracy, respectively. No real quantum leap in the development can be observed in these techniques recently but there is a steady evolution. With the increased interest in nuclear microprobes - a combination of microanalysis and microscopy - There has been a considerable increase in the simultaneous use of several techniques, e.g. PIXE, RBS, NRA, secondary electron imaging, ionoluminescence, scanning transmission microscopy, ion tomography etc.. The demands on data acquisition capability have increased and been mainly fulfilled because of the rapid development of computers during the last decade.

With the present technology for ion beam optics and ion sources, the best lateral resolution of a nuclear microprobe is about 1 micrometer. The ion current is also limited to within the range about a few pA to a few nA, depending on the ion beam size. This has initiated an on-going development of detection systems with larger solid angles both for X rays and charged particles. The progressive development in detector technology, for instance, the improved energy resolution and detector cooling by Peltier elements, has also been very beneficial for the IBA field.

The limitations of IBA in being capable of only determining information on elemental composition have been compensated, for instance, by the development of the use of IBA combined with thermal analysis: ion beam thermography, IBT. The only existing system, so far, has been entirely designed for the characterisation of atmospheric aerosols by making use of backward and forward ion scattering, PIXE and NRA while gradually heating the sample on a thin aluminium foil [5.4].

5.2. ADVANTAGES AND LIMITATIONS TO OTHER TECHNIQUES OF ANALYSIS

With the wealth of other analytical techniques available it is very difficult to summarise pros and cons. Some of the characteristics of the IBA methods are due to the penetration patterns of the impinging ions. The relatively shallow, but still significant, penetration depth of the ion beam can sometimes be an advantage and sometimes not – it depends on the particular analytical problem. One important advantage of IBA is that determinations can often be performed without any preparation of a solid sample, a property

IBA methods have in common with several other nuclear techniques. Another advantage connected to the use of nuclear microprobes is the micro-analytical capability. In addition, the well-known reaction cross-sections etc. often make it possible, in principle, to perform standard-less quantitative analysis. However, for accurate quantification it is highly recommended that accepted reference materials are used or an intercomparison is made with an independent analytical technique. For bulk analysis, suitable reference standards are commercially available — for microanalysis there is a general problem due to lack of adequate reference materials.

Among the more important disadvantages, one can identify beam-induced sample deterioration, limited mass analysed (representativity), somewhat limited sensitivity (not an ultratrace technique), and very limited chemical speciation capability. The users should be aware of these limitations and actively seek for alternative methods to either complement or replace IBA when justified by the analytical problem.

5.3. PRESENT AND EMERGING APPLICATIONS OF IBA

The fields of environmental studies and industrial applications are quite different. Most studies on environmental effects are carried out by agencies, institutes and universities. The development of the PIXE technique has been closely linked to general environmental applications and in particular atmospheric aerosols. The development of IBT described above followed along these lines. The recent renewed interest in atmospheric particles related to respiratory human health effects and for the modelling of climate change, has put the use of data from IBA studies in focus.

Several IBA research groups have been active for a long time in this field of application and have become well established, in particular when combining the IBA with other complementary methods and when collaborating closely with atmospheric chemists and physicists. The accumulated data on composition of atmospheric aerosols produced by many IBA groups world wide, is now very important as a input into enhanced models for global climate change. When combining these data with results from other groups working with XRF, INAA and other analytical techniques, pertinent information can be obtained for understanding a sustainable global future will be at hand.

The applications in industry of any accelerator-based technique are clearly limited by availability of instrumentation. Only a few semiconductor industries have in-house particle accelerators and the commercially available turnkey systems that might improve this situation have only recently been introduced. Investment costs are not prohibitively high but the requirement for highly skilled expert staff represents a serious problem. The normal route for interaction between industry and IBA facilities is by consulting or participation in joint R&D projects. These are mostly on material science, environmental issues, quality control or very specific analytical problems that have emerged during industrial activities. When scrutinising the recent literature on industrial applications the dominance of applications using RBS on complex, epitaxially-grown materials is evident. Part of the explanation for this is the fact that much of the collaboration is performed on the basis of 'commercial confidentiality' and is not published. Also in the field of economic geology, IBA techniques have had a major impact, in particular, by supplying trace element data by using the nuclear microprobe on mineral samples [5.4].

The development of a specific technique for using the concept of "geogas" in ore prospecting is based on the emission of minute amounts from deep underground deposits to the earth surface [5.5]. Small particles are collected on thin foils and after several weeks of exposure these foils are analysed using a millimetre ion beam. PIXE can then reveal the composition of the material deposited. By a complex interpretation procedure utilising geophysical principles it is possible to judge the mineral deposits in deep ground. This is a technique with a good potential for evaluating rock conditions (in particular rock crack characteristics) to investigate the suitability of sites for underground long-term storage of highly radioactive waste.

A slightly different industrial application is the use of focused ion beams for characterisation of the fibrous structure of newsprint paper and to characterise the characteristics of printing [5.6].

REFERENCES

[5.1] "Particle-induced X-ray emission spectrometry (PIXE), Chemical Analysis, Vol. 133 (Johansson, S.A.E., Campbell, J.L., Malmquist, K.G., eds), J.W. Wiley & Sons, New York (1995).

[5.2] CHU, W.K., NICOLET, M.A., MAYER, J.W., Backscattering Spectrometry, Academic Press, New York (1977).

[5.3] KRISTIANSSON, P., MARTINSSON, B.G., Nucl. Instr. Meth. **B132** (1977) 159.

[5.4] RYAN, C.G., GRIFFIN, W.L., Nucl. Instr. Meth. **B77** (1993) 381.

[5.5] MALMQUIST, L., KRISTIANSSON, P., Proc. 8th Int. PIXE Conf., Lund, 1998, Nucl. Instr. Meth. B (in press).

[5.6] KRISTIANSSON, P., MALMQUIST, L., SJÖLAND, K.A., SUNNERBERG, G., Nucl. Instr. Meth. **B104** (1995) 584.

6. CONCLUSIONS AND RECOMMENDATIONS

(1) Most of the NATs discussed in the present report, namely SR-XRF, IBA, and NAA techniques require access to sophisticated and expensive (in terms of both investments and maintanence costs) nuclear instrumentation, such as accelerators and experimental reactors. More effective use of these facilities can be achieved in the Member States, especially in the developing countries in the framework of bi- or multilateral co-operation. This approach may lead to the establishment of national or regional centres which would concentrate not only experts in NATs, but their existence should also attract attention of the potential users of NATs.

(2) An interdisciplinary approach is recommended to be employed or further extended in the Member States to fully exploit the analytical potential of NATs, in particular for the SR-XRF, IBA and NAA techniques. This can again be best realized in the national or regional centres with the added advantage that a more cost-effective and greater utilisation of facilities and their infrastructure should be achieved. Such centres should also run educational and training courses, organise specialised seminars and conferences on both regional and international scales to pool and expand knowledge and expertise in the relevant fields. It can also be presumed that funding of such centres by both national

and international bodies will be much more effective than establishing scattered and narrow-oriented institutions with incomplete instrumentation and/or infrastructure.

(3) The existence of such centres seems to be of particular importance for NAA. There is a real danger that because experimental reactors in the Member States, especially in the developed countries have been shut down and because a number of experts have retired, the strength of NAA may be depleted and the expertise gathered during the last three decades may be lost in the coming years.

(4) A more specific recommendation can be given for the other NATs discussed in this report. Users of TXRF in the Member States should be aware of the fact that a computer-controlled system was developed by the IAEA Laboratories at Seibersdorf. This module can significantly increase the performance of TXRF compared to manually adjusted instruments that are still in use in many laboratories.

(5) The IAEA Laboratories at Seibersdorf have also developed a modular table-top capillary-based micro-XRF system and acquired sufficient experience in methodology and applications of the technique. Thus, it seems reasonable and justified to implement the micro-XRF instruments in selected XRF laboratories, especially in the developing countries which have already acquired basic XRF facilities and experience in the conventional ED-XRF technique. Once micro-XRF facilities are established, the XRF laboratories can provide the unique analytical services to other countries in the region.

(6) Portable XRF is a rapidly moving field, both in the further development of instrumentation as well as new applications. There is, therefore, a need for exchanging topical information among the Member States so that they can be made aware and take advantage of the most recent developments. Furthermore, it is important that laboratories in the Member States appreciate both the advantages and disadvantages of portable XRF instrumentation. In particular, there is a danger that on the one hand, analytical results will be misused unless the limitations of what is essentially a surface analytical technique are taken into account when results are used to estimate the bulk composition of a sample. On the other hand, there is the danger that users may not take full advantage of the quantitative capabilities of the technique if sufficient care is not taken over the acquisition and correction of data. Both these points suggest that the mutual exchange of information and expertise between the centres in the developed and developing countries has a role in the adoption of this technique.

(7) In general, it is recognised that the existence of the above mentioned centres can also contribute to the faster development and implementation of new applications of NATs in specific fields, and significantly facilitate validating their results by developing suitable reference materials and organising interlaboratory comparisons and/or proficiency testing.

Annex

PAPERS PRESENTED AT THE WORKSHOP

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CURRENT APPLICATIONS OF XRF AND MICRO-XRF TECHNIQUES IN ENVIRONMENTAL AND INDUSTRIAL FIELDS

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Abstract

A general overview of current applications of X-ray Fluorescence methods are given, including detection limits for different methods and sample preparation procedures.

1. INTRODUCTION

There are few analytical techniques that can, even today, compete with X-ray fluorescence (XRF) regarding its simplicity of instrumentation, limited sample preparation requirements, speed of analysis and range of elements, especially for solid samples. Generally speaking, the XRF methods rival the accuracy of wet chemical techniques for the elemental analysis of Be to U. Most popular is XRF in: a) industries producing metals, semi-conductors, polymers, chemicals, mining and crude oil, cements and ceramics, building materials, motor vehicles and glass, b) environmental sciences, c) forensics, d) pharmaceuticals e) paints, g) films and coatings. The main drawback to the technique is in its relatively poor elemental sensitivity, with normal detection limits in the ppm-range.

Most XRF spectrometers today operate in the wavelength-dispersive mode (WDXRF) but the number of energy-dispersive (EDXRF) spectrometers is significant as well. WD-instruments are estimated at 15,000 world-wide, whereas there are some 3000 units of for EDXRF. Total-reflection (TXRF) devices are only efficient and available in the ED-version, and there may be about 300 presently in operation, while only a handful instruments are working in the grazing emission mode (GEXRF). There are at least 50 micro-XRF instruments in operation around a world at present, but this number is increasing rapidly.

The common EDXRF mode provides simultaneous determination of different elements, but its use in trace analysis is limited by insufficient sensitivity for low-Z elements and inter-element spectral effects. Such simultaneous detection offers a more rapid analysis than WD. On the other hand, the WDXRF version has a much better spectral resolution, its detection limits are usually lower and it permits the measurement of very light elements. Both techniques are multi-element and provide non-destructive analysis. TXRF is nowadays well established technique for microanalysis: less than 1 μg of a solid sample or 10 μl of a solution are required for an analysis in a ppt-range. TXRF can be applied to aqueous solutions, acids, airborne particular matter, biological materials, ultra-pure metals, wafers in the semiconductor industry (where contaminations at $1x10^{10}$ atoms.cm^{-2} can be detected), etc. A precondition is that the sample must be present as a very thin layer. The disadvantages of the technique are mainly related to the ED-system, such as a limited dynamic range of the detector and its poor spectral resolution. GEXRF is newly established technique that takes advantages of the grazing emission and the WD leading to better resolution and sensitivity for light elements. For the high-Z elements, GEXRF is not expected to be better than TXRF: detection limits in the range of ng are anticipated. Micro-XRF is a sort of microscopical variant of bulk EDXRF, where a microscopic X-ray beam is used to excite locally a small area (e.g., 10x10 μm^2). Considering fundamental algorithms, quantification is accurate and precise. It promises to be one of the best microprobe methods for inorganic analysis of various materials: it operates at ambient pressure and in contrast to particle-induced X-ray emission (PIXE) and electron probe X-ray micro-analysis (EPXMA), no charging occurs. In many instances, no sample preparation is necessary other than placing the material in a sample chamber.

2. WAVELENGTH-DISPERSIVE X-RAY FLUORESCENCE (WDXRF)

WDXRF is a well-established analytical technique for the determination of the elemental composition of raw materials, semi-finished products and final products in industrial environments. Recently, fewer publications have been reported on WDXRF, although enormous numbers of element determinations are daily undertaken, but mostly in industrial practice.

The market demand for quality in the microelectronics wafer industry stimulated on-line WDXRF analysis, which can measure both composition and layer thickness with sufficient accuracy and speed. Such a system can be fully integrated into the production line, and the only part of the instrument that is in the clean room area is its loading bay (Reader and Nieuwenhuizen, [19]). Hence, in the recent period, a rapid growth in the use of automatic diffraction systems (polychromatic or monochromatic) for industrial quality control was seen (Rich. Seifert & Co., Ahrensburg, Germany). Reported typical applications and developments in the field of semiconductors involve phase analysis of thin films, texture analysis, strain evaluation in multilayer structures, reflectivity and topography measurements. In the field of the automotive industry, WDXRF is frequently used on highly stressed material surfaces to determine their behaviour of engine or gear parts and to improve material properties. Furthermore, in the iron and steel industry, quantitative determinations of total Fe and trace elements, as well as Fe_2O_3 and Fe_3O_4 in iron ores or FeO in sinters are necessary for optimising various process parameters.

WDXRF has been confirmed as a valuable method in various environmental studies. In a case of multi-element analysis of plants, it is possible to perform a complete evaluation of the plants: their growth, nutrient deficiency, food value, resistance to disease, etc. Garivait et al., [7]. In the past decade, most geochemical analyses on routine basis were carried out by WDXRF. Recent published examples are the complete study of the mineralogy and mineral chemistry of the island Ponza (Gulf of Gatea, Italy) by Belkin et al. [2] and a case study of the mineralogical composition of the mine coals in Alberta (Canada) and theirs impact on plant performance and stack gass opacity, by Gentzis et al. [8].

Monitoring of environmental waters for trace heavy metals represents an ongoing challenge. In this prospect, a passive monitoring system for control trace metals in river waters was built. A woven textile fibre, based on polyacryloamidoxime as a chelating agent, was used as collector and further analysed by both EDXRF and WDXRF. For field experiments, small cloth pieces, of 3.5x4 cm^2 are placed inside a 3.5-cm conventional plastic slide holder, which can be transferred directly into water and used as a collector. Detection limits in the sub-mg l^{-1} range and a precision better than 6% suggest a good ability of the method to concentrate heavy metals.

3. ENERGY-DISPERSIVE X-RAY FLUORESCENCE (EDXRF)

EDXRF has traditionally being used in the field or in the laboratory for a variety of industrial and environmental applications. This technique is ideally suited for field screening work as a result of the minimisation of sample preparation and its potential portability.

Monitoring and control of stack gas emission from industrial furnaces is of great importance nowadays. For this purpose, an automated EDXRF monitoring system was developed (Spectro Analytical Instruments, Kleve, Germany) which enables a continuous emission sampling and a fast, non-destructive and robust determination of heavy metals in the emitted stack gases. In this setup, aerosols are collected through a heated-titanium probe onto a quartz-fibre filter and analysed "on-line" by EDXRF. Elements like As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Sn, Tl and V could be detected with a Rh-anode tube for excitation and a silicon drift chamber as the detection system. The non-destructive method allows storage of the samples for further investigations and comparison with other methods like ICP-OES and AAS.

X-ray techniques have already contributed to non-destructive in situ measurements in the metal processing industry. A few methods are, however, used to measure on-line the microstructural parameters such as stress, phase composition and texture. It is well known that the texture or preferred orientation is one of the most important microstructural characteristics of materials; it correlates with the elastic, plastic and magnetic properties of materials. On-line texture X-ray sensors can be used for example to evaluate the mechanical or magnetic properties of sheets and therefore serve for quality control and assurance of the final product. Universal X-ray equipment serves to test X-ray sensor designs suitable for texture analysis. Experimental testing with the laboratory sensor (developed at the Department of Metallurgical Engineering, McGill University, Montreal, Canada) gave good results for two sets of specimens: (1) a set of cold-rolled and annealed, interstitial-free steels and (2) a set of hot-rolled alloy aluminium sheets.

A totally automated on-line EDXRF has been used in nuclear power plants for several years to monitor metals in their feedwater at the ppb-level (DETORA Analytical. Inc., Alliance, OH). The first systems of this type comprised radioisotope source for excitation and proportional counter type detectors.

A very important environmental application of EDXRF is the analysis of airborne particulate matter (about 50 publications per year). It seems to be the method of choice, since aerosol loaded filters are an ideal target for EDXRF. As the part of the sample actually analysed has a surface of only few cm^2, it must be representative for the entire sample. Therefore, a critical step is in the selection of an appropriate filter material. Teflon and polycarbonate (Nuclepore) filters are ideal because of their high purity and because they are surface collectors. Whatman-41 cellulose filters have been used widely because of their low cost, but they are rather thick (namely around 9 $mg.cm^{-2}$ versus 1.1 $mg.cm^{-2}$ for Nuclepore), which leads to more X-ray scatter and higher detection limits, and they partially collect particulate matter within their depth, so that X-ray absorption corrections become more complicated. Glass fibre filters should be avoided in any case due to their high inorganic impurity. High-purity quartz fibre filters have recently been proposed. Table 1 gives detection limits obtained by WDXRF on Nuclepore filters and by EDXRF on Teflon filters.

With liquid samples there are two options for analysis: a) direct analysis with or without internal standard and b) preconcentration. With the latter approach, the samples can be physically evaporated and concentrated to determine ppb-levels or chemical preconcentration can be applied. A variety of methods can be used for the preconcentration of aqueous samples to lower the detection limits from the ppm to ppb level. These include extraction, precipitation, co-precipitation, use of ion exchange membranes and ion exchange resins. One of the most effective methods involves concentration of e.g. a litre of water on a cation exchange resin and direct analysis of the resin by EDXRF.

TABLE 1. Detection limits (μg.cm^{-2}) for wdxrf on nuclepore filters and for secondary-target edxrf on teflon filters. detection limits are based on the measurement of kα x-rays, unless otherwise indicated in parentheses.

	Detection limit			Detection limit	
Element	WDXRF	EDXRF*	Element	WDXRF	EDXRF*
Na	310	-	Ge	-	3
Mg	60	-	As	-	4
Al	7	130	Ss	-	2
Si	16	45	Br	16	2
P	8	-	Rb	-	3
S	8	15	Sr	20	3
Cl	6	13	Zr	-	8
K	2	6	Mo	-	5
Ca	3	5	Ag	-	5
Ti	1	30	Cd	8 (Lα)	6
V	4	20	In	-	6
Cr	2	16	Sn	5 (Lα)	8
Mn	1	12	Sb	7 (Lα)	8
Fe	3	12	Te	-	10
Co	2	-	I	-	13
Ni	6	5	Cs	-	24
Cu	6	6	Ba	5 (Lα)	40
Zn	5	5	Hg	-	7 (Lα)
Ga	-	4	Pb	21 (Mα)	8 (Lα)

* *Ti-secondary target for elements Al-Ca; Mo-secondary target for elements Ti-Sr; Hg and Pb; Sm-secondary target for elements Zr-Ba*

With this procedure, a Pb contamination of 10 ppb was easily determined in drinking water [6]. Anion exchange filters may be used to concentrate or selectively remove a particular component. An example is the determination of Cr^{+3} and Cr^{+6}. In acid medium, an anion exchange filter paper will collect Cr^{+6}, while Cr^{+3} passes through. Subsequently, the toxic Cr^{+6} can be directly analysed on the filter paper.

Many soil (sludge) samples have been analysed by EDXRF so far, and reported detection limits for e.g. As, Pb, Cd and Hg were at a few ppm [6]. Following recent requirements for rapid, field-based methods for environmental analysis, quite original EDXRF techniques were evaluated at the Los Alamos National Laboratory (Los Alamos, New Mexico) using laboratory, transportable, and portable instruments (Goldstein et al., [9]). Fundamental parameters provide reasonably accurate standardisation and detection limits are below background soil abundances for all elements of concern, with the exception of As. Results for certified materials indicate that the accuracy is typically better than ± 10 %, although some elements, like Se, Cd and Hg, have few or no suitable reference material to evaluate the accuracy. Comparison between portable and fixed based instruments is giving, typically, consistent results. The benefits of using EDXRF for a geochemical mapping were recently described by Civici and Van Grieken [4]. Using experimental systems with source and secondary target excitation and pressed pellet samples, 20-30 major and trace elements were determined. Detection limits and precision were evaluated and compared with required values.

The results showed that all determined elements meet the analytical requirements for geochemical mapping programs.

A correlated study on the concentration of 22 elements (P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Hg and Pb,) in various environmental samples (coal, water, sediment, soil, fish, trees, leaves, and spinach) from a coal mining area in Vietnam, was provided by Nguyen et al. [16]. This work illustrates how suitable EDXRF is for various environmental applications. Analyses were performed on dried, powdered samples, on water samples, and on digestion solutions of solid samples.

TABLE 2. Detection limits (μg. g^{-1}) for different powdered samples analysed by edxrf (ag - tube, 300 s analysis time, dry weight)

Element	Leaves	Fish	Hair	Coal	Sediment
S	70	74	180	620	930
Cl	20	15	20	60	90
K	8	3	7	60	80
Ca	2.5	2	5	30	50
Ti	1.5	1	1	9	13
Cr	1.2	0.9	1	8	12
Mn	1.1	0.9	1	6.5	10
Fe	1.1	0.8	1	5.6	8
Co	0.7	0.7	0.8	3.8	6
Ni	0.5	0.6	0.8	1.5	2
Cu	0.5	0.5	0.7	1.5	2
Zn	0.4	0.4	0.6	1.4	2
Se	0.3	0.3	0.2	0.4	0.6
Br	0.2	0.2	0.2	0.4	0.6
Rb	0.2	0.04	0.07	0.2	0.3
Sr	0.1	0.03	0.05	0.2	0.3
Ba	0.4	0.4	0.5	0.9	1.8
Hg	0.2	0.2	0.3	0.8	1
Pb	0.2	0.2	0.2	0.7	1

For coal samples, a mixture of HNO_3-H_2SO_4-H_2O_2 was recommended for digestion; for most other samples, a mixture of HNO_3-H_2O_2 can be used, while for digestion of sediments and soils a mixture of HNO_3-HCl was found to be the best. For sea water, the pretreatment procedure involves addition of HNO_3 and an internal standard, followed by overnight heating at 80°. Analytical results obtained from coal, waste water, river water, tap water, sediments and tree samples could be used not only to evaluate the impact of coal mining and coal combustion on the environment in Vietnam, but also to understand better the geology, elemental solubility, fractionation and transport mechanisms in geo-chemical research, and, in general, can give valuable guides in order to minimise the impact of coal mining on human health. In Table 2, mean detection limits for different powdered samples, as analysed by EDXRF are given. The application of EDXRF in monitoring Hg concentrations in environmental samples has not been widely used as the concentration of Hg in the environment is often below the detection limit of the technique. Suitable sample preparation methods for such studies involve the use of HNO_3-H_2O_2 and H_2SO_4-HNO_3-H_2O_2 mixtures. By performing an analysis on digested samples, the detection limit of EDXRF could be significantly decreased from 0.2 ppm to 0.058 ppm. This method was satisfactorily applied to environmental samples like coal, vegetation, fish, sediments and human hair (Nguyen et al., [16]).

Portable EDXRF instrumentation has experienced a fast development in recent times. Radioisotopes, that have been frequently used in such instruments, are now replaced with a pen-size small tube and a tiny ED detector (X-ray pen, Swedish Patent 95018111-5; U.S. Patent 5,633,908). Such device consists of a small X-ray source, a transmission tube, and a conical capillary that goes through a hole in the middle of the solid-state ED detector (drift chamber or diode). Small size transmission or microfocus tubes with low-power exigency are available from most manufactures. Such reductions in the size of detectors and X-ray tubes have made it possible to bring a XRF spectrometer at depths down to 50 m to measure e.g. heavy metal contaminants in the underground soils (Naval Research Laboratory, Washington, DC). XRF spectra are collected from a sensor which fits within the penetrometer pipe and produces high quality spectra in 100 s. The unit uses a miniature X-ray tube developed exclusively for this device and a commercial PIN diode detector. Detection limits have been observed as low as 100 ppm, even though the X-rays are transmitted through a rugged window. A major benefit of portable instrumentation is its unique capability for a non-destructive and *in situ* analysis of various geological, archaeological or architectural samples, artefacts and remote samples. On the other hand, its weak points are related to the lack of sample preparation, sampling precision and an accuracy being affected by a nature of the analysed surface.

Microsample X-ray analysis (MXA) is rather new technique developed by *Process Analytics* (Orem, USA). Basically, it is slightly adapted EDXRF instrumentation: collimation reduces the area that incident X-rays strike to a 2 mm diameter and hence, eliminates most scattering from a film sample support. The technique requires a thin film sample support designed to concentrate a small amount of solution (e.g. 50 μl) into a small spot. Prior to analysis, all liquids are dried into small residues (this eliminates scattering of X-rays from the matrix of the sample). The achievable limits of detection are in the sub-ppb region. For transition metals at the 50 ppb level, the method precision is from 2 - 9%, while the requested analysis time is less than 15 min.

4. TOTAL-REFLECTION X-RAY FLUORESCENCE (TRXRF)

Over the past decade, TXRF has been increasingly used world-wide for multielemental analysis in a variety of disciplines, including geology, biology, material and environmental sciences, medicine, forensics and art history (Klockenkämper, [14]).

Because of its simplicity, TXRF is a method of choice for quality control of ultrapure reagents, as needed in electronics, cosmetics and pharmaceutical industries. Some high-purity-grade acids, bases and solvents, including high-purity water, can be analysed almost directly, down to 1 ng.ml^{-1} (Prange et al., [18]). Further applications are concerned with high-purity metals, like aluminium or iron, and ultra-pure non-metals like silicon or silica (Klockenkämper, [14]). These solid products can be analysed in the sub-μg.g^{-1} region after an appropriate matrix separation. TXRF has been confirmed as especially useful for the determination of metal traces in light and heavy crude oils, in motor oils, and in diesel fuels. High-purity Si and SiO_2 are extremely important products for the semiconductor industry. The determination of impurities at the sub-μg.g^{-1} level is possible by a dissolution of the materials and a separation of Si as SiF_4, which is volatile (Reus, [20]).

Polished wafer disks are the basic materials for semiconductor devices. Since they are optically flat and even, they are an ideal target for TXRF. Several commercial instruments have been developed for wafer applications, and today more than 100 are in operation in the

USA and Japan. Numerous reports have appeared in the last decade and Hockett [10] gave overviews on different applications. In 1995, a new TXRF instrument, especially suitable for semiconductor research, was introduced by Yamada et al. [24]. It operates with an Au anode and with three different monochromators that can be changed within a few seconds to reach optimal analytical conditions. As regards its efficiency, Au L-excitation line appears to be a better choice than the conventional W L-line: the peak intensities for most elements are higher with simultaneously lower background.

By the use of SR and special X-ray tubes, which are more powerful than a commercial one, it is now possible to determine light elements, such as Na, Mg and Al, on Si-wafers down to 100 fg (Streli et al., [22]). Furthermore, with the SR, monochromatised with a multilayer, it is possible to determine 13 fg of Ni on Si-wafers (Wobrauschek, [25]).

Especially in the environmental sector, TXRF demonstrates strength, due to its multielemental capability for small sample amounts and its short analysis time. The analysis of water samples and air dust is routinely utilised, as well as the analysis of organic tissue, plant material and vegetable foodstuff (Klockenkämper and Von Bohlen, 1996). In case of rainwater or drinking water (both tap and mineral), the detection limit of $ng.ml^{-1}$ is directly assessable. For river water, seawater and waste waters, a sample preparation is recommended for separation of the suspended matter and for removal of the salt content. Recently, some international programs have been carried out for pollution control of environmental water bodies. Some European rivers were tested systematically for contaminants and appropriate actions were taken for their regeneration. Trace contaminants in the Atlantic Ocean were studied at several deep water stations, while heavy metal traces and pollutant transfers were investigated in the North Sea (Injuk et al., [13]).

Effective monitoring of air pollution assumes small sampling volumes and small collection times, as it is offered by TXRF. Collection of air dust can be carried out by filtration or impaction. If Nuclepore filters are used, the sampled material can be moved by ultrasonic treatment with a HNO_3 solution. The mixture of dissolved and particulate matter can be easily analysed by TXRF after internal standardisation. If membrane filters are used, the loaded filters (together with a standard), can be subjected to a pressure digestion with HNO_3 and analysed by TXRF as usual. Another possibility is to collect air directly on glass or plexiglass carriers that are ordinarily fitted for TXRF devices. Under such conditions, various elements can be determined down to < 0.1 ng. These detection limits are 3 orders of magnitude less than with conventional EDXRF. Consequently, the sampling time can be reduced to 1 h and the sampling volume to 0.5 m^3. Such analytical performances allow monitoring air pollution in the course of a day (Injuk and Van Grieken, [12]).

TXRF in not only suitable for analysis of inorganic materials, such as ashes, sludges, sediments and soil, but also organic materials like fruits, cereals, grasses and vegetables can be analyzed after digestion and preferably after matrix removal (Klockenkämper, [14]).

5. GRAZING EMISSION X-RAY FLUORESCENCE (GEXRF)

The new GEXRF technique has already been applied to the determination of submonolayer quantities of an absorbate as well as to measure ion implantation profiles. Urbach and de Bokx [23] dealt with wafer analysis and have developed a special algorithm for the calculation of layered samples. A good agreement between their theoretical and practical results was found. Furthermore, De Bokx et al. [3] analysed with GEXRF elemental contaminants on Si wafers and reached a detection limit of 6×10^{11} atoms.cm^{-2} for Mg.

In the field of environmental analysis, only direct analysis of tap water has been performed until now, and preliminary results showed for F and Mg detection limits of 300 and 1.9 ng.ml^{-1}, respectively [5].

6. MICRO-X-RAY FLUORESCENCE (MICRO-XRF)

The field of micro-XRF is currently subject to a significant evolution in instrumentation (lead-glass capillaries and polycapillary X-ray lenses; air-cooled micro-focus X-ray tubes; compact ED detector systems with a good resolution even at a high count-rate and no longer requiring liquid nitrogen cooling). This evolution allows the use of micro-XRF for a wide variety of investigations in material sciences, in various environmental studies and for traditional artefacts of a fine structure and design. Very often, micro-XRF is employed in the control of coating composition, thickness and homogeneity of various materials. Layer systems can be easily examined with a high sensitivity down to 5 nm. Furthermore, the small spot size allows measuring the coating thickness in different spots (homogeneity).

Most applications that have appeared in the literature are focused on demonstrating the spatial resolution of micro-XRF using line scans or mapping capabilities Adams et al [1]. The stromatolite analysis done by Hosokawa et al. [11] is a good example of the ability of an instrument to map multiple elements simultaneously over a wide area (200 x 200 mm^2). In addition, the rough surface of the sample had no effect upon the images because of the large solid angle of Hp-Si detector (0.4 sr). Also, by carrying out the measurement in air, sample decomposition due to loss of water of crystallisation was avoided. Another set of a data, associated with the analysis of a synthetic ruby (like for its crystalline homogeneity and Cr distribution) showed that it is useful to take diffraction mapping images as well as the common fluorescence mapping ones. By using diffracted mapping images, it was possible to determine the orientation of the crystal grains (Hosokawa et al., [11]). Other possible applications include the investigation of the bonding condition inside a plastic packaged light-emitting diode (LED). Elemental distributions of Au, As, Fe, Ni, Cu and Ga, in addition to the transmitted image, were observed non-destructively. In spite of the 1 mm thickness of the plastic package, the bonding conditions of 25 μm Au wire were easily observed. The micro-XRF technique was also applied to several industrial wastewater streams and for examination of rolled and annealed aluminium samples.

In the field of environmental studies, X-ray microprobe has been successfully employed so far e.g., an inorganic component investigation was employed for a wood sub-ring structure. The use of transmitted and scattered radiation revealed subtle changes in the wood density related to the changes in the temperature during the growth period (Kuczumow et al., [15]). Another detailed study of the leaves, taken from a garden in a neighbourhood of a metal refinery, clarified the air pollution from the refinery; elements like S, K, Ca, Ti and Fe were found to be "heavily" deposited on the leaves (Hosokawa et al., [11]). For air particulate matter, a significant improvement resides in the use of microanalytical mapping. At current micro-XRF facilities, only particles with a diameter above 10 μm can be readily analysed. Rindby et al. [21] have studied a cluster of fly-ash particles, that were deposited on a plant leaf, and then subjected to chemical treatment simulating the effect of acid rain. These types of samples are considered to be very inhomogeneous in terms of chemistry and topology and an analytical problem is to identify these two types of variations. Therefore, a quantitative method was developed, which is based on analysis of correlation graphs between the intensities from different fluorescent lines. This method is capable of distinguishing chemical variations from those variations that are due to the topography.

From the present view, it is clear that progress in the field of X-ray microanalysis with X-ray sources is advancing at a rapid rate. Commercial laboratory instrumentation using capillary optics combined with rapid scanning and compositional mapping capability is expected to grow. Already new systems from companies such as Horiba, EDAX and XCO have appeared (Pella and Lankosz, [17]).

During the 1980s, synchrotron facilities around a world have begun to implement X-ray microbeam capabilities on their beam lines for localised elemental analysis. A particular advantage in comparison with the conventional X-ray sources is the extremely high brilliance achieved with synchrotron radiation (SR) sources. SR can be 8-12 orders of magnitude more brilliant than the best conventional sources, and the achievable X-ray microbeam intensity is ultimately set by source brilliance. The most recent state of the art application using a micro-SR-XRF will not be discussed here and readers are referred to the review of Adams et al. [1] for more information.

REFERENCES

[1] ADAMS, F., K. JANSSENS AND A. SNIGIREV, Microscopic X-Ray Fluorescence Analysis and Related Methods with Laboratory and Synchrotron Radiation Sources. *Journal of Analytical Atomic Spectrometry.* 13 (1998) 319-331.

[2] BELKIN, H.E., B. DE VIVO, A. LIMA AND K. TÖRÖK, *Eur. J. Mineral.* 8 (1996) 1401-1420.

[3] DE BOKX, P.K., C. KOK, A. BAILLEUL, G. WIENER AND H. P. URBACH, Grazing-Emission X-Ray Fluorescence Spectrometry: Principles and Applications. *Spectrochimica Acta.* B52 (1997) 829-840.

[4] CIVICI, N. AND R. VAN GRIEKEN, Energy-Dispersive X-Ray Fluorescence in Geochemical Mapping. *X-Ray Spectrometry.* 26 (1997) 147-152.

[5] CLAES, M., R. VAN GRIEKEN AND P. DE BOKX, Comparison of Grazing Emission XRF with Total Reflection XRF and Other X-Ray Emission Techniques. *X-Ray Spectrometry.* 26 (1997) 153-158.

[6] DRISCOLL, J.N., Field Analysis of Metals in the Environment by XRF. *International Environmental Technology.* 8/5 (1998) 10-12.

[7] GARIVAIT, S., J.P. QUISEFIT, P. DE CHATEAUBOURG AND G. MALINGRE, Multi-Element Analysis of Plants by WDXRF Using the Scattered Radiation Correction Method. *X-Ray Spectrometry.* 26 (1997) 257-264.

[8] GENTZIS, T., F. GOODARZI AND A. HICKINBOTHAM, Mineralogical Composition of the Highvale Mine Coals and its Impact on Plant Performance. *Energy Sources.* 17 (1995) 681-699.

[9] GOLDSTEIN, S., A.K. SLEMMONS, AND H.E. CANAVAN, Energy-Dispersive X-Ray Fluorescence Methods for Environmenal Characterization of Soils. *Environmental Science and Technology.* 30/7 (1996) 2318-2321.

[10] HOCKETT, R.S. *Advances in X-Ray Analysis.* TXRF Semiconductor Applications, 37 (1994) 565-575.

[11] HOSOKAWA, Y., S. OZAWA, H. NAKAZAWA AND Y. NAKAYAMA, An X-Ray Guide Tube and a Desk-Top Scanning X-Ray Analytical Microscope. *X-Ray Spectrometry*. 26 (1997) 380-387.

[12] INJUK, J. AND R. VAN GRIEKEN, Optimisation of Total-Reflection X-Ray Fluorescence for Aerosol Analysis. *Spectrochimica Acta*. Part B, 50 (1995) 1787-1803.

[13] INJUK, J., R. VAN GRIEKEN AND G. DE LEEUW, Deposition of atmospheric trace elements into the North Sea: coastal, ship, platform measurements and model predictions. *Atmospheric Environment*. 32 (1998) 3011-3025.

[14] KLOCKENKÄMPER, R. Total Reflection X-Ray Fluorescence Analysis. John Wiley & Sons, Inc. New York, NY (1997).

[15] KUCZUMOW, A., A. RINDBY AND S. LARSSON, Tree Sub-Ring Structure Analyses by X-Ray Microprobe Analysis. *X-Ray Spectrometry*. 24 (1995) 19-26.

[16] NGUYEN, T.H., J. BOMAN, M. LEERMAKERS AND W. BAEYENS, Mercury Determination in Environmental Samples Using EDXRF and CV-AAS. *X-Ray Spectrometry*. 27 (1998) 277-282.

NGUYEN, T.H., J. BOMAN, M. LEERMAKERS, EDXRF and ICP-MS Analysis of Environmental Samples. *X-Ray Spectrometry*. 27 (1998) 265-276.

[17] PELLA, P.A. AND M. LANKOSZ, Highlights of X-Ray Spectrometry for Microanalysis. *X-Ray Spectrometry*.6 (1997) 327-332.

[18] PRANGE, A., K. KRAMER AND U. REUS, Determination of Trace Element Impurities in Ultrapure Reagents by Total-Reflection X-Ray Spectrometry. *Spectrochimica Acta*. 46B (1991) 1385-1392.

[19] READER, A. AND K. NIEUWENHUIZEN, *Solid State Technology*. September (1996) S16-S19.

[20] REUS, U. Total-Reflection X-Ray Fluorescence Spectrometry: Matrix Removal Procedures for Trace Analysis of High-Purity Silicon, Quartz and Sulphuric Acid. *Spectrochimica Acta*. 44B (1989) 533.

[21] RINDBY, A., P. VOGLIS AND A. ATTAELMANAN, Analysis of Inhomogeneous and Irregularly Shaped Samples by the Use of XRF Micro-beam Correlation Analysis, *X-Ray Spectrometry*. 25 (1996) 39-49.

[22] STRELI, C., P. WOBRAUSCHEK, V. BAUER, P. KREGSAMER, R. GÖRGL, P. PIANETTA, R. RYON, S. PAHLKE AND L. FABRY, Total Reflection X-Ray Fluorescence of Light Elements with Synchrotron Radiation and Special –X-Ray Tubes, *Spectrochimica Acta*. B52 (1997) 861-872.

[23] URBACH, H.P. AND P. K. DE BOKX, Calculation of Intensities in Grazing-Emision X-Ray Fluorescence, *Physical Review*. B53 (1996) 3752-3763.

[24] YAMADA, T., T. SHOJI, M. FUNABASHI, T. UTAKA AND T. ARAI, Development of a High Sensitivity TXRF with a Novel Monochromator Having Three Selectable Crystals, *Advances in X-Ray Analysis*. 38 (1995) 313-337.

[25] WOBRAUSCHEK, P., R. GÖRGL, P. KREGSAMER, C. STRELI, S. PAHLKE, L. FABRY, M. HALLER, A. KNÖCHEL AND M. RADTKE, Analysis of Ni on Si-wafer surfaces using Synchrotron Radiation Excited Total-Reflection X-Ray Fluorescence Analysis, *Spectrochimica Acta*. B52 (1997) 901-906.

CURRENT ENVIRONMENTAL AND INDUSTRIAL APPLICATIONS OF XRF TECHNIQUE AT THE UNIVERSITY OF COSTA RICA

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Abstract

A review of the application of nuclear analytical techniques in Costa Rica is given.

1. INTRODUCTION

Neutron Activation Analysis was the first nuclear analytical technique introduced in Costa Rica in 1974. Using Cf^{252} neutron sources the analysis were done over very few matrices, basically due to the low activity of the sources and the conditions of the laboratory. NAA activities ended in 1988. Now a days, the old neutron sources, including an Am-Be source, have been used to perform neutron-alpha reactions to follow tracks of Boron in fruit leaves, detecting the alpha particles from the reaction $B^{10}(n,\alpha)Li^7$ and using nuclear track detectors.

The X-ray Fluorescence (XRF) technique was introduced in Costa Rica by the year of 1979. After an expert meeting in San José, Costa Rica in 1977, the International Atomic Energy Agency decided to support a project at the University of Costa Rica to start with the use of XRF, including the basic instruments. By that year Dr. Peter Kump was sent to train the people at the local laboratory. Luz Maria Moya and Alfonso Salazar, professors of the School of Physics, were working with him.

The instruments used at the beginning were the isotope sources of Cd^{109} and Fe^{55}, a Si(Li) detector from Ortec and a multichannel analyzer from Canberra. Pre-Columbian ceramics were studied at that time, in a joint project with the Archeology Department. In this study, special attention was dedicated to the trends of three elements, Strontium, Zirconium and Rubidium, comparing the results from different archeological regions and looking for natives commerce routs.

Since the beginning the Agency supported several fellowships for training. Mr. Salazar attended two courses, one held at the Ruder Boskovic Institute, Zagreb Croatia (1985) under the supervision of Dr. V. Valkovic, and the other at Argonne National Laboratory, Chicago and Florida State University, Florida, USA (1988) working with Dr. W. Nelson in the application of PIXE for aerosol analysis. Ms. Moya participated in a training course in Bangkok, Thailand.

The laboratory has been visited by several Agency supported experts in the x-ray field. After Dr. Peter Kump, we worked with Dr. Vlado Valkovic during the installation of the x-ray tube in 1986, with Dr. Jon Tiss for alloy analysis in 1989 and with Mr. Ronny Ayala during the installation of the Total Reflection system in 1990. Dr. Woubrachek helped us to calibrate de total reflection system in 1995.

Three graduated students have worked with us during the last fifteen years; two are working in another institution (Instituto Tecnológico de Costa Rica) but they are doing only teaching. The third one is finishing his Ph.D. degree at the University of Minnesota and will return to Costa Rica next year to join the XRF group.

Professor Luz Maria Moya retired in 1986. Mr. Manuel Zapata from Cuba joined our laboratory, and worked preferentially with Total Reflection x-ray Fluorescence. He spent one and half year at the laboratory and left at the end of last year.

At present time, Mr. Alfonso Salazar M. carries out the applications of the x-ray fluorescence analysis, with the assistance of four students, three from Physics and one from Chemistry.

The applications of the x-ray fluorescence analysis have been done throughout several research projects sustained mainly by the University of Costa Rica. Some aerosol analysis projects have received complement help from the government.

The laboratory has also made analysis of alloys. This job is normally done for private companies, who are principally interested in knowing the composition of the samples.

The most relevant applications that have been carried out are related with environmental studies and with alloy composition.

- Element composition of pre-Columbian gold pieces of the Central Bank Museum of Costa Rica.
- Heavy metals analysis of aerosol particles from San José metropolitan area using PIXE and x-ray direct irradiation.
- Determination of trace elements in sediment and coral samples from the Caribbean coast.
- Alloys composition using Mo secondary target (sell service).
- Trace element in rain water using total reflection x-ray fluorescence.

2. ENERGY DISPERSIVE X-RAY FLUORESCENCE

Energy dispersive x-ray fluorescence has been a useful technique in the analysis of different material, solid and liquid. The multichannel x-ray spectrometer provides the means of measuring many elements simultaneously. The great advantage of this technique is given essentially by its nondestructive property. A wide range of well-analyzed calibration standards and the use of appropriate algorithms relating x-ray emission intensity and elemental composition is allowing the use of this x-ray method in a wide variety of analytical disciplines.

The different types of the samples require the adjustment of the irradiation setup; different sample preparation and counting time. The characteristic x-rays of the elements are affected by sample density, the element composition, the thickness, the inter-element effects or the so called matrix effects. It is also important to take into account the geometry of the irradiation system, the peak-background ratio, dead time and the calibration curve needed for an appropriate quality of the analytical results.

The Applied Nuclear Physics Laboratory (LAFNA) is using three types of irradiation setups. The Mo type x-ray tube has two windows for primary irradiation of the samples. One window is settled for the use a secondary target and for direct irradiation, and the other window is used for the total reflection system.

The primary radiation that is coming directly from the x-ray tube, besides the Mo photopeak, also introduces bremsstralung x-rays. This produces a very high background and the radiation is not monochromatic. The algorithms used by the QXAS software are based on monochromatic primary radiation. There are two ways to get almost monochromatic x-rays:

- Using a secondary target between the radiation from the tube and the sample, normally on a 45 degree setup. The sample is then irradiated with the characteristic x-rays of the target. Any kind of metal can be used as a secondary target, it only depends on the elements of interest. With each target it's necessary to calculate a calibration curve using several standards. For trace analysis of heavy metals in different samples, we normally have used a Molybdenum secondary target, and for the analysis of gold pieces a Tin secondary target is used.

- Using a filter between the sample and the x-ray from the tube, the bremsstralung radiation is reduced. A 0.5 mm foil of Molybdenum or Zirconium reduces the bremsstralung and lets only the Mo photopeaks through, as monochromatic radiation. The background on the spectra and the dead counting time reduces this technique to the analysis of thin samples. With this setup a very low tube current has to be used, usually down to 5 mA. For aerosol analysis it is a very good technique. The loaded Nuclepore filters are presented directly to the XRF unit, with the loaded side towards the instrument. Calibrating the system with appropriate standards, no correction for the X ray absorption in the aerosol material is usually necessary.

We have also introduced in the laboratory the **Total Reflection X-ray Fluorescence (TXRF)** technique. It is a more accurate and sensitive analytical technique. All samples to be analyzed need to be in an aqueous solution and a drop less than 10 µl is put on a quartz sample carrier for irradiation. The primary x-rays impinge on the sample with a scattering angle less than 5 min. The reduction of background is almost 100% and the secondary x-ray comes from the elements present in the sample. The minimum detection limit goes as low as 50 ng/L. A TXRF module designed by Dr. Peter Wobrauchek has been mounted at the laboratory. For rain water analysis one of the advantage is that the sample need very little chemical preparation. This is the main application that we are giving to TXRF method. Digestion of the sample is needed for most biological samples. Recently the laboratory received a microwave digestion system, which has been tested with some samples with good results, but so far it is not in routine use.

PIXE (Proton Induced X-ray Emission) analysis was carried out also at the laboratory, due to special cooperation between LAFNA and the PIXE Laboratory of Florida State University (FSU). PIXE analysis is a very sensitive technique for trace element analysis, especially used for aerosol composition studies. Small amount of material on a tiny area is very easy to irradiate with high energy protons. Aerosol samples collected in Costa Rica were irradiated at FSU Van der Graaff accelerator. Complement spectra and data analysis was done in Costa Rica. During six years of cooperation, several aerosol studies were done, selecting sites in the San José urban area and at the countryside. The aerosol sample is collected using a streaker system with two filters, one of 8 µm at the main entrance and one of 0.4 µm. The filter disk rotates on a moving system to collect a 1x8 mm^2 sample. The sample collection is done every hour during a complete week, giving 160 samples. The sample disk is mounted in a vacuum chamber for high energy proton irradiation. The x-ray spectrum is evaluated using a HEX code, developed by the PIXE Laboratory at Florida State University. The data obtained for more than fourteen elements are analyzed by statistical commercial software. Element profile and origin can be established with this procedure for pollution studies on the sites selected.

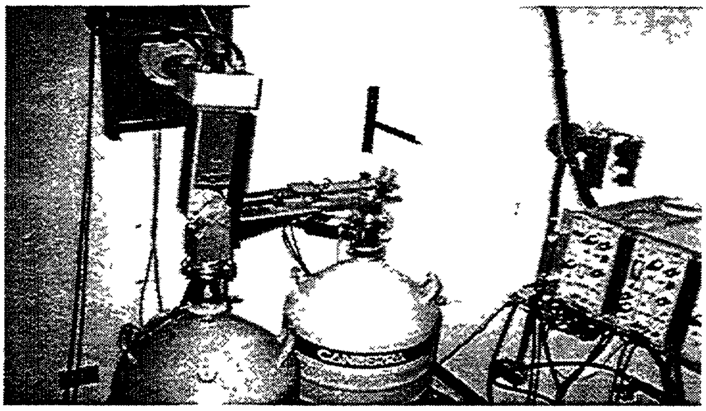
2.1 EQUIPMENT

Irradiation system: Since 1986 The laboratory has an X ray tube, ISO DEBYEFLEX 2002 from Seifert, with a Molybdenum anode. The model has four separated parts, a high voltage generator, a control chassis, a regulation chassis and the tubehousing with a SN60 Mo, K-Anode. The cooling system was changed, in 1990, to a unit from Electro Impulse Inc. Model 36332. The tube has two windows, one is used for the 45 degree setup and the other for the total reflection system. There are three Si(Li) detectors from Canberra, Models SL 30170 and SL 30165. One is not operating because a damage on the Be window. The electronics is completed with two High Voltage supplies, Canberra models 3102, and two spectroscopy amplifier, Canberra models 2020. The sample support for the secondary target setup consists of an Aluminum base with three collimators of pure Al. They are oriented for the source-secondary target, the secondary target-sample and the sample-detector.

Direct irradiation with regenerative monochromatic filter uses the same base, only with two collimators, one from source to sample and from sample to detector. Thin foil filter, of Mo, is used between source and sample.

Besides the X ray tube, an annular ^{109}Cd source of 25 mCi (April 97) is used when the X ray tube is out of operation. Recently it has not been used very frequently.

The total reflection module consists of several components. A height adjustable steel support with connecting base plate. The X ray tube housing is mounted downright a 6 degrees deviation from the vertical line, thus the X ray beam propagates in the horizontal plane. On the Al base there are the brass collimator, the cut-off reflector, the beam stopper, the adjustable quartz reflector holder. The total reflection is accomplished by adjusting the three micrometers by hand, looking at the two lines of the x-ray formed by Zn-S screen. This procedure makes one of the biggest difficulties of the system considering the radiation hazard during calibration and mechanical sensitivity. For the Mo anode with characteristic radiation energies of 17.48 keV and 19.6 keV, the cut off angle is 1.6 mrad. If the Zn-S screen is located at 0.5 m, the angle can be reached if the two beam lines are separated from each other by 1.6 mm. A view of the irradiation facility is given in the picture.



Counting system: The X ray spectra and general data is collected using: a) A Nucleus II, personal computer analyzer (PCA-II), installed on 486DX2 IBM compatible personal computer. The PCA card contains a 100 MHz Wilkinson analog to digital converter (ADC). An input from a shaping amplifier is the only external signal necessary for pulse height analysis (PHA).The software utilizes a windowing technique with pull down menus for user friendly operation. b) ACCUSPEC, personal compute analyzer from Canberra. It consists of both hardware and software components which are installed in an IBM PC compatible system. An acquisition interface board with an on-board Analog-to-Digital Converter. This system is not in operation because memory problems with computer has not been solved. All the spectra collected is transferred to the AXIL system.

Sampling and sample preparation: The laboratory has used some basic equipment for sampling and sample preparation. Most of the X ray fluorescence applications has been done with samples that need little preparation. It is necessary to follow some simple rules in sampling and sample preparation, like: a) take large samples if it is possible, b) avoid contamination of the sample, c) avoid losses of the elements during transportation and storage, d) take account of parameters that may influence the sample composition and e) use simple sample preparation procedure before any chemical method.

For analysis of airborne particulate matter, two sample collectors have been used. a) PIXE analysis and direct irradiation with filter, can be done on Nuclepore filters used with a "streaker" type collector and mounted on a 160 position disk. Each sample is formed by an area of 8 mm^2 every hour and represents the material transported by 60 l of air. For PIXE analysis the sample is irradiated with 3.5 MeV protons from a Van der Graaff accelerator (Florida State University). b) The "GENT" air collector works for 24 hour period, using a two stage filter support to select the particles with size less than 10 µm. Both instruments use a vacuum pump, a simple integrating dry gas meter and a rotameter. After weighting, the filters are irradiated without any further chemical preparation.

Marine and geological samples are collected direct on the field. After collection the sample is crushed , milled to about 0.5 mm grain size, a fraction is grinned to coarse powder and finally to a fine powder. The sample is homogenized and pressed into a 5 mm diameter pellet without a binder. For this procedure we have a Fritzch mill, some mortars and sieves. With coral samples we are using the "slurry" technique in order to get a thin sample.

For digestion needed for Total Reflection XRF there is a Pressurized Microwave Decomposition System from PAAR, using Quartz and Teflon bombs. The sample preparation room is not complete. The water purification system and the fume hoods have not been installed because new room space is needed.

Spectra and data analysis: The laboratory has used the QXAS software package very extensively. It has been used for quantitative evaluation of the spectra and for quantitative determination of element concentration on the samples, using several methods. The evaluation and processing the X-ray spectra is performed using the AXIL package (Analysis of X ray spectra by Interactive Least-squares fitting) after the spectra has been transfer from the MCA (Nucleus II or ACCUSPEC).

We have used three of the quantitative methods:

1. Elemental sensitivities method.
2. NBS method
3. The Fundamental Parameters Method.

To accomplish the methods is necessary to specify the excitation source, the detector characteristic, the geometry of the irradiation facility, and perform the calculation of the calibration curve or the sensitivities using appropriate standards. Following the steps, the unknown samples can be analyzed for the concentrations of all of the elements detected. Matrix corrections are very important on this procedure. The elemental sensitivities method has been used for thin samples, mainly for aerosol samples. For quantitative evaluation of marine and geological samples using thick samples, the Fundamental Parameters method has been implemented. Alloys have been quantify by the NBS method.

Statistical studies of the elements data have been carried out with a commercial software (STATISTICA for Windows, v 4.5). Factor Analysis has been used for aerosol source profiles.

2.2 XRF APPLICATIONS IN COSTA RICA

2.2.1 Glass-fiber filter for analysis of aerosol particles using energy-dispersive X ray fluorescence

Energy dispersive x-ray fluorescence was used to analyze aerosol particles deposited on glass-fiber filters. The blank filter contained several elements that interfered with trace elements found on the particles. The loaded filters were studied for composition and particle distribution of the few elements that can be analyzed, which include lead. Samples were provided by the Costa Rican Health Ministry. The study was carried out with ^{109}Cd isotope source. The filters have dimensions of 20x25 cm^2 and were used exclusively for monitoring airborne particulate matter density. The study was a complement in order to evaluate those elements not present in the blank filter.

The homogeneity of the matter and the element distribution on the filter are calculated when only a fraction of the total filter is irradiated. The distribution for eighteen different measurement points on the filter, showed good homogeneity of the particle distribution on the filter. Three small areas for each filter were analyzed. Figures 1 and 2 shows the trace elements detected on the blank filter and the loaded filter. Copper and lead were the only two elements possible to analyze under the conditions imposed by the filter. The results of this experience were used by the Health Ministry to measure the lead levels present. At that time (1990) gasoline with lead was sold in Costa Rica.

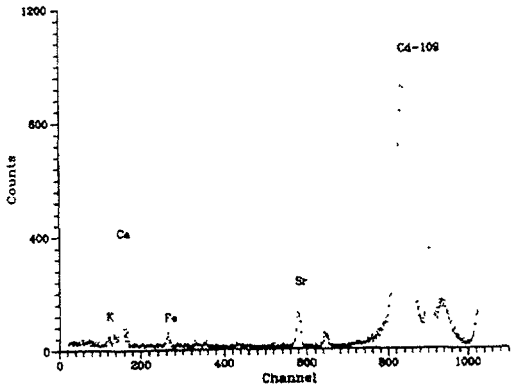


Figure 1. Trace elements identified on a blank glass-fibre filter. Counting time: 3000 s.

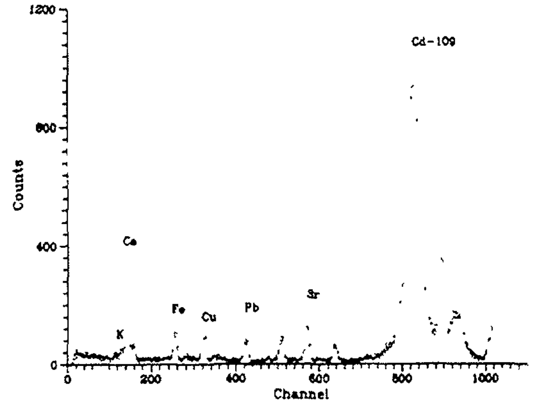


Figure 2. Trace elements identified on a loaded filter. Counting time: 3000 s

2.2.2 Time variation of trace elements in airborne particles from San José, Costa Rica

The measurements were carried out in cooperation with Dr. J.W. Nelson and Mr. P. Thonnard from the Florida State University. Trace elements in airborne particles are important to identify possible pollution sources. Evaluating the concentration of several elements allows to establish a reasonable understanding of wind cleaning processes in San Jose. Three different sites were chosen. The sites were selected based on the facility to collect meteorological information and to identify possible pollution sources by sight. These places chosen were:

(a) Site 1: The wheeled intersection Hispanidad, San Pedro de Montes de Oca, 2 km east of San José downtown, where the sampler was placed about 5 m from the street with high traffic. The samples were colleted between may 15 to 22, 1995.

(b) Site 2: The Instituto Costarricense de Electricidad (ICE) building, besides La Sabana metropolitan park, 1.5 km west of San José downtown, in front of a big park, but also surrounded of high traffic. The samples were collected between February 12 to 16, 1995.

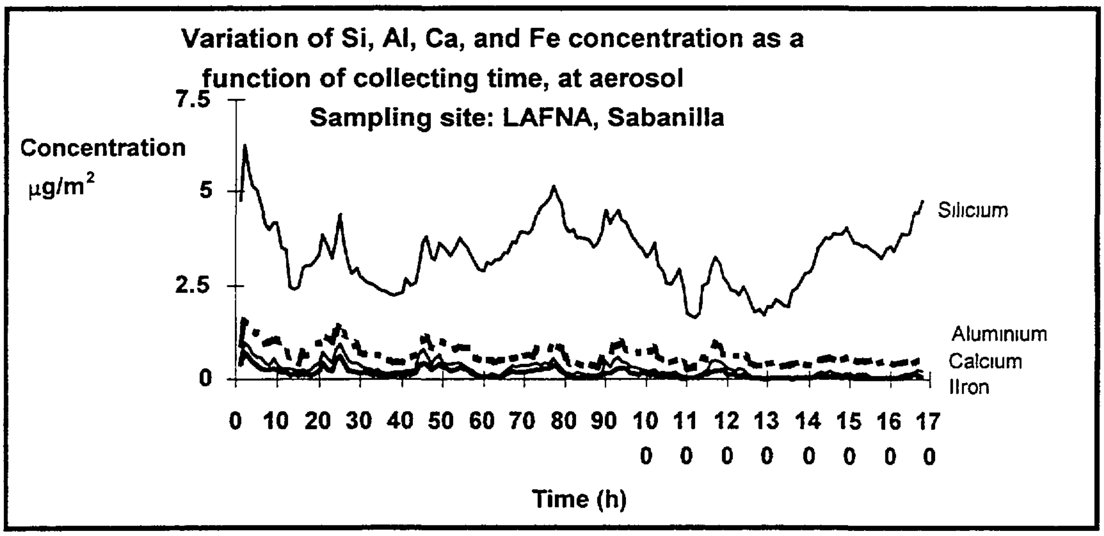
(c) Site 3: The outside of the Laboratorio de Física Nuclear building, located on an open field at the University campus, located 2.5 km east from downtown. There is no car influence over this place. The samples were collected between November 22 to 25, 1994.

During the last ten years two political decisions contributed to understand the roll of airborne particles in atmospheric pollution on the city of San Jose. First, the reduction on import taxes over used cars has contributed to increase the amount of cars, which give more particles into the air. Second, the elimination of any lead compound in gasoline has contributed to reduce respiratory problems. . During the period of sample collection, no lead was detected (1995).

The samplers used were circular streaker of one-week duration, which collects airborne particles every each hour, for a total of one hundred and sixty samples.

Elemental concentrations of aerosol contents were determined using PIXE analysis, performed at PIXE Lab., Florida State University, Fl. USA. Data reduction was done using the computer software Hex code both at FSU and at the Laboratorio de Física Nuclear Aplicada, Universidad de Costa Rica. Commercial statistics and data analysis software is used for factor analysis in order to establish groups of the trace elements.

Up to 14 elements are measured on particles collected on a nuclepore filter using PIXE. The results show that about 85% of the particles are formed by soil dust and automobile combustion, with some elements from the marine breeze. The average values for all elements (except Si) are less than 1 $\mu g/m^3$.The concentration levels go down during the night due to less anthropogeny activity. San José is not an industrial city so industry contribution to pollution is very low. The figure shows the time variation of the concentration of some elements (Si, Al, Ca and Fe) measured on the filter.



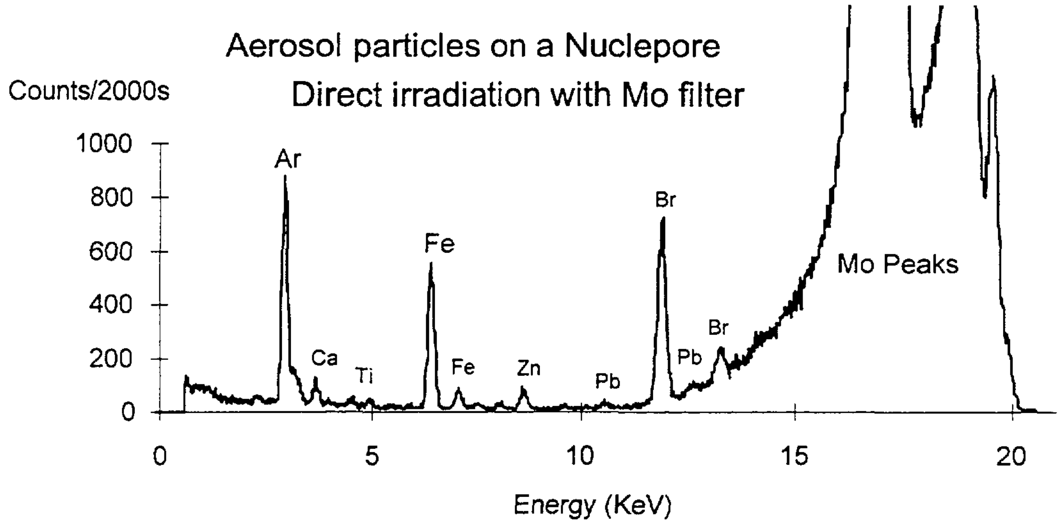
2.2.3 Irradiation of aerosol filters using regenerative monochromatic filter

In order to continue the monitoring of trace elements in aerosol particles, new possibilities for irradiating the filters were studied. When the sample is irradiated directly with the main beam of the x-ray tube, the trace element peaks sit on a very high background and tend to be obscured by the large statistical fluctuations in this background. The reduction of the bremsstrahlung in regions containing the trace element peaks is done using a selective filter, according with anode material.

A Molybdenum foil of 0.5 mm is used between the x-ray tube and the sample to attenuate the bremsstrahlung continuum at lower energies than the Mo K lines. Trace elements in the energy range from 3 to 13 KeV will be efficiently excited by the Mo K lines, while the background beneath these trace element peaks will be extremely low. This background depends of the tube current and to achieve a good peak-background ratio a 5 mA is used. This monochromatic excitation is very useful only with thin samples. If an intermediate thick or thick sample is placed a distance of 2.5 cm from the x-ray window, the counting dead time is over 10%.

For aerosol analysis this excitation method is appropriate. A new sample collector is necessary in order to have more aerosol mass on the filter. This is achieved using a "GENT" type collector. This system has a filter holder with two positions on cascade. The filters (8 µm, 0.4 µm) are separated 5.0 cm. The collecting time goes to 24 hours, with an air flow rate of 17 l/m. The particle distribution on the filter was measured on several spots.

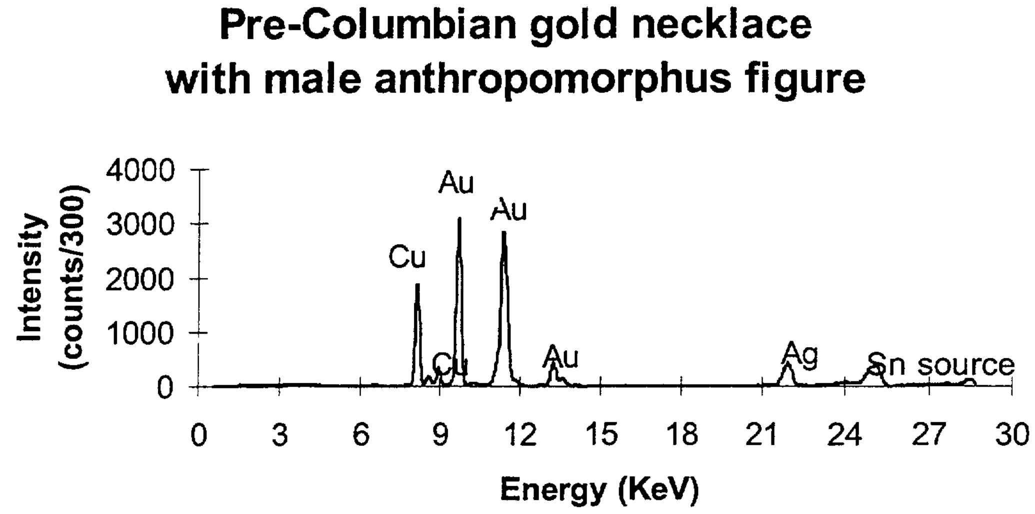
The minimum detection limit(MDL) shows that the sensitivity is appropriated to evaluate the heavy metals on aerosol filters. The samples have been collected from the same places selected before for PIXE analysis.



2.2.4 Gold and Silver relation in pre-Columbian gold pieces of the Costa Rican Central Bank Museum

The Central Bank Museum is classifying pre-Columbian gold pieces made by the natives handicraft work. They are interested to look at the relation between the gold and silver concentration in order to find out commercial routes and the origin of manufacturing. These pieces have mainly anthropomorphic forms, representing human and animal figures. They have only a few flat parts where irradiation is possible. Several measurement were done over different spots of the figures at different distances from the source, with a range of 2-4 mm. When the concentration of all the elements are normalized to 100%, we found that individual concentration varies less than 2% in absolute value. These procedure permits to assure the results, because some of the pieces have a very irregular form.

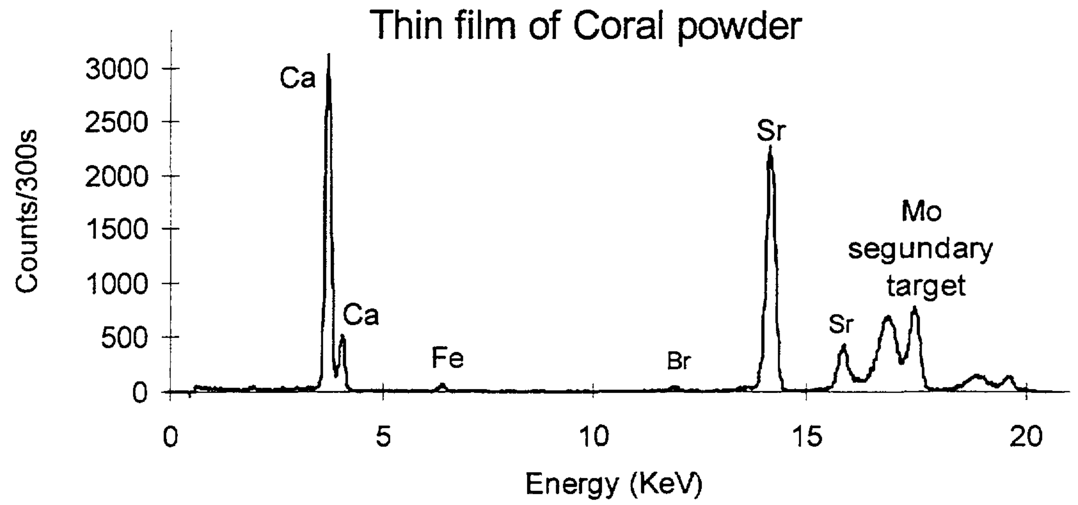
The irradiation system was calibrated using a Tin secondary target. Its excitation energy is high enough to get the silver K peaks and the gold L peaks. Copper is the third element present in this kind of sample. A few samples have some others elements due to the contamination during the treatment. Pure metal standards and the NBS software were applied to evaluate the concentrations. The results show good similarities with a evaluation made by Dr. David A. Scott from the GCI Museum Laboratory, Ca. He also analyzed pre-Columbian gold pieces from Costa Rica and Panama.



2.2.5 Calcium-Strontium ratio for marine sediment and coral samples

The Center for Atmospheric and Oceanographic Studies of the University of Costa Rica has been collecting marine sediment and coral samples from the Caribbean coast of Costa Rica. They have been interested in the study of the composition of the marine sediment and the coral. Pollution studies have shown that the contamination of the sea water modified the growth of the coral, and altered radically the habitat. The study involves calcium-strontium ratios and the evaluation of some other trace elements.

After the samples are collected and classified, they are cleaned, dried and pulverized. Pressed pellets are made from the fine powder of both samples. The irradiation system is based on Molybdenum secondary target, with a tube current of 30 mA and voltage of 40 kV. The concentration is calculated for each one of the elements observed using thick samples and the Fundamental Parameters method of the QXAS software.



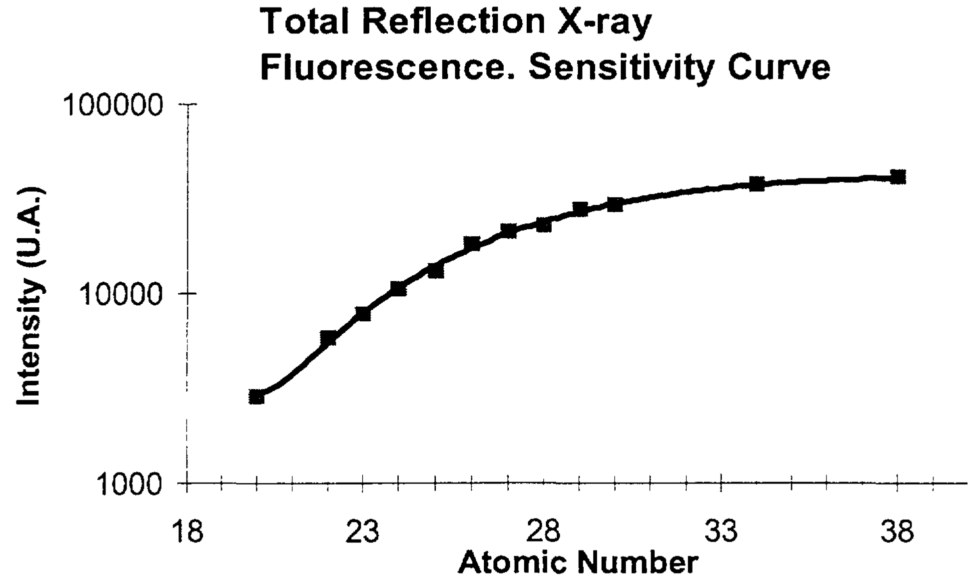
2.2.6 Trace elements in rainwater by total reflection X-ray fluorescence (TXRF)

Costa Rica is a tropical country with high rain precipitation during six months of the year. The amount of trace elements found in aerosol is affected by the rain. Rainfall is a form of deposition for trace-element input from the atmosphere to terrestrial and aquatic environments. The determination of trace elements in rainwater is becoming important because many heavy metals contribute to the hazards and destruction of forest, lakes and coastal waters.

Total-reflection X-ray fluorescence is a special variant of energy-dispersive XRF, with substantially improved detection limits. The rain water is collected manually on 1-L polyethylene bottle. When the sample is taken to the laboratory, an aliquot is used for pH determination and the rest is acidified to pH about 1.7 with concentrated HCl, sealed in polyethylene bags and stored in a refrigerator until analysis. The conditions of the laboratory is going to be improved to get a good purification of all components of the sampler.

The analytical technique used to quantify the trace-element concentration is based on the direct measurement of rain water sample. An amount of 50 μL of Co-standard solution (10 ppm) is added to 20 mL of rainwater and mixed thoroughly. An aliquot of 25 μL is transferred to a siliconized quartz sample carrier and vacuum-dried for measurement. We chose this procedure in order to avoid chemical treatment of the samples.

The TXRF system has been calibrated using pure standards from Merck. The detection limit for the elements measured with direct deposition goes down to 10-50 ng/L. The application of the TXRF has been limited by the absence of personal with chemistry knowledge. Some difficulties with sample preparation has reduced the number of samples analyzed.



REFERENCES

[1] BERTIN EUGENE P. Principles and Practice of X-Ray Spectrometric Analysis. Plenum Press. N.Y. 1975

[2] JENKINS RON, GOULD R.W., GEDKE D. Quantitative X-ray Spectrometry. Marcel Dekker Inc., N.Y. 1981

[3] DEBERTIN KLAUS, HELMER R.G. Gamma and X-ray Spectrometry with semiconductor Detectors. North Holland, Amsterdam. 1988

[4] IAEA. Manual for QXAS Quantitative X-ray Analysis System (Version 1.2 1995-1996)

[5] IAEA. Sampling, storage and sample preparation procedures for X-ray fluorescence analysis of the environmental materials. IAEA-TECDOC-950. 1997

[6] BOUMANS P. Total Reflection X-ray Fluorescence Spectrometry. Spectrochimica Acta, Part. B: Atomic Spectroscopy. Proceedings of the Fourth Workshop on TXRF, Geesthacht, F.R.G., 1992.

[7] ADAMS, F.C.; VAN GRIEKEN, R.E. Absorption correction for x-ray fluorescence analysis of aerosol loaded filters. Analytical Chemistry, Vol. 4, 123-127,1975

[8] V. VALKOVIC. Sample preparation technics in trace element analysis by X-ray emission spectroscopy. Technical document. IAEA, 1983

[9] VOGT, JAMES R., PARKINSON T.F.,CARTER, R.L. Nuclear Methods in Environmental Research. Published by University of Missouri-Columbia, 1980

[10] IAEA. Sampling and Analytical Methodologies for Energy Dispersive X.ray Fluorescence Analysis of Airborne Particulate Matter.Division of Life Sciences IAEA, 1993.

ENVIRONMENTAL AND INDUSTRIAL APPLICATIONS OF XRF AND RELATED TECHNIQUES AT THE INSTITUTE OF NUCLEAR SCIENCE, UNIVERSITY OF NAIROBI, KENYA

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Abstract

A comprehensive review of the application of nuclear analytical techniques, in Kenya, to different areas are given. High levels of Mercury in beauty creams are reported.

1. SUMMARY

For the past one year, the Institute staff and students have hosted and participated in regional and national conference/workshops, locally and abroad. These workshops/conferences have dealt on issues such as harmonization of health related environmental measurements using nuclear techniques, scientific writing, repair and maintenance of nuclear and other scientific laboratory instrumentation, computer networking and research on African grassland fires. Research activities undertaken in 1997 include: *Traditional medicines in anticonvulsant therapy and the implications of trace elements in health and diseases*, for an award of a Ph.D. degree and *Non-destructive analysis of mercury in beauty creams* for the award of M.Sc. degree. The aim of the latter study was to develop a faster analytical technique for mercury analysis especially for organic samples. This is because other well known chemical analytical procedures take too long, owing to the lengthy sample preparation procedures which require expensive and toxic reagents. In addition, this study revealed that the mercury in the beauty creams sold in Kenya was in levels that were above the local and WHO acceptable limits. These mercury levels were not constant in different batches of same products sampled at different periods. The results have far reaching implications on the quality control processes during the manufacture and it is possible that some of the products in the market could be having higher levels of mercury than those sampled during this work. The interest on the study of traditional medicines was inspired by the fact that for a long time bioinorganic scientists have attempted to extract the active curative ingredients from plants without success. This work addressed the important therapeutic role being played by the essential trace elements. Various elements were identified in various levels in the plant-derived preparations and in medicinal plant extracts which are often used in the preparation of herbal medicines in Kenya for anticonvulsant therapy. The analytical techniques used in this study were EDXRF, AAS, Colorimetry, ICP-MS and PIXE. When administered traditional anticonvulsants depresses the central nervous system (CNS). Rats treated with one traditional anticonvulsant used by one traditional healer registered longer pentobarbital sleeping time

(71.2±18.1) minutes while the control group had a sleeping time of (39.3±9.3) minutes. This study showed the important role being played by the essential trace elements present in some traditional medicines and medicinal plant extracts available in Kenya. Some of these medicines made our forefathers survive for many years without modern allopathic drugs because they provided the essential therapeutic agents with minimum side effects. Future challenges of this work include: the speciation determination of the essential trace elements in the medicinal plant extracts and preparations; determination of the existence of radicals such as NO which is now known to be important in cognition and neurotransmission; the determination of metabolic pathways and mechanisms on the possible roles being played by essential trace elements in drug functions. Some current studies by our M.Sc. students include the following projects: *Analyses of food crops grown along Nairobi river for their heavy metal content using EDXRF technique*. This study by Sirengo S.J. aims to: (i) determine the heavy metal content of Nairobi River waters and the soils on which the food crops are grown, and (ii) determine the available heavy metals for plant. The second study: *Trace element analysis of local pollen, honey and its by-products using EDXRF technique* is another study by Wamwangi M.D. and aims at: (i) determining the trace elements distribution in the pollen, raw and local refined honey and its by-products; (ii) determining the different trace element profiles of the honey samples from selected areas of the country, and (iii) determining the extent of trace element contribution on the quality of local refined honey. The third study: *Trace element analysis of environmental samples from Webuye Town using x-ray fluorescence analysis technique* is by Akinala J.M. This study aims at determining trace element levels in: (i) the industrial effluent discharges from Pan African Paper Mills; (ii) water and sediment samples from river Nzoia, (iii) particulate matter settling on buildings and land in Webuye Town; (iv) plants and fungi (*Lichens & Mosses*). The fourth study is: *The determination of radio-nuclides in food-stuffs and environmental samples found in Nairobi by gamma spectroscopy*. This study is by Maina J.W.A. and has the following objectives: (i) calibration of the newly acquired hyperpure germanium detector for gamma measurements; (ii) analysis of food and environmental samples from Nairobi for the presence of gamma emitters for baseline data on radioactivity levels in the country, and (iii) assessing the radiation exposure from natural and man made sources for the evaluation of activity levels in cereals, milk products and fertiliser applications.

Other studies by staff include the following: *Characterisation and Transport of Aerosols Sampled at a high altitude on Mt Kenya*. This is a Ph.D. Project by C.K. Gatebe. He is registered at the University of Witwatersrand, Johannesburg, South Africa and is supported by IPPS, START, UON, University of Witwatersrand and DAAD. The work aims at the development of an air transport climatology model for Kenya and to characterize aerosols samples obtained from Mt Kenya. This is a remote site located next to the equator while the air sampling was by use of a Streaker Sampler and was started in June 1997 and continues to date. A number of good samples have been collected and analysed at PIXE International, Tallahassee, USA. Other samples are being analysed at Schonland Research Center for Nuclear Sciences, University of Witwatersrand, Johannesburg. Good progress has been made and initial results show that there is inter-hemispheric transport of aerosols across the equator; *Investigation of Kenya aerosols by size characterisation, chemical constituents and deposition in the perspective of air pollution and climate change*. This is a Ph.D. project by M.J. Gatari. He is registered at the University of Gothenburg, Sweden and is supported by IPPS. At present he is undertaking the necessary coursework to strengthen this investigation. *The Physics of Radon Daughters in Relation to Smoke Aerosols and their Role in Human Dosimetry*. This is also a Ph.D. Project by D.M. Maina. He is registered at the University of Witswatersrand, South Africa. The aim of this project is i) to measure the size distributions of smoke particles; ii) to measure the size and activity distribution of radon daughters attached to smoke particles;

and iii) determine the exposure due to these radioactive aerosols. The distribution of smoke particles using a Differential Mobility Aerosol Analyser has already been done at Chalmers University, Sweden while the radon measurements are being done using E-PERM System at the Institute of Nuclear Science, University of Nairobi. Other studies by our staff members include: *Suspended particulate matter (SPM) sampling at the Nairobi Industrial Area and Workplaces, analysis of water samples and effluents collected from factories- sugar and a tannery; mercury (Hg) analysis of beauty creams sold in Nairobi; and heavy metal and sulphur analysis of waste engine oils.* Air sampling exercise in the industrial area was done twice a week for a period of two months (November and December, 1996) and twice monthly for a period of six months (January-June 1997). Each sample was collected after approximately 24 hours using the 'Gent' Stacked Filter Unit (SFU). The SPM values were found to vary from 16 to 83 μgm^{-3} during the sampling period. The results of the analysis of dust collected inside a workplace indicated that there was poor filtration of the air being drawn into the building. Recommendations on the improvement of the air filtration and conditioning unit within the building plus a reduction of emissions emanating from a neighboring tyre factory were made to the proprietors.

EDXRF analysis of beauty creams showed that there was mercury present in significant amounts (0.14 - 3.0%) in various cosmetic brands being sold in Nairobi. The health implications on the presence and of these high levels of mercury in some of these beauty creams is also discussed.

The presence of sulphur (0.9 - 439 μg/ml) in the water samples from the River Nyando showed that industrial waste from the sugar and agro-chemical factories upstream did affect the water quality of the river. These high levels were registered at a waste treatment pond of an agrochemical factory. Heavy metal analysis of the water samples collected from River Nyando showed phosphorus and lead being below detection limits which ranged from 30-180 g/ml and 30-150 ng/ml respectively. The occurrence of the high levels of sulphur suggests some random release of industrial wastes into the river plus poor effluent control measures by the industries. Other parameters measured include conductivity, salinity and BOD which indicated the need to improve on the effluent control measures by the industries. The analysis of waste engine oils shows high levels of heavy metals and sulphur. The heavy metals were mainly from wear and tear of engine parts.

From the above studies, it is evident that XRF can be utilized in many fields and when complemented with other techniques, the analytical results are useful for multidisciplinary research studies. Our laboratory has for many years collaborated with other institutions on a number of research projects. Some examples are shown below as a testimony of the utility of nuclear analytical techniques for industrial and environmental studies. It is hoped that this will enhance human resource development, introduce new analytical techniques and regional collaboration.

2. INTRODUCTION

The utility of nuclear techniques in Kenya dates way back before Kenya's independence in 12th December 1963. This was at institutions such as the former Royal Technical College (presently the University of Nairobi), some agricultural research institutes and the Medical Research Laboratory which was formed in 1958. Documentation of these activities is not available but can be speculated that some work was being carried out in tracer techniques in agriculture, quality control and basic nuclear science experiments. Other activities were in medical-radiology at the former King George Hospital (now Kenyatta National Hospital).

The United Nations General Assembly in 1977 passed a Resolution, (32/50-1977), which, among other things, stated that: *"the use of nuclear energy for peaceful purposes is of great importance for the economic and social development of all countries"*. The following year, Kenya formulated a project on the establishment of a Nuclear Science Laboratory. This was financed by the Government and the International Atomic Energy Agency (IAEA) to serve as a nucleus for the introduction and development of nuclear science and technology in the country. It was implemented in 1979 with creation of the Centre for Nuclear Science Techniques (CNST) under the Faculty of Engineering at the University of Nairobi. Since then, CNST developed into an Institute of Nuclear Science in 1993. The major emphasis of the Institute has been the training of postgraduate students on the use of nuclear techniques in material analysis, environmental pollution monitoring and basic nuclear science research. This led to the introduction of an M.Sc. Programme in nuclear science which has benefited research institutions in the country and others from East, West and Central African region.

Since 1978, various Technical Co-operation (TC) projects and Co-ordinated Research Projects (CRP) funded by the IAEA have been implemented in the country. Some examples of these projects are: radiation protection and dosimetry; environmental pollution monitoring using nuclear analytical and related techniques; non-destructive testing of materials; nuclear instrumentation; nuclear waste management; isotope techniques in the efficient use of fertilizers; improvement of dairy productivity; pesticide research and the use of radio-nuclides in quality control and production of medical kits.

Apart from these TC and Co-ordinated Research projects, Kenya also participates in the African Regional Co-operative Agreement (AFRA). These activities are co-ordinated by the IAEA and include: nuclear techniques in plant breeding and biotechnology; local preparation and use of radio-immunoassay reagents, non-destructive testing, repair and maintenance of nuclear instrumentation.

3. OVERVIEW OF SOME CURRENT ACTIVITIES

3.1 AIR POLLUTION STUDIES

(i) SPM measurements at Nairobi Industrial Area

Air sampling exercise at this site was done in November 1996 - August 1997 and continues to date. This site is located some 13 km from the city centre and to the south eastern side. Surrounding the sampling site are residential estates with high population densities particularly to the western and northeastern sides where there are also two main soccer stadiums within ~3 km. The Jomo Kenyatta International Airport is approximately 5 km to the southwestern side of this site. It is difficult to estimate the population density around this site, since the information was not available by the time of compiling the data. However, it can be estimated to be around 2500 persons per square kilometer. Within this area are found various industries (metal, chemical, motor assembly and food processing).

Sampling of SPM was done using a 'Gent' Stacked Filter Unit (Maenhaut, [31]; Gatebe et al., [8]). Nucleopore filter membranes (0.4μm, and 8μm) were weighed in an air conditioned laboratory controlled at 50% relative humidity and 20°C. A ^{241}Am α-emitting source (5μCi) was used to remove the static build-up within the filter. Prior to weighing, all filters were left to equilibrate for at least 24 hours. Before the start of each sampling exercise, the SFU was properly cleaned with ethanol to remove any particles, which may have previously embedded inside. Filters were handled with care using plastic tweezers to avoid grease from fingers and heavy metal contamination. Information recorded was: (i) volume of air sucked by the pump and (ii) average weather conditions like temperature, humidity and wind direction. During the sampling, the sampler was run at flow rate of 1m^3/hour for 24 hours. The fine and coarse mass concentrations were obtained through gravimetric measurements of nucleopore filter membranes with 1μg sensitivity (Ainsworth, type 24N) weighing balance. Before weighing, the filters were equilibrated for 24 hours at 50% relative humidity and at 20°C temperature. Electrostatic charges were controlled by use of ^{241}Am radioactive source(5μCi). The filter membranes were then weighed before and after air filtration.

The EDXRF system utilized in this analyses has previously been described (Kinyua, [17]). It consists of 28 mm^2 x 5 mm thick ORTEC Si(Li) detector with beryllium window thickness of 25 μm, a Canberra amplifier/pulse processor with pile-up rejector Model 2020, and a Canberra S100 PC based multichannel analyzer system. The detector resolution (full width at half maximum-FWHM) was 190 eV at Mn K_α line at 5.9 keV, while the pulse shape time constant was 10 μs. The excitation source used was ^{109}Cd (20mCi). Ten samples were also analysed using a tandem accelerator facility at Schonland Research Centre for Nuclear Science, University of Witwatersrand, South Africa. The samples which had earlier been analysed with EDXRF, were cut into an area of 2.7cm^2 using a punch. A Proton beam (collimated with a rectangular collimator) with an energy of 3.2 MeV, and a beam current of 10nA was used. Irradiation times were 600 seconds. The PIXE system was calibrated by a large number of Micromatter Standards (mono and bi-elemental) of known area density (5% uncertainties certified). The fitting of the x-ray spectra and quantitative analysis were performed using the AXIL-PC software and WITS-HEX (Lipworth et al., [30]).

For both PIXE and EDXRF analytical systems, the detection limits were evaluated based on three sigma criterion (Wobrauschek, [46]). Table 1 shows the analytical results of SRM-2676d and the detection limit for the EDXRF based on the above criterion. Table 2 shows an intercomparison of the analytical results of the analysis of coarse and fine filters by both PIXE and EDXRF techniques. There was some good agreement in some of the results especially the major elements such as iron. The differences noticed in some of the results are mainly due to loss of the sample material during transportation, preparation and inhomogeneity. However, the precision of the elemental concentration measurements is typically less than 10% for elements with concentration near the detection limit. Table 4 shows some analysis of standards by both XRF systems utilized in this work.

TABLE 1(a) EDXRF analysis of a Standard Reference Material - NIST 2676d: metals on filter media

Element	Expt. Value (μg/filter)	Certified Value(μg/filter)	Filter Number
Mn	16.06 ± 0.41	19.83 ± 0.38	III
Zn	82.05 ± 1.52	99.31 ± 1.77	III
Pb	26.55 ± 0.72	29.77 ± 0.61	III
Mn	10.54 ± 0.21	9.83 ± 0.14	II
Zn	55.54 ± 0.83	49.47 ± 0.73	II
Pb	17.76 ± 0.34	14.82 ± 0.26	II
Mn	2.84 ± 0.05	2.09 ± 0.03	I
Zn	13.33 ± 0.18	10.17 ± 0.13	I
Pb	10.84 ± 0.15	7.44 ± 0.10	I

Results over the eight months of sampling shows almost similar trends for most of the elements (Kinyua et al., [24]). The concentration of potassium(K), calcium(Ca), and iron(Fe) varied from 0.2 to 2 μg/m^3, with Ca showing a higher level than Fe and K over the entire

TABLE 1(b) Experimental Detection Limits for SPM analysis by EDXRF

Element	Atomic Number	Detection Limits(μg/filter)	Detection Limits(ng/m^3)*
Ca	20	2.15 ± 0.21	89.5 ±8.5
Mn	25	0.41 ±0.03	17.0 ± 1.0
Fe	26	0.33 ± 0.01	13.5 ± 0.5
Cu	29	0.18 ± 0.03	7.5 ± 1.5
Zn	30	0.15 ± 0.02	6.0± 1.0
Pb	82	0.19 ± 0.02	8.0 ±1.0

*Nb * - based on 24 hrs sampling time at a flow rate of 1m^3/hour using Gent SFU*

TABLE 2 Comparison of EDXRF and PIXE Analysis of Aerosols Samples(μg/m^3)

	Fine Filter (0.4μm)		Coarse Filter (8μm)		Period
	EDXRF	PIXE	EDXRF	PIXE	
K	0.0956	0.167	0.544	0.667	Night 1
Mn	0.0629	0.014	0.0765	0.108	"
Fe	0.165	0.149	0.909	1.154	"
Zn	0.177	0.137	0.119	0.153	"
Pb	0.0741	0.047	0.0944	DL	"
K	0.187	0.075	0.517	0.317	Day 2
Mn	0.0752	DL	0.0752	0.021	"
Fe	0.137	0.061	0.322	0.247	"
Zn	0.0852	0.036	0.028	0.026	"
K	0.60	0.159	0.0305	0.229	Day 4
Mn	0.107	0.015	0.187	0.047	"
Fe	0.151	0.145	0.549	0.54	"
Zn	0.133	0.147	0.109	0.045	"
K	0.20	0.106	0.0751	0.319	Night 4
Mn	0.0678	DL	0.0619	0.064	"
Fe	0.0992	0.048	0.64	0.693	"
Zn	0.0637	0.024	0.0679	0.055	"
K	0.0221	0.068	0.409	0.072	Day 5
Mn	0.0661	DL	0.12	DL	"
Fe	0.0671	0.05	0.231	2.219	"

NB DL - Detection limit

period. Zinc(Zn) is conspicuously high in all the months varying from 1.0 to 8 μg/m^3. This points out to the presence of industry(ies) dealing with/or producing Zn or its products. Comparison of these results with the ones from the suburban sites shows higher concentration levels for most elements (Gatebe et al., [8]). This indicates some enrichment from the industries around the sampling site at the industrial area. With this data it will now be possible to sensitize the government on the need to monitor closely the impact of the emissions from industries on our air quality.

(ii) Workplace monitoring for Air Quality-Voucher Processing Centre

The Voucher Processing Unit Centre is a modern three storey building for banking activities located in the Industrial Area. The first two floors have several computer hardware and installations used for processing of the bank's financial transactions. The top floor of the

building houses the air conditioning unit for the Centre. The air conditioner used has inlet ducts located on the same side with the diesel power generator exhaust whose outlets face the Prisons Staff Quarters, Avon Tyre Factory bay and an unpaved road next to the premises. There are other various industrial activities near this building. The aim of the study was first to characterize the dust particles collected by analysis of the elemental contents and if possible determine the origin of dust and also to recommend to the client the ways to eliminate it so as to protect the workers and the sensitive equipment installed. The exercise was successfully completed. Among other recommendations, the client was advised to include determining the air particulate levels inside and outside the building by way of PM-10 system. This campaign for air particulate monitoring in this area is still going on.
Sample characteristics and other general observations included:

[1] Dust samples from the Computer Server room were "black" in appearance.

[2] Dust samples from the air conditioner located on top floor and from the back-up power supply room were brown in colour.

[3] The dusty "black" samples were fine powder that can easily be transported in air. However, due to the small quantities collected, it was not possible to determine the particle sizes.

Construction activities, unpaved roads around the Voucher Processing did contribute to increased dust particles in the workplace. Other air polluting activities include, industrial and traffic emissions (Gatebe et al., [8]). There were no significant reductions in the levels of heavy metals; iron (Fe), zirconium (Zr) and zinc (Zn) for samples collected from the air conditioner room and those from the computer server room. This implied poor filtration of the air. Carbon and sulphur in the samples analysed seemed to be of the same origin. It was therefore concluded that the air filtration system in the premises was not efficient because the room entrances and exits are not properly constructed hence allows the dust into the building. Secondly, the openings for the cable installation on the ground floor are not properly sealed against the dust inlets. It was therefore recommended that a closed/or open-loop air filtration system for the premises be installed. This system is capable of filtering out air particles sizes less than 10μm or less depending on the filter membrane installed. It was also recommended that some dialogue and negotiations on the possible ways and means to reduce the particulate matter in air by way of clean production practices be initiated between the bank, the neighboring firms and relevant authorities.

(iii) Characterization and transport of aerosols at Mt. Kenya

Aerosol samples are being collected using a two-stage streaker sampler (Annegarn et al., [2]). It has a size selective inlet with an upper cut-off point of 10 μmad defined by impaction onto a fixed substrate, followed by impaction through a rectangular orifice onto a rotating substrate. This is followed in turn by a filter stage with an upper cut-off point of 2.5 μmad. The impaction stage consists of a mylar foil mounted on an identical plastic frame to that used for filter stage, allowing for the same convenience of handling, analysis and storage. The frame rotates at 1 revolution per 32 days. The mylar foil and filter passes over 0.5x3 mm and 1x7 mm impaction slit and sucking orifice respectively, leaving behind a streak of dust. Aerosol samples were collected at Mt. Kenya using a two-stage streaker sampler (Gatebe et al., [11]; Annegarn et al., [2]). The sample which is reported is for the period 12 August to 9 September 1997. Elemental analysis of the mylar foil (coarse stage) and nucleopore (fine stage) was performed by Particle Induced X-ray Emission (PIXE) analysis (PAL, [38]). The sample was analysed in 1 mm segments corresponding to a 4 hr increment, yielding 168 steps per frame, for 28 days. Elements between sodium and uranium were analysed. Five elements, silicon, sulphur, chlorine, potassium and iron (accounting for about 95 % of the total observed inorganic aerosol loading) were chosen for analysis of source regions of the air masses impacting on the site during the sampling period. A 36-hour moving maximum function was used to remove the diurnal variations, followed by a 36-hour moving average for smoothening the resultant maximum curve (Gatebe, [10]).

Of the 21 elements identified in the aerosols reaching Mt. Kenya, silicon, sulphur, chorine, potassium and iron account for ~95% of the total mass transport (Table 3). Silicon is the major elemental contributor to the total inorganic aerosol loading, accounting for 38 % in the coarse mode (particle size >2.5 μmad) and 61% in the fine mode (size <2.5 μmad) of material transported to Mt. Kenya. Fine-fraction sulphur constitutes the second highest constituent (22 %) of the total fine mass. Chlorine in the coarse mode (6 %) constitutes a significantly less important contribution and fine-fraction potassium (4 %) and iron (3 %) an even smaller contribution to the total loading.

TABLE 3 Percentages of weight fraction of the elements present in the sample on Mt. Kenya at 4420 m above mean sea level *

Coarse Fraction	% Mass	Fine Fraction	% Mass
Si	37.8	Si	61.0
Fe	14.1	S	21.6
Ca	13.0	Cl	5.8
Na	10.8	K	3.9
Al	6.5	Fe	2.6
Cl	6.5	Ca	1.8
P	6.3	Na	0.6
K	3.3	Ti	0.3
Zn	1.6	Br	0.2
Ti	1.6	Zn	0.1
Pb	0.6	V	0.1
Mn	0.5	Cu, Cr, Mn, P, Ni, Pb, Se & As	< 0.1
Cu	0.1		
Sr, As, V, Ni, Cr & Br	< 0.1		

* - *(Gatebe et al., [11])*

Iron accounts for 3 % of the total mass transport to the site in the fine fraction and 14 % in the coarse mode and reached its highest concentration of ~0.1 μgm^{-3} from 23-25 August. Usually iron is mainly associated with dust from crustal material (Priest et al., [39]; Maenhaut et al., [32]). However, in this case despite the fact that transport pathways for iron, silicon and sulphur are similar, the variation of the element (Fe) with time is more similar to that of sulphur than silicon. This suggests that the two elements S and Fe may have similar source or source regions and that fine iron may be anthropogenic as well as crustal particularly as steelworks are to be found in the industrial region over which the air passed. Potassium is also used as a signature of biomass burning component (Crutzen and Andreae, 1998). The highest concentration of potassium was < 0.3 μgm^{-3}. From the transport pathway associated with the peak occurrence of potassium, it is clear the source of burning was over the horn of Africa region. For the observations considered, there is little evidence of pyrogenic products reaching Kenya from the usual Angola, Zambia, Zimbabwe, Malawi and Tanzania areas of southern Africa region identified as the primary source of intensive fire activities from August to October (Cahoon et al., [4]; Andreae, [1]).

3.2 WATER POLLUTION STUDIES

(i) River Nyando

This is one of the most recent work undertaken to assess river water quality. This site is at Muhoroni which is about 400 km from Nairobi in western Kenya. It is located nea .e

Victoria in the sugar belt of Kenya. Along the River Nyando a lot of sugar and other agro-chemical industries are based. Discharge of industrial effluents into this river is a common phenomenon and hence the need for this study. Water samples were collected using one litre polyethylene plastic bottles, which had been thoroughly washed with water and 10 % nitric acid then rinsed with copious amounts of double distilled water (Maina et al., [33]). The water bottles were immersed while closed, then opened at a depth of about 20 cm from the surface to avoid contamination by surface debris (Maina et al., [33]).

3.2.1 Total Reflection X-ray Fluorescence

Total Reflection X-ray Fluorescence system was used for analysis (Korir, [26]). The system consists of a Vienna Prototype TXRF Module attached to the line focus of the Type D Housing of Mo target water cooled Siemens Model FK 60-04 X-ray tube. The high voltage generator used was the Kristalloflex 710H from Siemens with a maximum of 53.5 kV and current of 40 mA. The x-ray detector used was Canberra Si(Li) Model 2008 of resolution 174 eV (at Mn-K_α line), active crystal volume of 30 mm^2 and thickness 5mm. For this study, the x-ray tube was operated at 40 kV and 20 mA. No other extra spectral modification of the Mo primary beam was done due to the low intensity. The TXRF module was optimized for the Mo-K lines with the cut off at 20.0 keV. The angle of incident with the sample used was about 0.6 mrad. The counting dead time for most samples averaged 1%. X-ray spectra were collected for 2000s by way of an MCA emulation software - S100 from Canberra. The quantitative analysis was done with QXAS (IAEA, [12]) after calibration of the spectrometer using a set of multi-element standard solutions with Co as internal standard (Kregsamer, [28]). The sample carriers used were the SUPRASIL discs, 30 mm in diameter and 3 mm thick.

3.2.2 Sample preparation for TXRF analysis

One millilitre of each sample was pipetted onto a clean vial and 1 μg of cobalt per ml of sample was added as internal standard. The content of the vial was mixed thoroughly by shaking and after which 10 μl was pipetted on a cleaned sample carrier. The samples were seen to spread to about 6 mm in diameter. The sample substrate liquid was then dried in a low-pressure chamber at room temperature (23 °C). For each sample, 3-4 replicates were measured.

3.2.3 Preconcentration of water samples for TXRF analysis

The pH of 100ml of the sample with 10 μg of Co internal standard and 5 μg of Ni added as a carrier was adjusted to between 5 and 6. It was then mixed with 10 ml of freshly prepared 2% NaDDTC solution and stirred for 15 minutes. The precipitate formed was filtered by a Millipore filter of porosity 0.4 μm. The filter substrate formed was then dissolved in 1 ml of MIBK solution into a clean container. 10 μl of the solution was then spiked onto each of the clean sample carriers, dried and analysed.

Results of TXRF analysis of the water samples (no preconcentration with organic reagents) collected from River Nyando (along it are sugar and agro-chemical food industries) indicate that phosphorus (P) and lead (Pb) were below detection limits which ranged from 30-180 μg/ml and 30-150ng/ml respectively (Table 5). The presence of sulphur in these water samples was an indicator of poor effluent control measures not effected by the industries. Other parameters (Table 6) measured include conductivity, pH, salinity, total dissolved solids (TDS), hardness, biochemical oxygen demand (BOD) and dissolved oxygen (DO). The pH remained relatively very basic in most of the samples analysed. However, the conductivity levels of industrial effluents were about four (4) times those of the river water while the salinity levels were about eight (8) times. The BOD levels of the waste from the sugar factory is about 100 times that of the river water before any industrial waste discharge points while that from the agro-industry is about 13 times that of the river water. Although the river seems to recover, the industrial wastes certainly do elevate the BOD levels of the river waters and requires constant monitoring to ensure that the limits are not exceeded.

3.2.4 Water Sample Analysis using EDXRF

The water samples were preconcentrated and filtered through a millipore paper then irradiated using ^{109}Cd source for 3000 seconds and the spectra data were stored in a computer. Spectra de-convolution and fitting was carried out by AXIL (Analysis of X-ray Spectra by Iterative Least-Squares Fitting) modular program of the Quantitative X-ray Analysis System (QXAS) (IAEA, [12]), while quantitative analysis was by a software for Quantitative Analysis of Environmental Samples (QAES) (Kump, [27]). Quality control assessment of the technique was done by analysis of standard reference material from National Institute of Standards and Technology (NIST), SRM 2676d and some in-house standards.

TABLE 4a.TXRF analysis of a In-house Water Standard

Element	Experimental (μg)	Expected value (μg)
Ti	3.18 ± 0.04	4.0
Fe	4.25 ± 0.03	"
Ni	4.17 ± 0.03	"
Cu	3.65 ± 0.03	"
Zn	3.86 ±0.03	"
Sr	3.43 ± 0.03	"
Pb	.46 + 0.05	"

TABLE 4b. EDXRF analysis of an In-house Water Standard

Element	Experimental (ppb)	Expected value(ppb)
Ti	84.1± 21.5	100
Fe	125.0 ± 11.3	"
Cu	105.0 ± 8.6	"
Zn	78.7 ± 6.6	"
Pb	108.0 + 8.2	"

The results of analysis of the effluents from the River Nyando showed that waste from the factories was certainly affecting the water quality of the river. High levels of sulphur (0.9 - 439 μg/ml) were registered at a waste treatment pond in the factory. The occurrence of these high levels during some sampling visits, suggests some random release of industrial wastes into the river. Other parameters affected by the industrial wastes included the conductivity, salinity and BOD. This calls on the authorities to initiate some strident monitoring of the industrial waste.

TABLE 5. Elemental Analytical Results in μg/ml (ppm)

Sample	Phosphorous	Sulphur	Calcium	Lead
A1	DL	3.6±0.5	99±2	DL
A2	"	0.90±0.02	16±0.6	"
A3	"	1.2±0.2	18±0.1	"
A4	"	1.1±0.2	18±0.5	"
A5	"	1.1±0.3	18±0.02	"
B1	"	439±2	47±1.0	1.46 ± 0.1
B2	"	182±2.3	19±1.0	DL
B3	"	190±4.2	18±1.3	"
B4	"	259±4.7	20±3	"
B5	"	166±14	17±0.1	"
C1	"	169±5	88±3.8	"
C2	"	164±20	13±1.1	"
C3	"	434±2.2	36±2.3	"
C4	"	228±8.1	31±1.6	"
C5	"	165±13.1	13.9±0.3	"

TABLE 6. Results of other Parameters

Sample	Conductivity (mg/l)	pH	Salinity (mg/l)	TDS (mg/l)	Hardness (mg/l)	B.O.D. (mg/l)	D.O. (mg/l)
A5*	246	7.31	0.1	116	124	15	4.4
B5*	140	8.02	0.1	102	126	50	2.0
C5*	237	7.26	0.1	109	118	10	4.2
A2**	205	8.65	0.1	97	84	380	2.8
B2**	321	8.3	0.1	187	99	420	3.6
C2**	188	8.07	0.1	82	91	320	2.6
A1#	1344	7.30	0.7	654	184	2640	1.6
B1#	1286	9.6	0.9	715	193	2450	1.8
C1#	1256	6.9	0.9	701	203	2360	1.8
A3##	201	9.01	0.1	103	92	250	2.4
A4##	233	8.03	0.1	110	98	30	2.2
B3##	302	8.1	0.1	115	89	310	2.0
B4##	285	7.9	0.1	132	72	305	2.0
C3##	192	9.2	0.1	121	81	300	2.2
C4##	201	8.11	0.1	97	104	25	2.4

Key:- Samples collected before factory discharge points
*** - Samples collected after the Agro-chemical discharge point*
 # - Samples collected after waste treatment ponds of the sugar factory
- Samples collected after the discharge point of the sugar factory

(ii) Tannery Effluents

A recent study (Kinyua et al., [22]) on water samples collected on the up-and-down streams of a tannery factory discharge point to Kamiti river has been done. The heavy metal analysis was done by TXRF (Korir, [26]) while BOD and COD parameters were done as per the standard method for the examination of water and waste water (Rad et al., [40]). Sample collection, storage and preservation was carried out as set out previously (UNEP, [43]). Polyethylene containers were used to minimize trace metal contamination. Sample preparation for analysis was carried out within 48 hours.

TABLE 7. Kamiti River Water Analysis (ppb unless otherwise stated)

Parameter	Upstream	Downstream		
BOD	7 mg/L	20 mg/L		
COD	28 mg/L	112 mg/L		
S	1651 ± 251	1852 ± 497	3186 ± 335	3094 ± 267
Cl	6652 ± 275	5417 ± 398	4430 ± 229	5593 ± 161
K	12826± 253	11246 ± 312	9406 ± 201	10227 ± 158
Ca	10000 ± 15	10099 ± 150	15533 ± 129	16332 ± 136
Ti	155± 15	236 ± 23	159 ± 15	119 ± 10
Cr	< 23	< 37	34 ± 10	< 23
Mn	127 ± 12	143 ± 19	687 ± 15	550 ± 12
Fe	1590± 30	2181 ± 32	3279 ± 27	2748 ± 25
Cu	40 ± 10	< 48	< 19	< 16
Zn	24 ± 7 ppb	41 ± 11	25 ± 6	23 ± 6
As	< 34	< 56	< 32	< 26
Br	42 ± 13	61 ± 20	42 ± 11	104 ± 8
Rb	< 32	< 60	< 30	< 26
Sr	91 ± 13	103 ± 25	52 ± 15	89 ± 9
Pb	< 81	< 137	< 78	< 90

Results of recent analysis of water samples from Kamiti River (Table 7) (Kinyua, [23]) shows that the influence of the tannery had greatly reduced compared to some previous analysis (Kinyua, [18]). This reduction was because the industry's operations had been curtailed due to its poor record on control of emissions (Muriuki, [34]).

3.3 OTHERS

iii) Beauty Cream Samples

Samples (n=100) of beauty creams were bought randomly from various retail shops in Nairobi and its environs (Kinyua et al., [22]). Each sample was squeezed into a clean beaker then heated on a water bath at 40-50°C until melting was complete. The melt was then poured onto a 2.5 cm diameter Mylar (Spectro-Film grade, Somar INC., USA) supported on aluminum ring (Kinyua et al.,[21]) so as to acquire the configuration of a homogenous pellet ($0.3g/cm^2$) when cooled. No other physical and/or chemical treatments were applied to the sample.

Results of mercury level measurements and analysis (Kinyua et al., [22]) showed that the cosmetic cream "Madonna"(green) had the highest level (μg/g) of mercury - 29000±2800 followed by "Madonna" (red) cream with 18000±1700. Significant differences ($p<0.001$) in the analytical results for "Madonna" (red), "Pimplex" and "Shirley" (original) were observed for the samples bought March and September, 1995. The creams, "Shirley" (new), "Dermovate" and "Topshirley", registered values below the detection limit (3 μg/g).

Two significant findings of this study are: mercury is present in some of the beauty products being sold in Kenya. This confirms previous findings which reported levels of mercury above 1μg/g (Wandiga and Jumba, [45]). Secondly, the level of mercury is not constant in different batches bought during the sampling periods. For example, the mercury levels (μg/g) during the month of March 1995 for "Madonna" (red) was 16080±1030 (n=5); "Pimplex" cream (n=5) had 4350±290 while "Shirley" (original) had 18090±890 (n=5). For the month of September 1995, the mercury levels (μg/g) were: 20900±1400 (n=5), 9644±630 (n=5) and 10895±690 (n=5) respectively. This has the implication on the quality control during manufacture of these products and it is possible that some products could be on sale with even higher levels of mercury than those shown in this work.

Mercury levels in some of the products analysed were above the World Health Organization (WHO) limit of 5 µg/L in human blood (WHO, [48]). Although the levels absorbed through the skin is less, the health implications on the uses of some of these products need to be investigated further. This is especially when traces of mercury previously reported in the nails and hair of some young people in Machakos (IAEA, [13]) plus the increased incidences of renal problems and hypertension, reportedly attributed to heavy metals especially among the youth in this country (Kinyua et al., [19]). In their studies involving African women in South Africa, Barr et al., 1972, attributed damaged kidneys to the effect of mercury in the skin lightener creams used to improve facial appearances. However, previous studies (Kinuthia et al., [25]) observed that there was no single etiological factor of major significance in nephrotic syndrome in Nairobi.

The major risks to human health arises from the neurotoxic effects of mercury in adults (Bakir et al., [3]) and its toxicity to the foetus if women are exposed to methyl mercury in their pregnancy (Cox et al., [5]). There is therefore a great need for the local authorities to implement stringent measures to curb the sale of these products, more so especially when the level of mercury is high in comparison to those reported in a previous survey (Wandiga and Jumba, [45]). Organic mercury has greater affinity for the brain, and in particular, posterior cortex as well as adipose tissue beneath the skin (WHO, [48]). The technique developed is fast and has the added advantage of permitting multi-elemental analysis. Other well known chemical analytical techniques take too long due to lengthy sample preparation procedures, and also require expensive and toxic reagents.

The EDXRF system utilized in these analyses has previously been described (Kinyua, [17]). The excitation source was ^{109}Cd (20mCi) with a run time of 300 seconds. The spectra data deconvolution was by AXIL based software (IAEA, [12]), while quantitative analysis was by QAES Software (Kump, [27]). The detector system was calibrated using an oil standard reference material - NIST-SRM-1634b and some in-house standards for L-lines. Calculation of the mercury concentration in the samples was based on intensity recorded (I), being taken as equal to a product of sensitivity (S), concentration of a given element (C), absorption coefficient (A), and enhancement factor (E) (Kump, [27]). For mercury, enhancement is absent (E=1) since there is no additional excitation of mercury by other fluorescent radiation emitted by other elements present in the sample. The absorption correction factor was measured experimentally by use of pure target of molybdenum, whereas the sensitivity curve was generated from the use of the oil standard reference material and in-house standard for other L-lines which were not present in the oil standard. The intensity (area under the mercury peak) was read from the spectrum fitting by AXIL.

For quality control an AAS unit was also used for this work. This is as previously been described [Jumba, 1980]. The unit is a Perkin Elmer Model 2380 a microprocessor controlled unit. It measures the concentration of metallic elements and provides integrated readings in absorbance and concentration. For this work, the AAS unit was used for intercomparison and verification of results of the mercury levels in beauty creams. A few of the samples were extracted and analysed as previously described (Wandiga and Jumba, [45]). Aliquots (0.5g) were digested first with H_2SO_4 (1hr) and then 6% aqueous potassium permanganate (2 hrs). The excess permanganate was destroyed with hydroxylamine and the aqueous extract analysed by flameless cold vapour atomic absorption spectrometry (AAS) - Pye Unicam SP 90A, at 253.7nm. The detection limit obtained was better than 4 ng.

REFERENCES

[1] ANDREAE, M.O. (1993). Global distribution of fires seen from space, *Eos Trans.* AGU, 74, 129.

[2] ANNEGARN, H.J., CAHILL, T.A., SELLSCHOP, J.P.F. & ZUCCCHIATTI, A. (1988). Time sequence particulate sampling and nuclear analysis, *Physica Scripta* 37, 282-290.

[3] BAKIR, F., DALMUJI, S.F., CLARKSON, H.I.(1973). Methyl mercury poisoning in Iraq, *Science* 181, 230-241.

[4] CAHOON, D.R., JR, STOCKS, B.J., LEVINE, J.S., COFER III, W.R. & O'Neil, K.P. (1992) Seasonal distribution of African Savannah fires, *Nature* 359, 812-815.

[5] COX et al., Dose-response analysis of infants prenatally exposed to methyl mercury: an application of a single compartment model to single strand hair analysis, *Environmental Res.* 49 (1989) 318-332.

[6] CRUTZEN, P.J. & ANDREAE, M.O. (1990). Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science* 250, 1669-1678.

[7] GATEBE, C.K. AND KINYUA, A.M. (1994). Total Suspended Particulate Matter in Air of Some Urban Areas in Kenya - A Review. *Int. J. BioChemiPhys.* 3, 1-4.

[8] GATEBE, C.K.(1996). UNEP/WHO 1996 Air Quality Management and Assessment Capabilities in 20 Major Cities, United Nations Environmental Programme, World Health Organization, Monitoring and Assessment Research Centre, London. p.178-182.

[9] GATEBE, C.K., A.M. KINYUA, M.J. MANGALA, R.KWACH, L.N. NJAU, E.A. MUKOLWE, D.M. MAINA (1996). Determination of Suspended Particulate Matter of Major Significance to Human Health using Nuclear Techniques in Kenya. *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 203, No. 1, 125-134.

[10] GATEBE, C.K. (1998). Characterisation and transport of aerosols sampled at a high altitude on Mt. Kenya, unpublished Ph.D. thesis, University of Witwatersrand, Johannesburg, South Africa.

[11] GATEBE, C.K., TYSON, P.D. ANNEGARN, H.J., HELAS, G., KINYUA, A.M. AND PIKETH, S. (1998). *Inter-Hemispheric Transport of Aerosols over Continental Africa* (submitted for publication).

[12] International Atomic Energy Agency (IAEA) (1995). Quantitative X-ray Analysis System (QXAS, Version 3.2), Vienna.

[13] International Atomic Energy Agency (IAEA) (1978). Activation analysis of hair as an indicator of contamination of man by environmental trace element pollutants, IAEA/RL/50, 105.

[14] JUMBA, I.O., personal communication, 1996.

[15] KAHENYA, P.N.P. (1996). A review of studies on occupational diseases in Kenya. *African Newslett on Occup. Health and Safety Supplement* 2/96: 46-49.

[16] KENNY, T. (1996). Northern Corridor Transport Project: Adverse social and environmental impacts caused by the rehabilitation of the Westlands-St. Austins and Kabete-Limuru roads, Kenya. Oxfam UK/Ireland Policy Department.

[17] KINYUA, A.M. (1982). X-ray fluorescence analysis of solid and liquid samples, M.Sc. Thesis, University of Nairobi.

[18] KINYUA, A. M., OWERA-ATEPO, J. B., JUMA, F. D., MANGALA, M. J., MWANGI, L. W. AND NDWARU, T.W. (1990a). *Heavy Metal Analysis of Industrial Effluents in Nairobi City.* Proceedings of the 11th KEMRI/KETRI Annual Medical Scientific Conference, Nairobi, Kenya.

[19] KINYUA, A.M., OWERA-ATEPO, J.B., KANYIMA, J., ORIOKOT, G., JUMA, F.D., OTIENO, L.S., MWANGI, L. W.(1990b), Trace Element Analysis of Urine obtained from Patients with Renal Failure. Proc. 11th Ann. Med. Sci. Conf. KEMRI/KETRI, Kenya Medical Research Institute.

[20] KINYUA, A. M. AND PACINI, N. (1991). The Impact of Pollution on the Ecology of the Nairobi-Athi River System in Kenya, *Int. J. BioChemiPhys.* 1(1),5-7.

[21] KINYUA, A. M., MAINA, D. M., MANGALA, M. J., GATARI, M. J.(1994). Energy Dispersive X-ray Fluorescence (EDXRF) in Non-destructive Testing of Oil Samples. Proceedings of 1st African Regional Conference on Non-destructive Testing (ARCNDT), Kenya NDT Society, 76-82.

[22] KINYUA, A.M., MAINA, D.M., MAINA, C., MANGALA, M.J., JUMBA, I.O., GATEBE, C.K. AND GATARI, M.J. (1997a). Non-destructive analysis of Mercury(Hg) by Energy Dispersive X-ray Fluorescence (EDXRF) Technique in Beauty Creams sold in Kenya. IAEA-SM-344/49 Proceedings of International Symposium on Harmonization of Health Related Environmental Measurements using Nuclear and Isotopic Techniques, Hyderabad, India, 4-7 November 1996, p. 361-368.

[23] KINYUA, A.M., MANGALA, M.J., KORIR, A.K., ODHIAMBO, G.O. AND BARTILOL, S.(1997b). Analysis of River Kamiti water samples (unpublished results).

[24] KINYUA, A.M., GATEBE, C.K., MANGALA, M.J., MAINA, D.M., KORIR, A.K., BARTILOL, S., KWACH, R., NJAU, L.N. MUKOLWE, E.A., ODHIAMBO, K., KONJI, V.N., KWASA, T., MWARE, A., BOR, P.K. AND WACHIRA, J.K. (1997c). Heavy Metal Analysis of Suspended Particulate Matter(SPM) and other Samples from some Workplaces in Kenya using Nuclear and Related Analytical Techniques, CRP KEN/9478, International Atomic Energy Agency (IAEA).

[25] KINUTHIA, D.M.W., ONGERI, S.K., ABDULLAH, M.S, OTIENO, L.S., REES, P., HUTCHEON, R.(1981). Clinicopathological aspects of nephrotic syndrome in patients at Kenyatta National Hospital 1973-1977, *East Afri. Med. J.* 58(11), 818-827.

[26] KORIR, A.K. (1998). M.Sc. Thesis, University of Nairobi.

[27] KUMP, P. (1993). Quantitative Analysis of Environmental Samples(QAES), Ljubljana, Slovenia.

[28] KREGSAMER, P.K.(1995), Manual for QXAS, *Quantitative X-ray analysis system* (Version 3.2), IAEA.

[29] LALOR, G.C., H. ROBOTHAM, M.DAVIS, A. JOHNSON, J. PRESTON, C. GRANT (1993). The Development of Air Pollution Studies in Jamaica. Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques, a Report on the second Research Coordination Meeting, Menai, Australia, 27-31, March, 1995, NAHRES-26, International Atomic Energy Agency, Vienna, 12-1.

[30] LIPWORTH, A.D., H.J. ANNEGARN, M.A. NEON (1993). Advanced, enhanced HEX program for PIXE, *Nuclear Instruments and Methods in Physics Research* 75, 127-130.

[31] MAENHAUT, W. (1993) The 'Gent' Stacked Filter Unit (SFU) Sampler for the collection of Atmospheric Aerosols in Two size Fractions; Description and instructions for installation and use, Report No. NAHRES-19, International Atomic Energy Agency, Vienna, 249-263.

[32] MAENHAUT, W., SALMA, I., CAFMEYER, J., ANNEGARN, H.J. AND ANDREAE, M.O.(1996) Regional atmospheric aerosol composition and sources in eastern Transvaal, south Africa, and impact of biomass burning, *J. Geophys. Res.*, 101, 23631-23650.

[33] MAINA, D.M., KINYUA, A.M., MANGALA, M.J. AND GATARI, M.J. (1997). Assessment of heavy metal pollution of L. Victoria (*in press*).

[34] MURIUKI, A.W. (1995). Report of Air Emissions in and around Kamiti Tanners Ltd., Directorate of Occupational Health and Safety Services, Ministry of Labour, Government of Kenya.

[35] NJUGUNA, S.G. (1978). A study of the effects of pollution on a tropical river in Kenya. M.Sc. Thesis, University of Nairobi.

[36] ODHIAMBO, G.O. (1997). The Impact of Muhorni Sugar Factory on the Water Quality of River Nyando, Kisumu District, Final year project, Dept. of Environmental Science, Kenyatta University.

[37] OKETCH, T.G.N. (1994). Air Quality Based Service flow rates for Urban arterials, A study of some arterials in Nairobi, Kenya, M.Sc. Thesis, International Institute for Infrastructural, Hydraulic and Environmental Engineering, Netherlands.

[38] PAL, (1998). PIXE Analytical Laboratories, Tallahassee, USA.

[39] PRIEST, P, NAVARRE, J-L., RONNEAU, C. (1981). Elemental background concentration in the atmosphere of an industrialized country, *Atmos. Environ.* 15, 1325-1330.

[40] RAD, M.C., GREENBAG, A.F. AND TARAS, M.J. (eds) (1975). Standard Method for the examination of water and waste water, 14 Edition, American Waterworks Association and Water Pollution Control Federation, Alpha-AWWA-WPCF, p.959.

[41] SCHWELA, D.(1997). Health Effects of Air Pollution, Healthy Cities-Air Management Information System-AMIS, WHO/UEH.

[42] SUESS, M.J. AND CRAXFORD, S.R. (1976). (Ed.) WHO Manual on Urban Air Quality Management, WHO Regional Publications, Europeans Series No. 1.

[43] UNEP (1987). Guidelines for determining inputs of inorganic contaminants into estuaries. Reference Methods for Marine Pollution Studies No. 41.

[44] UNEP/WHO (1992). Urban Air Pollution in Megacities of the World, Blackwell Publishers, UK, ISBN 0-631-18404.

[45] WANDIGA, S.O. AND JUMBA, I.O., Determination of mercury in body beauty soaps and creams sold in Kenya and Norway, *Kenya J. Sci. and Tech.* A3 (1982) 89-91.

[46] WOBRAUSCHEK, P. (1995). Total Reflection X-ray Fluorescence analysis with Polarized Radiation, *J. Trace and Microprobe Techniques*, 13(2), 83-96.

[47] WHO (1987). Air Quality Guidelines for Europe, Regional Publications, European Series No. 23, Copenhagen

[48] World Health Organization (WHO), Trace Elements in Human Nutrition and Health, Geneva (1996) 206-209.

PORTABLE X-RAY FLUORESCENCE ANALYSIS

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Abstract

Different applications of portable XRF instruments are described. Measurement methods are described and detection limits for field portable XRF instruments are given

1. INTRODUCTION

X-ray fluorescence is a well established technique which is used for the chemical analysis of materials in many laboratories around the world. In conventional instrumentation, samples are normally excited by a high power (3 to 4 kW) X-ray tube and fluorescence spectra are detected by one or more wavelength dispersive spectrometers. These latter devices serve as X-ray monochromators, the X-ray spectrum being diffracted off a crystal or multilayer device into an X-ray counter. The analytical power of WD-XRF instrumentation is derived from its multielement capability, the wide range of elements that can be determined (by convention from Na to U in the periodic table and in some routine applications down to C), and the low detection limits, which for some elements fall below the $\mu g\ g^{-1}$ level. A second category of instrumentation is based on the use of energy dispersive X-ray spectrometers. In many laboratory ED-XRF instruments, samples are again normally excited by an X-ray tube, but the fluorescence spectrum is detected by the interaction of X-ray photons with a solid state semi-conductor crystal - most commonly a lithium-drifted silicon detector. ED-XRF instruments have an unrivalled capability to finger print samples, since the full spectrum is detected simultaneously and can be displayed and interpreted during data acquisition. ED-XRF instrumentation is also very effective for quantitative analysis, although detection limits are often 5 to 10 times worse than WD-XRF, mainly because the spectrum resolution characteristics of ED detectors are substantially worse than those of WD spectrometers, especially in the lower energy region of the X-ray spectrum (below 8 keV). To compensate for this deficiency, there is considerable advantage in using a polarised excitation geometry, since the scattered background in the fluorescence spectrum can be considerable reduced in this way, with a corresponding favourable improvement in detection limit performance.

In addition to the two main categories of laboratory XRF instrument described above, a number of hybrid instruments have been developed, some incorporating an XRD detector to permit the simultaneous determination of phases (e.g., in the analysis of cement), some combining ED and WD spectrometers to exploit the best characteristics of both in a single instrument, some optimised for specific applications (for example S in oil). However, one of the most exciting developments in recent years has been the introduction and application of portable XRF instrumentation, based largely on ED-XRF technology.

2. PORTABLE INSTRUMENTATION

When considering portable analytical instrumentation, it is important to distinguish between instrumentation that can be installed and operated in a mobile laboratory, and can, therefore, be used for the on-site analysis of samples and true portable instrumentation that can analysis samples in the field *in situ*. Portable XRF can be used in both types of application but the important advantage enjoyed by portable X-ray fluorescence is the capability for the direct, non-destructive analysis of samples in the field. Few techniques offer this capability in respect of non-organic species, the closest rival being spark source optical emission spectrometry. This latter technique can be used effectively for the analysis of metallurgical samples, in applications such a scrap metal sorting, but which is ineffective in the analysis of non-conducting samples and inappropriate for the analysis of museum and archaeological samples or works of art, because it cannot satisfy the non-destructive criteria.

3. DESCRIPTION OF PORTABLE XRF INSTRUMENTATION

Although portable XRF instrumentation is largely based on ED-XRF technology, a number of design compromises are necessary to satisfy the portability criteria. Instrumentation comprises an X-ray excitation source, X-ray detector and a data acquisition and analysis unit and an overview of the design of a hand-held portable analyser is shown in Figure 1. The analytical characteristics of these principal components will now be summarised.

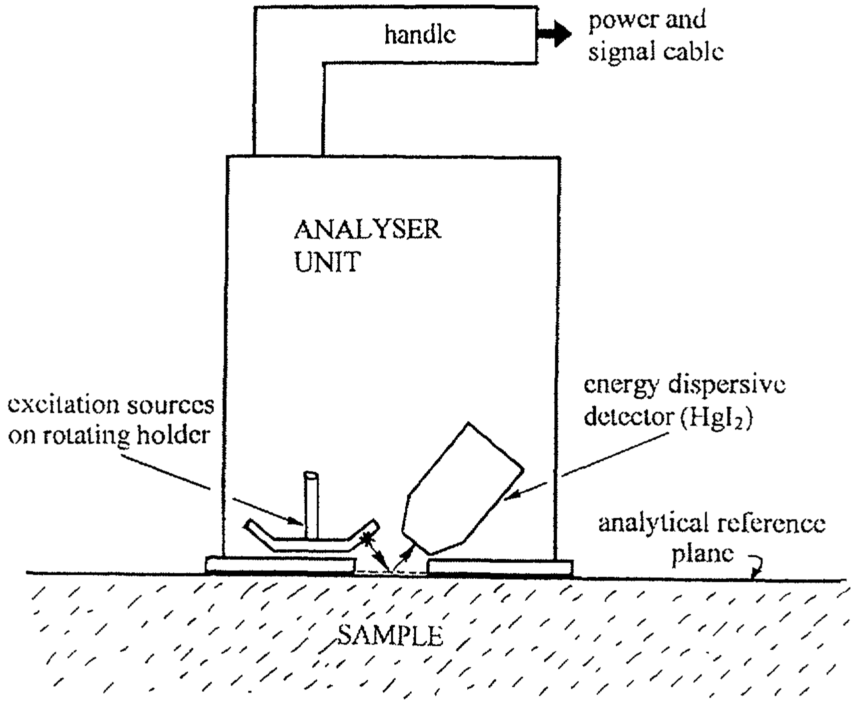

FIG. 1 Hand-held portable X-ray fluorescence analyser showing the overall configuration of components.

3.1 EXCITATION SOURCE

By far the most widely used excitation source in portable XRF instrumentation is one or more radioisotopes that decay emitting X-ray or gamma ray radiation capable of exciting the range of X-ray fluorescence lines of interest. In fact very few radioactive sources have suitable characteristics (in terms of emission energies and long half lives) for use in portable XRF. Furthermore, several sources are required to excite effectively the full range of elements if appropriate for an application. The sources most commonly used are ^{55}Fe, ^{109}Cd and ^{241}Am and their decay characteristics are listed in Table 1. Additionally, ^{238}Pu has been used in some earlier instruments. Miniature X-ray tubes are becoming available and have the potential to extend the capabilities of P-XRF instrumentation. However, the requirement for additional power consumption is an important consideration in assessing their successful application to portable battery-powered instrumentation for use at remote sites.

TABLE 1 Decay characteristics of radioactive excitation sources used in portable XRF

Source	Half life (years)	Emission characteristics Energy (keV)	Element range that can be determined (K-lines)	WD-XRF tube anode equivalent
^{55}Fe	2.7	5.9/6.5 (Mn K-lines)	(Cl)-V	Cr
^{109}Fe	1.24	22.2/25.0 (Ag K-lines)	Cr-Mo	Rh (Ag)
^{241}Am	433	59.9	Ru-LREE	W (100 kV)

LREE = light rare earth elements

In terms of analytical capabilities, ^{55}Fe is capable of exciting the K-lines of elements below Cr in the periodic table. The fluorescence Cr K lines suffer a severe overlap interference from the Mn Ka line emitted from the source and scattered off the sample and more reliable determinations can normally be made using the ^{109}Cd excitation source. The determination of lower atomic number elements is increasingly affected by attenuation of the corresponding fluorescence radiation in air. As a consequence, detection limits for elements below K increase substantially. The ^{109}Cd source has a wide range of applicability, being capable of determining the K-lines of elements typically in the range Cr - Mo. Best sensitivity is shown for elements in the range Rb - Nb. Immediately higher atomic number elements suffer enhanced backgrounds due to scatter of Ag K lines off the sample. The sensitivity with which elements of lower atomic number than Rb can be excited by the ^{109}Cd source falls off significantly. In addition, the L-lines of higher atomic number elements (e.g. Pb) can be excited by this source. The 59.9 keV gamma emission from the ^{241}Am source extends the analytical capability to the K lines of elements in the range from Mo up to the light rare earth elements (LREE). Higher atomic number elements than the LREE suffer enhanced background interferences caused by scatter in the sample of the source 59.9 keV lines.

An approximate correlation can be drawn between the analytical characteristics of these sources and conventional X-ray tube excitation sources. The ^{55}Fe source behaves in a similar manner to a Cr anode tube and the ^{109}Cd source to a Rh (or Ag) anode tube. The principle difference is that in radioactive source excitation, there is no continuum (bremsstrahlung) component to the excitation spectrum, offering a potential improvement in portable XRF detection limits due to the absence of a background enhancement due to continuum scatter. This benefit must be balanced by the reduced intensity available from the sources in comparison with X-ray tubes because of practical limitations on the maximum activity that can be incorporated in portable instrumentation. The excitation capabilities of an ^{241}Am source are not as readily matched to an X-ray tube since modern WD-XRF X-ray tube generators often have a maximum rating of 75 kV, inadequate to excite efficiently 60 keV radiation. Perhaps the closest equivalent is a tungsten anode tube powered at 100 kV.

The other principal difference in comparison with conventional X-ray tube sources is that it is not possible to 'turn-off' a radioactive source, a factor that has safety implications for the design of interlocked shielding mechanism for when the source is not in use.

3.2 DETECTORS

Portable XRF instrumentation invariably incorporates energy dispersive detectors of which three types are widely used. Some characteristics of these detectors are listed in Table 2, particular features being as follows:

3.3 PROPORTIONAL COUNTER

The proportional counter is well known as the detector commonly used on WD spectrometers where it essentially serves as a single channel analyser to measure the intensity of the monochromatic diffracted beam. However, in portable XRF applications, the proportional counter is used as an energy dispersive detector, the output signal being fed into a multichannel analyser, rather than a pulse height analyser. Proportional counters are simple, light-weight and robust devices. The major draw-back is the energy resolution. By convention, energy resolution is measured as the full width at half maximum (FWHM) of the peak detected at 5.9 keV (corresponding to Mn Ka radiation), usually measured from a ^{55}Fe source. The industry standard is the 140 eV (or better) achievable with a Si(Li) detector. by contrast, gas proportional counters can only achieve about 900 eV. As a consequence, spectrum overlap interferences require serious considerations and applications are often restricted to samples that give relatively simple XRF spectra using matrix matched calibration samples which offer some compensation for spectrum interference effects.

3.4 Si(Li) DETECTOR

The Si(Li) detector is the best established energy dispersive detector, widely used in laboratory XRF instrumentation as well as SEM and electron microprobe systems. To achieve optimum resolution performance, Si(Li) detectors must be cooled , most commonly to liquid nitrogen temperatures using a dipstick connected to an integral liquid nitrogen container. Although detector systems can be designed for portable *in situ* field measurements, the requirement to provide liquid nitrogen is not particularly convenient. As an alternative, electronic Peltier cooling can be used to provide a reasonable degree of cooling, although with the penalty of additional power consumption. As referred to above, Si(Li) can achieve FWHM resolutions of better than 140 eV, but with Peltier cooling, this is likely to be degraded to 180 to 200 eV.

3.5 MERCURY (II) IODIDE DETECTOR

Contemporary research on alternative energy dispersive detectors has seen the development of thallium-drifted mercury(II) iodide as a practical semiconductor detector. One advantage of this material is the low degree of electronic cooling required to achieve stable operation. Another is the high stopping power offers improved higher energy X-ray detection efficiency from physically small detector crystals. Typical energy resolution is about 280 eV (FWHM at 5.9 keV) - not as good as can be achieved with a Si(Li) detector, but more than adequate to allow the successful analysis of complex multielement materials, particularly for higher atomic number elements that give fluorescence lines above 8 to 10 keV.

TABLE 2 Characteristics of detectors used in portable XRF instrumentation

Detector	Advantages	Disadvantages	Typical energy resolution (FWHM @ 5.9 keV)
gas proportional counter	simple, light, robust	Poor energy resolution limits applications	900 eV
Si(Li)	industry standard technology. Best energy resolution of current solid state devices	relatively fragile, liquid nitrogen cooling for optimal resolution	<140 eV (liq N_2 cooling) 180-200 eV (Peltier)
Hg(II)I_2	compact, no external cooling required, adequate resolution	relatively fragile, longevity?	ca. 280 eV

3.6 DATA ACQUISITION AND SPECTRAL ANALYSIS

Being based on ED-XRF technology, portable XRF instrumentation incorporates a full multichannel analyser data acquisition system, which for the higher resolution detectors would normally extend to 2048 channels. The rate of data acquisition is controlled by the source activity an source-sample-detector geometry, so deadtime performance is largely fixed by design. Spectrum analysis requirements are similar to other ED-XRF systems in the need to measure fluorescence line intensities and correct/compensate for overlap interferences. There are several well established methods of doing this, including digital filtering/fitting library spectra, fitting model peaks and backgrounds, region of interest integration. In view of its simplicity, region of interest integration is often used on portable instruments - data are integrated over a certain number of channels centred on the fluorescence line of interest. Overlap corrections can then be applied by subtracting the appropriate proportion of an un-interfered peak of the interferent from the analyte peak intensity. To give satisfactory results, a procedure is required to monitor drift in the spectral acquisition system and to recalibrate periodically the channel versus spectral energy calibration function.

3.7 MATRIX CORRECTION

There are some special considerations in assessing the most appropriate matrix correction procedures for portable XRF instrumentation. Principal among these is the problem that for a significant proportion of samples, it is not possible to analyse all matrix elements. This limitation arises from the attenuation in air of fluorescence X-rays from low atomic number elements such that it is unlikely that elements below potassium in the periodic table can be determined with adequate sensitivity. This limitation is particularly relevant in the analysis of silicate materials, including soils, sediments and rocks. One approach to accommodate this limitation is to use a fundamental parameter matrix correction procedure in which the difference is assumed to be SiO_2, or some other compound that is judged to best represent the X-ray attenuation properties of the unanalysed constituents of the sample. Another approach is to use matrix matched calibration samples that will compensate for both matrix effects and, to some extent spectrum overlap interferences. These approaches are usually more acceptable for portable as opposed to laboratory XRF because the fitness-for-purpose criteria in terms of accuracy and precision in many portable XRF applications are not as stringent as those for laboratory XRF.

3.8 ANALYTICAL PERFORMANCE

In order to demonstrate the analytical performance of portable XRF instrumentation, results are presented from an investigation in the authors laboratory using one specific instrument, a Tracor Northern Spectrace TN9000 instrument, which incorporates ^{55}Fe, ^{109}Cd and ^{241}Am excitation sources and a $Hg(II)I_2$ detector. This instrument was used in a laboratory assessment of the analysis of silicate rocks using a wide range of reference materials prepared as compressed powder pellets.

3.9 DETECTION LIMITS

Representative detection limits are listed in Table 3, where a comparison is made between (i) the manufacturer's portable XRF detection limits for a ‘siliceous matrix’, (ii) measured portable XRF detection limits derived from the analysis of a wide range of representative silicate rock reference materials and (iii) conventional laboratory ED-XRF in which silicate rock reference materials were excited with a Ag-anode X-ray tube. The siliceous matrix data represent ideal 'instrumental' detection limits achievable on favourable samples. The 'working' silicate rock reference material data represent detection limits that can be achieved in day-to-day performance in the analysis of rock (and soil) samples.

TABLE 3 Comparison of detection limits obtained by field portable XRF (μg g^{-1})

Source	Element	Portable XRF 'instrumental' (siliceous matrix) (manufacturer's data)	Portable XRF 'working' (silicate rock) (reference material)	Laboratory ED-XRF (Ag-tube excited) (silicate rock)
^{55}Fe	K	150	360	
	Ca	70	225	
	Ti	55	120	
	V	50	49	24
	Cr	90	1080	30
^{109}Cd	Mn	200	354	
	Fe	110	424	
	Co	100	354	14
	Ni	65	116	12
	Cu	50	80	8
	Zn	40	63	7
	Ga	35	58	6
	Rb	5	13	3
	Sr	4	14	3
	Y	4	9	3
	Zr	3	9	3
	Nb	4	6	3
	Pb-L	15	39	7
^{241}Am	Ba-K	9	21	-
	La-K	8	-	-
	Ce-K	8	14	-

'Instrumental': 200 s count time per source on a siliceous matrix (Spectrace TN9000, Manufacturers data).
'Working': 200 s count time per source on a silicate rock matrix (based on an analysis of silicate rock reference materials), taken from Potts et al. [3].
Laboratory ED-XRF: 800 s count time, Si(Li) detector, Ag tube excited (Potts 1987).

Comparison with laboratory XRF show that detection limit performance by portable XRF is not dissimilar for a range of elements excited by the ^{109}Cd source, if differences in count time are taken into account (200 s for P-XRF compared with 800 s for the laboratory ED-XRF data). An exception to this general observation is the poorer P-XRF detection limits for the lower atomic number elements, where detector resolution, source excitation intensity and attenuation in air are all factors that count against P-XRF performance. The portable XRF data listed in Table 3 are representative of count times of 200 s per source but in practical situations, a shorter count time would normally be used, depending on fitness-for-purpose criteria. If the count time is halved, the detection limit is expected to increase by a factor of $\sqrt{2}$ (i.e., 1.4), a conversion that can be used to estimate detection limits if shorter count times are selected.

3.10 PRECISION

From the same evaluation of the performance of portable XRF instrumentation in the analysis of silicate rock reference materials, an review of results was undertaken to assess precision and accuracy. Precision data in the repetitive analysis of a dolerite rock (Whin Sill) are listed in Table 4 using count times of 100 s and 200 s per source. Taking into account the affect of concentration, these data indicate that repeatabilities in the order of 1 to 3 % (relative standard deviation) can readily be achieved by portable XRF instrumentation.

TABLE 4 Precision (repeatability) in the analysis of Whin Sill dolerite (powder pellet)

element	expected (μg g^{-1})	100 s count time (n=10)			200 s count time (n=8)		
		analysed (μg g^{-1})	s (μg g^{-1})	RSD (%)	analysed (μg g^{-1})	s (μg g^{-1})	RSD (%)
K	8302	13046	512.2	3.9	13093	210.2	1.6
Ca	64540	70152	794.9	1.1	70239.9	313.0	0.45
Ti	14560	17799	382.0	2.1	17445.1	311.2	1.8
V	349	470.5	60.6	12.9	484.3	484.3	4.0
Mn	1320	1531.0	375.2	24.5	1523.2	206.3	13.5
Fe	93380	104020	1396	1.3	104079	1585	1.5
Rb	27	38.8	8.3	21.4	42.0	4.0	9.5
Sr	422	513.9	22.2	4.3	508.4	11.1	2.2
Y	34	37.5	6.3	16.8	31.4	4.4	14.0
Zr	206	240.4	8.1	3.4	234.5	7.5	3.2
Nb	18	14.2	3.8	26.8	13.6	4.0	29.4
Ba	350	385.3	27.7	7.2	392.9	7.7	2.0

Data abstracted from Potts et al. [3].

3.11 ACCURACY

Accuracy can be assessed visually from graphs of expected versus analysed values for a wide range of geological reference materials shown in Figure 2. These results demonstrate that quantitative results can be achieved with confidence by the technique, taking into account detection limit performance.

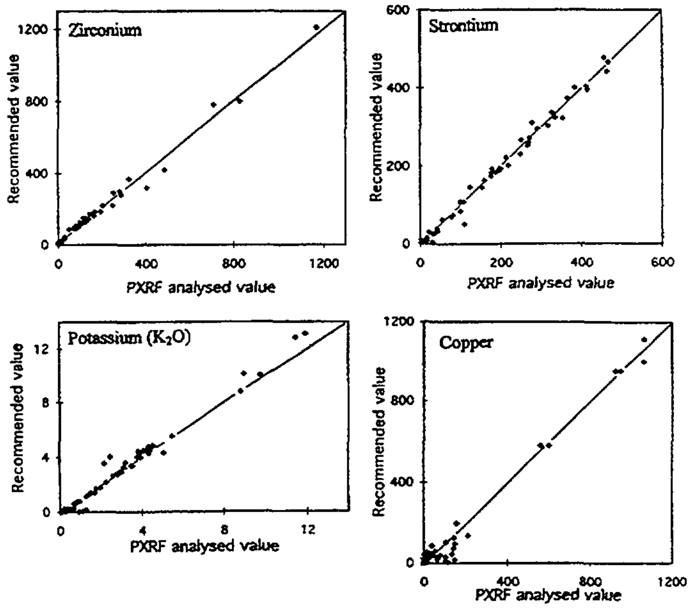

FIG. 2. An example of the accuracy of P-XRF results in which expected results are plotted against analysed values for a series of silicate rock reference materials, prepared as compressed powder pellets. Results are plotted for the elements K, Cu, Sr, and Zr (taken from Potts et al. 1995).

4. QUANTIFICATION AND INTERPRETATION OF P-XRF DATA

4.1 SAMPLE SURFACE IRREGULARITY EFFECTS

The results in the previous sections show that portable XRF is capable of achieving excellent accuracy and precision under well controlled conditions in the laboratory. All the results presented above were derived from standard compressed powder pellets. Although not always recognised as such, one of the factors that affects the quality of laboratory XRF data is sample presentation in terms of the requirement to prepare samples for analysis with perfectly flat surfaces which are positioned accurately in the analysis position in relation to the source-sample-detector X-ray optics. This too can be achieved by portable XRF by carefully positioning a flat sample in the 'analytical plane' of the instrument over the analyser window. However, these stringent requirements for sample presentation are not usually met in the direct field analysis of real samples by portable XRF. In particular, real samples (especially rocks, archaeological samples, museum artefacts and even soil surfaces levelled for analysis) are unlikely to be perfectly flat and indeed may have significant curvature and surface roughness effects. In these circumstances, portable XRF results will suffer from inverse square law phenomena whereby the intensity observed from a point source varies in proportion to the inverse square of the distance between source and detector.

When fitness-for-purpose criteria indicate that results of the highest accuracy are required (as in provenancing geological or archaeological samples, for example), surface irregularity effects may represent a serious limitation. For many samples, analytical results are likely to be lower than expected (mean surface of sample lies above the analytical plane of the analyser). Exceptionally they might be greater (part of the sample protrudes towards the analyser window).

A detailed investigation of this problem was undertaken by Potts et al. [4] with a view to seeking a correction. Results demonstrating the magnitude of the problem are shown in Figure 3. Data in this diagram show the apparent concentration of Sr obtained by analysing broken surfaces of an irregularly shaped silicate rock sample. An estimate of the 'air gap' (that is the distance between the mean surface of the sample and the analytical plane of the instrument) could be made from a separate series of measurements in which the distance between the analyser plane and a flat polished surface of the same rock type was accurately varied between 0 and about 13 mm. At each height, corresponding to a known air gap, the intensity of the ^{241}Am scatter peak was measured. By comparing the same scatter peak intensity measured off the broken surface of the sample, an estimate of the effective air gap could be made.

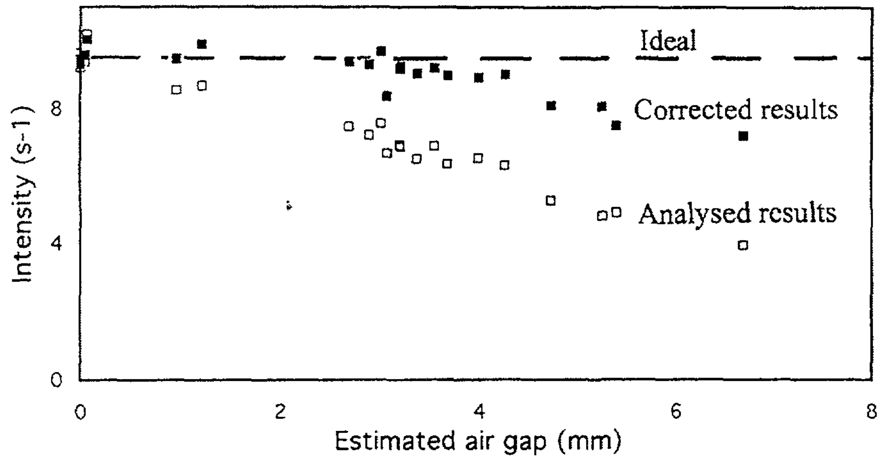

FIG 3. Apparent P-XRF concentration of Sr obtained from determinations made over the irregular surface of a silicate rock with varying surface roughness. The degree of surface roughness was estimated as the effective air gap (in mm). Uncorrected results are compared with corrected data based on ^{55}Fe scatter peak intensities (taken from Potts et al. [4]).

Results in Figure 3 show that even with the broken surface of the rock sample resting on the analyser, considerable discrepancies could arise in analytical results. The simulated air gaps observed in this sequence of measurements on broken surfaces was between about 0 and 7 mm, the latter values being achieved by deliberately raising one edge of the rock. If quantitative results are required, a correction is clearly required to compensate for these discrepancies. The correction proposed by Potts et al. [4] involved measuring the scatter peak intensities from the irregular sample surface and comparing it with an 'ideal' measurement, observed from a perfectly flat sample, where the surface lies exactly in the analytical plane of the instrument. It was found that if fluorescence intensities were multiplied by the ratio of the scatter peak intensity from the flat surface ratioed to the same intensity from the sample being analysed, the influence of surface irregularity effects could largely be eliminated. There are, however, some limitations to this approach. One is that the scatter peak intensity is itself matrix dependent. In the case of the ^{55}Fe scatter peak, this matrix dependency was not very great, so a 'typical' silicate rock could be used to derive the reference intensity. In the case of the ^{109}Cd source, a more significant matrix dependence was observed so that a reference rock of matched matrix composition must be chosen as the reference sample. Results for ^{241}Am were obscured by the fact that the reference samples investigated for matrix dependency (powder pellets of geological reference materials) were not infinitely thick with respect to 59.9 keV radiation.

The other major limitation of this approach is that other factors affect scatter peak intensities when sample to analyser distances are changed. The most serious of these is the additional air attenuation which affects the 5.9 keV ^{55}Fe scatter peak and the change in intensity which occurs when the mean scatter angle increases as the effective air gap becomes larger. These factors mean that increasing errors affect results if this correction procedure is applied to sample surfaces with effective air gaps that exceed 3 to 4 mm. However, it should be noted that experience in the analysis of rock materials indicates that except for samples of unusual shape, the effective air gap rarely exceeds these values.

Results obtained when the proposed correction procedure based on normalising to ^{55}Fe scatter radiation are plotted on the same graph as uncorrected results in Figure 3. These data indicate a significant improvement in results when compared with the expected composition, though with the correction becoming increasingly unreliable above about 4 mm.

4.2 EXCITED VOLUME AND STATISTICAL EFFECTS ASSOCIATED WITH SAMPLING

Like all XRF techniques, the fluorescence signal is derived from and excited volume whose depth is dictated by the critical penetration depth of the fluorescence line of interest. This parameter is normally defined as the depth below the surface of the sample from which 99% of the analytical signal is derived. Beyond this depth, there is a high probability that fluorescence photons will be absorbed within the sample. By its nature, the critical penetration depth varies with photon energy, since higher energy photons have higher penetrating powers than lower energy photons. Data in Table 5 gives estimates of the critical penetration depth of a range of characteristic X-rays, varying from about 30 μm for the K Ka line (3.3 keV) to no less than 8.6 mm for the Ba K-lines at 32.2 keV. The simplistic implication of these data are that the potassium signal is derived from the mass of sample represented by a cylinder 25 mm in diameter (the diameter of the analytical window) by 30 μm deep, whereas Ba is derived from a much larger mass, the height of the cylinder representing the excited volume now being over 8 mm. However, the interpretation is complicated by the fact that contributions made by various layers within the excited volume will decrease approximately exponentially with depth, down to the critical penetration depth and that the surface of the sample adjacent to the analytical window is not likely to be excited uniformly by the excitation source. As an example of the latter phenomenon, the excitation capabilities of a near point source are plotted in Figure 4, showing how different regions on the sample adjacent to the analyser window contribute to the detected signal. An annular source would be expected to show different characteristics.

TABLE 5 Critical penetration depths

Element, energy of K-line (keV)	K 3.31	Ca 3.69	Ti 4.51	Fe 6.40	Rb 13.39	Zr 15.77	Ba 32.19	Ce 34.72
Critical penetration depth (mm)	0.030	0.035	0.047	0.16	0.82	1.2	8.6	9.6

Critical penetration depth represents the depth within an silicate rock of andesitic composition from which 99% of the X-ray fluorescence signal originates.

Despite these complications, the overall effect is that P-XRF elemental data will be derived from a relatively small mass of sample. There are two important analytical consequences which derive from these observations. The first is that for some elements, analytical results will be affected to a disproportionate extent by the composition of the surface. For this reason, turf and other vegetation must be removed prior to the analysis of soil and the presence of weathering, fallout contamination or lichen growing on the surface of rock materials or corrosion products on metals and alloys which have been exposed to the environment for any length of time, will disproportionately affect results if the aim is to estimate the bulk composition of the sample. Conversely, if the aim is to characterise weathering or corrosion products, P-XRF may be able to contribute useful results.

A second important consequence concerns the effect that statistical variations in the random distribution of phases within the analysed volume will have on the overall precision of results derived by averaging replicate measurements. This effect has been demonstrated by replicate determinations made on the surface of flat and polished blocks of a range of silicate rocks containing an assemblage of minerals of increasing coarseness. The hypothesis is that although all minerals in this assemblage may be randomly distributed in the bulk sample, there will be significant differences in the proportion of minerals in the excited volume of any individual P-XRF measurement. The precision, based on replicate measurement at random positions on the surface may then be dominated by sampling precision (reflecting statistical variations in the distribution of individual minerals). To assess the magnitude of this effect, replicate measurements were made on polished blocks of the five rock types listed in Table 6 (Potts et al., 1997). These varied from a fine grained dolerite in which in which grains were mainly less than 1 mm across, occasionally up to 2 mm, through various medium-grained granite (with a grain-size of typically 1 to 4 mm), through to an coarse grained granite having a ground mass of quartz and plagioclase grains up to 7 mm long and exceptionally potassium feldspar grains of up to 35 mm long. Results of replicate measurements were then averaged and the standard deviation calculated. These data were then recalculated for each sample to estimate the number of replicate measurements that would have to be made to achieve a specified overall analytical precision (calculated as the standard deviation of the mean) of 2, 5, 10 and 20%. A simplified summary of the results is listed in Table 7 and shows that for the fine grained dolerite, target precisions of 10 and 20% relative can be achieved from a single determination, 2 measurements must be averaged to achieve a precision of 5% relative, but an average of 8 measurements are required to achieve a precision (standard deviation of the mean of 2%.

TABLE 6 Estimate of the number of individual determinations that must be averaged to achieve a measurement precision of 2, 5, 10 and 20% (relative standard deviation of the mean) in the direct analysis of a range of rock samples of varying grain size.

Target precision	Dolerite	Quartz andesite	Microgranite	Medium-grained granite	Coarse-grained granite
Typical grain-size	1-2 mm	1-3 (-5) mm	1-4 mm	1-3 mm	3-7(-35) mm
Target precision	Number of replicates to be averaged (representative data)				
20% STD	1	1	1	1	6
10% STD	1	1	1	1	21
5% STD	2	4	4	3	82
2% STD	8	20	23	17	512

STD = standard deviation of the mean. Data abstracted from Potts et al. (1997)

Corresponding figures for the number of determinations that must be averaged for the medium-grained rocks to achieve 20, 10 5 and 2% precision are typically 1, 1, 4, 20 analyses, respectively. For the coarse-grained granite, no less than 512 determinations would need to be averaged to achieve 2% relative precision (in terms of standard error of the mean), indicating that such a requirement has extended beyond the practical limits of the performance of the technique.

Although this precision assessment is specific to the samples investigated, the results are presented to serve as a guide to the influence of sampling precision on P-XRF measurements, relevant to soils and sediments, as well as rock samples. An important practical issue is that the contribution of sample mineralogy to overall measurement precision cannot be detected from a single measurement, or from replicate measurements on the same spot. It is essential that the analytical procedure includes a requirement to undertake replicate measurements on different positions on the same sample so that an assessment can be made to judge whether the overall measurement precision is acceptable in comparison with the relevant fitness-for-purpose criteria.

5. AN OVERVIEW OF APPLICATIONS

It is not the intention of this section to undertake a comprehensive review of applications of the technique published to date but to give an indication of the categories of measurement to which the technique is appropriate. A general overview is listed in Table 7. One of the more common applications is in environmental studies, particularly related to the remediation of contaminated land. It is appropriate, therefore, to examine the capabilities of the P-XRF technique in this area. These capabilities are influenced by two factors. One is the detection limit performance of the P-XRF instrumentation; the other is the target concentrations of contaminants at which decisions on remediation must be made for the relevant category of land use. Corresponding data are listed in Table 8 in which a comparison is made between the P-XRF detection limits and ICRCL action levels published by the UK Government Department of the Environment. To be generally applicable, P-XRF detection limits should be between 5 and 10 times lower than the action level and an evaluation of these data shows that this condition is easily satisfied for Pb and almost so for Zn. For the other toxic elements, P-XRF does not have a sufficiently low detection limit to evaluate contamination at the appropriate action level. However, the technique may provide valuable data in assessing substantial levels of contamination of these other elements, particularly in the location of 'hot spots' that may provide information on the source of contamination.

TABLE 7 Representative applications of P-XRF

Remediation of contaminated land

- Land associated with abandoned lead mining activities
- Contaminated soil painted with leaded paint from adjacent wooden buildings
- Soil contaminated with arsenic around sheep dips

Analysis of paint

- In-situ analysis to see if lead paint used (can detect layers beneath the surface)

Archaeological provenancing

- Roman granite columns
- British stone axes
- Coinage metal

Analysis of museum samples and valuable artefacts
(To research historic techniques and provide information for restoration)

- Paintings / works of art
- Medieval illuminated manuscripts
- Building stone

Industrial use

- Recover for recycling of precious metal catalysts
- Others

Health and Safety

- Analysis of dust deposits to assess hazards in the work place.
- Workplace analysis of air filters

Geochemical exploration and mining

- Field use in the exploration for ore bodies
- Locating ore seams in working mines

Investigation of surface processes

- Weathering of building stone and geological samples
- Corrosion products on metals (e.g., Cl on steel)

TABLE 8 P-XRF detection limits compared with ICRCL trigger levels for various toxic elements of environmental interest.

Element	P-XRF detection limit (μg g^{-1})	ICRLC action level (μg g^{-1})		
		(i)		(ii)
As	60	10	-	40
Cd				
Cr (total)	1080	600	-	1000
Cu	80	-	130	-
Hg	Hg			
Ni	116	-	70	-
Pb	39	500	-	2000
Zn	63	-	300	-

P-XRF detection limits: 200 s count time

ICRCL data for As, Cr, Pb are trigger concentrations for:

(i) domestic gardens and allotments and

(ii) parks, playing fields and open spaces.

ICRCL data for Cu, Ni and Zn are trigger concentrations for any use of land where plants are grown.

For the reasons outlined above, one of the principal environmental applications of the P-XRF technique is in the analysis of lead in contaminated land. To this extent, the use of P-XRF is compatible with draft EPA method 6200 for contaminants in soils. It is also relevant to note the detailed evaluation undertaken by Argyraki et al. [1] of the performance of P-XRF in the analysis of lead in soil at a medieval smelter site in comparison with conventional laboratory analysis of samples collected from the site. P-XRF data was obtained by removing turf to a depth of about 30 mm with a spade and analysing directly the exposed soil. Laboratory results were obtained by using a screw auger to remove a 100 mm column of soil from the same sites. On returning to the lab, these soil samples were sieved, dried and disaggregating with a pestle and mortar. Lead was then determined by ICP-AES using a mixed acid (nitric and perchloric) leach. Providing the field analyses were corrected for the moisture content of the soil (noting the laboratory results were representative of a dried sample) and were further corrected for surface irregularity effects using the scatter ration correction described above, no significant bias was detected between the two sets of results. These results give confidence to the capabilities of P-XRF in contributing to lead/soil contamination studies, provided account is taken of the sampling limitations summarised above.

ACKNOWLEDGEMENTS

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REFERENCES

[1] ARGYRAKI, A., RAMSEY, M.H. AND POTTS, P.J. (1997), Evaluation of portable X-ray fluorescence instrumentation for in situ measurements of lead on contaminated land. Analyst, 122, 743-749.

[2] POTTS P.J. (1987), A handbook of silicate rock analysis. Blackie (Glasgow), 622pp.

[3] POTTS P.J., WEBB, P.C., WILLIAMS-THORPE O. AND KILWORTH, R. (1995) Analysis of silicate rocks using field-portable X-ray fluorescence instrumentation incorporating a Mercury (II) iodide detector: A preliminary assessment of analytical performance. Analyst, 120, 1273-1278.

[4] POTTS P.J., WEBB, P.C. AND WILLIAMS-THORPE O. (1997a), Investigation of a correction procedure for surface irregularity effects based on a scatter peak intensities in the field analysis of geological and archaeological rock samples by portable X-ray fluorescence spectrometry. Journal of Analytical Atomic Spectrometry, 12, 769-776.

[5] POTTS P.J., WILLIAMS-THORPE O. AND WEBB, P.C. (1997b) The bulk analysis of silicate rocks by portable X-ray fluorescence: Effect of sample mineralogy in relation to the size of the excited volume. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 21, 29-41.

ACCELERATOR-BASED ANALYTICAL TECHNIQUES USING ION AND PHOTON BEAMS — ENVIRONMENTAL AND INDUSTRIAL APPLICATIONS

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Abstract

An overview of different Ion Beam Analysis (IBA) techniques is given. Examples of applications of the PIXE techniques to varoious types of samples are presented.

1. INTRODUCTION

The use of particle or electron accelerators for analytical purposes has significantly developed over the last decades. Compact, dedicated and commercially available electrostatic accelerators have been installed in many laboratories all over the world, mainly intended for use with nuclear analytical techniques. Several large electron accelerator facilities for production of synchrotron radiation have been established. This access to intense X-ray sources in the keV region has lead to a rapid development in synchrotron radiation induced X-ray fluorescence techniques. The obvious disadvantage to require an accelerator facility is balanced by the powerful analytical properties of these techniques. The applications are numerous in many fields. Here we will concentrate on environmental and industrial applications.

2. ION BEAM ANALYSIS

The term Ion Beam Analysis (IBA) denotes techniques based on use of MeV ions from particle accelerators to induce reactions suitable for elemental and structural characterisation (see Fig. 1). Some of the more important techniques will be presented briefly.

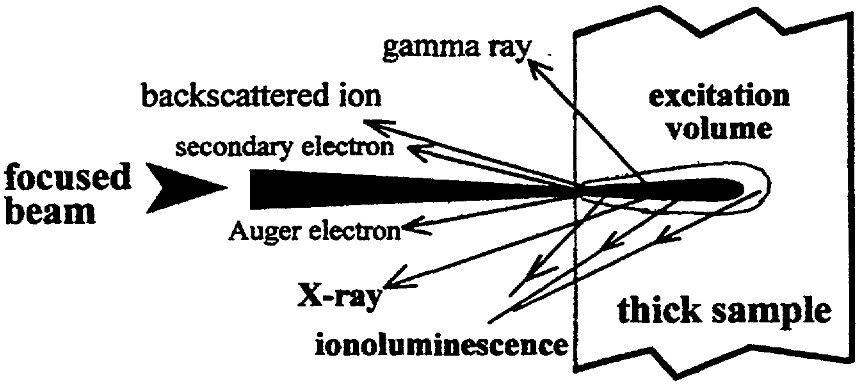

FIG. 1: Processes in MeV ion-solid interaction

2.1 PARTICLE-INDUCED X-RAY EMISSION (PIXE)

An impinging MeV ion has a high probability to eject an inner shell electron from its orbit and the resulting vacancy is rapidly filled by an electron from one of the outer shells. The transition leads to a release of energy that is equal to the energy gap between the adjacent shells, and characteristic of the parent atom. Measurement of characteristic X-rays using a high-resolution energy-dispersive X-ray detector provides information on the elemental constituents of the sample. The PIXE technique and its applications are comprehensively covered in a recent book [1].

PIXE is multielemental, sensitive (detection limits often at ppm level), quantitatively accurate (5-10%), and the PIXE energy spectrum is relatively easy to interpret With most elements being associated with a characteristic peak (see fig. 2). The analytical properties also include rapidity, relatively smoothly varying sensitivity and near non-destructiveness.

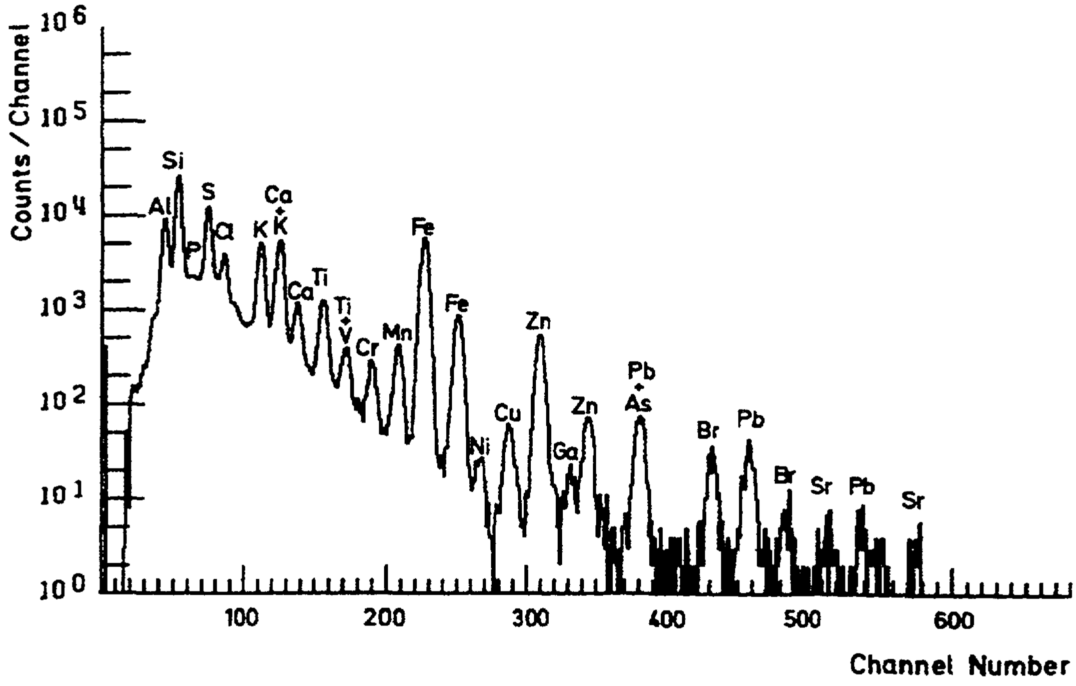

FIG. 2: X-ray spectrum from PIXE analysis of a sample of atmospheric aerosols.

2.2 RUTHERFORD BACKSCATTERING SPECTROMETRY (RBS)

The classical Rutherford scattering and other non-Rutherford modes of scattering are used both for mass normalisation and for measurements of depth distributions of elements. The RBS scattering probability can be calculated exactly and hence the accuracy is very high.

Rutherford Backscattering Spectrometry [2] is since many years a well-known technique based on the elastic scattering of incoming MeV ions by nuclei in the sample. The depth of the scattering nucleus in the sample can be determined from the energy loss suffered by the backscattered ion as it passes into and out of the sample. In Fig. 3 an example of a RBS spectrum from analysis of a thin specimen is shown. Its ability of depth profiling is important in many applications. For 2-3 MeV protons, penetration of the Coulomb barrier of many light elements occur. Therefore, the Rutherford scattering formula can be severely effected by the presence of nuclear resonances that are not described by simple classical theory. This problem is being addressed using the experimental determination of cross-sections for light elements at the backward angle.

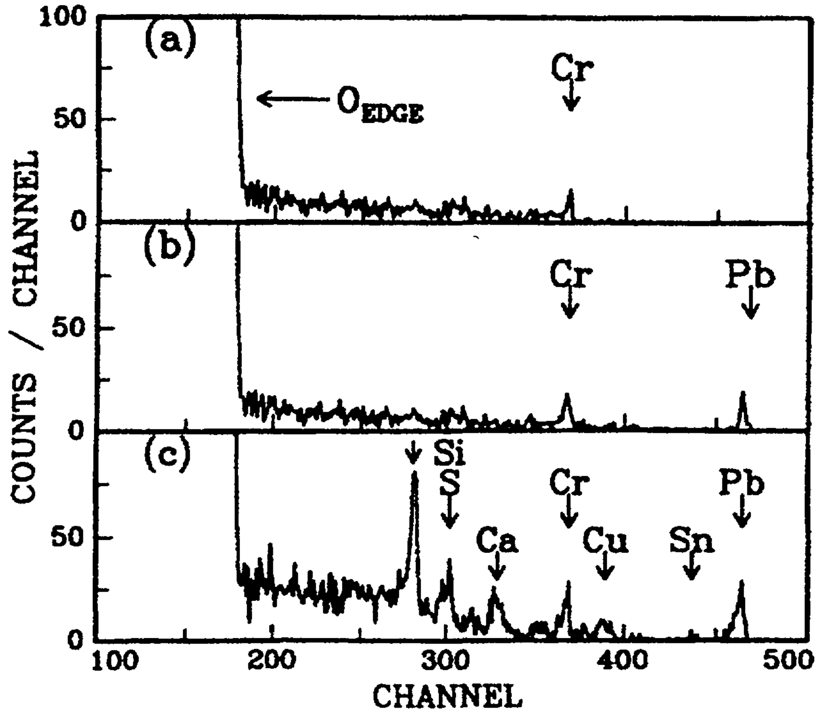

FIG. 3: Energy spectrum from RBS analysis of a thin sample of atmospheric aerosols

2.3 NUCLEAR REACTION ANALYSIS

The possibility of using nuclear reactions to determine light elements by specific nuclear reactions is quite common in addressing materials science problems. The relatively low cross-sections for most nuclear reactions makes this technique most suitable for determination specific isotopes with enhanced resonant cross sections. In an enhanced version, photon-tagged NRA [3] (pNRA), the background can be significantly suppressed by the use of fast (ns) electronics coincidence measurements and hence it can be used also with low ion beam currents. Some light elements, such as boron, fluorine, beryllium and sodium, can be determined using pNRA.

2.4 NUCLEAR MICROPROBE

Many applications require analytical procedures applicable to microscopic structures. The development of finely focussed ion beams to a microanalytical tool in the nuclear microprobe has extended the use of ion beam analysis in industrial and environmental studies even more. The nuclear microprobe is an instrument combining PIXE, RBS, NRA with imaging methods such as scanning transmission ion microscopy (STIM), secondary electron imaging (SEI) and ionoluminescence (IL). This instrument constitutes a powerful tool for characterisation of microscopic specimens (see Fig. 4)

2.5 SYNCHROTRON RADIATION INDUCED X-RAY FLUORESCENCE (SXRF)

X-ray fluorescence analysis (XRF) is a widely applied analytical technique that makes use of X-rays, both as a means of excitation and as analytical signal and it will be covered in detail in other chapters. With the development of advanced light sources based on synchrotron radiation in the keV region the SXRF analytical technique has been developed. The much

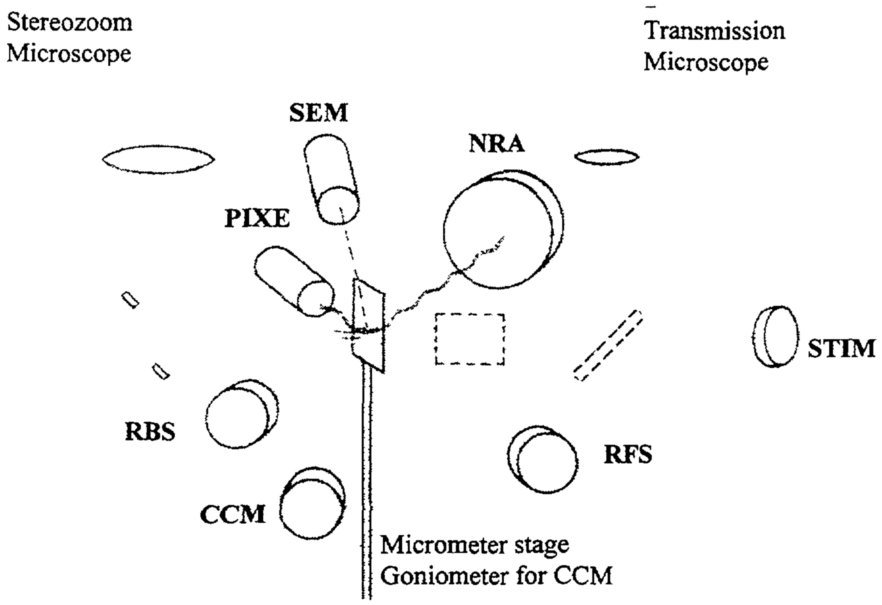

FIG. 4: Schematic arrangement of a nuclear microprobe

higher X-ray intensity available and the polarised light produced together enhance the analytical characteristics of SXRF. The advantages of X-ray spectrometry based on excitation by photons instead of charged particles is higher ionisation cross sections (see Fig. 5) and less radiation-induced damage [4].

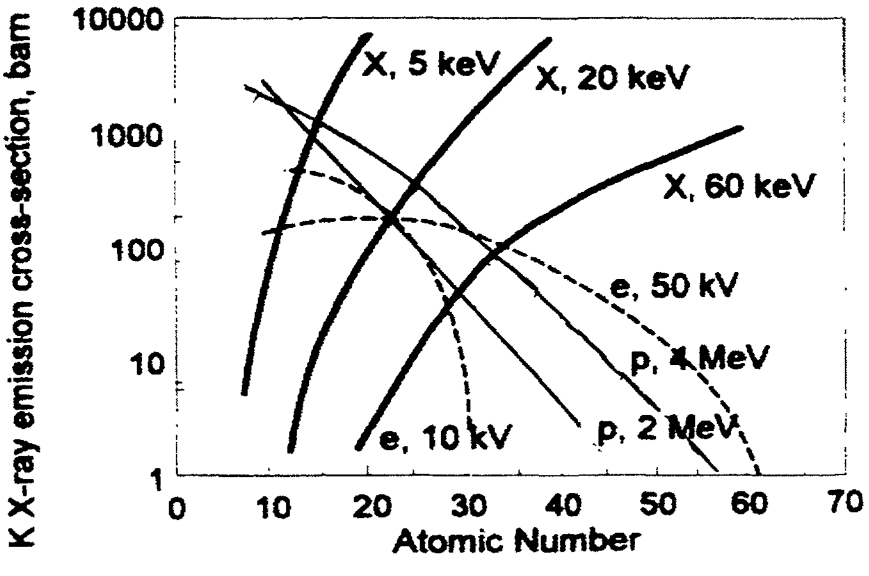

FIG. 5: Comparison of cross-section for K X-ray production using different means of excitation.

The major disadvantage of using photons is that, in contrast to charged particles, electrical or magnetic fields cannot be used to focus to small beam dimensions. However, because of new technological advancements in designing X-ray optics, for instance, glass capillary focusing devices (see Fig. 6), intense photon beams of a few micrometers in diameter can be produced to irradiate a specific location on the sample surface [5], much similarly to the ion beam in the nuclear microprobe.

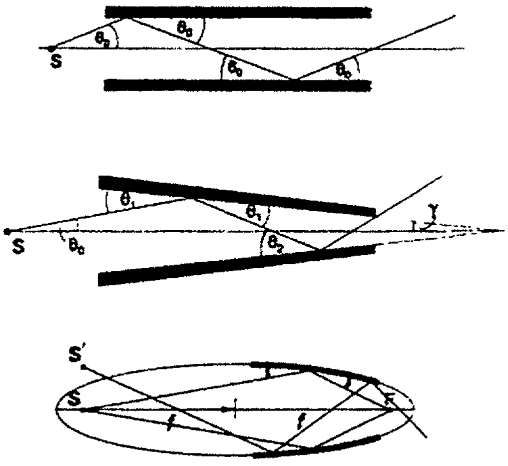

FIG. 6 Different geometries for designing capillary focusing devices using total reflection of X-rays.

When comparing the relative merits of a micro-SXRF facility and a nuclear microprobe it should be noted that also the SXRF can be supplemented by alternative techniques providing information additional to elemental composition, by using the techniques EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) and, if enough intensity is available, e.g. using a wiggler beam line, micro XRD (X-ray diffraction). The first two techniques are based on observed distortions due to chemical effects near absorption edges and the latter makes use diffraction patterns from interaction will crystalline material [6].

3. ENVIRONMENTAL APPLICATIONS

The energy-dispersive X-ray detection techniques, whether based on ions or photons, have been instrumental in many environmental studies in a variety of fields. Hear we will only discuss the use of PIXE and SXRF.

3.1 AIR POLLUTION STUDIES

For broad-beam excitation both PIXE and SXRF has been used for trace element analysis of collected aerosol samples. The more wide-spread and easier access to PIXE facilities has resulted in a more extensive use as routine analytical technique of large number of samples . A good example of this is the network operated in the USA by the PIXE group at the University of California, Davis [7]. Furthermore, the advantages of simultaneous use of several IBA techniques have facilitated the acceptance of PIXE as a standard technique in this field. Specially designed aerosol collection apparatus (see Fig. 7) has enhanced the usefulness of the analyses.

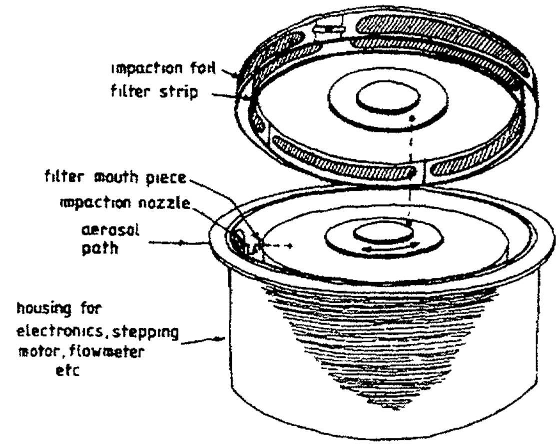

Fig 7 Specially designed equipment for unattended aerosol field sampling over extended periods producing samples well suited for rapid PIXE analysis.

In order to improve the characterisation of the aerosol composition a combination of thermal analysis and IBA has been developed into a technique called Ion Beam Thermography (IBT) (ref). By using simultaneous controlled heating and IBA analysis (see Fig. 8) of a sample IBT offers the capability of, in addition to elemental analysis, also produce chemical speciation, crucial to the basic understanding of atmospheric aerosols.

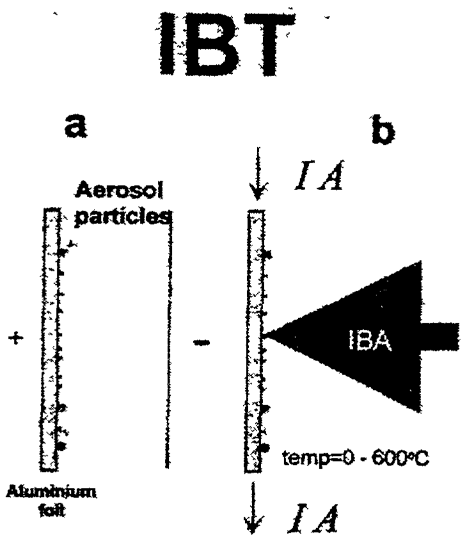

FIG. 8: a) Collection of aerosols on aluminium foils electrostatically
b) Heating of specimen in low vacuum chamber during IBA

When using millimetre size photon or ion beams the aerosol composition is averaged of a large number of particles. It is important also to study single aerosol particles in detail. The most common and feasible way of doing this is to use an automatic electron microprobe that by scanning and imaging identifies individual particles and analyses one after another. However, the limited sensitivity of this technique calls for the use of the more sensitive SXRF and PIXE techniques based on finely focused beams. An alternative, but less quantitative technique is the laser microprobe (LAMMA) [8]. In practise, micro-SXRF and micro-PIXE has been used only for a limited number of samples but with good results [9].

3.2 PLANT STUDIES

Plants are interesting from many aspects of environmental monitoring in that they often selectively preconcentrate, for instance, heavy metals. By analysing the various parts of the plant conclusions can be drawn regarding the metal loading in the environment. Some plants also show hyperaccumulation of specific elements as demonstrated in a study where specific plant species were shown to accumulate nickel from serpentine soil [10].

Forest decline is a particularly serious environmental problem in central Europe. Acidification of forests is a major threat, not only to forestry, but to the ecological system as a whole. Microprobe analysis based on ion and photon beams has played an important role in several studies of effects on trees and plants. By following the changes in the trace element content along a tree core it is expected that changes in the environment can be followed. Both X-ray fluorescence and PIXE based on millimetre size beams have been applied to this problem. Valkovic′ et al. [11] And Pernestâhl et al. [12] used PIXE for this kind of analyses.

One common objection to use mm-size beams to probe change in trees is the difficulties to interpret the results without a more detailed knowledge of elemental transport routes and mechanisms. This problem has been addressed in nuclear microprobe to investigate the microscopic elemental distribution in wood and bark from a young tree [13]. The conclusion from this study was that interpretation of macroscopic tree core analyses must be exercised with great care.

Fine roots of trees and plants are very sensitive to changes in the soil chemistry. A detailed understanding of how pH and metal availability affect the roots would help significantly in understanding the problem of forest decline. Using a nuclear microprobe several studies of roots [14], have produced accurate quantitative maps of root cross sections showing the distribution of aluminium and other elements.

In a continuation of one of these studies, the results from high resolution analysis of roots from onions cultivated in an Al-enriched growth medium indicate that aluminium is stored rather in the intra-cellular space than inside the cells. These findings, which seem to be confirmed by independent studies using different analytical methods could be very important for future work in this field [15].

Other examples of studies include heavy metal uptake in lichens and bracken in order to determine environmental parameter such as heavy metal load in soil in the vicinity of deposited sewage [16], [17]. Results from one of these studies indicate that a fungus from the roots of bracken from a polluted forest can concentrate specific heavy metals. No significant accumulations of heavy metals were observed elsewhere in the root, either in the plant or other fungal tissue.

3.3 CALCIFIED TISSUES FOR ENVIRONMENTAL MONITORING

The special properties of biominerals to preserve incorporated trace elements over long time spans can be used when monitoring heavy metal exposure. Environmental lead exposure to young children has been monitored by PIXE analysis of teeth [18]. A mm size beam of protons was used for analysis of extracted healthy teeth grown in the first years after birth. It was possible to demonstrate that lead levels were significantly higher in teeth from children living in urban compared to rural areas. By instead using a microprobe at µm resolution it would be possible to study the detailed distribution of elements in calcified material in greater detail. Jones and co-workers used micro-SXRF to investigate lead distributions in human tibia and deciduous teeth [19]. In Fig 9 results from a line scan across a deciduous tooth are presented as relative concentrations of several elements including lead. In an early study Lindh et al. used a nuclear microprobe to investigate the lead distribution in osteons in femur sampled from exposed workers [20].

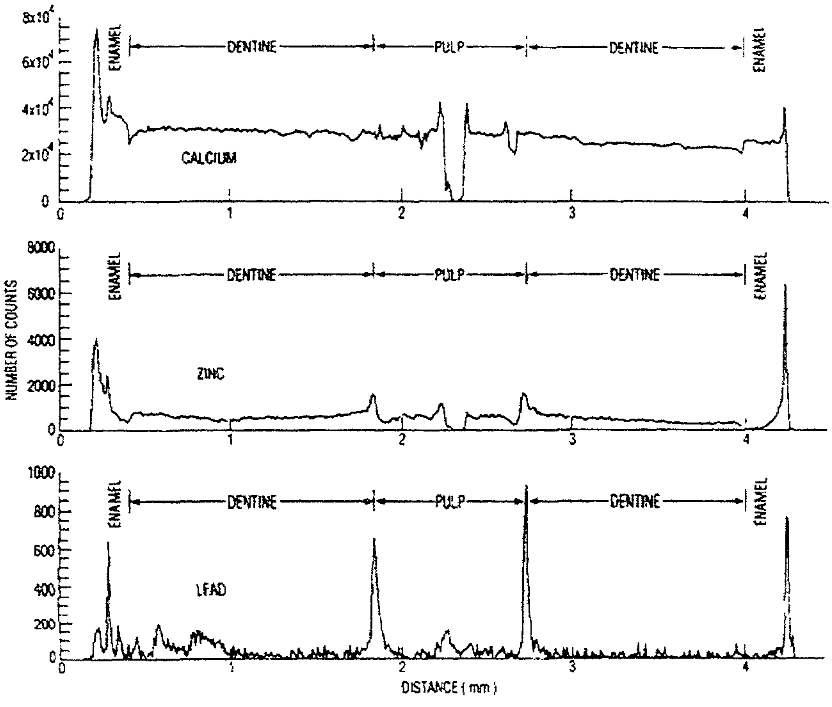

Fig. 9: SXRF analysis results from a line scan across the fresh surface of a cleeved deciduous tooth. The lateral resolution was 10 micrometers.

If these analytical techniques are applied to organisms that annually grow new material, there is a potential that the calcified material can be used as an environmental monitor with time resolution. It has been shown possible to observe elemental variations in the shells of bivalves. Several groups working with nuclear microprobes have performed studies to reveal aspects of environmental chemical changes in shells. Examples are ontogenetic distribution of elements in the shells of living oysters [21] and mussels [22] as a function of growing times in different environments. The pearl *mussel Margaritifera margaritifera* (L.) is a freshwater bivalve. The shell grows in the warm period of the year and ceases during the winter. The annual growth increments can be measured and nuclear microprobe analysis was performed as shown by Fig. 10 [23]. The thick black lines correspond to the line scans performed with the nuclear microprobe.

The PIXE results were quantified using standard reference material of similar composition. In Fig. 11 th easure annual variation of the elements manganese and strontium in a mussel shell is sh . Although the interpretation of such elemental variations is very difficult, because of biovariablity and complex relations between environmental parameters and analytical results, the micro-PIXE is a very promising tool in this field.

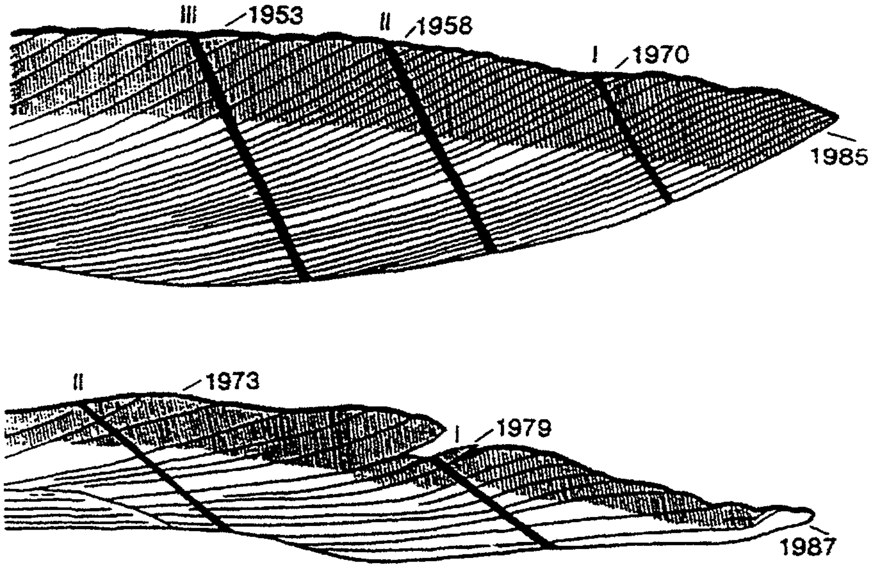

Fig. 10: Mussel shells with indicated annual growth segments and traces of line scans in the nuclear microprobe.

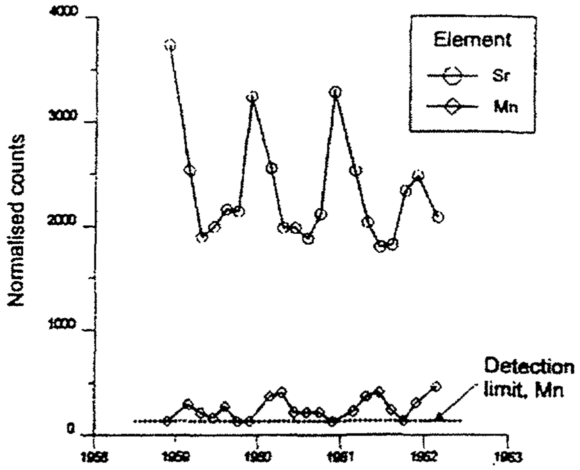

Fig. 11. Results from PIXE analysis in the study shown in Fig. 10.

4. INDUSTRIAL APPLICATIONS

Compared to the environmental field use of ion and photon beams from accelerators are clearly less common in industrial applications. The applications of the ion beam techniques on industrially relevant problems are mainly in the field of materials science. Extensive routine use of RBS in semiconductor industry is based on its capability of monitoring the composition of thin layers (see Fig. 12) during material processing, e.g. epitaxy. Several nuclear reactions offer opportunities for studying single selected elements in various materials such as metals or polymers.

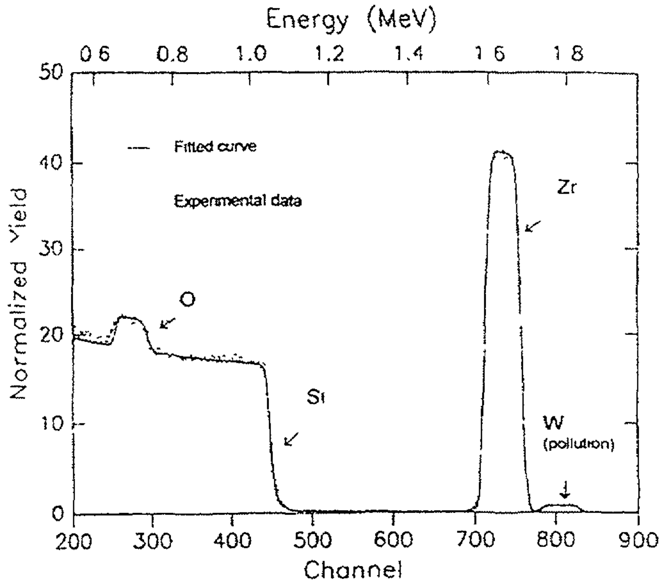

FIG 12 An example of results from RBS analysis on multi-layer materials: Thin ZrO_2 layer on top of silicon.

With a very wide interpretation the field of economical geology is a part of the industrial applications and then broad beam PIXE analysis as well as nuclear microprobes and micro-SXRF have had extensive use. For prospecting of mineral ores one good example is the geogas technique [24]. Thin polymer foils are buried into shallow ground and then exposed to minute amounts of material transported from great depth to the surface (see Fig. 13). Some small particles are collected on the foils and after several weeks the collectors are recovered. By analysing these foils using millimetre ion beam PIXE can reveal the composition of the material deposited. By general geophysical understanding and a complex interpretation processes it is possible to judge the mineral deposits in deep ground.

The fields of mineralogy and petrology are very important also for prospecting of ores. In the CSIRO laboratory in North Ryde, Australia, an ion beam analysis laboratory has been running micro PIXE for more than a decade, primarily serving the mineral industry with analyses for applied geology [25] At the ion beam laboratories in Heidelberg, Germany and Guelph, Canada, the PIXE programmes are also more or less dedicated to geology. The standard samples used for EMP analysis also lend themselves to micro PIXE analysis: approximately 30 μm thick polished sections mounted on a glass backing. Since the ion beam in the NMP penetrates deeper than the EMP, the analytical properties will be somewhat different. There is a potential risk of penetrating into an underlying region of completely different composition, and hence, the results of the analysis of such standard samples have to be evaluated with care. This disadvantage is even more pronounced for the SXRF analysis. However, this capability to see "below the surface" could also be used in investigating unopened liquid inclusions, which cannot be analysed with the traditional EMP technique.

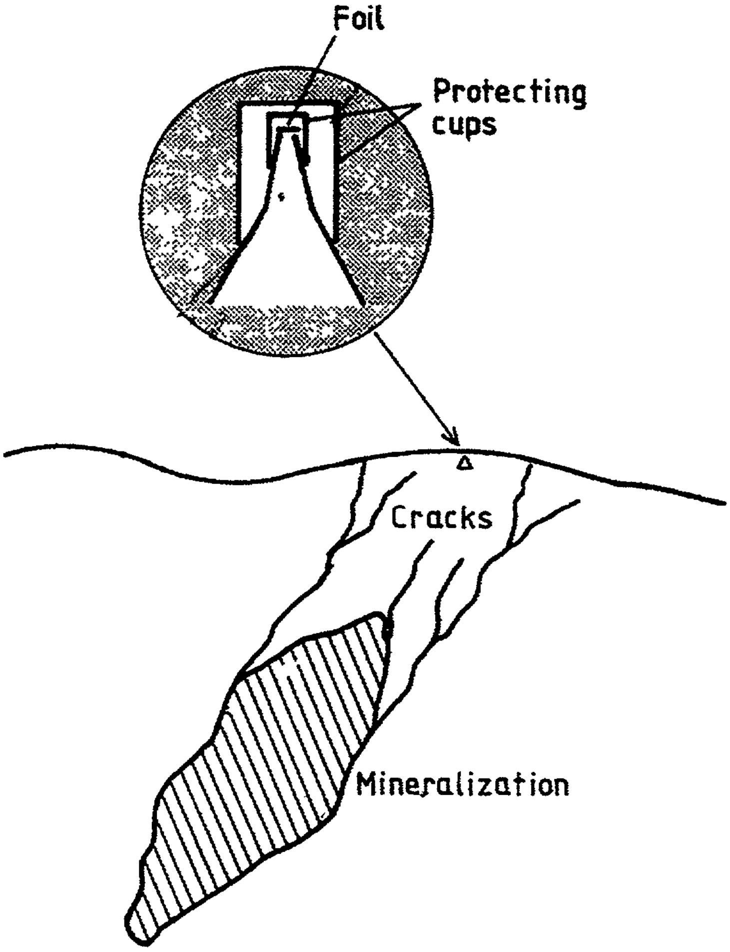

FIG 13 Schematics of geogas mineral exploration Large arrays of collectors are formed in geologically interesting areas Revealed mineralisation can be on several hundred meters of depth

The depth resolution available when combining micro PIXE with micro RBS makes information on the underlying structures obtainable. The distribution of elements in mineral grains can be used to facilitate the understanding and modelling of the formation and transformation of the mineral.

Ore genesis is one field in the earth sciences in which PIXE has been applied. It is especially suited for the study of trace element partition between co-existing minerals, which gives information about the chemical and physical conditions (e.g. temperature) during the ore-forming processes. Diamond genesis can be studied through the analysis of small grains, which have been trapped during the growth of the diamond [26]. As these inclusions have been shielded from any outside influence they carry important information on the physical and chemical parameters of the environment during the formation of the diamonds.

A slightly different industrial application is the use of focused ion beams for characterisation of the fibrous structure of newsprint paper and to characterise the printing characteristics [27]. The energy-loss technique, STIM, has been used to characterise the fibrous structure for different pre-treatment of the paper and PIXE is used to perform elemental analysis of the inks for printing.

5. CONCLUSION

The accelerator-based analytical techniques based on keV photons and MeV ions are in many ways complementary to each other and to many other analytical techniques used in environmental and industrial applications. Both SXRF and PIXE have the most analytical potential when used in their micro-analytical modes. With a careful selection of applications their respective merits more than account for the need for access to accelerator facilities. The ion beam facilities are of about the same complexity and cost as many other advanced analytical techniques and the more expensive and complex synchrotron radiation facilities are increasing in number and becoming more user friendly actually allowing access to large number of simultaneous users. Hence, the future of both techniques seems bright.

REFERENCES

[1] Particle-Induced X-ray Emission Spectrometry (PIXE), eds. S.A.E. Johansson, J.L. Campbell and K.G. Malmqvist, J.W. Wiley & Sons, New York, Chemical Analysis, vol 133, (1995).

[2] CHU W.K., MICOLET M.-A. AND MAYER J.W., Backscattering spectrometry, Academ. Press, N.Y., (1977).

[3] KRISTIANSSON P. AND MARTINSSON B.G., Photon-tagged nuclear reaction analysis for trace element determination, Nucl. Instr. Meth. B132 (1997) 159.

[4] JANSSENS, L. VINCE, B. VEKEMAN, A. AERTS, F. ADAMS, K.W. JONES AND A. KNÖCHEL, Microchim. Acta (suppl.) 13 (1996) 87.

[5] JANSSEN, F. ADAMS, K.W. JONES, Anal. Chim. Acta 283 (1993) 98.

[6] Jones in "Handbook of X-ray spectrometry – methods and techniques" eds. Van Grieken and Markowicz, M. Dekker, N.Y. (1992) 411

[7] CAHILL T., Nucl. Instr. Meth., B75 (1993) 217.

[8] JAMBERS AND VAN GRIEKEN R., TRAC- trends in analytical chemistry 15 (3) (1996) 114.

[9] ARTAXO, RABELLO M.L.C, WATT F., GRIME G. AND SWIETLICKI E., Nucl. Instr. Meth .B75 (1993)521

[10] MESJASZ-PRZYBYLOWICZ, W.J. PRZYBYLOWICZ, V.M. PROZESKY AND C.A. PINEDA, Quantitative-micro PIXE comparison of elemental distribution in Ni hyperaccumulating and non-accumulating genotypes of Senecio coronatus, Nucl. Instr. Meth. B130 (1997)368

[11] VALKOVIC V., RENDIC D., BIEGERT E.K. AND ANDRADE E., Environ. Int. 2 (1979) 27.

[12] PERNESTÅL K., JONSSON B., HÄLLGREN J-E. AND LI H-K., Int. J. PIXE 1 (1991) 281.

[13] LÖVESTAM, JOHANSSON E.-M., JOHANSSON S.A.E. AND PALLON J., Ambio, 19 (1990) 87.

[14] HULT M., BENGTSSON B., LARSSON N.P-O. AND YANG C., Scanning Microsc. 6/2 (1992) 581

[15] SCHOFIELD, PALLON J., FISKESJÖ G., AND MALMQVIST K.G., Planta (1998), in press.

[16] WATKINSON S.C. AND WATT F., The Bryologist 95 (1992) 181.

[17] WATT F., GRIME G.W., BROOK A.J., GADD G.M., PERRY C.C., PEARCE R.B., TURNAU K. AND WATKINSON S.C., Nucl. Instr. Meth. B54 (1991) 123.

[18] MÖLLER B., CARLSSON L-E, JOHANSSON G.I., MALMQVIST K.G., HAMMARSTRÖM L. AND BERLIN M., Scand. J. Work. Environ. Health 8 (1982) 267.

[19] JONES, SCHIDLOVSKY G., SPANNE P., DEJUN X., BOCKMAN R.S., RABINOWTZ M.B., HAMMOND P.B., BORNSCHEIN R.L., AND HOELTZEL D.A., X-ray Microsocopy III, Springer-Verlag (1992)

[20] LINDH U., Anal. Chim. Acta, 150 (1983) 233.

[21] CARRIKER, C.P. SWANN AND J.W. EWART, Marine Biology, 69 (1982) 235.

[22] COOTE W.J. TROMPETTER, Nucl. Instr. Meth. B77 (1993) 501.

[23] LINDH U., NYSTRÖM J. AND MUTVEI H., in: Environmental archives disclosed by nuclear microscopy of mussel shells,, thesis, J. Nyström, Acta Universitatis, Uppsala (1995).

[24] MALMQVIST L. AND KRISTIANSSON P., The geogas technique - an ideal industrial application of PIXE, Proc.8th PIXE Conf., Lund, June 1998, submitted

[25] RYAN C.G. AND GRIFFIN W.L., Nucl Instr Meth, B77 (1993) 381.

[26] GRIFFIN L., RYAN C. G., COUSENS D. R., SIE S. H. AND SUTER G. F., Nucl. Instr. Meth. B49 (1990) 318.

[27] KRISTIANSSON P, MALMQVIST L., SJÖLAND K.A. AND SUNNERBERG G., The Lund nuclear microprobe in newsprint research, Nucl. Instr. Meth. B104 (1995) 584

PORTABLE GAMMA-RAY SPECTROMETERS AND SPECTROMETRY SYSTEMS

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Abstract

The current state-of-the-art in portable gamma-ray spectrometers and portable spectrometry systems is discussed. A comparison of detector performance and features of commercially available systems are summarised. Finally, several applications of portable systems are described.

1. GENERAL

The basic components for any gamma-ray spectrometer system, portable or other wise, include a spectrometer, a spectroscopy amplifier, bias supply, data processing equipment, system power supply, and ancillary equipment: cables, tripods, shielding, etc. The issue of portability is primarily one of size and weight. For gamma-ray spectrometers and spectrometers systems, it is also desirable to have low power detectors that operate at ambient temperatures. Ultimately the issue of portability must be balanced by the requirements for system performance. Most gamma-ray detectors can be made small and compact, but the efficiency, dynamic range and energy resolution can vary significantly. The focus of this report will be to discuss readily available portable spectrometers and spectrometry systems in the context of their portability and performance.

2. GAMMA-RAY SPECTROMETERS

Presently, two types of gamma-ray detectors are readily available and commonly used in gamma-ray spectroscopy: semiconductor and scintillator. These two detector types offer a variety of possible detector choices. However, only three detectors are currently being used with portable gamma-ray spectrometry systems: high purity germanium (HPGe), thallium-activated sodium iodide (NaI(Tl)), and cadmium zinc telluride ($Cd_{0.9}Zn_{0.1}Te$ or CZT)

2.1 PORTABLE HPGE DETECTORS

HPGe detectors are solid state devices that were developed in the mid 1970's. There are two basic types of HPGe detectors: normal and reverse electrode. They are more commonly referred to as "p-type" and "n-type" respectively. The designation specifically refers to impurity concentration. The n-type or reversed electrode detector has a thin outer contact layer, which gives them good sensitivity to low energy photons. HPGe detectors are characterised by their efficiency relative to a 7.6 cm x 7.6 cm NaI(Tl) crystal for the 1332 keV photon at a source-to-distance of 25 cm. Currently HPGe detectors range from 10 % to 170% relative efficiency. The small bandgap[1] (0.7 eV) of germanium prohibit room temperature operation of HPGe

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[1] An energy region separating the conduction and valence band in insulators and semiconductors.

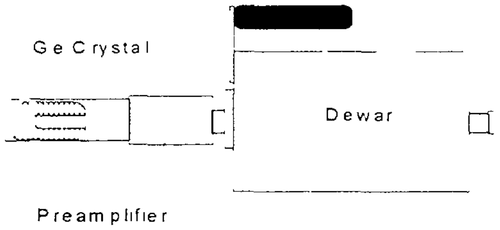

Fig 1 A schematic drawing of a portable HPGe detector indicating some key components

detectors. Leakage across the bandgap is sufficiently reduced by cooling the Ge crystal with liquid nitrogen[2] (LN_2). An HPGe detector is made portable by mounting the crystal and preamp. assembly to a small dewar, typically 1.2, 3 or 5 l. capacity. Fig. 1 is drawing of a portable HPGe detector.Despite the small dewars, portable HPGe detector can be heavy and rather large. A moderately sized detector can be over 40 cm long and weigh as much as 10 kgs when filled with LN_2. For continuous or prolonged operations portable HPGe detectors need a daily[3] supply of LN_2. Moreover, a room temperature detector requires a 'cool-down' period once the dewar has been filled. For a moderately sized crystal (100–200 cm^3), the cool-down period can range from 4-6 hrs. For larger detectors, the cool-down period can last 8 hrs. This can be a inconvenience for some emergency response applications. HPGe detectors require a bias voltage of 3000 to 5000 V. A complete spectrometry system using an HPGe detector consists of a preamplifier (usually incorporated as part of the detector), a shaping or spectroscopy amplifier, a multichannel analyser (MCA), and a laptop computer. A block diagram of a typical HPGe spectrometer system is shown in Fig. 2. Despite their size and need for LN_2, portable HPGe detectors are preferred for many *in situ* applications because of their broad energy range, large active volume, and superior energy resolution.

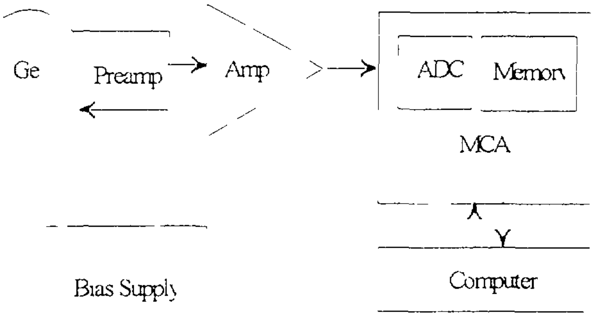

Fig 2 A schematic diagram of a HPGe spectrometry system

2.2 NaI SPECTROMETERS

Advantages of a NaI scintillator include high luminescence, room temperature operation and the ability to be machined in a variety of size and shapes. Typically the sizes range from 3 cm x 3 cm to 7.6 cm x 7.6 cm. Crystal sizes greater than 7.6 cm x 7.6 cm are readily available but are not recommended for portable systems. The crystals (and PMTs) are somewhat fragile and can be damaged by mechanical or thermal shock. Moreover, their

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[2] Other cooling options are available, but would not be considered portable.

[3] Detectors mounted to 3 and 5 l. dewars that can last several days between refills.

luminescence varies with changes in ambient temperature. Compared to HPGe detectors, NaI(Tl) have poor energy resolution. The energy resolution for a NaI(Tl) is typically expressed as a percent of the gamma-ray energy, for HPGe detectors the energy resolution is about 2 keV across the entire spectrum[4]. At 662 keV a NaI(Tl) detector will have an energy resolution of about 8% to 10%. Most portable NaI spectrometers employ an 'inline' design whereby the crystal and PMT are hermetically sealed in light-tight metallic cylinders. They usually require a bias voltage of about 600-800 V. A block diagram of a typical NaI spectrometer system is shown in Fig. 3.

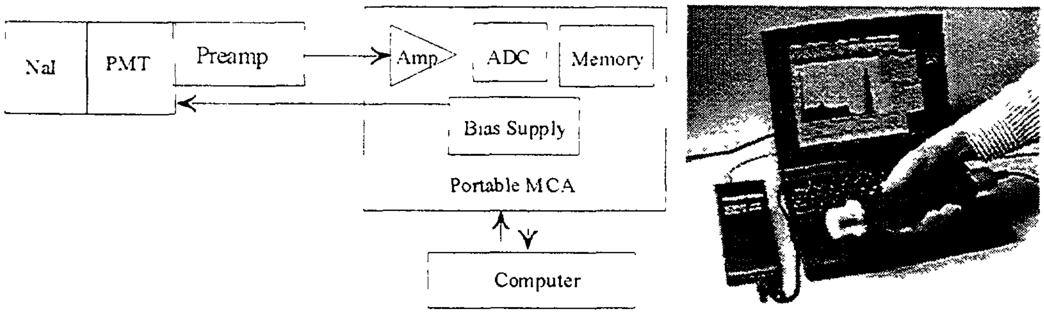

Fig. 3. A schematic drawing of portable NaI(Tl) spectrometry system (left). A picture of a portable spectrometry system (right) (Courtesy of Amptek, Inc., Bedford, MA)

2.3 CZT SPECTROMETERS

With a bandgap of 1.5 eV, the semiconductor CZT can operate a room temperature. This means good resolution without LN_2. Unfortunately, problems with crystal inhomogeneity, excessive charge trapping, and mechanical cracking have hampered fabrication of crystals with large active volumes. Currently the largest active volume available is about 1 cm^3; typical volumes for commercially available spectrometers are closer to 0.05 cc. CZT detectors are recommended for moderate to low energy applications. Fig. 4 shows a diagram of a CZT detector. Table 1 summarises the properties of HPGe, NaI(Tl), and CZT spectrometers.

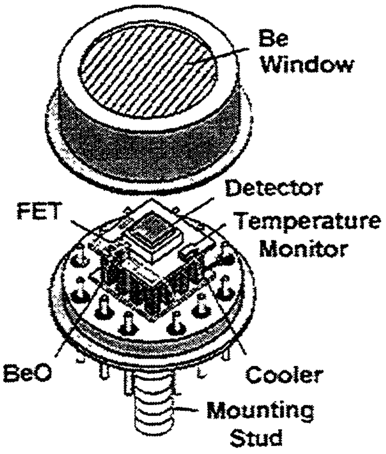

Fig. 4. A schematic drawing of a CZT detector (Courtesy of Amptek, Inc., Bedford, MA).

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[4] Resolution for HPGe detectors is expressed in terms of full with at half-maximum (FWHM). The resolution for a 40% relative efficiency detector at 122 keV can be less than 1 keV, at 1.33 MeV the resolution can be less than 2 keV.

TABLE 1. Comparison of portable spectrometers

Detectors	High Purity Germanium (HPGe)	Sodium Iodide NaI (Tl)	CdZnTe (CZT)
Type	Solid state	Scintillator	Solid state
Resolution	2-3 keV	8% @ 662 keV	1.5 keV @ 122 keV
Energy Range (typ.)	40* keV – 10 MeV	5** keV – 3 MeV	< 1 MeV
Size & Shape: Crystal	Coaxial and planar (30 – 400 cc)	Cylindrical (typ.) 3 cm x 3 cm, 5 cm x5 cm, 7.6 cm x 7.6 cm	Rectangular (~0.05 cc)
Size & Shape: Detector	Cylindrical shape 40-50 cm long 5-15 kg	Cylindrical shape 20-40 cm long 1-5 kg	Rectangular ~ 10 cm long ~ 1- 2 kg
Operating temp.	77 K	300 K	300 K
Cost (USD) (est.)	(10-100k)	10 k	5 k

**this refers to p-type detectors, n-type has good efficiency down to about 5 keV*
***for thin NaI crystals*

Clarke and Williams [3] reported a more recent entry to field of portable spectrometers. They examine the performance of a CsI(Tl) scintillator (1.8 cm x 1.8 cm x 4 cm) with integral p-i-n diode (1.8 cm x 4cm). Advantages of this detector include room temperature operation and no bias supply. However, no commercial version of this portable detector is readily available.

For a more complete discussion of the principles of gamma-ray detection and gamma-ray detectors we refer the reader to Debertin and Helmer [1] and Knoll [2].

3. PORTABLE SPECTROMETER SYSTEMS

3.1 INTEGRATED SYSTEMS

An integrated system is a complete, fully functional spectrometry system. While they are intended for general purpose surveys, some systems have been optimised for very specific applications such as the measurement of the isotopic composition of Pu or the enrichment of U. Most systems utilise NaI scintillator with a multichannel analyser with a built-in display. Some are hand-held and all weigh just a few kilograms. A brief summary of available integrated systems can be found in Table 2.

3.2 MODULAR SYSTEMS

Modular Systems provide the flexibility to construct a portable, laboratory grade spectrometry system for field applications. The portability of the HPGe systems results from small LN_2 dewars and compact, battery powered (MCAs). A configuration can be as simple as a HPGe detector, a set of cables and a portable MCA. A more typical configuration will consist of a detector, cables, and portable MCA and a laptop computer. Fig. 5 is a block diagram of a typical modular system. Note that the bias supply and amplifier are physically housed with MCA. A modular HPGe system can be quite heavy and rather cumbersome. For example a complete HPGe spectrometry system with a 40% relative efficiency detector

TABLE 2. A comparison of integrated spectrometry systems

Integrated Systems	Detector	ADC	Spectrum capacity	Size & Weight	Operating Time	Other
Scout512 (Quantrad)	NaI(Tl) (1”x1”, 2”x2”,3”x3”)		251 spectra w/time and date	11.5x5x19 cm 0.82 w/o detector	12 V Lead acid	
PN-114 (Princeton Electron Systems)	NaI(Ti) (1”x1”-3”x3”) or CdZnTe (CZT)	80 Mhz Wilkinson 1k resolution	configurable 2048 bytes	28x28x8.9 cm 6 kg	2.5 hrs 5 A-h lead acid	
EasySpec (Canberra)	NaI(Tl) (1”x1”, 2”x2”,3”x3”)	66 Mhz Wilkinson 1k resolution	90 spectra w/time and date	19x10x5 cm 1.3 kg	7 hrs NiMH	
GDM 40 PRS (GammaData)	NaI(Ti) 3”x3”	80 Mhz Wilkinson 2 k resolution	1600 spectra (256 ch.@ 2 bytes)	46x34x15 cm 12 kg	8 hrs	Has GPS capability
Gamma-X (Amptek)	NaI(Tl) (30x30 mm up to 152 x76 cm)	MCA 8000A (Successive Approximation FCT <5 μs 16k resolution		17x7x2 cm	16-24 hrs 2 AA cells	Needs computer
“ROVER” (Amptek)	CZT	MCA 8000A				Needs computer
GR-130 (Exploranium)	NaI(Ti) 74 cc, 0-3000 keV or 0-1500 keV	256 channels resolution	Up to 30000 readings or 200 full 256-channel spectra	10x23x9 cm 2.2 kg	+30 hrs 2 D cells	Hand-held survey instrument

mounted to a 1.2 l dewar with a ruggedized MCA and a laptop computer weighs about 20 kg. A brief summary commercially available battery powered MCAs can be found in Table 3.

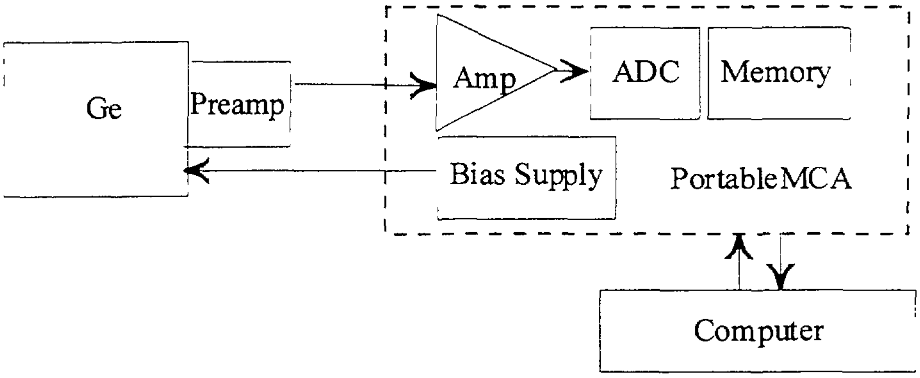

Fig. 5. A schematic drawing of a HPGe portable spectrometry

4. CURRENT APPLICATIONS OF PORTABLE SYSTEMS

Portable gamma-ray systems are primarily used for *in situ* measurements. Typical applications include cargo inspection, non-destructive testing, environmental, industrial, security, and surveillance applications.

4.1 ENVIRONMENTAL MEASUREMENTS AND DECOMMISSIONING OPERATION

In situ measurements are central to most environmental surveillance and site decommissioning operations. They usually involve measurements at a site for extended periods, often from a vehicle or other temporary shelters. They also involve low level measurements for environmental surveillance, or relatively hot samples in the case of decommissioning operations.

4.2 IN-SITU SPECTROMETRY OF SOIL USING PORTABLE GAMMA-RAY SPECTROMETRY SYSTEMS.

The Environmental Measurements Laboratory (EML) has been using portable and transportable spectrometry systems for nearly 30 years. The laboratory developed the technique of *in situ* gamma-ray spectrometry for a real-time assessment of gamma emitting radionuclides in surface soil. Currently, the method typically involves the use of a "downward-looking" uncollimated HPGe detector positioned 1 m above the ground. The activity per unit mass for a given radionuclide can be derived from the peak count rate using parameters that describe the soil characteristics and the depth profile of the radionuclide distribution. The *in situ* technique is well suited for quickly determining levels of contamination over large areas. A single uncollimated *in situ* gamma-ray measurement provides a position-weighted average over the detector's field of view, which is typically several hundred square meters. A comprehensive discussion of the technique may be found in Beck et al. [4] and ICRU Report 53 [5].

For general environmental applications the specific activity for the source is usually low and the gamma-rays of interest can range from 63 keV to 2.6 MeV[5]. The spectrum is

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[5] The 63 keV photon is from Th^{234}, a progeny of U^{238}. The 2.6 Mev photon is Tl^{208}, a progeny of Th^{232}.

TABLE 3. A comparison of portable MCAs

Portable MCAs						
	Bias Supply	Amplifier	ADC	Size & Weight	Operating Time	Other
MCA 8000A (Amptek)	N/A	N/A	Successive Approximation FCT <5 µs 16k resolution	17x7x2 cm 0.3 kg	16-24 hrs	Needs computer, Does not provide bias voltage or a spectroscopy amp
M^{3}CA (Aquila Tech. Group)	300-3500 V 200-1200 V 125 µA	Course Gain: 1,2,4,8,16,32, 64 2 selectable TC	100 MHz Wilkinson 4k resolution	10x22x9 cm		
InSpector (Canberra)	0-5000 V, 100 µA 0-1300 V 500 µA	Gain: x2 to x1500 STC 1 / 4µs	100 MHz Wilkinson 8k resolution	29x27x5 3.2 kg	6 hrs	
NaI InSpector (also CdTe)	0-1300 V 500 µA	Gain: x2 to x1500 STC 0.5 / 1 µs	100 MHz Wilkinson	29x27x5 3.2 kg	6 hrs	Optimized for NaI or CdTe scintillators
Vista (5002, 5004, 5008, 5016) (Aptec)	0-5000 V 0-200µA	No information available	Fixed Conversion 800 ns to 5 µs depending on model 2k-16 k res.	35 x 25 x 6 cm 5 kg	2 –4 hrs	4 model No. to choose from depending on performance requirements
OYDESSEY 6 (Aptec)	0-5000 V @100µA 0-2000 V @250 µA	Built-in high performance spectroscopy amplifier for HPGe or NaI(Tl) detectors	Flash, 16k	Brief case size		Includes computer W/ full I/O Housed in an ABS plastic alloy carrying case
NOMAD^{TM}Plus (EG&G)	0-5000 V @100µA 0-2000 V @250 µA	Gain x4 to x 1000 STC 1 / 6µs	Successive Approximation 16K resolution FCT <5 µs	46x33x15 cm 8 kg	6-8 hrs	Housed in a Zero-Haliburton aluminum case with removable lid
Dart (EG&G)	0-5000 V, 100 µA 0-1250 V 750 µA	Gain: x3 to x1000 STC 1 / 6 µs	Successive Approximation 8K resolution FCT <12 µs	9x14x30 cm 2.3 kg	6 – 7 hrs	Does not require a computer for data collection

usually complex, the gamma emitting progeny of radium and thorium combine for 33 individual lines having at least 1% intensity. It is recommended that for the analysis of environmental spectra a HPGe detector be used with an ADC capable of least 4K resolution, with 8K preferred. While HPGe detectors are preferred for environmental applications, they are not strictly necessary, especially if one is interested in Cs^{137} or Co^{60}. *In situ* measurements of the Mishelyak River were performed using an integrated system featuring a NaI detector (Wollenberg et al. [6], Drozhko et al. [7]). The count rate associated with most environmental applications is modest (< 0.5 kcps) and can be handled many, if not all, portable MCAs. A typical set-up that EML uses for environmental work consists of a 40% relative efficiency p-type HPGe detector mounted to a 1.2 L dewar, and a battery powered MCA with an ADC with 16k resolution. Data storage and data acquisition is accomplished with laptop computer running MCA emulation software. The limiting factor of this set-up is battery power. The computers will last for 2 hours, while MCA is a little better lasting about 7 hrs.

4.3 NUCLEAR SAFEGUARDS

Nuclear safeguards applications prevent unauthorized proliferation of nuclear material. Regulatory Agencies routinely make *in situ* measurements during inspection trips at various nuclear sites. Data collection times are often short, and sometimes must be conducted in hostile environments. A CZT detector can be useful for cargo inspections looking for enriched uranium and plutonium. Both U and Pu have low energy photons, the excellent resolution and compact size of a CZT make it a sensible choice for such applications.

REFERENCES

[1] DEBERTIN, K. AND HELMER, R.G., Gamma- and X-Ray Spectroscopy with Semiconductor Detectors, North-Holland, 1988

[2] KNOLL, G. F. Radiation Detection and Measurements, 2nd Ed. Wiley, New York, 1989.

[3] CLARK, X. X., WILLIAMS R. R., An in situ gamma ray spectrometer with CsI/p-I-n detector, Rev. Sci. Instrum. 66 (3) (1995).

[4] BECK, H.L., DECAMPO, J., AND GOGOLAK, C. In Situ Ge(Li) and NaI(Tl) Gamma-Ray Spectrometry, Report HASL-258, U.S.D.O.E. Environmental Measurements Laboratory, NY (1972)

[5] International Commission on Radiation Units and Measurements, “Gamma-Ray Spectrometry in the Environment”, Technical Report ICRU 53, Bethesda, MD (1994).

[6] WOLLENBERG, H., TSANG, C.-F., FRANGOS, W., SOLBAU, R. D., LOWDER, W. M., STEVENSON, K. A., FOLEY, M. G., DRZHKO, E. G., ROMANOV, G., GLAGOLENKO, Y. U., POSOCHOV, Y. G., YVANOV, L., SAMSONOVA, L. M., PETROV, A., TER-SAAKIAN, S.A., VASIL’KOVA, N. A., GLAGOLEV, A. V. Joint Russian-American Field Test at the Chelyabinsk-65 (Mayak) Site: Test Description and Preliminary Results, Lawrence Berkeley Laboratory Report LBL-36825, (1995).

[7] DRZHKO, E. G., GLAGOLENKO, Y. U., MOKROV, Y. G., POSTOVALOVA, G. A., SAMSONOVA, L. M., GLAGOLEV, A. V., TER-SAAKIAN, S.A., GLINSKY, M. L., VASIL’KOVA, N. A., SKOKOV, A. V., WOLLENBERG, H. A., TSANG, C.-F., FRANGOS, W., SOLBAU, R. D., STEVENSON, K. A., LOWDER, W. M., FOLEY, M. G., Joint Russian-American hydrogeological studies of the Karachai-Mishelyak system, South Urals, Russia, Environmental Geology 29, (1997)

PORTABLE GAMMA SPECTROMETERS FOR ENVIRONMENTAL AND INDUSTRIAL APPLICATIONS AT THE INSTITUTE OF PREVENTIVE AND CLINICAL MEDICINE IN BRATISLAVA

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Abstract

A survey of methods for in-situ measurements of gamma radioactivity in soil is done. Mathematical models for depth distribution of gamma radioactivity in soil are given.

1. INTRODUCTION

At IPCM there is a research centre for radiation protection, where methods for field gamma spectrometry are developed. Field gamma spectrometry is used for determination of photon energy spectra and for the rapid identification of radionuclides. When the source and/or shielding geometry is taken into account, the determination of radionuclide activity and exposure rate is performed. Applications have included:

- In situ measurement of gamma-ray emitting radionuclides in soil
- Measurement of radionuclides in bulky samples
- Searching for lost, buried or shipped radionuclides
- Gamma-ray dosimetry based on field spectrometry

2. INSTRUMENTATION

Field gamma-ray measurements are performed using a conventional coaxial HPGe detector with a 12.5% relative efficiency (compared to a 3x3 inch NaI[Tl] full energy peak net area at 1.33 MeV) and a resolution of 1.9 keV (FWHM @ 1.33 MeV). The useful energy of the detectors range from 40 keV to more than 10 MeV. In order to allow operation of the detector in any orientation without LN_2 spillage, a multi-attitude cryostat has been used. The cryostat is a Dewar with a capacity of 7.0 litres LN_2 and a holding time of 5 days. This allows the Dewar to be operated in the horizontal position, pointing vertically upward or downward, without loss of LN_2. Field measurements are made using a computer based spectroscopy system. High voltage, preamplifier and spectroscopy system are supplied through a portable power supply. The detector is supported by a tripod and the front of the detector is 1 m above the ground. The orientation of the detector is downward facing. A cylindrically-shaped collimator was used to modify the angular distribution of photons impinging on the detector surface. The collimator is a lead cylinder with an outer/inner diameter of 19/10 cm and a height of 10 cm. Detector calibrations field gamma-ray spectrometry have been performed by calculations and by using point like gamma-ray sources.

3. ENVIRONMENTAL AND INDUSTRIAL APPLICATIONS

3.1 IN SITU MEASUREMENT OF GAMMA RADIONUCLIDE ACTIVITY IN SOIL

Soil contamination by gamma-ray emitting radionuclides can be measured in two ways:

- soil sampling method (soil samples are measured in the laboratory)
- in situ spectrometry of the ambient gamma-ray radiation.

The conventional soil sampling method has two disadvantages:

- the samples may not be representative for a large area
- the determination of the depth distribution of a radionuclide requires measurement of several samples taken at different depths.

In situ measurement of radionuclide activity in soil are more sensitive and provide more representative data than data obtained by soil sample collection and subsequent laboratory analysis. In emergency situations when the time to assess the contamination is critical, a direct measurement of ambient gamma-ray radiation for rapid assessment of the deposited activity is used. In order to obtain accurate measurements of radionuclides in the soil, the Ge detector should be placed on relatively even and open terrain. Areas with large obstructions such as boulders or man made structures should be avoided. When working in wooded areas, the detector should be positioned as far as possible away from tree trunks. When measuring fallout radionuclides, the terrain under study should be undisturbed since natural wind and water erosion processes as well as any human activity, e.g. plowing would upset the distribution of deposited radionuclides. Although these site criteria can be difficult to fulfill for aged fallout, there is generally no problem for a fresh deposition event. For measurements in most undisturbed terrain's, one generally can assume a uniform distribution with depth for natural emitters and a negative exponential distribution with depth for fallout radionuclides. A positive exponential distribution of radionuclide activity in profile of deposited soil can be used. It is a common practice to place the detector 1 m above the soil surface. At this height, a tripod-mounted detector can be easily handled and still provide a radius of view for gamma emitting sources out to about 10m. The "field of view" actually varies, being somewhat larger for sources at upper layers of soil. Depending upon source energy, the detector effectively sees down to a depth of 15-30 cm. For most applications a more sensitive and representative measurement can be made by using a bare detector so that the full half-space is seen.

3.2 IN SITU SPECTROMETRY BY BECK

An excellent synthesis of the state of art of in situ measurements has been presented in the ICRU report 53 [1]. The primary advantage of the in situ method by Beck [2] is the ability to obtain information about the average activity of radionuclides in or on the soil. Furthermore, one can use this information about the radionuclide activity to determine their individual contribution to the ambient exposure. Beck's approach is characterised by expressing the conversion factor (from peak count rate to radionuclide activity) in terms of three quantities:

$$\frac{N_f}{A} = \frac{N_f}{N_0}\frac{N_0}{\Phi}\frac{\Phi}{A}$$

where:

N_f/N_0 = angular correction factor of the detector for a radionuclide distribution in the soil

N_0/Φ = peak count rate to flux density for parallel beam of photons that is incident-normal to the detector face.

Φ/A = primary photon flux density arising at the detector to radionuclide activity (inventory Bq m^{-2}, or concentration Bq kg^{-1}) for a given radionuclide distribution in the soil.

N_f/N_0 and Φ/A depend on the gamma-ray flux density reaching the detector, therefore the accuracy of the technique is a function of numerous parameters affecting the flux density. Some of these parameters include spatial and depth distribution of the contaminant which can vary significantly with time. For example, in early stages of an accident situation, the contamination is mainly on the surface. The gamma-ray fluence rate, in this situation, is very sensitive to variations in parameters such as roughness of the soil surface, vegetation, roads etc.. Later, as the radionuclides migrate into the soil, the contribution to the total fluence rate, from large distances, decreases [3].

3.3 CALCULATIONS OF BECK'S COEFFICIENTS

Calculation of the constants N_f/N_0 and Φ/A for a realistic model of in situ measurement takes into account:
- roughness of soil surface
- aged fallout (not exponential radionuclide activity distribution in soil profile)
- mixed ground level

The calculations are based on analytical equations of photon attenuation in soil and in air, and/or by interpolation of Beck's conversion factors [2,4].

3.4 METHODS OF CALCULATING THE DEPTH DISTRIBUTION OF THE RADIONUCLIDE CONCENTRATION IN SOIL.

The most important disadvantages of in situ spectrometry by Beck is that the accuracy of the analysis depends on separate knowledge of the radioactivity distribution as a function of soil depth. Several groups have been trying to obtain this information by calculation using data from in situ measurements. The calculations are based on the energy dependence of gamma-ray attenuation in soil, scattering of photons in soil and track length distribution of photons in soil. This method of calculation can be applied independently for radionuclides emitting gamma-rays with more than one energy. The ratio of fluence rates of unscattered photons of ^{137}Cs whose decay product ^{137m}Ba emits photons with energies of 0.662 and 0.032 MeV was used in post Chernobyl measurements [5]. The method is applicable a short time after the deposition of about 50 kBq m^{-2} ^{137}Cs. Several methods based on the ratio of the unscattered and scattered radiation in the whole energy region, total to peak ratio method [6], or forward scattered, peak to valley ratio method [7] exist. The peak to valley ratio is an attractive and quite sensitive method, when forward scattered photons of exactly determined energies are measured [8]. Photons with different track length distributions in soil can be measured by collimated and uncollimated detector. By restricting the solid angle, at which the detector registers gamma-rays, the average depth where the detected rays were emitted is changed [9].

3.5 IN SITU MEASUREMENTS BY UNFOLDING METHOD

The in situ measurements by the unfolding method utilises a combination of two methods: the peak to valley method and the change of track length distribution of photons in soil, registered by collimated and uncollimated detector [8]. The detector response N(i) to the i:th characteristic of the gamma-ray field above ground, with a homogenous distribution of radionuclides in the horizontal direction, is described by the integral equation:

$$N(i) = \int \sigma(i,\zeta)\, A(\zeta)\, d\zeta \qquad i = 1,2,\ldots,n \qquad (1)$$

where:

ζ (kg m^{-2}) = depth in the soil in units mass-per-area,

$\sigma(i,\zeta)$ (Bq^{-1} m^{-2}) = the detector response in gamma-field of plane source of unit activity per-area in soil,

$A(\zeta)\, d\zeta$ (Bq m^{-2}) = activity of the plane source to be determined.

Quantities presented in terms of soil mass-per-area characterise the related field in air better than the linear depth of the source element in ground. The unknown activity A(z) as a function of depth is obtained by unfolding equation (1). The method is based on the unfolding of four various responses $\sigma(i,\zeta)$ of in situ measurements at the same place. The measurements consist of collimated and uncollimated detector responses in full energy peak net areas of 0.662 MeV primary and 0.62-0.655 MeV forward scattered photons. Fig. 1 shows the pulse high distribution in the energy interval 0.55-1.0 MeV measured by an uncollimated HPGe detector. The background continuum in the valley between the Compton edge and the 0.662 MeV photo peak is compounded from contributions of photons from natural sources and ^{137}Cs scattered in the detector and in the detector housing material.

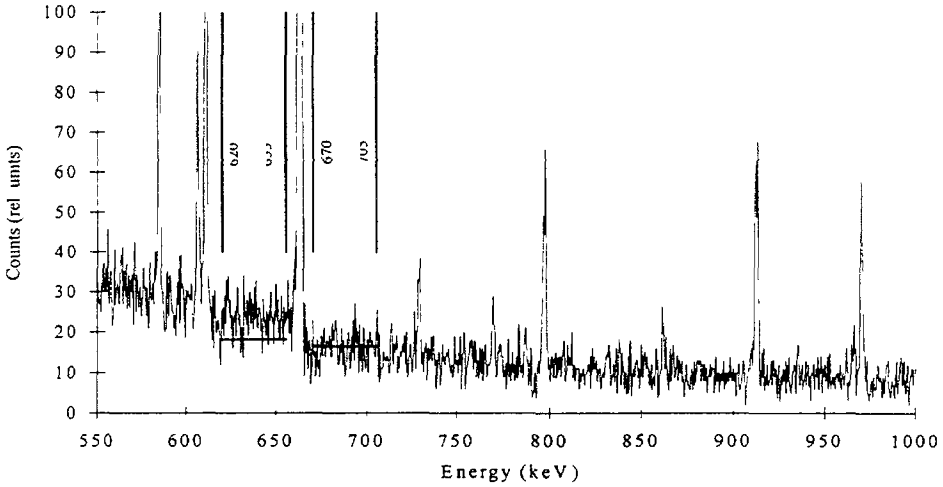

Fig 1 Pulse height spectrum of HPGe detector

The contribution from natural sources to the background continuum in the energy region from 0.62 to 0.655 MeV can be obtained by the ratio of integral counts in the channels corresponding to the energy regions 0.62-0.655 keV and 0.670-0.705 keV. This ratio is constant in field spectra, because the shapes of the HPGe continua are relatively constant. This is because Compton scattered gamma-rays from natural emitters in the soil dominate in HPGe spectrum and the spectrum is relatively invariant to the amount of U, Th and K in the soil or to the size of the individual total absorption peaks in the continuum [2]. The detector response $\sigma(i,\zeta)$ to the i:th characteristic of the gamma-ray field with a flux $\phi(i,\zeta,\theta,E)$ per-unit-activity of plane radionuclide at the depth ζ in the soil can be described as follows:

$$\sigma(i,\zeta) = \int\Phi(i,\zeta,\theta,E)\, R(i,\theta,E)\, d\theta\, dE \quad (Bq^{-1}\, m^{-2}) \qquad (2)$$

where $R(i,\theta,E)$ is the detector response in peak of the total absorption of a parallel photon beam of energy E at angle θ. eqn. (2) can be simplified by assuming that $R(i,\theta,E)$ is constant in the energy range from 0.62 to 0.662 MeV:

$$\sigma(i,\zeta) = \int\Phi(i,\zeta,\theta)\, R(i,\theta)\, d\theta \qquad (3)$$

where $\Phi(i,\zeta,\theta)\, d\theta$ is the photon flux at angle θ integrated over the energy and $R(i,\theta)$ is the angular dependence of the detector response for a parallel, 0.662 MeV, photon beam. The photon flux Φ has been calculated by using our Monte Carlo code SOILSC. A homogeneous and isotropic plane source of thickness 0.5 cm was simulated up to 85 g cm^{-2} of soil depths, starting with the plane source on the ground. The plane source radii were asumed to be 100 m to represent an infinite plane soil contamination with radionuclide ^{137}Cs. Photon interaction processes of photoelectric absorption and Compton scattering [13] had been taken into account by the Monte Carlo program. The calculation results for angular distribution of photon fluences $\Phi(1,\zeta,\theta)\, d\theta$ 100 cm above the soil with a density of 1 g cm^{-3} and a plane ^{137}Cs source located at various depths are given in Table 1 (primary photons) and $\Phi(2,\zeta,\theta)\, d\theta$ in Table 2 (scattered photons with energies in the interval 0.62 - 0.655 MeV). The incident directions of photons are expressed as cosines of a normal vector to the soil surface. The depth of the plane source is related to the centre of the source layer with a thickness of 0.5 cm. Responses of uncollimated and collimated detector to primary photons are given by the equations:

$$\sigma(1,\zeta) = \int\Phi(1,\zeta,\theta) R(1,\theta)\, d\theta$$

$$\sigma(3,\zeta) = \int\Phi(1,\zeta,\theta)\, R(2,\theta)\, d\theta$$

Where: $R(1,\theta)$ and $R(2,\theta)$ = angular dependence of response in peak of total absorption of uncollimated and collimated detector to a parallel 0.662 MeV photon beam, respectively. Responses of uncollimated and collimated detector to 0.62 - 0.655 MeV photons consist of two components, photons that are scattered in soil and in detector housing material

$$\sigma(2,\zeta) = \int\Phi(2,\zeta,\theta)\, R(1,\theta)\, d\theta + \int\Phi(1,\zeta,\theta)\, R(3,\theta)\, d\theta$$

$$\sigma(4,\zeta) = \int\Phi(2,\zeta,\theta)\, R(2,\theta)\, d\theta + \int\Phi(1,\zeta,\theta)\, R(4,\theta)\, d\theta$$

Where: $R(3,\theta)$ and $R(4,\theta)$ = angular dependence of response in the energy interval 0.62-0.655 MeV of an uncollimated and an collimated detector to a parallel 0.662 MeV photon beam, respectively. The angular responses $R(i,\theta)$ of the detector have been measured by using a point like ^{137}Cs source which was positioned at different angles at a fixed distance of 0.7 m from the detector. The detector responses $\sigma(i,\zeta)$, $i = 1,2,3,4$ (response matrix of the detector) to scattered and unscattered photons of the plane ^{137}Cs source in depending of depth in mass-per-area are shown on Fig. 2. For unfolding of detector responses the iteration procedure SAND II [10] has been found reliable and capable of calculating the depth distribution of ^{137}Cs in soil with adequate accuracy for environmental monitoring purposes. Fig. 3 shows the depth distribution of the ^{137}Cs activity in the soil at Bled [17].

TABLE 1. Angular distribution of the fluence of primary photons at 1m height per unit source intensity of plane source of 0.662 MeV photons at different depths in the soil (m^{-2} per photon m^{-2})
Depth in ground (g cm^{-2})

cos	Depth in ground (g cm^{-2})									
cos	1,00E-01	2,00E-01	3,00E-01	4,00E-01	5,00E-01	6,00E-01	7,00E-01	8,00E-01	9,00E-01	1,00E+00
0,0	7,73E-01	3,42E-01	2,53E-01	1,77E-01	1,65E-01	1,52E-01	1,39E-01	7,60E-02	2,03E-02	2,60E-03
1.7	4,53E-03	1,24E-01	1,13E-01	9,98E-02	8,34E-02	8,55E-02	9,70E-02	3,60E-02	2,06E-02	2,06E-03
3,4	7,82E-03	4,93E-02	6,44E-02	7,28E-02	7,82E-02	7,28E-02	7,80E-02	4,92E-02	1,82E-02	1,29E-03
6,8	3,30E-04	9,76E-03	2,38E-02	3,52E-02	4,09E-02	4,31E-02	5,11E-02	4,66E-02	1,82E-02	1,07E-03
10.2	1,50E-05	1,85E-03	8,45E-03	1,62E-02	2,08E-02	2,66E-02	3,24E-02	3,59E-02	1,62E-02	1,51E-03
13,6	8.19E-07	3.60E-04	2,96E-03	7,28E-03	1,09E-02	1,59E-02	1,93E-02	2,50E-02	1,71E-02	1.14E-03
17.0	5.26E-08	7,89E-05	9,90E-04	3,59E-03	5,98E-03	8,80E-03	1,32E-02	1,79E-02	1.55E-02	1.91E-03
23,8	0,00E+00	3,93E-06	1,20E-04	7,40E-04	2,03E-03	3,22E-03	5,24E-03	7,15E-03	1,01E-02	2,38E-03
34,0	0.00E+00	0,00E+00	7,28E-06	7,98E-05	3,30E-04	8,50E-04	1,64E-03	2,23E-03	4,22E-03	1,64E-03
51,0	0,00E+00	0,00E+00	5,50E-08	1,98E-06	1,76E-05	7,81E-05	2,00E-04	4,20E-04	8,10E-04	6,70E-04
68,0	0,00E+00	0,00E+00	5,71E-11	5,91E-08	9,92E-07	7,92E-06	2,81E-05	7,22E-05	1,50E-04	2,00E-04
85,0	0,00E+00	0,00E+00	0,00E+00	1,48E-09	6,47E-08	7,76E-07	3,97E-06	1,29E-05	3,23E-05	4.99E-05

TABLE 2. Angular distribution of the fluence of scattered photons of energies 0.62 - 0.655 MeV at 1m height per unit source intensity of plane source of 0.662 MeV photons at different depths in the soil (10^{3}m^{-2} per photon m^{-2})

cos	Depth in ground (g cm^{-2})									
	1,00E-01	2,00E-01	3,00E-01	4,00E-01	5,00E-01	6,00E-01	7,00E-01	8,00E-01	9,00E-01	1,00E+00
0,0	9,80E-03	5,60E-03	2,60E-03	5,40E-04	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00
1,7	3,38E-03	6,04E-03	5,34E-03	3,20E-03	2,14E-03	1,07E-03	9,78E-04	8,10E-05	6,40E-05	3,47E-05
3,4	1,80E-03	5,10E-03	5.10E-03	4,40E-03	3,50E-03	2,90E-03	1,80E-03	9,20E-04	8,20E-04	4,00E-04
6,8	3,30E-04	5,20E-03	3,50E-03	4,20E-03	3,40E-03	2,50E-03	2,20E-03	1,90E-03	1,80E-03	4,30E-04
10,2	1,05E-04	1,05E-03	2,40E-03	2,90E-03	2,95E-03	2,70E-03	2,10E-03	2,10E-03	2,10E-03	4,30E-04
13,6	9,00E-05	9,20E-05	1,38E-03	1,80E-03	2,10E-03	2,10E-03	2,35E-03	2,35E-03	2,35E-03	6,70E-04
17,0	1,20E-04	2,20E-05	4,80E-04	1,14E-03	1,55E-03	1,88E-03	1,70E-03	2,37E-03	2,00E-03	7,80E-04
23,8	0,00E+00	5,70E-06	8,50E-06	4,80E-04	8,20E-04	8,60E-04	1,47E-03	2,10E-03	1,90E-03	9,80E-04
34,0	0,00E-00	7,40E-06	6,70E-06	6,30E-05	1,40E-04	3,80E-04	4,00E-04	7,00E-04	9,00E-04	3,50E-04
51,0	0,00E+00	0,00E+00	9,00E-08	1,40E-06	8,50E-06	6,00E-05	1,30E-04	2,10E-04	3,10E-04	1,07E-04
68,0	0,00E+00	0,00E+00	0,00E+00	1,09E-06	1,09E-06	1,06E-05	1,06E-05	5,90E-05	1,06E-04	3,30E-05
85,0	0,00E+00	0,00E+00	0,00E+00	1,60E-07	3,00E-07	6,00E-07	7,00E-07	1,70E-05	1,70E-05	1,90E-05

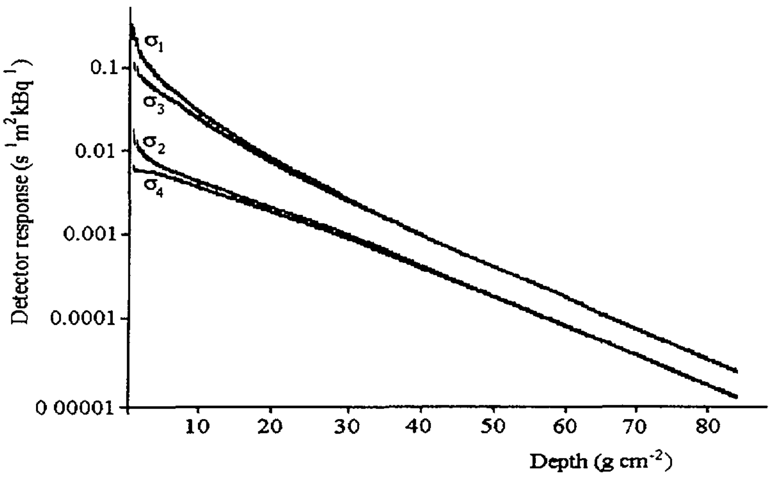

Fig.2 Response matrix of HPGe detector

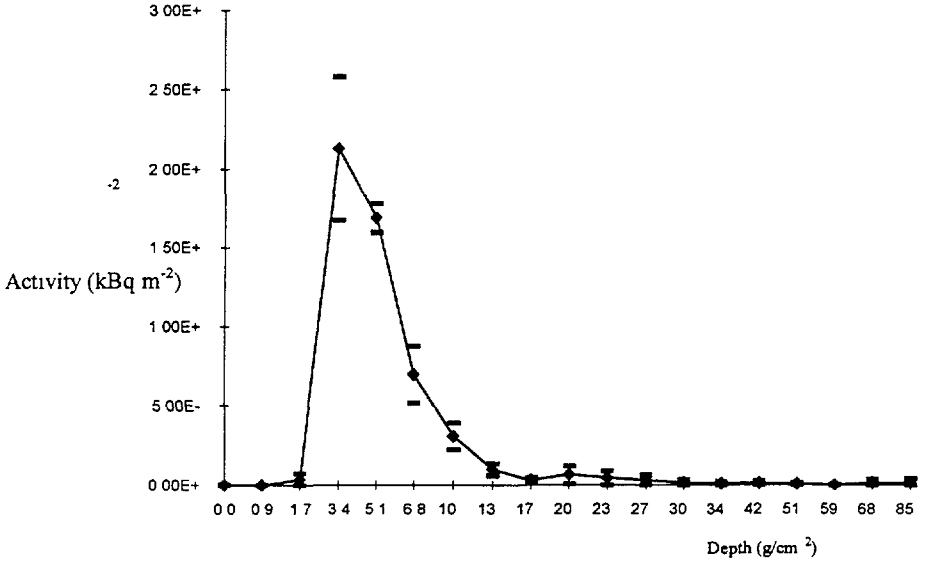

Fig.3 Distribution of Cs in soil at the airport Bled

This was calculated by unfolding method. Fig. 4 shows the same as Fig. 3, but the depth distribution in the soil was measured at Hinterrhein [18] Our experiences indicate that ^{137}Cs concentration in soil 10 years after Chernobyl accident would be measurable using a middle sized HPGe detector (20-30% relative efficiency), and a counting time of the order of 1 hour. Even with smaller detectors (12-15% relative efficiency), ^{137}Cs concentration of 5 kBq m^{-2} are measurable and the depth distribution of ^{137}Cs activities above 10 kBq m^{-2} in the soil can be estimated by the presented method when a counting time of the order of 3 hours is used.

3.6 INHOMOGENEOUS DISTRIBUTION OF RADIONUCLIDES IN SOIL – HOTSPOTS

For site characterisation for environmental restoration, or in emergency removal actions it is necessary to identify areas within a defined boundary that have levels of radionuclide contamination greater than given limit. The method utilises a collimator for limiting the field of view of a detector to measure a small section of ground, allowing for a more selective searching procedure of detecting a hotspot. Monitoring of an area with hotspots is time consuming and expensive, therefore a careful planning of the data collection should be undertaken in order to:

- provide sufficient data to make the required decisions within a reasonable uncertainty
- collect only minimum amount of necessary data.

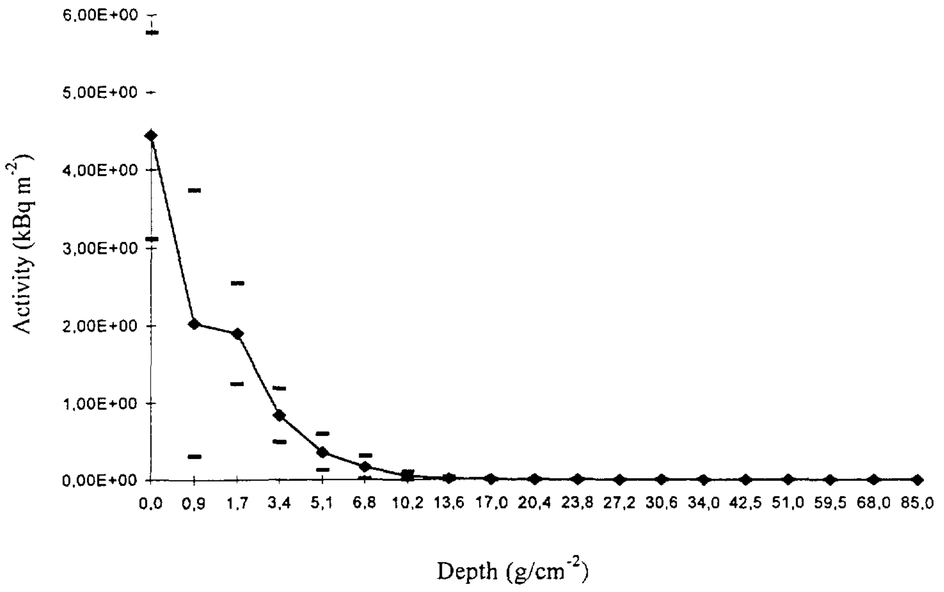

Fig.4. Distribution of ^{137}Cs in soil at Hinterrhein

There are several steps in the planning procedure, to be considered, in order to obtain reasonable type, quantity and quality of data for environmental decision making [11]:

State the problem:

There are two approaches to this problem. One is hypothesis testing where decisions are made by comparing an average radionuclide activity to a given limit. The second is to calculate the probability of detecting a hotspot. The diameter of the smallest hotspot, which can be detected by using an ionisation chamber or a sensitive survey ratemeter, should be estimated. The case study states that if a hotspot is found, a further study will have to take place in order to determine the extent of contaminated area.

Specify limits of the decision:

Limits on the probability of finding a hotspot and the area to be covered should be stated.

In situ spectrometry design alternatives:

Development of general sampling and analysis design alternatives. For each design alternative, the mathematical expressions, needed for solving the design problem, should be formulated. For each design alternative, the optimal grid size for a given probability of finding a hotspot, or standard deviation of radionuclide activity in soil should be chosen. One can use two monitoring plans: simple monitoring (a grid for in situ measurements with a constant density of nodes) and sequential monitoring (with higher density of nodes at locality of a hotspot).

For a continuous distribution of activity a_0 of a radionuclide in soil. An equation for calculation of the standard deviation of activity, determined by in situ measurements with a collimated detector, was derived [12]:

$$\sigma_{a_0}^2 = \frac{8\pi R^2 a_0}{\varepsilon t \rho K_z \Delta x^2 \left(1 - \frac{\Delta x^2}{24\,\xi^2 R^2}\right)^2}$$

Where : R = distance from detector to soil surface
ε = detection efficiency
ξ = detector collimation factor [12]
ρ = soil density
t = time of measurement
Δx = grid density (density between two nodes)
K_z = factor of radionuclide distribution in soil profile [12]

$$K_z = \frac{1}{\mu}\left(1 - e^{-\mu h}\right) \text{ = radioactive waste on landfill}$$

$$K_z = \frac{1}{\mu + \frac{\alpha}{\rho}}\left(1 - e^{-\left(\mu + \frac{\alpha}{\rho}\right)h}\right) \text{ = radioactive fallout}$$

$$K_z = \frac{1}{\mu}\left(1 - e^{-\mu h}\right) - \frac{1}{\mu + \frac{\alpha}{\rho}}\left(1 - e^{-\left(\mu + \frac{\alpha}{\rho}\right)h}\right) \text{ = deposition of earth with a radionuclide}$$

The standard deviation of activity depending on grid size (distance between nodes of the grid) and for various distances of the detector from the soil surface is shown in Fig. 5.

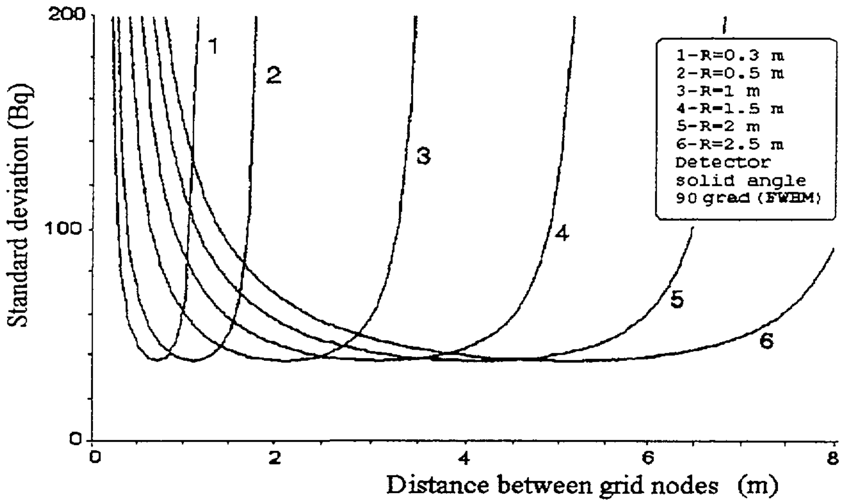

Fig. 5. Standard deviation of activity of ^{137}Cs in soil measured by collimated detector at various distances from the soil surface

The activity a_0 of ^{137}Cs in soil was 500 Bq kg^{-1} and the solid angle of the detector with collimator (FWHM) was 90°. The standard deviation of activity depending on grid size (distance between nodes of the grid) and for various solid angles of the detector with collimator (FWHM) is shown on Fig 6. The distance from the detector to the soil surface was 1 m

4. BULKY SAMPLES WITH RADIONUCLIDES.

- Industrial waste on landfill
- Radioactive waste in containers
- Indoor gamma spectrometry

A combination of field gamma spectrometry and calculation of photon transport in sample material by analytical equations and/or by the Monte Carlo code MCNP (13) is used for estimation of radionuclide activity in the measured sample.

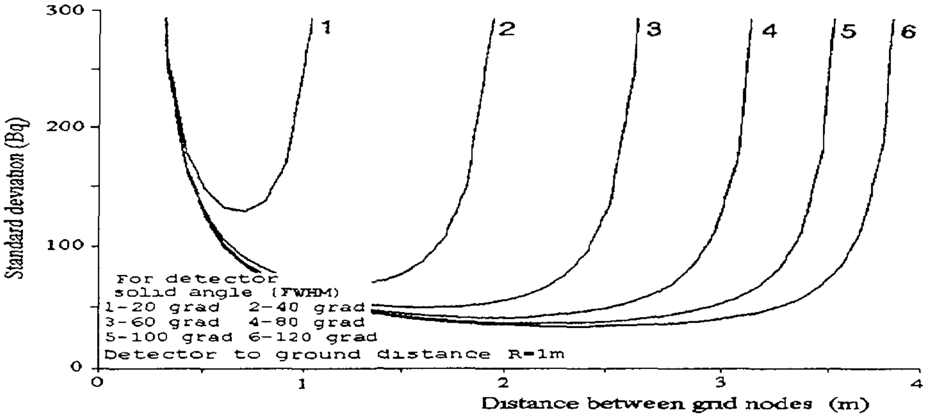

Fig 6 Standard deviation of activity of ^{137}Cs in soil measured by collimated detector

5. SEARCHING FOR LOST, BURIED OR SHIPPED RADIONUCLIDE

- Identification of radionuclides
- Lost radionuclides
- Buried or shipped radionuclides

Field gamma spectrometry is used for a rapid identification of radionuclides and when measurements are performed at various distances between source and detector, the source activity can be deduced.

6. GAMMA DOSIMETRY BASED ON FIELD SPECTROMETRY

At present the most popular technique for evaluation of semiconductor gamma-ray spectra is the net area calculation of the total absorption peak In dosimetry of gamma radiation, the peak net area method allows one to calculate dosimetric values only for sufficiently discrete gamma spectra without consideration of contribution of scattered photons to the total gamma dose The gamma dose due to scattered photons is often a great part of the total dose (14) Further, continuos spectra are often typical cases in gamma-ray dosimetry due to single and multiply scattering, in internal and external bremsstrahlung investigation etc

Therefore for determination of ambient dose it is necessary to know photon energy spectrum in locality of interest. There are two ways to estimate the photon energy spectrum:

- The calculation of the angular distribution of the gamma-ray energy spectrum by considering the source and shielding geometry [2, 14]. Only gamma dose from radionuclide of interest is determined. For photon transport calculation we used the MCNP code.
- Calculation of the photon energy spectrum from measured detector pulse height spectrum [15, 16]. In this case the total gamma dose from radionuclide and cosmic radiation is determined.

6.1 IN SITU SPECTROMETER AS A GAMMA DOSIMETER

The evaluation of the photon energy spectrum from detected pulse spectra can be performed by unfolding the detector responses in channels of the multichannel analyser. The response matrix was created by combining point source measurements with an estimation of the scaling and loading coefficients and by a confirmatory least squares technique of factor analysis [15]. In Fig.7 the response matrix of our semiconductor detector to 0.040 – 1.8 MeV photons is shown. The calculation of photon energy incident spectra was performed by an iteration procedure SANDII.

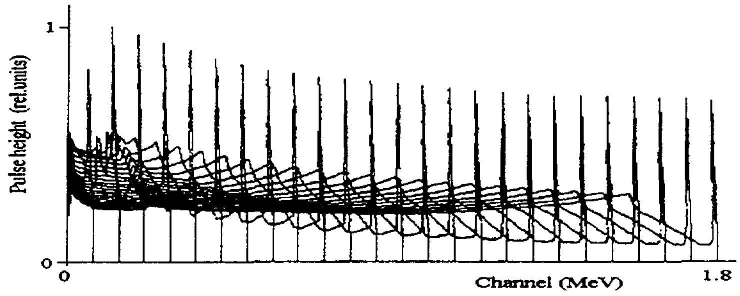

Fig. 7. Pulse spectra from the HPGe detector

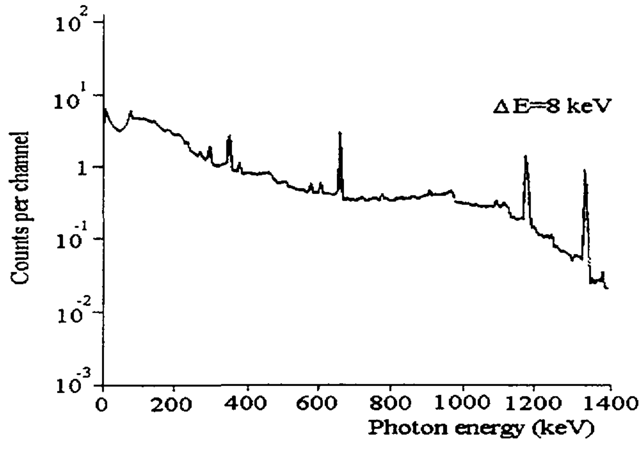

Fig.8. Pulse heigh spectrum of the HPGe detector

In order to demonstrate the application of the method, four gamma-ray sources ^{133}Ba, ^{137}Cs, ^{60}Co and ^{152}Eu on the ground and at various distances from the detector were measured. In Fig.8 the pulse height spectrum of the HPGe detector is shown. The value of kerma in air (or any other dosimetric parameter) can be obtained by an integration of multiplication of photon flux density and photon to kerma conversion factor over the photon energy.

7. CONCLUSION

Development of methods of field gamma-ray spectrometry at the Institute of Preventive and Clinical Medicine has been stimulated during the last several years by our participation on Regular Workshops on Mobile Radiological Laboratories. Measurements on these Regular Workshops have provided good occasions for verification and inter-comparison of methods among laboratories for field gamma-ray spectrometry in European countries. The Regular Workshops on Mobile Radiological Laboratories are organised annually in different countries. For example in 1996 the Regular Workshop took places in Slovenia (16 Mobile Laboratories from 9 countries), in 1997 in Switzerland (17 labs from 8 countries) and in 1998 in Slovak Republic (20 labs from 7 countries). The Regular Workshops on Mobile Radiological Laboratories became important action for laboratories for monitoring of radionuclides in environment. Also organisation of the Regular Workshops with so many participating mobile laboratories is difficult and pretentious. Therefore organisations of the Regular Workshops on Mobile Radiological Laboratories should be performed in co-operation with a supervisor and sponsor of an international authority such as IAEA.

REFERENCES

[1] International Commission on Radiation Units and Measurements: Gamma-Ray Spectrometry in the Environment, Technical Report ICRU 53, Bethesda, MD (1994).

[2] H. L. BECK, J. DECAMPO AND C. GOGOLAK: In Situ Ge(Li) and NaI(Tl) Gamma-Ray Spectrometry, Report HASL-258, U.S.D.O.E. Environmental Measurements Laboratory, NY (1972)

[3] J.-P. LAEDERMAN, F. BYRDE AND C. MURITH: In-situ gamma-ray spectrometry: influence of topography on the accuracy of activity determination, Journal of Environmental Radioactivity, 38 (1997) 1

[4] I.K. HELFER, K.M. MILLER: Calibration factors for the Ge detectors used for field spectrometry, Health Physics, 55 (1988) 1

[5] K. RYBAÈEK, P. JACOB: In situ determination of deposited radionuclide activities: Improved method using derived depth distribution from the measured photon spectra, Health Physics 62 (1992) 6

[6] O. KARLBERG: In-situ gamma spectrometry of the Chernobyl fallout on urban and rural surfaces, Studsvik Nuclear, Report NP-89/108 (1990)

[7] P. ZOMBORI, A. ANDRÁSI, I. NÉMETH: A new method for the determination of radionuclide distribution by ib situ gamma-ray spectrometry, Budapest, KFKI-1992-20/K (1992)

[8] FÜLÖP, P. RAGAN: In-situ spectrometry of ^{137}Cs in soil by unfolding method, Health Physics, 72 (1997) 6

[9] KORUN, R. MARTINÈIÈ: In-situ γ-ray spectrometry, Acta Chimica Slovenica, 42 (1995) 3

[10] DIERCKX: Unfolding method in neutron spectra measurements by foil activation techniques, Nucl. Instrum. and Meth., 105 (1972) 1

[11] Data Quality Objectives, U. S. Department of Energy Office of Environmental Management (EM-76), Pacific Northwest National Laboratory, (1996)

[12] LIPKA, S. KRNÁÈ: Standardisation of procedures for monitoring of radionuclides in soil, (in slovak), HZ 86/10/94, FEI Slovak University of Technology, Bratislava (1994)

[13] F. BRIESMEISTER: MCNP-A general Monte Carlo code for neutron and photon transport, Version 4.2, Los Alamos, NM: Los Alamos National Laboratory; Technical Report LA-7396-M; (1990)

[14] SAITO, P. JACOB: Gamma-ray fields in the air due to sources in the ground, Radiation Protection Dosimetry, 58 (1995) 1

[15] KRNÁČ, P. RAGAN: HPGe spectrometer as a gamma-ray dosimeter in situ, Radiation Protection Dosimetry, 58 (1995) 3

[16] Kamboj, B Kahn: Evaluation of Monte Carlo simulation of photon counting for germanium detectors, Health Physics, 70 (1996) 4

[17] 9th Regular Workshop on Mobile Radiological Laboratories, Ljubljana, Slovenija (1996)

[18] 10th Regular Workshop on Mobile Radiological Laboratories, Gordola, Switzerland, (1997)

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SELECTED INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS

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Abstract

A review of the applications of Instrumental Neutron Activation Analysis (INAA) in the industrial and environmental fields is given. Detection limits for different applications are also given.

1. INTRODUCTION

In the last three decades, neutron activation analysis (NAA), namely its non-destructive mode (instrumental neutron activation analysis - INAA), has been found to be very useful for the determination of trace and minor elements in many industrial and especially environmental applications. This is due to advantageous features of the technique in both modes, i.e. INAA and radiochemical NAA - RNAA, which have recently been discussed in detail [1-3] and have also been mentioned in Ch. 4 of this document. Therefore, only two specific advantages are mentioned here which concern an inherent potential for accuracy and the completely independent principle compared to the other trace element analytical techniques. This makes NAA indispensable for quality control of chemical analysis, namely for the preparation of certified reference materials, i.e. for both homogeneity testing and certification analyses. Besides chemical metrology itself, these advantageous features are also very important in industrial and environmental applications, because use of inaccurate analysis results in any decision process would incur vast financial and other losses.

2. INDUSTRIAL APPLICATIONS

In industrial applications of NAA, the most appreciated advantages involve low up to extremely low detection limits of elements, and the nondestructive and multielemental character of analysis. The matrices analysed mostly include high purity and high-tech materials, plastics, often also geological materials, and in general, such materials that are difficult to convert quantitatively into a solution for subsequent analysis by other analytical techniques. Numerous NAA procedures have been developed for process research, testing, process control, and product-quality improvement since the sixties [4-7].

In the last ten years, most frequent industrial applications or most frequently analyzed industrial-related matrices in which predominantly trace and ultra-trace concentrations of elements were determined by various NAA procedures involve: alloys, catalysts, ceramics and refractory materials, coatings, electronic materials, detection of explosives, fissile and other safeguard materials, fertilizers, graphite, high purity and high-tech materials, integrated circuit packing materials, on-line, flow analysis, oil products and solvents, pharmaceutical products, plastics, process control applications, semiconductors, pure silicon and silicon processing, silicon dioxide and NAA irradiation vials, textile dyes, thin metal layers on various substrates, while in geology and geochemistry analysis of the following specimens was most frequently performed by NAA: asbestos, borehole samples, bulk coals and coal products, coal and oil shale components, crude oils, kerosene, petroleum, cosmochemical samples, cosmic dust, coral, diamonds, exploration and biogeochemistry, meteorites, ocean nodules, rocks, sediments, soils, glacial till, ores and separated minerals [8-12]. However, it should be realized that in the competition with other trace element analytical techniques, namely ICP-MS, only those applications have remained viable until now which have also economic advantages of low cost and speed or where NAA has an indispensable position. Some examples are given in this report.

2.1. INAA FOR SILICON INTEGRATED CIRCUIT TECHNOLOGY

Very pure silicon wafers are needed for fabrication of integrated circuits, because concentrations of impurities in silicon are considered to be critical even at levels of 10^2 pg/g. However, during a large number of process steps, contamination may easily occur in the wafers and their top structure, often adversely affecting the properties of the product of a process step. A stringent control of contamination is therefore required throughout the entire manufacturing process as exemplified by various producers, for instance, in the Philips Research Laboratories, Eindhoven, The Netherlands. For this purpose, INAA proved to be extremely useful as demonstrated by contents of the impurities found and limits of detection of other elements in a very pure silicon wafer given in Table 1.

TABLE 1. Content of the impurities found (bold values) and detection limits of other elements in a Si wafer (for experimental details see [13])

Element, content, pg g^{-1}	Element, content, pg g^{-1}	Element, content, pg g^{-1}	Element, content, pg g^{-1}
Na < 500	Se < 2	Cs < 0.5	Hf < 0.3
K < 150	Br **2.4**	Ba < 60	Ta < 0.5
Ca < 10000	Rb < 10	La < 0.15	W 25
Sc < 0.03	Sr < 250	Ce < 0.9	Re < 0.3
Ti < 3000	Zr < 150	Pr < 6	Os < 0.7
Cr < 2	Mo < 6	Nd < 10	Ir < 0.004
Mn < 15000	Ru < 1.5	Sm < 0.03	Pt < 4
Fe < 300	Pd < 60	Eu < 0.07	Au **1.6**
Co < 0.5	Ag < 3	Gd < 6	Hg < 0.6
Ni < 150	Cd < 15	Tb < 0.1	Tl < 3000
Cu **560**	In < 4	Ho < 3	Th < 0.2
Zn <15	Sn < 200	Er < 40	U < 1
Ga < 1.5	Sb **180**	Tm < 3	
Ge < 1000	Te < 4	Yb < 2	
As **33**	I < 8000	Lu < 0.04	

In this case, the matrix is very favourable since the half life of the induced radioisotope (^{31}Si) is only 2.6 hours, and induced radionuclides of the elements of interest (mostly transition metals and Au which are highly undesirable in semiconductor silicon) are much longer-lived and therefore extremely low detection limits can be obtained.

Bulk analysis of the quartz used in the furnace for Si wafer processing is another example where INAA is highly suitable, and is routinely done either by the chip manufacturers or their quartz suppliers. Other materials that need bulk analysis in semiconductor industry include SiC (used in vertical furnaces), thin films of silicon dioxides, Ti, TiN, W, etc., and also determination of U and Th as precursors of α-particle emitters in various plastic packaging materials is highly required [3]. Besides NAA, other techniques based on neutron interactions with matter, such as neutron depth profiling (NDP) and prompt gamma activation analysis (PGNAA), e.g. for depth profiling of boron in thin silicon oxide films prepared by chemical vapour deposition (CVD) and for measuring bulk hydrogen content of thin films produced in CVD process, respectively, play also an important role in the semiconductor industry [3].

2.2. APPLICATIONS OF INAA IN CHEMICAL INDUSTRY

Recently, numerous applications of INAA were reported from DSM Geleen, a Dutch company producing chemicals and materials [14]. Although INAA was introduced at DSM Research primarily for the determination of trace elements in high-purity silica, nowadays the use of this technique is much more diversified to meet special analytical requirements of the chemical plant.

One of many applications is panoramic analysis of liquid hydrocarbons (LHCs), the emphasis being placed on the determination of mercury and arsenic. LHCs, such as gas oil and naphtha, are used in very large amounts in huge chemical plants. Since oil and natural gas, from which LHCs are derived, contain significant amounts of Hg and As as contaminants, both elements are contained in LHCs. These elements can cause extensive damage to process equipment, affect adversely the performance of catalysts and pose a potential hazard to plant workers and to the public if released into the environment. INAA proved to especially useful for this purpose for the following reasons:

- both elements and/or their compounds are volatile and can thus be lost during sample preparation for other analytical techniques, while no special sample preparation is needed in INAA
- possible matrix variations can cause problems to other analytical techniques, but not to NAA
- more other analytical techniques would be needed to deliver full panoramic quantitative information, resulting in much higher costs.

Another kind of samples for which INAA is especially suitable are Ziegler-Natta catalysts, based on the elements Ti, Cl, Mg, Al and V. Determination of these elements is quite difficult to carry out by other analytical techniques, because very often the catalysts are present in a slurry of organic materials which is difficult to handle with other analytical techniques, and because the catalysts readily decompose upon contact with ambient air and moisture, making sample preparation for other analytical techniques very difficult. A survey of typical samples at DSM Research analyzed at DSM Research by INAA and elements being determined is given in Table 2.

TABLE 2. Typical samples analyzed at DSM Research by INAA [14]

Sample type	Elements to be determined	Concentration
Liquid hydrocarbons	panoramic analysis	μg/kg to mg/kg
Catalyst slurries	Ti, Cl, Mg, Al, V	mg/kg to %
Catalytic systems	Co, Pd, Mn, As, Rh, Fe, Ni	μg/kg to %
Plastics	Cu, I, F	mg/kg to %
	heavy metals (Cr, Cd, Hg, Ni, Zn, Cu, As)	μg/kg
	Br, Sb	%

Determination of halogens and other impurities, such as Mn and Sb in polymers also appears to be a very important application of NAA in chemical industry [3,14]. On the other hand, fluorine compounds are added to some plastics to improve the behaviour of the polymer during processing and determination of this element by INAA is one of the best possibilities.

NAA is also in demand in photographic industry [3]. A very important process of the manufacturing of the photographic films is the precise doping of the silver halide crystals with ultra low level impurities, such as Ir, Rh and Au. Determination of these dopants was found to be best performed by NAA with a pre-irradiation separation. Most photographic films are chemically mixed halides, e.g. AgBrCl, AgBrI, etc. The mole ratio of the halides determines the sensitivity of colour films. The halide ratio in these mixed halides can be readily and reliably measured by INAA using a ^{252}Cf neutron source. Gelatine used as the emulsion in which Ag halides are dispersed is required to be of high purity. Presence of trace impurities such as Hg and Se is highly inhibitive to the photoactive process and latent image formation. A nuclear reactor based NAA (as in most of the above applications) of the gelatine was found to provide superior quality trace analytical data when compared with other techniques, such as hydride generation, and cold vapour atomic absorption spectrometry [3].

2.3. OTHER INDUSTRIAL APPLICATIONS

Determination of rare earth elements (REE), most of which can easily and reliably be performed by INAA, in geological materials is frequently required. Ratios of individual REE or the pattern of their contents normalized to those of C1 chondrites are extremely useful indicators in geochemistry of the origin and processes involved in the evolution of geological formations, structures, rocks, etc.

Related to NAA are analytical techniques used in the geochemistry and geophysics for well logging, i.e. to measure properties of reservoirs of gas and oil from inside the well casing. In this type of well logging, a probe consisting of a pulsed source of fast neutrons and γ-ray detectors, is pulled through the formations traversed by the borehole. As the logging probe is pulled slowly (e.g. at 2 m/s) along the borewell, the formations are irradiated and measured at the interface. Spectra are collected during the source pulse (mixed energy neutron field) and after the pulse (thermal neutron field). The data from the mixed energy neutron field is separated into capture and inelastic scattering events. These resolved spectra are mapped to elemental constituents; of particular interest are inelastic scattering by carbon and oxygen (oil and water). More information about this technique and other applications of nuclear techniques in the exploitation of mineral resources can be found in proceedings of an IAEA specialized symposium on these topics [15] and in proceedings of a topical meeting on Industrial Radiation and Radioisotope Measurements and Applications [16].

Of the emerging techniques, analysis of large samples (kg-size) by NAA should be mentioned. Most analytical techniques deal with portions in the order of µL to mL, and of mg to grams, whereas the amount of sampled material may easily be in the order of litres to kilograms, due to aspects of representativity and ease of operation. Thus it is usually necessary to reduce the particle size and to homogenize the sample before the subsampling takes place; sometimes the material characteristics are such that homogenization to a representative sample of a few mg is almost impossible. Further, in all these sample preparation processes, contamination and/or element loss may occur, while care is needed to avoid segregation. Therefore, a facility has been developed at the Interfaculty Reactor Institute, Delft, The Netherlands for INAA of kg-size samples. The maximum dimensions of the samples that can be handled in the facilities for irradiation and counting are 1 m in length, 15 cm in diameter, and about 50 kg in mass [17]. Applications of large sample INAA should be sought for in the first place with materials difficult to dissolve, which may be considered macroscopically homogeneous but which are grossly too inhomogeneous for direct subsampling without extensive homogenization. Examples are materials from the waste recycling industries, e.g. plastics, shredded materials from electronic devices, domestic waste, waste from construction sites, etc. Also, the geological market segment might be interested in large sample INAA, particularly for analysis of samples (rocks, drill-cores, as well as sediments) with inhomogeneously distributed depositions [17].

3. ENVIRONMENTAL APPLICATIONS

Applications of reactor-based NAA in environmental studies are by far more extensive compared to industrial applications. It is therefore hardly possible to provide a comprehensive and exhaustive review of such applications in this type of report. Therefore, the importance of employing NAA in environmental applications will be demonstrated mostly using examples of air pollution monitoring and biological monitoring of environmental pollution.

3.1. AIR POLLUTION STUDIES

Large amounts of pollutants are yearly discharged into various compartments of the environment world-wide, although many countries have already establishing measures towards decreasing pollution of the environment. Many pollutants enter primarily the atmosphere in the form of inorganic or organic gases and inorganic or organic particulates. The major sources of atmospheric pollution are generally recognized to be industry, power generation and home-heating, transport, and waste incineration. The material discharged into the atmosphere is dispersed in aerosols, tiny liquid or solid particles. The processes involved in the formation of the atmospheric aerosol are schematically depicted in Fig. 1 [18]. The solid component of this aerosol, which has diameters in the range from about 1 nm to „giant" particles of several hundred µm, is frequently referred to as airborne particles or air particulate matter (APM). However, most of their mass is in the size range from about 0.1 µm to 10 µm. Depending on the particle size and the atmospheric conditions, APM resides in the air for various periods of time, typically from a few days to a few weeks, and can be transported by the winds over distances of thousands of kilometres. Eventually, APM is removed by precipitation in rainfall or by gravitational fallout. Therefore, there is a continual transfer of contaminants from the atmosphere into the hydrosphere or into the soil, so that the air provides a route for the contamination of the rest of the biosphere.

Because of the variability in production and the relatively short lifetime, the concentrations, size distributions and chemical composition of APM vary widely in time and space. Although aerosols form only a small part of the total mass of the atmosphere (about 1 part in 10^9), they play an important role in atmospheric chemistry, have effects on human and animal health and welfare, and they influence climate [19]. The climatic effect of aerosols is in the direction of cooling (under most circumstances) and is of a magnitude comparable to that of the greenhouse gas warming [20,21]. However, there is still a large uncertainty associated with the estimate of climate forcing which reflects the unsatisfactory knowledge regarding the sources, distributions, and properties of atmospheric aerosols.

APM larger than 1 µm show a high sedimentation velocity and can move independently of the wind, while APM smaller than 1 µm show a low sedimentation velocity and move with the wind. It is probable, therefore, that APM smaller than 1 µm exert a strong influence on human health and the environment [22]. The potential negative effects of aerosols on human health have been recognized many years ago. Recently, renewed interest in the health risks of aerosols has been generated by the finding of a correlation between the increased mortality and the concentration of airborne particles in metropolitan areas in the United States [23]. The US studies, together with similar research in the European Union, Brazil and elsewhere, consistently link higher levels of APM to increased risks of respiratory-, cardiovascular-, and cancer-related mortality, as well as pneumonia, lung functions loss, hospital admissions, asthma, and other respiratory problems. In most studies, the correlations examined were those between mortality and PM 10 particles (smaller than 10 µm equivalent aerodynamic diameter - EAD), but other studies indicated that the association with increased mortality was even higher when PM 2.5 particles were examined instead of those with PM 10. This is probably due to the relationship between the diameter of the APM and its precipitation in the human lungs. The respiratory air passages begin at the nasal cavity, pass through the trachea, bronchi and bronchioles, and end at the alveoli. The diameter of these passages and the velocity of air flow through them also decrease in this order. Larger APM are therefore unable to penetrate into the narrow branches of passages, but smaller particulates can easily reach the alveoli (Cf. Fig. 2). Clearly, therefore, it is important to investigate the size distribution of APM in addition to simple quantitative observations on their total mass. For these purposes, various sampling techniques of APM exist which has already been reviewed [23,24]. Details of INAA methodology and a survey of reference materials available for quality assurance of air pollution studies have also been described [24].

3.1.1. Data reporting and treatment

Results for the element concentrations in APM are usually expressed in a mass of an element per cubic meter of air, i.e. in ng m^{-3}, µg m^{-3}, etc. Therefore, it should be emphasised that at least the same attention should be given to the appropriateness and quality assurance of sampling of APM, i.e. calibration and control of the air flow through a collection device, checking of tightness of the device to avoid possible leakages, etc., as to its analysis, because otherwise larger uncertainties of results may be expected due to the sampling process than those of analysis. In addition, the concentration of an element in APM can be calculated as a mass fraction. However, in this case the exact mass of the material collected must be known. This means that proper weighing procedures must be followed [24].

A first exploratory step in the interpretation of the element concentrations determined is to compare the level of pollution in the impact (polluted) and clean (background) regions, and to evaluate time trends, especially if sampling was performed in regular intervals for a sufficient period of time. More broadly, this type of the data treatment concerns evaluation of spatial and seasonal variability of elemental composition of APM.

A useful way of the data evaluation is the use of enrichment factor (EF) calculations. An EF is defined as the double ratio of the concentration of the element of interest, c_x, in APM to that of a reference element, c_r, in APM divided by the ratio of the same elements in a reference material (e.g. the earth crust, soil, seawater, etc.) according to the relation

$$EF = \frac{\left(\frac{c_x}{c_r}\right)_{APM}}{\left(\frac{c_x}{c_r}\right)_{ref}} \tag{1}$$

In general, for EF calculations in APM, aluminium or scandium is taken is taken as the reference element both in APM and the reference material for which the earth crust is most frequently employed. Evaluating of EF presumes that the atmosphere is always loaded with

APM originating both from the natural (soil erosion, sea aerosol) and anthropogenic (man-made) sources. An EF value close to one is indicative that the main source is of the crustal and/or marine origin, while values of EF exceeding ten (sometimes these values can reach several thousands) are indicative of significant anthropogenic contribution.

In order to develop rational and effective strategies for improving air quality, it is necessary to have an understanding of the relationship between the pollutant sources and their impact at receptor sites. Qualitative information of this kind can be inferred from the increased occurrence of specific elements which serve as markers for particular source emissions. Examples of marker elements are given in Table 3 [24]. More sophisticated approaches involve source or dispersion models which predict the concentration of pollutants at a receptor site using diffusion models with emission inventories and meteorological data. The predicted element concentrations can then be compared with the measured ones.

TABLE 3. Characterization of emission sources according to marker elements [24]

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

There is a number of mutlivariate statistical techniques which can be used for these purposes. *Receptor modelling* infer source contributions at receptor sites using statistical models with the data measured at the receptor site. *Principal component analysis* (PCA) is frequently employed for identifying pollutant sources. PCA attempts to explain the variance of a large set of intercorrelated variables (measured element concentrations in APM) with a smaller set of independent variables (the principal components). PCA is one of method of qualitative and quantitative techniques for data analysis which are collectively termed *factor analysis*. An introduction to data analysis of airborne particle composition has recently been published within the framework of one the IAEA Research Co-ordinated Programmes in this field [25] and there are numerous literature sources on this topic, as well, for instance [26,27]. Moreover new techniques are being developed, such as APCA, “Source profiles by unique ratios technique“ (SPUR), “Positive matrix factorization“ (PFA) [28,29]. *Chemical mass balance* (CMB) methods are designed to apportion the APM mass of each sample quantitatively amongst a number of contributing sources. This is possible if each source is characterized by a specific chemical pattern (source profile) and as many variables are available as sources.

Studies of elemental composition of APM in remote (background) and impact regions reveal the extent of environmental pollution due to various anthropogenic activities, time trends, geographical variations of pollution, and how various pollution sources, e.g. combustion processes, industrial activities, transport, etc. contribute to the overall level of pollution. However, in order to be able to control the level of pollutants and/or their abatement, it is very important to study the elemental composition of APM in the place of its origin.

Since the combustion processes are the main sources of anthropogenic APM in many countries, a study has recently been started in the author's laboratory on elemental composition of APM originating from the combustion of lignite using an experimental fluidized bed combustor with the thermal output of 100 kW. The samples analyzed included bottom ash, coarse fly ash collected by a hot cyclone (five fractions were obtained with the particle size range of < 40 up to > 200 μm) and fine fly ash separated by a cascade impactor into eleven fractions with the aerodynamic cut-off diameters from 0.016 to 14.3 μm. Using INAA (and PIXE for some elements), significant enrichment was found for many trace elements, including toxic ones, such as As, Cd, Ni and Pb, in the finest particles compared to bottom ash [30]. In the presence of additives, such as limestone and lime hydrate, the volume concentrations of most of these and also matrix elements in combustion aerosols decreased [31]. This is especially important for the abatement of the toxic elements in power plants, because namely the ultrafine particles easily penetrate through the common separation devices. Thus, use of the INAA (and PIXE) data on elemental composition of combustion aerosols helped in explaining of the mechanism of the abatement of both trace and matrix elements on lignite combustion with the additives. It has been shown that both a reduction of the total mass of emitted particles and specific absorption of some elements, namely As, in the additives employed were responsible for the abatement of the pollutants, and consequently for a reduction of the environmental pollution due to combustion of lignite [32].

3.2. BIOLOGICAL MONITORING OF ENVIRONMENTAL POLLUTION

Biomonitoring, i.e. the use of biological indicators to detect changes in the physical and chemical properties of the abiotic environment, represents an interesting alternative to direct measurements of the physical and chemical properties of the environment. Biological indicators are those tissues, organisms or populations of which their occurrence, vitality and responses change under the impact of environmental conditions [33]. Biomonitoring takes one of two approaches: i) direct monitoring which is based on measuring the quantity of pollutants in suitable organisms rather than in samples from the environment; ii) indirect monitoring which is based on interpreting of biological signals due to changes of the environment such as the study of morphological, physiological and cytological responses of organisms, changes of abundances of certain species, etc. Only the former approach is discussed in the present report.

Although data provided by physical and chemical monitoring are indispensable for evaluating the changes of the environment, application of an (ideal) biomonitor can show several advantages compared to the use of direct monitoring techniques:

- the concentration of pollutants in the monitor tissue or organism are often higher than in the system to be monitored. This may facilitate accurate sampling and analysis, which are very difficult at the low levels occurring in many compartments of the environment;
- sampling of the tissue or organism used as a biological monitor is in general easier than most direct sampling procedures and no long term use of expensive sampling equipment is required;
- the intricated equilibria existing in many parts of the environment can easily be distorted by sampling itself, which may lead to erroneous results. When using biological monitors, this distortion is minimized;
- most tissues and organisms reflect external conditions averaged over a certain time, depending on e.g. the biological half-life of a specific substance in that organism. This is important when monitoring levels may change rapidly in time;

- concentrations of pollutants in organisms may give insight into the bio-availability of that pollutant. This information may be as relevant as the absolute concentration in a certain part of the environment;
- biological monitors are already present in the environment and monitoring continuously.

In direct biomonitoring of atmospheric element pollution, the relevant information is deduced from concentrations of elements in the monitor tissues. They have to meet specific requirements which have been described elsewhere [34].

Many human, animal and plant species can be used for air pollution monitoring, because they can meet most of the requirements. Human and animal species and/or tissues usually reflect complex changes of the environment, i.e. air, water, soil pollution, and element intake from their diet, so that their use for studying only air pollution may be rather difficult to interpret. Nevertheless, some of them proved to be very useful, such as analysis of human and/or animal hair and other ectoderm derivatives, for instance nails. Certain plant species appear to be especially suitable to indicate elemental air pollution and therefore their use as biomonitors of air pollution is also briefly discussed.

3.2.1. Hair

The feasibility of human hair as a material easily accessible for non-invasive sampling in individuals or population groups, to demonstrate criminal, occupational or environmental exposure to toxic elements has received a great deal of attention in the literature. Besides many papers scattered in various journals, two monographs, one chapter in another monograph, and two review articles have been published [35-39]. Hair analysis is also facilitated by the availability of the generally recognized washing procedure which has been suggested in one of the IAEA Research Co-ordinated Programmes in the mid- seventies [40]. It this is very important to use a standardized hair cleaning, because there is no single washing procedure which would completely remove the external contamination without influencing the endogenous element contents. While a generally accepted washing procedure exists for hair (for monitoring of environmental pollution) and thus comparable data on elemental hair composition are available from many countries, no such standardized washing is widely used for nail cleaning which can also be used for biological monitoring as another ectoderm derivative.

Numerous examples of application of hair analysis for studying environmental pollution can be found in the above (and other) literature sources. Therefore, the usefulness of hair analysis for these purposes will only be shown in one example which demonstrates a correlation between arsenic content in hair of children living in various distances from a pollution source and the expected degree of arsenic contamination of the air (Cf. Fig. 3 [41]). Noteworthy, a similar correlation was obtained when urinary arsenic levels of children were determined (Cf. Fig. 4 [41]). This demonstrates that urine is also a very suitable indicator to assess environmental exposure, however, the arsenic (and many other elements) determination in urine is much more difficult compared to hair, because RNAA is required for this purpose to eliminate high matrix activity.

Similarly to human hair, the hair of some rodents, such as the Common Hare (*Lepus europaeus*) and the Common Vole (*Microtus arvalis*) proved to be a very useful indicator of environmental pollution. This can be supported by the finding that similar haematological changes were found in hares as in children living in regions burdened with industrial emissions [42].

TABLE 4 Detection limits of 45 elements in selected environmental matrices by INAA*

Element	Coal mg/kg	Coal fly ash mg/kg	Atmospheric particulate matter, ng m^{3}	Soil, sediment mg/kg	Spruce needles mg/kg
Ag	0 5	1 5	0 04	0 7	0 05
Al	20	35	5	30	15
As	0 05	0 25	0 015	0 45	0 05
Au	0 001	0 01	0 005	0 01	0 001
Ba	20	100	3	50	3
Br	0 05	0 3	0 1	0 4	0 04
Ca	100	500	30	500	300
Cd	0 5	4	0 1	5	0 3
Ce	0 15	1 5	0 15	1	0 2
Cl	50	300	15	400	50
Co	0 015	0 1	0 03	0 05	0 01
Cr	0 5	3 5	1	1 5	0 2
Cs	0 05	0 1	0 03	0 1	0 015
Cu	1	5	1	15	0 4
Dy	0 05	0 05	0 01	0 05	0 03
Eu	0 015	0 04	0 005	0 03	0 005
Fe	30	150	10	75	10
Ga	0 5	3	0 2	10	0 08
Hf	0 05	0 15	0 01	0 1	0 015
Hg	0 05	1	0 02	1	0 05
I	2	15	0 4	20	1
In	0 02	0 05	0 03	0 05	0 02
K	20	100	10	300	20
La	0 03	0 07	0 05	0 15	0 01
Lu	1	2 5	0 25	1	0 05
Mn	2	5	0 5	8	1
Mo	0 1	2 5	0 35	2 5	0 3
Na	2	4	10	10	0 3
Ni	10	40	2 5	60	10
Nd	2	4	0 2	5	1
Rb	5	10	0 5	7 5	0 5
Sb	0 03	0 1	0 015	0 075	0 01
Sc	0 005	0 010	0 003	0 005	0 001
Se	1	4	0 1	3	0 15
Sm	0 01	0 02	0 005	0 03	0 005
Sr	30	100	2	50	5
Ta	0 05	0 2	0 01	0 07	0 01
Tb	0 05	0 3	0 02	0 1	0 05
Ti	300	500	6	400	150
Th	0 03	0 1	0 015	0 05	0 015
U	0 1	0 5	0 03	0 5	0 01
Yb	0 1	0 3	0 05	0 3	0 03
	0 3	1	0 05	1 5	0 05
W	0 2	0 5	0 03	1	0 05
Zn	2	10	1	5	0 5

**Experimental conditions* Short- and long-time irradiation of 100-200 mg samples (except for APM which mass amounts to 0 5- 1 mg) in a neutron fluence rate of 5 10^{13} cm^{2} s^{1} for 1 min and 10 h respectively, followed by gamma-ray spectrometric measurements using a HPGe detector (rel efficiency 21%) For other details see Ref [50]*

3.2.2. Other biomonitors

Recently, a review has been published on using herbaceous plants, trees, bryophytes, and lichens for biomonitoring of air pollution [34]. Of these recognized biomonitors, bryophytes, especially some moss species, lichens, needles of coniferous trees, and tree bark showed many advantages which are important for their application in this field as can be inferred from frequency of their use in various national and international programmes.

Mosses have been very popular in both local and long-term, large-scale studies in Nordic countries since seventies and use of these bioindicators have also been included in the Convention on Long-Range Transboundary Air Pollution [43,44]. In the Netherlands, national trace-element air pollution monitoring survey using epiphytic lichens has been started in 1982 and continues on international scale until now. These studies followed by a specific multivariate statistical procedure known as "Target Transformation Factor Analysis" have successfully been employed for apportionment of emission sources within and outside the country [45-47]. To obtain the relevant information of this kind, multielement analysis is required and INAA proved to be very effective tool for this purpose. Currently, the International Atomic Energy Agency is also conducting Co-ordinated Research Programme on “Applied Research on Plants as Biomonitors of Trace Atmospheric Pollution“ using nuclear and related analytical techniques in which more than 10 countries participate.

On the other hand, it should be realized that without extensive calibration under all relevant conditions, the use of even the most suitable biomonitors frequently yields only qualitative information on the atmospheric level of pollutants as a function of time or place [48].

There are many more biomonitors and other matrices suitable for the assessment of the environmental pollution. For instance, from nation-wide surveys of natural surface soils in Norway it has become evident that the long-range atmospheric transport of heavy metals apparent in the moss survey is also reflected in the chemical composition of surface soil [43]. A similar relationship as for the level of pollution of the atmosphere and that of surface soil is usually found between surface waters and sediments and/or water suspended matter. Stratigraphic distribution of elements and other biomarkers in undisturbed lake sediments may even be used to trace the history of atmospheric and water pollution several hundred years back [49]. While for water analysis other analytical techniques are predominantly used, such as AAS, electrochemical methods, ICP-MS (because water is almost an ideal matrix for these techniques), for soil and sediment analysis INAA offers many advantages as it follows from detection limits for 45 elements in selected environmental matrices shown in Table 4.

REFERENCES

[1] A.R. BYRNE, FRESENIUS J. Anal. Chem., 345 (1993) 144-151.

[2] A.R. BYRNE, J.KUCERA, Proc. Int. Symp. Harmonization of Health Related Environmental Measurements Using Nuclear and Isotopic Techniques, Hyderabad, India, 4-7 November 1966, IAEA Vienna 1997, pp. 223-238.

[3] IAEA TECDOC on Enhancement of Research Reactor Utilization for Neutron Activation Analysis, IAEA Vienna, to be published

[4] W.W. MEINKE, B.F. SCRIBNER (Eds.), Trace Characterization; Chemical and Physical, NBS Monograph 100, U.S. Department of Commerce, U.S. Government Printing Office, Washington DC, 1966.

[5] R.F. BUNSAH (Ed.), Modern Analytical Techniques for Metals and Alloys, Part 2., Interscience, New York 1970.

[6] M. ZIEF AND R. SPEIGHTS (Eds.), Ultrapurity: Methods and Techniques, Marcel Dekker, New York, 1972.

[7] T. BRAUN AND E. BUJDOSO (Eds.), Proceedings, Int. Conf. on Modern Trends in Activation Analysis, Paris, 1972, Elsevier, Amsterdam, 1972.

[8] W.D. EHMAN, S.W. YATES, Anal. Chem., 58 (1986) 49R-65R.

[9] W..D. EHMAN, S.W. YATES, Anal. Chem., 60 (1988) 42R-62R.

[10] W.D. EHMAN, J.D. ROBERTSON, S.W. Yates, Anal. Chem., 62 (1990) 50R-70R.

[11] W.D. EHMAN, J.D. ROBERTSON, S.W. YATES, Anal. Chem., 64 (1992) 1R-22R.

[12] W.D. EHMAN, J.D. ROBERTSON, S.W. YATES, Anal. Chem., 66 (1994) 229R-251R.

[13] M.L. VERHEIJKE, H.J.J. JASPERS, J.M.G. HANSSEN, M.J.J. THEUNISSEN, J. Radioanal. Nucl. Chem., Articles, 113 (1987) 397-404.

[14] D.A.W. BOSSUS, R. VAN SLUIJS, Proc. 13th Radiochemical Conference, Mariánské Lázne, Czech Republic, 19-24 April 1998, in press in Czech. J. Physics.

[15] Nuclear Techniques in the Exploration and Exploitation of Energy and Mineral Resources, Proc. IAEA Symp., Vienna, 5-8 June 1990, IAEA, Vienna, 1991.

[16] Industrial Radiation and Radioisotope Measurements and Applications (IRRMA), 1996, Proc. IRRMA Meeting, Appl. Rad. Isotopes, 48 (1997) 1273-1708.

[17] R.M.W. OWERWATER, P. BODE, J.J.M. DE GOEIJ, ANAL. Chem., 68 (1996) 341-348.

[18] J. O. BUFFLE, H. P. VAN LEEUWEN (Eds.), Environmental Particles, Vol. 1., Lewis Publishers Inc., Boca Raton, Chelsea, Michigan, USA.

[19] R. J. CHARLSON, J. HEINTZENBERG (Eds.), Aerosol Forcing of Climate, John Wiley & Sons, Chichester, 1994.

[20] J. T. HOUGHTON et al. (Eds.), Climate Change 1994: Radiative Forcing of Climate and an Evaluation of the 1992 Emission Scenario, Intergovernmental Panel on Climate Changes (IPCC), Cambridge University Press, Cambridge, UK.

[21] S.E. SCHWARTZ, J. Aeosol Sci. 27 (1996) 359-382.

[22] K. OIKAWA, Trace Analysis of Atmospheric Samples, A Halsted Press Book, Kodansha Ltd., Tokyo, John Wiley & Sons, New York, London, Sydney, Toronto, 1977.

[23] T. REICHHARDT, Environ. Sci. Technol., 29 (1995) 360A.

[24] Sampling and Analytical Methodologies for Instrumental Neutron Activation Analysis of Airborne Particulate Matter, Training Course Series No.4, IAEA, Vienna, 1992.

[25] P. K. HOPKE, Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques, NAHRES-19, IAEA, Vienna, 1994, p. 215.

[26] P. K. HOPKE, Receptor Modelling in Environmental Chemistry, J. Wiley & Sons Inc., New York, 1985.

[27] H. MARTENS AND T. NAES, Multivariate Calibration, John Wiley & Sons, Chichester, UK, 1989.

[28] P. PAATERO, AND U. TAPPER, Chemom. Intell. Lab. Syst., 18 (1993) 183.

[29] P. PAATERO, AND U. TAPPER, Environmetrics 5 (1994) 111.

[30] J. SMOLÍK et al., Environ. Sci. Technol., submitted (1998)

[31] J. SMOLÍK et al., J. Aerosol. Sci. 29, Suppl. 1, S451-S452 (1998).

[32] J. KUCERA et al., Proc. Int. Conf. Nucl. Anal. Methods in the Life Sciences (NAMLS), October 26-30, 1998, Beijing, China, p. 71, Biol. Trace El. Res., submitted (1998)

[33] M. KOVACS, (Ed.), Biological Indicators in Environmental Protection, Akadémiai Kiadó, Budapest 1992.

[34] J. KUCERA, Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques, NAHRES-19, IAEA, Vienna, 1994, p. 265.

[35] V. VALKOVIC, Trace Elements in Human Hair, Garland Publ. Inc., New York. 1977.

[36] S. A. KATZ, A. CHATT, Hair Analysis, Application in the Biomedical and Environmental Sciences, VCH Publishers, Inc., New York, Weinheim, 1988.

[37] T. SUZUKI, Hair and Nails: Advantages and pitfalls when used in biological monitoring, In: T. W. Clarkson, L. Friberg, G. F. Nordberg, P. R. Sater (Eds.), Biological Monitoring of Toxic Metals, Plenum Press, New York and London, 1988, pp. 623-640.

[38] K. BENCZE, FRESENIUS J. Anal. Chem., 337 (1990) 867.

[39] K. BENCZE, FRESENIUS J. Anal. Chem., 338 (1990) 58.

[40] YU. S. RJABUCHIN, Report IAEA/RL/50, IAEA, Vienna, 1978.

[41] V. BENCKO, Toxicology, 101 (1995) 29.

[42] J. KUCERA, Chemosphere, 34 (1997) 1975.

[43] E. STEINNES, Proc. Int. Symp. Appl. of Isotopes and Radiation in Conservation of the Environment, Karlsruhe, 9-13 March 1992, IAEA Vienna, 1992, IAEA-SM-325/174, p.387.

[44] Convention on Longe-Range Transboundary Air Pollution (LRTAP), Field and LRTAP laboratory manual, National Board of Water and Environment, Environmental Data Centre, Helsinki, 1989.

[45] M.DE BRUIN, P. M. VAN WIJK, J. Radioanal. Nucl. Chem., 123 (1988) 227.

[46] J. E. SLOOF, H. TH. WOLTERBEECK, Water, Air, and Soil Pollution 57-58 (1991) 785.

[47] J. E. SLOOF, H. TH. WOLTERBEECK, Lichenologist 23 (1991) 139.

[48] M. DE BRUIN, Applying biological monitors and neutron activation analysis in studies of heavy-metal pollution, IAEA Bulletin 4/1990, 22.

[49] J. VESELÝ et al., J. Paleolimnol., 8 (1993) 211.

[50] J. KUCERA, L. SOUKAL, J. Radioanal. Nucl. Chem., Articles, 121 (1988) 245.

REACTOR NEUTRON ACTIVATION FOR MULTIELEMENTAL ANALYSIS

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Abstract

Neutron Activation Analysis using single comparator (K_0 NAA method) has been used for obtaining multielemental profiles in a variety of matrices related to environment. Gold was used as the comparator. Neutron flux was characterised by determining f, the epithermal to thermal neutron flux ratio and α, the deviation from ideal shape of the neutron spectrum. The f and α were determined in different irradiation positions in APSARA reactor, PCF position in CIRUS reactor and tray rod position in Dhruva reactor using both cadmium cut off and multi isotope detector methods. High resolution gamma ray spectrometry was used for radioactive assay of the activation products. This technique is being used for multielement analysis in a variety of matrices like lake sediments, sea nodules and crusts, minerals, leaves, cereals, pulses, leaves, water and soil.Elemental profiles of the sediments corresponding to different depths from Nainital lake were determined and used to understand the history of natural absorption/desorption pattern of the previous 160 years. Ferromanganese crusts from different locations of Indian Ocean were analysed with a view to studying the distribution of some trace elements along with Fe and Mn. Variation of Mn/Fe ratio was used to identify the nature of the crusts as hydrogenous or hydrothermal. Fe-rich and Fe-depleted nodules from Indian Ocean were analysed to understand the REE patterns and it is proposed that REE-Th associated minerals could be the potential Th contributors to the sea water and thus reached ferromanganese nodules. Dolomites (unaltered and altered), two types of serpentines and intrusive rock dolerite from the asbestos mines of Cuddapah basin were analysed for major, minor and trace elements. The elemental concentrations are used for distinguishing and characterising these minerals. From our investigations, it was concluded that both dolomite and dolerite contribute elements in the serpentinisation process. Chemical neutron activation analysis is applied to determine the concentration of REEs in quartzites and other minerals from the Cuddapah basin to understand the REE patterns and mineralogical processes. A comprehensive programme of analysing air, water and soil samples around the mining area is under progress to obtain the correlations between the environmental load with toxic elements and possible health implications vis-a-vis human beings and plant materials. Elemental concentrations of a few varieties of cereals, pulses and leaves were measured. The obtained values were utilised to examine the role of major and minor elements in terms of dietary and curative value of these leaves, cereals and pulses. Trace elements in the leaves could be determined more reliably using radiochemical neutron activation by separating the bulk elements like Na, K and Br, with enhanced sensitivity. A programme to determine nutrient elements and their availability for the plants through soil and water, and nature of species present is initiated. In each set of the experiments, the precision and accuracy were evaluated by determining the concentration of the elements in standard materials. In the studies of minerals USGS standard reference materials AGV-1 and W-1, for nodules and crusts NOD-A-1, for sediments SOIL-7 and for leaves SRM-1571 were analysed along with the samples of interest. CNAA and RNAA were applied for trace element analysis of the SOIL-7 and SRM-1571.

1. INTRODUCTION

Environment concerns with water, air, land and their interrelationship viz. human being, fauna and flora. Natural environmental changes may be invisible in a short span of time, but are likely to appear over long periods of time. Rapid industrialisation, deforestation and use of fertilizers, pesticides etc. in modern agriculture, in addition to the urbanisation and vehicular emissions have resulted in serious environmental changes. This reflects in the imbalance of elemental concentrations. The impact of imbalance of elemental concentrations could be understood in the context of health aspects by looking into trace/ toxic element content in our environment. The effect of toxic elements on the environment depends not only on the total concentration but also on their physico chemical state in which they exist. The overall problem of environmental protection is intrinsically linked to man's understanding and interaction with natural biospheric processes. This needs information on the factors that affect the stability of the biological systems and various ways the anthropogenic loads interact with in these systems. To understand this environmental problem, the natural systems like land, water and air are to be studied. In view of this, it is essential to determine the concentration of elements present in varied matrices like water, food, plant materials, minerals, soil, sediments, particulate matter and air and if possible the chemical states of these elements.

The elements are mainly grouped [1] based on their influence on the environment as (i) As, Be, Cl, Mn, Pb, Sb, Se, Tl and V which characterise the overall ecological situation, (ii) indicator elements that often introduce matter into ecologically important materials: Al, Ba, Fe, Zr, REEs and (iii) toxic elements: As, Cd, Cr, Hg, Ni, Pb and others. Since these elements are present in trace to major concentrations in different environmentally important materials, there is a need for multi-element analysis. Due to relative simplicity, inherent selectivity and sensitivity, Instrumental Neutron Activation Analysis (INAA) occupies an important position among the various analytical methods [2]. Advent of high resolution HPGe based gamma ray spectrometers and on line computer analysis techniques enhanced the simultaneous multielement analysis capability in many cases with or without radiochemical separations [2]. Single comparator NAA known as K_0 NAA [3-5] is now an established semi-absolute method with multielemental analytical capability. It has several advantages as compared to the more frequently used comparative method.

In the present paper, principle of K_0 NAA method, determination of α and f, results on the elemental concentrations of standard reference materials, and analysis of sediments, nodules, minerals, plants, leaves, cereals and soil are described. Additionally application of Chemical Neutron Activation Analysis (CNAA) for REE determination in quartzite minerals and Au and Pd determination in matrices containing uranium, copper or iron and Radiochemical Neutron Activation Analysis (RNAA) for the determination of trace elements in leaves are described. Future out look and the thrust areas are also mentioned. Possible application of other nuclear analytical techniques such as RBS, NRA, PIXE, XRF and PGNA are outlined.

2. EXPERIMENTAL

2.1 SAMPLING

2.1.1 Sediments from Nainital lake

The core samples were collected at different locations in the lake using gravity corer, its inner and outer diameters being 6.0 and 5.2 cm respectively. The length of the core obtained varies from 45 to 51 cm with the help of adjustable piston rod within the silicon packing. Obtained cores were extruded vertically and sliced at 2 cm intervals, were oven dried and homogenised. The textural composition of core samples were mainly clay and slits [6].

2.1.2 Ferromanganese Nodules and Crusts

The samples from different locations and water depth of the Indian Ocean, collected during the Scandi Surveyor and the 35th Sagar Kanya cruises, were obtained from National Institute of Oceanography, Goa, India. The geographical locations and water depth of these nodule samples are given in ref.[7] and that of crusts are given in ref.[8]. Samples were ground to uniform size and oven dried before using for analysis.

2.1.3 Serpentines and Quartzites

The altered and unaltered dolomites, dolerite and two serpentines were collected in the underground asbestos mines making traverses across the formations around Brahmanapalle village of Pullivendla Taluq, Cuddapah district, Andhra Pradesh, India. They were carefully crushed to bring down to the size of 100 mesh (ASTM) sieve. The homogenised materials were subjected to cone and quartering method to prepare the samples for the analysis. The geological set up of these mines are described in ref [9].

2.1.4 Leaves, Cereals, and pulses

The leaf samples (L1-L10) were collected in and surrounding areas of Tirupati, Andhra Pradesh, India. On an average 20-50 leaves from the very bottom to top part of the plant were collected giving equal weightage to the tender as well as old leaves. For seeing the effect of soil and environment on the mineral content, Neem leaves were collected both from Tirupati (L10) and Anushaktinagar, Mumbai (L11), India. Leaf samples were washed with deionised water and then with double distilled water. The samples were air dried in a clean drying chamber and dried at 80^0C over night in an oven. They were crushed to a homogeneous fine powder by pulverisation before sampling. The samples of cereals (C1-C5) and pulses (P1-P7) were collected from different representative places of Tirupati. They were crushed to a homogeneous fine powder by pulverisation and were dried overnight at 105^0 C. Samples are prepared from this powder [10].

2.1.5 Gold Standard

A known amount of gold foil (99.999% pure) was dissolved in aqua regia. It was evaporated to dryness and was made up in 0.1M HNO_3 This solution was used as a standard gold solution.

2.2 IRRADIATION

Samples weighing about 25- 50 mg of each were sealed in polypropylene tubes (2mm ID). The sealed tubes containing samples along with gold (5-15μg) were doubly sealed in alkathene, placed in a standard bottle and irradiated in a suitable irradiation position of APSARA reactor, BARC, Trombay, Mumbai. The duration of irradiation was varied from 5 minutes to 7 hours depending on the half life of the nuclide of interest. The neutron flux is around $\sim 10^{12}$ $n.cm^{-2}.s^{-1}$. The sub-cadmium to epi-cadmium flux ratio (f) and the deviation from the ideal epithermal neutron flux distribution (α) which are important input parameters in K_0 NAA method, were determined experimentally for each position using cadmium ratio method and/or multi isotope detector method [11,12]. The values of f and α are given in refs. [11,5]. For the nuclides of short half lives eg.,^{28}Al, ^{27}Mg, the cooling period was minimum and it was about a few hours to days for long lived nuclides.

2.3 RADIOACTIVE ASSAY

After providing necessary cooling time, polypropylene tubes containing sample and comparator were washed under running tap water, wiped and mounted on a standard perspex plate. Samples were assayed for gamma activity of the activation products using an 80 cc HPGe detector coupled to a PC based 4K channel analyser in an efficiency calibrated position with reproducible sample to detector geometry. The resolution of the detector was 2.1 keV at

1332 keV. Gamma ray standards, e.g., ^{152}Eu, ^{125}Sb, ^{134}Cs and ^{133}Ba were used for efficiency calibration of the detector in a stable source to detector geometry [13]. Efficiency values were periodically checked using ^{152}Eu standard sources. The sample to detector distance was maintained between 12 and 15 cm depending upon the level of activity to avoid pile-up and coincidence effects. The activities of radionuclides were followed as a function of time to ensure purity and identity.

2.4 CALCULATIONS

Peak areas corresponding to different gamma lines were obtained either by using the SAMPO programme in the case of complex gamma ray spectra or summing the counts under the peak and subtracting the linear Compton background in relatively simple spectra. The peak area was converted to specific count rate (A_{sp}) by the equation:

$$A_{sp} = (CL / LT).\ [(P_A\ .\lambda)/\ (1-e^{-\lambda t}).\ e^{-\lambda T}(1-e^{-\lambda CL})] \qquad (1)$$

where, t = time of irradiation, T= cooling time, CL = clock time, LT = live time, λ=decay constant of the radionuclide of interest, P_A = peak area and w = weight of the element in micrograms (mg).

The concentration of the ith element (C_i) in ppm was calculated using the relation,

$$C_i\ (\mathrm{ppm}) = [\ A_{p,\,i} / (A_{sp}^*.\ K_{anal})\ ] \qquad (2)$$

where, $A_{p,\,i}$ = the specific count rate of the ith nuclide normalised per gram of the sample, A_{sp}^* = the specific count rate of the ^{198}Au per mg of the comparator and the symbol * refers to the parameters of the comparator. K_{anal} is the specific count rate ratio of the individual element in the sample to comparator and is calculated using the following equation:

$$K_{anal} = K_{0,exp}\ [(f + Q_0(\alpha)\ /\ (f + Q_0^*(\alpha))]\ \varepsilon\ /\ \varepsilon^* \qquad (3)$$

where, ε = the detection efficiency of the detector for the gamma ray energy used, f = the sub-cadmium to epi-cadmium neutron flux ratio, α = the deviation from the ideal epithermal neutron flux distribution and $Q_0(\alpha)$ = the ratio of cross sections and is equal to $I_0(\alpha)\ /\ \sigma_{th}$, where, $I_0(\alpha)$ = infinitely dilute resonance integral corrected for the non-ideal epithermal neutron flux distribution and σ_{th} = the thermal neutron cross section. Equation (3) is the simplified form of K_{anal} as the contribution due to neutron self shielding is negligible. The self shielding correction factor for thermal (Gth) and epithermal (Ge) are approximately equal to 1, as the sample sizes chosen for irradiation were small Relevant nuclear data were taken from the compilations of Browne and Firestone [14] and from the IAEA compilations [15].

2.5 RESULTS AND DISCUSSIONS

2.5.1 K_0 values

K_0 is a ratio of four constants of corresponding to the element of interest and the comparator and is given by eqn.(4)

$$K_0 = (\theta\ \sigma_{th}\ M^*\ \gamma\ )\ /\ (\theta\ ^*\sigma_{th}^*\ M\ \gamma\ ^*) \qquad (4)$$

where θ is the isotopic abundance, σ_{th} is the thermal neutron cross section, M is the atomic mass of the element and γ is the emission probability of the gamma line used. We have measured K_0 factors for fifteen isotopes and obtained a good agreement between the calculated and measured K_0 values. A library of K_0 values for 111 isotopes spanning from fluorine to uranium was made by using the latest nuclear data [14,15] and are given in ref. [11]. The accuracy and consistency of the nuclear data play a significant role in the standardisation of reactor neutron activation analysis. Out of the these nuclear constants, data on cross sections and gamma ray emission probabilities are sometimes reported with large uncertainties. Therefore, the accuracy and consistency with respect to the above mentioned constants should be judged individually, consistency being the prime concern.

2.5.2 Determination of f and α

Sub-cadmium to epi-cadmium neutron flux ratio (f) was determined for all the irradiation positions of APSARA reactor using cadmium cut off method where as for PCF at Cirus and tray rod position at Dhruva reactor this ratio was determined by multi isotope method. Another important parameter α, the extent of deviation from ideal shape of neutron spectrum for each irradiation position was determined using multi isotope/element method. Details of measurements and calculations are given elsewhere [11].

2.5.3 Analysis of Standard Reference Materials

Since there is a large variation in the nature of the samples and the concentration of the elements present, it is essential to validate this analytical technique. In this context, a variety of the standard reference materials were analysed. Some of the SRMs analysed by this technique are USGS standard reference materials AGV-1 and W-1, NOD-A-1, SOIL-7 and SRM-1571. A good agreement between the measured values and the reported data was obtained. Percentage deviation of the measured and certified values are plotted in Fig. 1. The over all accuracy is between 2 to 10%. In our studies, as a control of the method of analysis, an appropriate standard was analysed along with the samples in each set of experiments.

2.5.4 Sediments from Nainital lakes

The knowledge of sedimentation rates and the elemental concentration levels in sediments from lakes and other water bodies might provide clues to unfold the chronology of the input of pollutants to the water bodies. Eight sets of sediments corresponding to depths from 6 to 51cm were analysed. The IAEA lake sediment standard SL-3 was analysed as a control of the method. Using the experimentally determined sedimentation rate of 0.32 cm/y [6], sedimentation age was calculated for these eight samples and was found to be in the range of 19 to 160 years. The data from different sections of the sediment core are given in Table 1 and represent the history of natural absorption/desorption pattern of the previous 160 years. The elemental concentration of As, Cr, Br, Zn and Cs are found to be more or less constant from bottom to top which could be taken as an indication that there is no anthropogenic pollution of trace elements to Lake Nainital. Samples from different locations of Lake Nainital were analysed and the data show similar trend of elemental concentrations as a function of the depth. A positive correlation of Fe-REE-Th is observed. Thorium is thought to be coprecipitated with REEs as $Th(OH)_4$ from water bodies and is absorbed in Fe phases The condrite normalised REE [16] Ce shows negative anomaly and Eu shows moderate and negative anomaly indicating a reduced atmosphere in the bottom sediments.

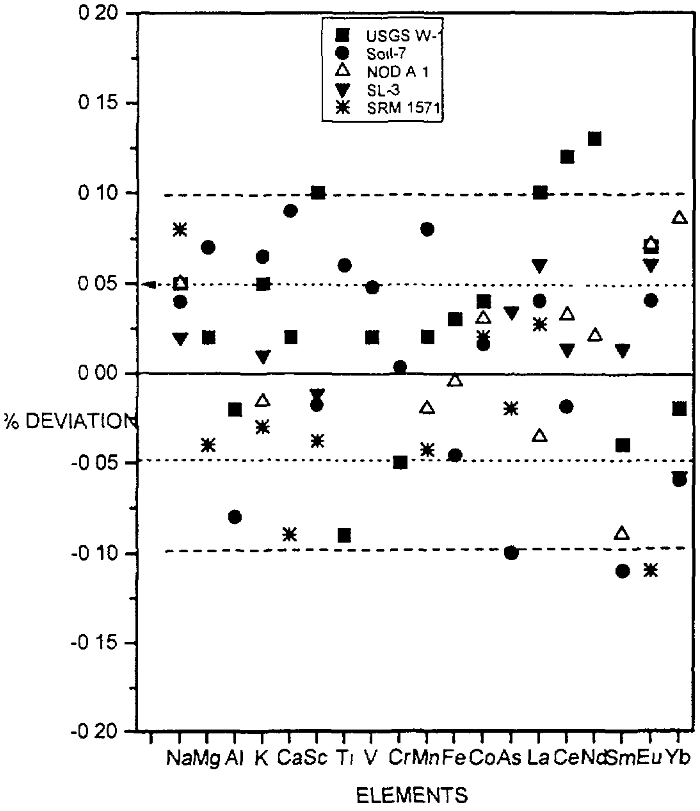

Fig 1 Comparison of measured and certified elemental concentrations of some standard reference materials

2.5.5 Ferromanganese encrustations from Indian Ocean

Ferromanganese oxide encrustations are common depositional features on exposed rock outcrops in the deep sea. They are mostly found on mid-oceanic ridges, seamounts and raised areas of sea floors of world oceans and significantly differ in their composition and mineralogy [17]. Multielemental analysis together with a varying Mn/Fe ratio is relevant in understanding their distribution in Mn and Fe phases. Three ferromanganese crusts from different locations of the Indian Ocean and another crust from the Lau basin of the Pacific Ocean were analysed by K_0 NAA method for studying the influence of different oceanic conditions on the trace element distributions in ferromanganese crusts. The precision and accuracy of the method were confirmed by measuring the elemental concentrations in a USGS nodule standard NOD A-1. The measured concentrations of elements ferromanganese oxide encrustations (C1, C2, C3 and C4) are given in Table 2. Cobalt was found to be highly enriched in the Afanasiy Nikitin seamount crust. The hydrothermal oxide deposit from Mid Indian Ocean Ridge (MIOR) exhibits a negative Ce anomaly and is associated with a low concentration of trace elements, whereas hydrogenous crusts are enriched in most elements and exhibit a positive Ce anomaly. The crust from north Rodriguez Triple Junction of the MIOR was characterised as of mixed hydrothermal and hydrogenous type, while the crusts from the Afanasiy Nikitin seamount and a topographically elevated region exhibit hydrogenous properties. The rare earth elements were found to be highly enriched in the crust of the Afanasiy Nikitin seamont and elevated region compared to the crust from MIOR. The thorium content was remarkably high for hydrogenous crusts. A Co-Sb correlation was observed particularly in seamount crust.

TABLE 1. Elemental concentrations of Sediment samples (in ppm unless % is indicated). N. D. = not detected

Element Depth(cm)	S1 51	S2 45	S3 39	S4 33	S5 27	S6 19	S7 12	S8 6
Na%	0.54±0.01	0.42±0.02	0.48±0.02	0.40±0.02	0.49±0.02	0.44±0.03	0.46±0.03	0.42±0.02
K%	3.22±0.15	2.28±0.12	2.45±0.18	2.42±0.02	2.74±0.06	2.44±0.02	2.39±0.12	2.30±0.11
Sc	14.60±0.45	12.07±0.55	12.70±0.81	11.32±0.62	14.85±0.72	13.83±0.71	12.38±0.52	12.13±0.90
Cr	113.82±4.50	90.58±3.60	91.90±4.20	91.60±5.07	96.00±4.17	103.49±5.02	104.23±4.11	85.83±3.12
Mn%	0.172±0.01	0.128±0.01	0.126±0.01	0.117±0.01	0.142±0.01	0.119±0.01	0.129±0.01	0.136±0.01
Fe%	5.23±0.18	4.18±0.27	4.01±0.21	4.14±0.09	5.00±0.0.09	4.22±0.13	4.11±0.24	3.88±0.07
Co	32.27±1.81	20.60±1.01	21.65±1.20	20.00±0.54	22.28±1.12	20.45±0.42	21.76±0.90	23.86±1.01
Zn	N. D.	75.23±4.03	110.90±5.10	105.32±4.31	126.93±4.17	97.38±5.72	111.45±6.32	66.07±2.72
Ga	8.96±0.52	13.52±0.82	N. D.	18.64±1.01	N. D.	9.39±0.73	10.52±0.85	9.84±0.72
As	20.39±0.85	19.91±1.31	13.50±0.80	10.77±0.25	17.46±1.07	17.10±1.10	16.51±1.05	18.17±1.24
Br	0.85±.02	N. D.	1.13±0.06	1.00±.03	1.40±0.06	1.38±0.06	1.30±0.10	1.85±0.11
Rb	115.38±6.50	100.23±5.40	128.20±7.10	N. D.	136.64±5.39	110.69±4.13	N.D.	100.74±3.52
Sr	N. D.	496.10±22.00	350.20±15.21	190.00±14.21	232.10±16.20	332.05±17.00	375.10±20.10	532.00±10.23
Cs	21.34±1.52	12.44±0.82	14.28±0.83	14.14±0.94	14.73±0.62	11.05±0.52	14.05±0.43	13.85±0.61
Ba	645.23±15.20	881.00±30.10	794.00±18.00	798.00±45.12	752.10±32.00	780.00±25.10	821.00±30.10	838.00±35.50
La	42.16±2.44	29.31±1.14	31.40±1.30	32.04±2.10	37.06±1.96	33.17±2.01	33.13±1.48	32.55±2.03
Ce	50.32±3.21	33.98±2.10	44.15±2.70	42.04±2.11	47.42±1.43	43.70±2.13	35.00±2.21	41.60±2.70
Nd	25.97±1.51	14.97±1.05	20.21±1.14	17.91±1.15	N. D.	19.64±1.18	18.47±1.23	11.56±1.12
Sm	6.19±0.18	5.03±0.32	5.63±0.41	5.71±0.12	7.26±0.22	5.86±0.14	6.46±0.71	5.61±0.26
Eu	1.09±0.08	1.12±0.08	1.00±0.07	0.97±0.06	1.15±0.04	0.89±0.05	0.96±0.04	0.96±0.07
Dy	3.79±0.20	1.76±0.12	3.65±0.17	3.30±0.18	4.10±0.21	3.70±0.18	4.30±0.24	4.21±0.23
Yb	4.12±0.21	6.45±0.41	2.63±0.14	3.28±0.15	3.87±0.25	2.58±0.16	2.21±0.13	2.24±0.12
Lu	0.61±0.04	0.96±0.04	0.95±0.05	1.08±0.06	0.89±0.05	1.04±0.06	N. D.	0.72±0.05
Hf	N. D.	1.83±0.07	1.97±0.10	2.88±0.11	2.35±0.07	2.46±0.14	2.51±0.08	2.85±0.17
Th	12.31±1.01	13.04±1.10	11.27±0.91	13.81±1.00	11.28±0.85	13.57±1.02	11.48±1.03	13.88±1.12

TABLE 2. Elemental Concentrations of ferromanganese Oxide Encrustations (in $mg.kg^{-1}$ unless % is indicated).

Element	C1	C2	C3	C4
Na%	1.12 ± 0.07	0.80±0.04	2.79 ± 0.13	1.51±0.09
K	5798 ± 246	3814±151	2316 ± 117	1280±76
Sc	9.83 ± 0.41	10.76±0.38	7.11 ± 0.28	16.69±0.78
Cr	N. D.	51.70±	70.6 ± 6.4	N. D.
Mn%	16.5 ± 0.9	21.2±1.4	12.1 ± 0.7	N. D.
Fe%	19.2 ± 0.9	16.9 ±0.7	21.9 ± 0.8	37.2±1.4
Co	12300 ± 396	2331±98	879 ± 39	74±5
As	121 ± 9	163.5±12	247 ± 14	449±22
Sb	80.4 ± 3.1	16.2±0.7	12.2 ± 0.6	8.73±0.4
Cs	301±26	851±64	136 ± 9	83±9
Hf	N. D.	4.64±0.34	7.67 ± 0.53	N. D.
W	101.4 ± 6.5	82.7±3.6	12.2 ± 0.5	N. D.
Th	81.2 ± 5.4	114.2±8.3	3.7 ± 0.2	N. D.
La	239.4 ± 11.2	286.0 ±12.2	201.4 ± 8.2	14.7±0.9
Ce	2037 ± 106	1530±78	169 ± 9	11.12±0.6
Nd	184.3 ± 9.7	222.5±13.2	125.3 ± 7.1	N. D.
Sm	37.6 ± 2.2	48.5±2.5	38.2 ± 2.3	N. D.
Eu	8.21 ± 0.48	12.20±0.68	11.32 ± 0.63	N. D.
Tb	3.2 ± 0.33	3.83±0.33	2.62 ± 0.33	N. D.
Ho	2.78 ± 0.34	3.46±0.39	N. D.	N. D.
Yb	16.85 ± 0.89	21.85±1.13	13.94 ± 0.83	1.51±0.08
Lu	2.68 ± 0.14	3.43±0.22	2.24 ± 0.09	N. D.
Ce*	+0.61	+0.407	-0.37	-
Mn/Fe	0.86	1.25	0.55	-

N. D. - not detected, Ce = Cerium anomaly calculated as log[3Ce/(2La+Nd)] as given in ref.[16]*

2.5.6 Ferromanganese Nodules from Indian Ocean

The ferromanganese nodules are mostly found at the interface of Ocean waters and the underlying sediment on the ocean bed and are associated with minor and trace constituents of alkali, alkaline earth metals, transition metals, REEs and other heavy elements. Characterisation of nodules might provide information on physical, chemical and biological activities taking place in the ocean. A total of five ferromanganese nodules from different locations and water depth of Indian Ocean were analysed along with SRM NOD P1. The measured concentrations of various elements in the nodule samples are presented in Table 3. A few elements, namely, Sc, Sb, Hf, W and Th have been estimated for the first time in the Indian Ocean nodules.

The Fe enriched hydrogenous nodules were associated with higher concentration of most of the minor and trace elements. Slow growth rate, high retention time and favourable depositional environment are attributed to their enrichment. Hydrogenous nodules characterised by low Mn/Fe ratio, found at shallow region of the Indian Ocean, indicates lower mobility of Fe component compared to the Mn in the oceanic environment, leading to the precipitation of Fe as its oxyhydroxide. Cobalt was found to have strong affinity towards Fe. . Tungsten and thorium are found positively correlated with iron and are reasonably enriched in the hydrogenous nodules compared to the diagenic one. Rare earth elements are probably incorporated on iron oxyhydroxide phase by adsorption processes. The REE abundance increases with the increase in the Fe content and is in good agreement to the earlier reports on the nodules of Pacific Ocean. It has been shown that the rare earth elements (REEs) are adsorbed but not co-precipitated with the iron oxyhydroxide phase.

TABLE 3.Elemental Concentrations of ferromanganese nodules of Indian Ocean (in ppm unless % is indicated).

Elements	N1	N2	N3	N4	N5
Na %	2.44±0.21	2.56±0.23	1.75±0.18	2.08±0.14	2.32±0.13
K %	0.57±0.04	0.58±0.04	0.40±0.03	0.50±0.04	0.48±0.04
Mn %	15.3±0.6	19.1±0.9	18.6±0.8	16.9±0.7	17.2±0.4
Fe %	16.5±0.7	21.2±0.8	13.9±0.7	11.3±0.4	5.5±0.3
Sc	15.65±0.32	22.92±0.81	13.72±0.36	15.33±0.78	10.92±0.42
Co	3220±163	5362±214	2180±96	2174±106	1128±49
As	76±8	110±9	77±6	61±5	39±4
Sb	18.9±0.7	21.6±0.8	19.5±0.8	17.9±0.6	12.2±0.6
Cs	321±7	379±16	216±12	267±9	718±24
Hf	6.52±0.37	6.61±0.35	8.54±0.46	7.14±0.49	3.40±0.22
W	67.1±4.3	77.8±6.8	49.2±3.9	46.6±4.5	42.5±4.4
Th	42.5±2.4	50.5±3.3	48.5±2.9	47.2±2.9	24.6±1.4
La	142.2±6.4	257.5±10.2	204.8±7.9	184.4±8.6	98.6±8.2
Ce	951±34	1862±83	1246±48	948±39	502±23
Nd	137.4±7.2	196.6±9.8	167.7±7.6	138.4±9.7	88.3±7.2
Sm	28.2±1.1	42.8±2.1	42.1±2.1	34.4±1.1	20.3±0.9
Eu	6.74±0.56	11.14±0.66	8.70±0.83	7.55±0.72	4.76±0.38
Tb	3.24±0.33	4.82±0.34	3.31±0.37	3.09±0.29	2.62±0.33
Ho	4.78±0.64	6.89±0.91	6.53±0.87	5.78±0.64	2.97±0.32
Yb	19.32±0.59	32.43±1.08	24.22±1.03	21.41±0.98	9.85±0.63
Lu	3.48±0.13	6.22±0.24	4.62±0.13	3.82±0.13	1.58±0.11
Ce*	+0.24	+0.21	+ 0.18	+ 0.16	+ 0.24
Mn/Fe	0.93	0.90	1.34	1.50	3.11
(La/Lu)*	0.76	0.81	0.82	0.88	0.98
ΣREE	1296.36	2420.40	1707.98	1346.85	730.98
Ce/La	6.68	7.24	6.08	5.14	5.09

Ce = Cerium anomaly, calculated using the relation Log[3Ce/(2La+Nd)], as given in ref.[16] (La/Lu)* = (La_{sample} / La_{NASC}) / (Lu_{sample} / Lu_{NASC})*

2.5.7 Dolomites, Dolerite and Serpentines

Serpentines are a class of secondary minerals derived by alteration in magnesium rich silicate minerals. It is reported that serpentine and associated asbestos are formed due to hydrothermal solutions accompanying the dolerite intrusives into dolomite host rock. The black and green serpentines are potential sources of asbestos. With an aim to understand the process of serpenisation, investigations on the composition of two types of dolomites (unaltered and altered dolomites) and two types of serpentines along with intrusive rock dolerite obtained in the asbestos mines of Brahmanapalle in Cuddapah basin, Andhra Pradesh, India were carried out .As many as 23 elements are measured. The elemental concentrations for the serpentines as well as the unaltred and altered dolomites and dolerite obtained from four independent determinations are given in Table 4. The major elements present in the five varieties are Mg, Ca, Al and Fe. From the variation of Mg concentration, it is clear that both dolomite and dolerite contribute Mg to serpentines. Absence of Ca in black serpentine could be that it is replaced by Mg in the serpentinisation. The REEs decrease in the order: dolerite → black serpentine → yellow serpentine → dolomite .Elements like Ti, V, Cr and a few REEs are absent in unaltered dolomite where as these elements are present in serpentines and dolerite. From these observations, it is clear that these elements were contributed in the serpentinisation only by dolerite.

TABLE 4. Elemental Concentrations of Intrusive rock (Dolerite), two Serpentines and Dolomities (in mg.kg^{-1} unless % or ng.g^{-1} is indicated).

S.N	Element	Dolerite	Black serpentine	Yellow serpentine	Altered dolomite	Unaltered dolomite
1	Na	1325.47±79.51	162.37±7.46	93.28±5.02	86.90±5.87	654.67±18.15
2	Mg%	9.22±1.1	22.72±1.86	18.11±0.58	8.28±0.18	12.91±7.4
3	Al%	1.89±0.11	4.00±0.17	0.11±0.005	0.11±0.005	0.17±0.01
4	Cl	N. D.	400.10±11.20	255.23±2.92	288.67±9.12	132.33±5.21
5	Ca%	8.75±1.15	N. D.	0.55±0.02	18.10±1.32	25.46±1.76
6	Sc	27.13±1.12	25.29±1.07	0.16±0.01	0.50±0.02	0.22±0.01
7	*Ti %*	*0.48±0.03*	*0.70±0.04*	N.D.	N.D.	N.D.
8	V	209.50±14.12	172.42±8.53	N.D.	N.D.	N.D.
9	Cr	N. D.	53.66±3.23	N. D	N. D.	N. D.
10	Mn	2921±160	2722±54	28.69±.0.09	144.02±9.45	145.31±3.59
11	Fe%	7.94±0.20	5.00±0.38	0.22±0.01	N.D.	N.D.
12	Co	30.51± 1.85	37.31±2.33	4.36±0.23	5.63±0.31	4.73±0.26
13	As	N.D.	4.99±0.18	13.41±1.16	6.21±0.11	0.76±0.05
14	Ba	N.D.	N.D.	545.00±53	222.02±17.06	158.58±9.23
15	La	13.72±1.05	10.94±0.68	1.82±0.04	3.07±0.06	1.28±0.08
16	Ce	41.32±2.16	24.25±1.51	N.D.	N.D.	8.32±0.67
17	Sm	2.97±0.15	1.77±0.08	0.48±0.03	0.23±0.01	0.22±0.02
18	Eu$^{\#}$	990.05±60.10	350.23±20.11	100.16±5.10	50.28±2.12	20.06±1.13
19	Dy	N.D.	9.19±0.57	0.27±0.01	N.D.	N.D.
20	Yb	2.99±0.00	2.22±0.10	N.D.	N.D.	N.D.
21	Au$^{\#}$	N.D.	13.20±1.01	N.D.	20.25±1.52	10.12±0.85

N. D. - not detected, ‘ # ’- ng. g^{-1}

2.5.8 Edible and Medicinal Leaves, Pulses and Cereals

The role played by micro nutrients and trace elements in the biochemical functions of human life and their impact on human life are important. These are supplied through food chain. Additionally carbohydrates, proteins and minerals are provided through food items like cereals, pulses and leaves. The investigations are aimed at measuring the concentrations of minerals required for human beings viz: major elements like Ca, P, K, Mg, Na, Fe and trace elements like Zn, Co, I, Cu, Mn, Mo, F, Se, Ni, Cr, Cd, Si, V and Sr. Phosphorous could not be measured by gamma spectrometric based NAA. It is also important to know the variation of these elements in these items from different places and environment. A comprehensive programme of determining the elemental profiles in soil, water, seeds and leaves is initiated.

Elemental concentrations of a few varieties of leaves which are used either as a natural ingredient in ayurvedic medicine preparations or as reliable items for human diet and SRM-1571 are determined by K_0 NAA method. The leaves analysed, their local names and scientific names are given in Table 5 Data obtained on one of the varieties studied (Neem), collected from two different places are given in Table 6. These data have been used to see the effect of soil condition on the trace element concentrations in these leaves. Elemental concentrations of a few varieties of cereals and pulses which are used as natural ingredients for human diet are determined. The cereals and pulses analysed, their local names and scientific names are given in Table 7. Al, Cl, Mg, Mn, Na, K and Ca were determined using short irradiation times, where as Br, Zn, Co, Fe, La, Sm, Cr, Rb, Se, Sn and Hg required long irradiation times and the elemental concentrations for 17 elements measured in cereals and pulses, in the present studies are given in Tables 8 and 9. An attempt has been made to analyse the results on the measured concentrations of major and minor elements in terms of the average intake and the dietary value of these leaves, cereals and pulses. The data obtained on the major and minor elemental concentration of the cereals and pulses can be used to evaluate the potentiality of these grains in their use for average intake and the dietary values. A programme is initiated on evaluating the uptake of elements by plants from different soils.

2.5.9 Palladium and gold determination by CNAA

Measurement of trace elements in presence of large amounts of Fe, Cu and U by NAA is very difficult due to the spectral interferences and also becomes complicated due to the fission product contribution from the fission of uranium. In such cases, it becomes imperative to preconcentrate elements of interest and decontaminate from the major elements and measure the concentrations by NAA. A reliable Chemical Neutron Activation Analysis (CNAA) method was developed to measure the trace amounts of Au and Pd present in matrices that may contain uranium, copper and iron [18,19]. Pd and Au were preconcentrated on a mini column containing anion exchanger Dowex 1X8 (100-200 mesh) in Cl^- form. The column was irradiated and the activities produced were measured using a this window HPGE and a Si(Li) systems. Concentrations were evaluated by comparison method. Standard addition method was used to arrive at the lowest detection limits. Under the ideal interference free conditions, an absolute detection limit of 0.12ng for Pd and 0. 1ng for Au were achieved. This is being used routinely to measure trace amounts of Au and Pd in different matrices.

Table 5 Sample Description of the leaves

Sample Ident.	Local Name	Scientific Name	Medicinal Uses
L1	Kadi patta	Murraya koenigii (L.) spr	Dysentery, Bruised, Snake bite, Eruptions
L2	Chauli(small)	Amaranths polygamus L.	Diarrhoea, Seminal debility, Leucorrhaea and Monorrhagia and Antidote for Snake poison
L3	Kanuga.	Pongamia pinnata (L.) pierre	Flatulence, Dyspersia, Diarrhoea, Cough, Leprosy, Gonorrhoea, Foul ulcers, Sores, Rheumatic pains and Bleeding piles
L4	Drum stick	Moringa oleifera Lam	Dental caries, Swellings, Hydrocele, Headache and Paralysis
L5	Eucalyptus	Eucalyptus globulus Labill	Rheumatism, Burns, Mosquito repellent, Infections of the Upper Respiratorytract, Chronicbronchitis, Asthma, Phthis, Insect and Vermin repellent and Some skin diseases.
L6	Methi	Amaranthus hybridus L.	Gonorrhoea, Eczema, Scorpion-sting, Snake bites, Cough, Dysentery
L7	Ambadi	Hibiscus cannabinus L.	Purgative, Healing
L8	Chauli	Amaranths gangetilus L.	Astringent, Menorrhagia, Diarrhoea, Dysentery, Haemorrhage, Ulcerated conditions of throat and mouth

L9	Pudina	Mentha spicata L	Fewer, Bronchitis, aphthae and antidote to poison
L10	Neem	Azadirachta indica A juss	Ulcers, Boils,czema,Smallfox,Blood purification, Skin diseases and as a antiseptic solution

TABLE 6 Elemental concentrations of Orchard Leaf (NIST SRM-1571) and Neem leaves

Element	Units	SRM 1571 Measured	Reported	Neem Leaf Tirupati(L10)	Mumbai(L11)
Na	µg/g	88 7±6 8	82 0±6 0	100 4 ±6 5	541 5±17 7
Mg	%	0 59±0 02	0 62±0 02	0 49 ±0 03	0 76±0 03
Al	µg/g	330 5±7 5	310-410	116 2±7 2	309 3±21 3
Cl	µg/g	650 0±30 0	690	5300±400	8300±500
K	%	1 42±0 09	1 47±0 03	2 84±0 09	1 11±0 06
Ca	%	1 89±0 03	2 09±0 03	3 06± 034	4 02±0 051
Sc	ng/g	86 5±5 1	90 0	-	-
Ti	µg/g	56 9±4 2	-	-	-
V	µg/g	0 52±0 02	-	1 66±0 06	4 26±0 08
Mn	µg/g	87 0±8 2	91 0±4 0	16 97±1 16	36 5±2 1
Zn	µg/g	29 3±4 3	25 0±0 3	-	-
As	µg/g	8 3±0 6	10 0±0 2	-	-
Br	µg/g	8 5±0 7	9 5±1 1	7 07±0 5	3 86±0 24
Sr	µg/g	34 1±1 5	37 0±1 0	115 0±10 1	138 3±4 4
Sb	µg/g	2 6±0 3	2 9±0 3	-	-
I	µg/g	-	-	3 09±0 6	-
Cs	µg/g	-	-	-	1 89±0 13
Ba	µg/g	-	-	74 98±3 41	-
La	µg/g	1 13±0 07	1 1±0 07	0 33±0 005	-
Sm	ng/g	130 0±10 0	114±20	-	-
Eu	ng/g	20 2±2 3	24±3	-	-

- *not detected*

TABLE 7 Sample Description of the cereals (C1-C5) and pulses (P1-P7)

Sample Identification	Local Name	Scientific Name
C1	Wheat	Triticum aestivun L
C2	Paddy	Oryza sativa L
C3	Bajra	Pennisetum typhoides (Burm f) Staff & Hubb
C4	Ragi	Eleusine Coracana(L) Gaertn
C5	Jowar	Sorghum vulgare Pers
P1	Methi	Trigonella foenum graecum L
P2	Moong	Phaseolus aureus Roxb
P3	Chanadal	Cicer arietinum L
P4	Til	Sesamum indicum L
P5	Chanli	Vigna sinensis (L) Hassk
P6	Horse Gram	Dolichos biflorus L
P7	Tur Dal	Cajanus cajan(L) Mill

TABLE 8. Elemental Concentrations of Cereals (in mg.kg^{-1} unless % is indicated)

Element	C1	C2	C3	C4	C5
Na	42.3±2.3	195.9±12.8	84.77±2.87	114.8±1.4	106.62±3.55
Mg%	0.24±0.025	0.92±0.032	0.703±0.014	0.44±0.034	0.69±0.019
Al	2.6±0.43	1801.88±47.7	995.27±98.46	N. D.	886.8±50.6
Cl%	0.17±0.004	0.33±0.033	0.262±0.006	0.106±0.002	0.14±0.006
K%	0.43±0.011	0.48±0.095	0.54±0.051	0.57±0.28	0.65±0.263
Ca%	N. D.	0.11±0.04	N. D.	0.35±0.023	0.048±0.003
Mn	40.88±3.83	151.6±7.99	32.9±1.87	267.3±6.99	19.72±2.04
Br	2.63±0.38	2.38±0.52	0.38±0.022	0.97±0.082	1.65±0.077
Zn	191.81±14.12	92.60±5.59	154.22±10.12	61.79±2.52	77.62±4.65
Co	1.33±0.09	0.51±0.02	0.96±0.04	0.37±0.02	2.71±0.14
Fe	1915.30±98.71	816.75±54.28	467.11±11.56	489.57±21.12	1376.21±50.21
La	0.172±0.032	0.46±0.053	N. D.	4.8±0.06	N. D.
Sm	N. D.	0.14±0.003	N. D.	N. D.	0.16±0.01
Rb	N. D.	165.94±10.72	115.12±8.58	71.59±4.51	N. D.
Cr	N. D.	55.70±2.23	N. D.	N. D.	N. D.
As	N. D.	0.144±0.032	N. D.	N. D.	N. D.

N D Not detected

TABLE 9. Elemental concentration of Pulses (in mg.kg^{-1} unless % is indicated)

Element	P1	P2	P3	P4	P5	P6	P7
Na	391.2±23.6	27.65±3.51	167.88±12.78	230.68±4.16	149.05±8.5	54.53±0.92	52.58±5.8
Mg%	0.87±0.04	0.88±0.035	0.87±0.025	1.15±0.05	0.79±0.030	051±0.023	0.34±0.025
Al	N. D.	N. D.	649.6±41.29	778.3±6.93	1079.3±67.73	586.81±37.8	185.6±10.6
Cl%	0.273±0.008	0.108±0.001	0.19±0.003	0.095±0.002	0.064±0.0016	0.07±0.001	0.04±0.002
K%	1.62±0.04	1.32±0.03	1.24±0.152	0.93±0.11	1.91±0.015	1.55±0.042	1.6±0.2
Ca%	0.297±0.013	0.173±0.015	0.24±0.014	1.16±0.018	04±0.086	0.344±0.035	0.115±0.017
Mn	20.6±0.8	15.53±0.4	31.12±1.19	22.57±1.9	43.9±1.25	48.82±0.86	10.1±0.6

Br	0.63± 0.02	0.5± 0.009	13.22± 0.4	5.7± 0.34	2.27± 0.12	2.81± 0.24	5.12± 0.25
Zn	167.12± 12.02	155.29 ±10.05	86.56± 2.13	82.94± 3.16	96.54± 1.84	127.91± 8.12	60.93 ±2.35
Co	3.02± 0.21	2.14± 0.11	0.74± 0.04	1.78± 0.04	0.45± 0.02	0.75± 0.05	0.54± 0.02
Fe	1261.16 ±88.40	855.90 ±25.23	1181.45 ±63.35	934.51 ±29.53	806.04± 25.43	1466.65 ±32.28	912.64± 35.21
La	N. D.	N. D.	0.174± 0.023	14.45± 0.76	0.25± 0.025	0.027± 0.0012	0.74± 0.032
Se	54.38± 3.15	N. D.	30.22± 0.93	28.3± 1.35	8.77± 0.364	N. D.	44.2± 4.85
Sm	0.089± 0.004	N. D.	N. D.	0.033± 0.002	0.084± 0.025	N. D.	N. D.
Rb	203.52± 11.24	83.4± 5.32	77.11± 3.45	125.61 ±7.53	191.67± 11.20	N. D.	51.9± 5.84

2.5.10 Rare Earth Elements (REE) in quartzites by CNAA

Trace amounts of uranium are present in the quartzites of Cuddapah basin. estimation of REEs in quartzites by NAA becomes erroneous due to the contribution from the fission of uranium. A preconcentration chemical procedure was developed and tested to estimate REEs in quartzites. This procedure was standardised using radiotracers in the separation of REEs from synthetic mixtures to arrive at the chemical yields and applied to quartzites. Quartzites were brought into solution by digesting with HCl in presence of HF. Boric acid was added to remove the excess fluoride and the solution was brought to 1MHCl .REEs and U were coprecipitated as oxalates by adding calcium chloride. The precipitate was dissolved in 9M HCl and loaded on an anion exchange (Dowex 1X8, Cl^- form) column to adsorb uranium. The effluent containing REEs was subjected to NAA.

2.5.11 Determination of trace elements in leaves by RNAA

In many naturally occurring materials like biological and minerals, Na is a major element .In leafy materials, in addition to sodium, Br and K are present as major constituents. In NAA activation products of these elements make the measurements nearly impossible. In view of this, it is essential either separate these major element prior to activation (CNAA) or after the activation (RNAA). If the matrix does not contain fissionable materials, then it would be better if the chemical separations are carried out after the activation. Trace elements are determined in leaf samples and in SRM-1571 by RNAA with enhanced sensitivity [20]. Irradiated sample was digested in perchloric acid medium to expel radiobromine. Radiosodium and radiopotassium were separated from the solution by passing it over HAP column in 8M HNO_3 for Na removal and 1M HNO_3 for K removal. For the first time elements Ti and V were measured in SRM-1571. These were compared with the results obtained by CNAA on the same standard. A similar programme of measuring the trace elements in blood samples after removing radiosodium is initiated. Preliminary data indicate that trace elements like Cr, Fe and Zn could be measured reliably.

3. FUTURE OUTLOOK

3.1 ENVIRONMENTAL MONITORING AROUND CUDDAPAH BASIN

Cuddapah basin is rich in minerals like asbesots, lime stone, barytes and uranium bearing rocks. Mining of these minerals load the environment with particulate matter which is a health concern. A comprehensive programme of monitoring air, soil, water and plants around this area is initiated in collaboration with Department of Mineral Chemistry, S.V.U. P.G. Centre, Cuddapah.

3.2 ENVIRONMENTAL MONITORING AROUND AGRA

Agra is an industrially developing area. A programme of monitoring the soil, water and dew in and around Agra is initiated to evaluate the impact of the pollutants by Dayalbagh Educational Institute, Agra and we are extending the required analytical services.

3.3 NUCLEAR ANALYTICAL TECHNIQUES

Apart from utilising NAA for analysing varied matrices, nuclear anlytical techniques using ion beam analysis are being developed with a view to utilise them for material characterisation. We are setting up facility for RBS, NRA and PIXE at the Folded Tandem Ion Accelerator (FOTIA) in B.A.R.C. where low energy ion beams will be made available. The main areas of research and development envisaged are depth profiling of low Z materials in different industrially important materials using NRA, high tech materials using RBS and multi elemental analysis in biolgically and environmentally important materials using PIXE. It is also proposed to set up PGNA for analysing low Z materials in environmental samples.

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REFERENCES

[1] G.M. KOLESOV, Analyst, **120**, 1457 (1995).
[2] A. CHATT AND R.E. JERVIS (Guest Ed), Proc. of the Second Intl. Symp. on Nuclear Analytical Chemistry, NAC-II, J. Radioanalytical Nucl. Chem, **179(1)** (1994).
[3] A. SIMONITS, F.DE CORTE AND J. HOSTE, J. Radioanal. Chem., **24**, 31 (1975).
[4] F. DE CORTE, A. SIMONITS, A. DE WISPELAERE AND A. ELEK, J. Radioanal. Chem., **133**, 43-130 (1989).
[5] R.N. ACHARYA, P.P. BURTE, A.G.C. NAIR, A.V.R. REDDY AND S.B. MANOHAR, J. Radioanal. Nucl. Chem., **220(2),** 223 (1997).

[6] R.N. ACHARYA, S.K. JHA, P.P. BURTE, A.G.C. NAIR, U.S. KUMAR, A.V.R. REDDY, T.M. KRISHNA MOORTHY AND S.B. MANOHAR, Proc. 5th Nat. Symp on Environment, p.209, February 1996, SINP, Calcutta, India.

[7] R.K. DUTTA, R.N. ACHARYA, A.V.R. REDDY, A.G.C. NAIR, V. CHAKRABORTTY, S.N. CHINTALAPUDI AND S.B. MANOHAR, to be communicated, J. Radioanal. Nucl. Chem.

[8] R.K. DUTTA, R.N. ACHARYA, V. CHAKRABORTTY, A.G.C. NAIR, A.V.R. REDDY, S.N. CHINTALAPUDI AND S.B. MANOHAR ,J. Radioanal. Nucl. Chem (in press).

[9] P.V. NAGENDRA KUMAR, R.N. ACHARYA, K. HARIKRISHNA, N. SURESH KUMAR, L.K. REDDY, N.B.Y. REDDY, A.G.C. NAIR, A.V.R. REDDY AND S.B. MANOHAR, Ninth Annual Conference of Indian Nuclear Society (INSAC-98), Mumbai, June 1-3, p.4 (1998).

[10] BALAJI, R.N. ACHARYA, A.G.C. NAIR, P.P. BURTE, A.V.R. REDDY, G.R.K. NAIDU AND S.B. MANOHAR, (to be communicated)

[11] R.N. ACHARYA, A.G.C. NAIR, P.P. BURTE, A.V.R. REDDY AND S.B. MANOHAR, B.A.R.C. Report, BARC/ 1995/E/0071995.

[12] F. DE CORTE, L. MOENS, K. SORDO-EL HAMMAMI, A. SIMONITS AND J. HOSTTE, J. Radioanal. Chem, **52,** 305 (1979).

[13] S.S. RATTAN, S.P. DANGE, T. DATTA, S.B. MANOHAR, P.P. BURTE, S. PRAKASH AND M.V. RAMANIAH, BARC Report

[14] Table of Radioactive Isotopes, E. Browne and R.B. Firestone: Ed.V.S. Shirley, John-Wiley and Sons (1986).

[15] Hand book of Nuclear Activation Data , Technical Report Series, No.273, IAEA, Vienna(1987).

[16] H. ELDERFIELD AND M. J. GREAVES, Earth Planet.Sci. Lett., **55**, 163(1981).

[17] G. P. GLASBY, Marine Chemistry, **1**, 105 (1973).

[18] A.G.C. NAIR, A.V.R. REDDY, R.N. ACHARYA, P.P. BURTE AND S.B. MANOHAR, 16th Conference of Council of Chemists, Mangalore, India, p. 166 (1997).

[19] A.G.C. NAIR, A.V.R. REDDY, R.N. ACHARYA, P.P. BURTE AND S.B. MANOHAR, Communicated to J. Radioanal. Nucl. Chem.

[20] A.G.C. NAIR, R.N. ACHARYA, A.V.R. REDDY AND S.B. MANOHAR, 33rd Convention of Chemists, Coimbatore, India, (1997).

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