IDENT, a Radioisotope Identification Subroutine for Use with the Gamma-ray Spectrum Analysis Program SAMPO

W. Carder and T. D. MacMahon

University of London Reactor Centre, Silwood Park, Sunninghill, Ascot, Berkshire, SL5 7PY

and A. Egan

Physics Department, University of Surrey, Guildford, Surrey, GU2 5XH

The versatile gamma-ray spectrum analysis program SAMPO[1,2] is now used in many laboratories for the analysis of the complex spectra encountered in neutron-activation analysis. The SAMPO program includes routines for peak finding, peak fitting and peak intensity and energy determinations. The addition of the subroutine IDENT, described here, increases the usefulness of SAMPO by carrying out radioisotope identifications and elemental mass determinations following both simple and cyclic thermal neutron-activation analysis.

The Nuclear Data Library

The nuclear data library, which forms part of the sub-routine IDENT, contains the following information for each of about 750 gamma-rays that are likely to be encountered in thermal neutron-activation analysis:

(*i*)   a reference number for each gamma-ray;
(*ii*)   the energy of the gamma-ray;
(*iii*)   the name of the isotope emitting the gamma-ray;
(*iv*)   the number of gamma-rays of this energy emitted per disintegration of the isotope (I_a);
(*v*)   the half-life of the isotope ($t_{\frac{1}{2}}$);
(*vi*)   the relative atomic mass of the target nucleus;
(*vii*)   the product of the thermal neutron absorption cross-section of the target nucleus and its natural fractional abundance (σf);
(*viii*) if the isotope concerned is the daughter of another isotope produced by thermal neutron capture, then a reference to the parent nucleus is included.

The library also includes information on naturally occurring radioisotopes and also a few of the more common isotopes produced by fast neutron reactions that may occur in the mixed neutron field of a nuclear reactor. The data library has been compiled using information listed in Appendix VII of reference **3**, together with data obtained from the "Table of Isotopes"[4] and recent issues of "Nuclear Data Sheets."[5] The library contains sufficient information for the identification of radioisotopes contributing to a gamma-ray spectrum, and is also used by the subroutine to determine the masses of the elements present in a sample that has undergone thermal neutron activation, provided that the following information is also input to the program:

(*i*)   thermal neutron flux (ϕ) (cm^{-2} s^{-1});

(*ii*) duration of irradiation (t_i) (s);

(*iii*) time between irradiation and gamma counting (t_d) (s); and

(*iv*) gamma detector efficiency (ϵ).

The mass (in grams) is then given by the equation

$$\text{Mass} = \frac{A\ W\ \lambda\ e^{\lambda_a}}{0.6\ \epsilon\ I_a\ \phi\ \sigma\ f\ (1-e^{\lambda_i})\ (1-e^{\lambda_c})} \qquad .. \qquad .. \qquad (1)$$

where A is the number of counts in the photopeak concerned, W is the relative atomic mass of the target nucleus, λ is the radioisotope decay constant $= \ln2/t^{\frac{1}{2}}$ (s^{-1}), t_c is the live counting time for the gamma-spectrum (s) and the other symbols are as already defined.

It should be noted that equation (1) is strictly true only when the fractional dead time remains constant during the counting time, which should therefore be kept short compared with the decay rate of the sample being studied.

In cyclic activation analysis where the sample is repeatedly transferred back and forth between the irradiation and counting position with a constant periodic time T, the mass (in grams) is given by the equation

$$\text{Mass} = \frac{B\ (1-e^{-\lambda T})^2}{n(1-e^{-\lambda T})-e^{-\lambda T}(1-e^{-n\lambda T})} \qquad .. \qquad .. \qquad .. \qquad (2)$$

where B is the right-hand side of equation (1) and n is the total number of cycles.

Radioisotope Identification by the IDENT Subroutine

The subroutine takes the first peak (lowest energy peak) found by the main SAMPO program and compares its energy and energy uncertainty with the energy of the first and subsequent peaks in the data library until a library peak is encountered whose energy is greater than the sum of the energy and energy uncertainty of the SAMPO peak. Whenever a library peak is found whose energy differs from that of the SAMPO peak by less than its energy uncertainty, a flag is put on the library peak indicating that it has been found in the spectrum, and the reference number of the library peak is recorded as a possible identification of the SAMPO peak. At this stage, depending on the magnitude of the energy uncertainty, there may be several possible identifications of each SAMPO peak, and the subroutine allows for up to 15 before an error message is given. If no identification is made a message to this effect is also given. Having dealt in this manner with the first SAMPO peak, the subroutine treats each subsequent SAMPO peak in the same way, except that it does not go back to the beginning of the data library each time but only goes back 20 library peaks from where it stopped with the previous SAMPO peak. This means that only a small part of the data library needs to be searched for each SAMPO peak.

For the sake of convenience in adding new peaks to the library, the library is made up of two sections: a fixed section of 714 gamma-rays, and an updatable section to which additions can be made and which at present contains 36 gamma-rays. As the updatable section is relatively short, each SAMPO peak is compared with every library peak in the updatable section and therefore the peaks in this section do not need to be in any particular order.

When this stage of the subroutine is complete, several of the library peaks will have flags indicating that they have been linked with peaks found by SAMPO, and most of the SAMPO peaks will have been associated with one or more library peaks.

The next stage of the program carries out the following checks:

(*i*) is the gamma-ray of highest intensity of the isotope concerned present in the spectrum? (if the energy of the highest intensity gamma-ray is outside the energy range of the spectrum, this check is ignored);

(*ii*) if the isotope identified is ^{81}Se, ^{80}Br or ^{124}Sb$^{m'}$ then a special calculation is carried out taking into account the fact that each isotope is produced by neutron irradiation together with its parent ^{81}Se^m, ^{80}Br^m or ^{124}Sb$^{m''}$;

(*iii*) if the energy of the SAMPO peak is 511 keV, it is identified as annihilation radiation and no further calculations are carried out;

(*iv*) if the isotope identified occurs in the natural background then only a simple calculation is carried out in which the total peak area is divided by the gamma-ray intensity (*i.e.*, gammas/disintegrations) and the live counting time;

(*v*) if the isotope identified is the daughter of a radioactive parent produced by neutron capture, a calculation is carried out to determine the mass of the parent element;

(*vi*) if the time between irradiation and counting of the sample is greater than 20 half-lives of the isotope identified, that identification is rejected;

(*vii*) if the absolute intensity of the gamma-ray is unknown, then no further calculations are carried out.

Having carried out the above checks, the program then calculates the disintegration rates of the identified isotopes both at the beginning of the counting time and at the end of the irradiation period, taking into account dead-time corrections and decay of the isotope during counting. This calculation uses the delay time between irradiation and counting which is fed into the program on the IDENT control card.

If the isotope concerned is not produced by a fast neutron reaction, and if its thermal neutron cross-section is known, then the program uses data on the sample irradiation time and thermal neutron flux also on the IDENT control card to determine the mass of the element concerned in the activated sample. If the resulting mass is negative or is greater than the total mass of the sample, the identification is rejected.

As well as the straightforward activation analysis process in which a gamma-ray spectrum is accumulated after a single irradiation, the subroutine also deals with spectra accumulated in cyclic activation analysis.

Because cyclic activation is used for isotopes having half-lives of the order of seconds, an additional criterion is included for acceptance of possible identifications. The formation of active daughter products is most unlikely to have had time to occur and so peaks assigned to such nuclides are rejected. Furthermore, those isotopes which may be formed directly by (n, γ) reactions and by decay of an isomer (Se, Br, ^{124}Sb) are considered, for calculation purposes in the cyclic activation option, to have been formed only by the former process.

For dead-time corrections two options are available:

(*a*) If the spectra are acquired cycle by cycle they can be corrected for an assumed constant, fractional dead-time by a simple CLOCK-TIME/LIVE-TIME multiplication, and then spectra for the same sample added together. This is accomplished by relevant characters on the DATAIN and IDENTIFY control cards.

(*b*) If the analyser is left to acquire data for the *whole* of the experiment, so that only a single spectrum is acquired, then a simple dead-time correction can be made, on the assumption that the dead-time arises only during the count section of the period. This mode of analysis can be defined by a relevant character on the DATAIN card.

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Analysis of Metals by Means of Energy-dispersive X-ray Fluorescence

P. Verbeke, H. Nullens and F. Adams

Department of Chemistry, University of Antwerp (U.I.A.), 2610 Wilrijk, Belgium

Energy-dispersive X-ray fluorescence has hitherto mainly been used as a quick, cheap and multi-element method for the analysis of thin samples. In the X-ray fluorescence of thick samples a major problem is that due to the occurrence of the so-called matrix effects.

Especially for the analysis of metallic samples these absorption-enhancement effects can be important. The correction method used in this work for the calculation of the elemental concentrations is based on the fundamental parameters algorithm given by Criss and Birks.[1] The physical parameters required are the mass absorption coefficients, the fluorescence yields and the excitation intensity distribution. The use of an energy-dispersive apparatus with secondary target set-up simplifies the application of the correction procedure considerably, as the excitation beam merely consists of the characteristic lines of the secondary target material instead of a broad polychromatic energy distribution. This eliminates the integration over a broad range of excitation energies or the introduction of a "most effective excitation energy" for each element.

The characteristic physical parameters were gathered from literature sources. The mass absorption coefficients were taken from the tabulations of McMaster *et al.*[2] and the fluorescence yields from the paper of Bambynek *et al.*[3] The elemental calibration factors were determined by the measurement of thin pure-element films. The accuracy on the factors thus obtained was within 5%, which was checked by measuring a number of thick samples consisting of pure elements.

The net spectral intensities were obtained by using a computerised fitting procedure, based on a non-linear least-squares algorithm, developed by Van Espen *et al.*[4] The fitting function consists of a number of Gauss functions and a polynomial background contribution. Some complex spectra with large $K\alpha$ - $K\beta$ overlap gave rise to difficulties in the fitting, and the accuracy of the results was correspondingly affected. Other interferences due to the occurrence of escape peaks, at 1.74 keV below the full energy peak, and sum peaks, appearing at high count rates, were also examined.

As there is no explicit equation for the concentrations, the net elemental intensities were used in an iterative approximation procedure, based on a fundamental parameters working equation:

$$C_i = \frac{(P_i + S_i)/\mathrm{Zr}}{P_i{}^*/\mathrm{Zr}^*} \times \frac{\displaystyle\sum_{k=1}^{N_\mathrm{E}} \frac{\mu_i(k)\, I(k)/I_\mathrm{tot}}{\mu_i(k) + \mu_i(i)}}{\displaystyle\sum_{k=1}^{N_\mathrm{E}} \frac{\mu_i(k)\, I(k)/I_\mathrm{tot}}{\mu_\mathrm{M}(k) + \mu_\mathrm{M}(i)}\left[1 + \frac{1}{2\mu_i(k)}\sum_{j=i'}^{N} C_j K_j \mu_i(j)\mu_j(k) X\right]}$$

with

$$X = \frac{1}{\mu_\mathrm{M}(k)\sqrt{2}}\ln\left[1 + \frac{\mu_\mathrm{M}(k)\sqrt{2}}{\mu_\mathrm{M}(j)}\right] + \frac{1}{\mu_\mathrm{M}(i)\sqrt{2}}\ln\left[1 + \frac{\mu_\mathrm{M}(i)\sqrt{2}}{\mu_\mathrm{M}(j)}\right]$$

$$K_j = \left(1 - \frac{1}{J_j}\right) R_j \omega_j \quad \text{and} \quad \mu_\mathrm{M}(i) = \sum_{j=1}^{N'} C_j \mu_j(i)$$

where

C_i is the mass fraction of element i in the sample.

P_i is the fluorescence intensity of element i due to primary excitation.

S_i is the fluorescence intensity of element i due to secondary excitation.

$P_i{}^*$ is the fluorescence intensity of pure element i (calculated).

N_E is the number of fluorescent lines in the excitation spectrum.

$I(k)$ is the intensity of line k in the excitation spectrum.

I_tot is the total excitation intensity.

$\mu_i(k)$ is the mass absorption coefficient of element i for line k.

$\mu_\mathrm{M}(k)$ is the mass absorption coefficient of the matrix for line k.

J_j is the absorption jump ratio for element j.

ω_j is the fluorescence yield of element j.

R_j is the intensity fraction of line j in its series.

i' is the first line for which the energy is larger than the absorption edge of element i.

N is the number of fluorescent lines.

N' is the number of elements present.

Zr, Zr* are correction factors resulting from the use of an external reference signal (zirconium wire) during measurements.[5]

It appeared that in some instances, the enhancement contribution could attain more than 50% of the total fluorescence intensity.

For a complete and practical investigation of the method, different types of metallic samples were examined. Most of them were standard materials, which were treated as unknowns in order to verify the accuracy. The results for a series of three nickel-base alloys are presented in Table I. The X-ray fluorescence values in columns 1 and columns 2 appear to compare closely. The applied correction scheme provides reliable results for the samples analysed. The intense peaks of major elements may, however, hamper the de-convolution of low-intensity adjacent lines and affect their precise analysis.

In order to appreciate the importance of the correction for the inter-element effects, Table II summarises the data obtained for SRM 1207–1 by different approaches: (1), considering

TABLE I

CERTIFIED AND MEASURED PERCENTAGE COMPOSITION OF NBS REFERENCE MATERIALS (NICKEL ALLOYS)

Element	SRM 1206–2			SRM 1207–1		SRM 1208–1		
	Certified	Measured		Certified	Measured	Certified	Measured	
		1*	2†		1*		1*	2†
Al	1.7	1.5	1.2	1.26	1.5	(0.15)	0.40	0.33
Si	0.21	0.22	0.18	0.47	0.59	0.43	0.38	0 31
Ti	2.9	3.4	2.9	3.09	3.58	0.46	0.51	0.43
Cr	19.17	19.57	19.17	18.88	19.35	17.5	18.3	17.7
Mn	0.030	0.078	0.075	0.34	0.35	0.38	0.41	0.39
Fe	0.46	0.39	0.40	2.22	2.13	19.2	19.3	20.1
Co	11.5	10.9	11.6	13.0	12.35	0.82	1.01	1.07
Ni	53.3	53.2	53.9	56.1	55.5	51.9	50.6	52.6
Cu	0.04	0.02	0.06	0.026	0.010	0.14	0.13	0.35
Nb	NC‡	<0.002	—	NC‡	<0.002	5.3	5.6	—
Mo	10.3	10.7	10.5	4.50	4.62	3.2	3.4	3.4

* Calibration based on thin-film standards.
† Calibration based on SRM 1207–1.
‡ Value not certified.

TABLE II

RESULTS FOR SRM 1207–1 OBTAINED BY DIFFERENT APPROACHES

Element	Concentration, %			
	Full correction	Correction for Kα enhancement and absorption	Correction for absorption only	No correction
Al	1.5	1.5	1.2	0.05
Si	0.59	0.58	0.46	0.03
Ti	3.58	3.66	4.87	3.37
Cr	19.35	19.74	25.51	23.26
Mn	0.35	0.36	0.47	0.51
Fe	2.13	2.19	2.83	2.09
Co	12.35	12.74	11.49	10.04
Ni	55.5	54.7	49.5	48.5
Cu	0.010	0.009	0.008	0.008
Mo	4.62	4.51	3.61	12.16

full absorption-enhancement corrections; (2), considering the absorption effects and only enhancement by the $K\alpha$ line; (3), neglecting all enhancement contributions but taking into account absorption; and (4), neglecting both absorption and enhancement effects. In each instance the concentration was scaled to 100%.

The results obtained show that the combination of the fundamental parameters approach with energy-dispersive X-ray fluorescence with secondary target set-up allows the quantitative and accurate analysis of metallic samples. The method is quick and versatile and can be used for the analysis of thick samples with widely varying composition.

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Analytical Applications of X-ray Photoelectron Spectroscopy in Archaeological Chemistry

M. Thompson and E. T. Leventhal

Department of Chemistry, University of Toronto, Lash Miller Chemical Laboratories, 80 *St. George Street, Toronto, Ontario, Canada, M5S 1A1*

X-ray photoelectron spectroscopy (XPS) has become a powerful tool for the investigation of chemical structure and bonding. The reason for this lies in the ability of the technique to convey several levels of information. For example, a wide-scan spectrum can be used to carry out an identification of all elements in the Periodic Table, with the exception of hydrogen and helium. Also, it is possible to infer structural information from core-level binding energies, *viz.*, the chemical shift effect. For solids, the potential exists for using XPS in concentration - depth profiling through the monitoring of electron count in conjunction with argon-ion etching. Finally, information can also be gleaned from other aspects of XPS such as shake-up and shake-off transitions, multiplet splittings and angular dependence studies.

The potential of XPS for the analysis of objects of archaeological interest has been cited.[1-3] Recently we demonstrated the advantages of XPS in this field through a multi-element analysis of a sample of mummy cartonnage.[4] Depth profiling of the resin and pigment layers of the sample was also carried out. In the present paper we report further examples of the use of XPS in archaeological chemistry.

Experimental

XPS analyses were carried out using a McPherson ESCA 36 spectrometer. Spectra were excited by either Mg $K\alpha$ or Al $K\alpha$ radiation.

Results and Discussion

An interdisciplinary study has recently been concerned with Holocene ecology and subsistence in North Africa.[5] According to many prehistorians, one of the facets of Capsian cuisine was a diet that was based primarily on land snails. Microstratigraphy of several sites (escargotières) was carried out in order to investigate snail species ecology. Analytical results from soil samples for hydrogen ion concentration, calcium, iron, phosphorus, nitrogen and total carbon were used in the arguments. It was felt that analysis for carbonate-carbon

and organically bound carbon would provide a sounder basis for these studies in view of the presence of the former in snail shells.   Fig. 1 shows a typical wide-scan spectrum from soil (homogenised) and Fig. 2 the peaks corresponding to carbon in the two different chemical environments.   Although a quantitative analysis for these two species was not achieved, the ratios of the peak areas and the total carbon result from layers of soil were used success-fully in correlation with snail-shell occurrence.
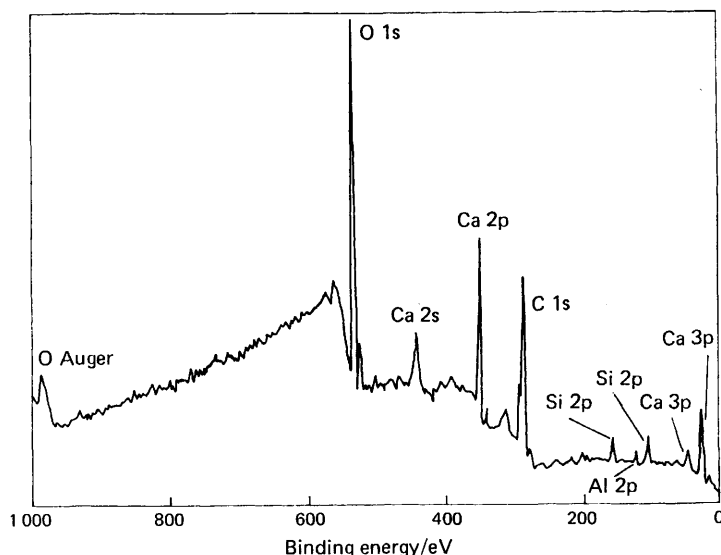
Fig. 1.   XPS spectrum of soil from Capsian site.

Naturally, this type of analysis can be carried out by other means; however, use of a multi-sample carousel in the target area of the spectrometer can result in many samples being studied in a short time by means of XPS.
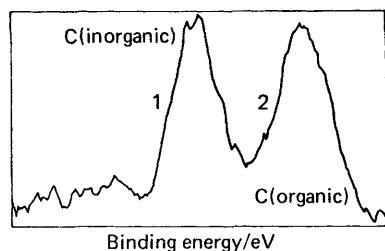

Fig. 2.   Carbon region in XPS spectrum of soil from Capsian site. 1, B.E. = 291.5 eV; and 2, B.E. = 286.5 eV.
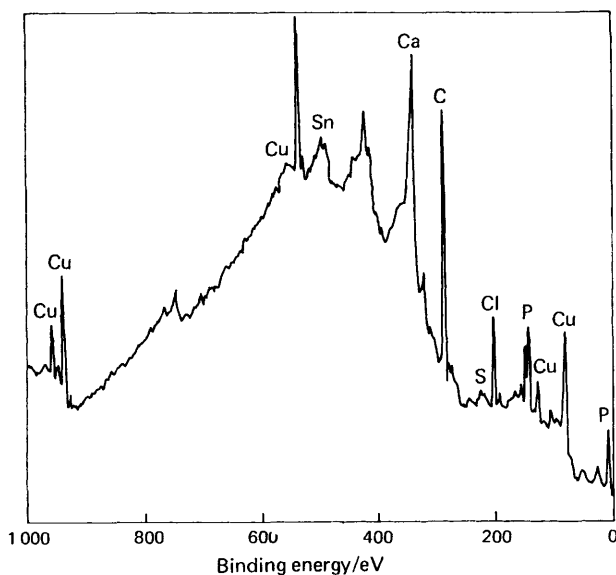

Fig. 3.   XPS spectrum of corrosion layer of Egyptian lamp.

It has been suggested recently that corrosion products on the surfaces of ancient artifacts may well contain "trapped" information that is important to the archaeological study.[6] An example might be organic material that the object may have been in contact with when buried. Chemical analysis of such products, particularly if performed together with *in situ* argon-ion etching for depth profiling, may reveal this information. Fig. 3 shows a wide-scan spectrum of the corrosion layer on a bronze Egyptian lamp, showing the number of elements present, some as anions, *e.g.*, chloride. (In this instance the sample, weighing about 1 mg, was powdered and placed on a small aluminium plate.) We believe that in this specific area concentration - depth profiling should prove to be very useful.

The number of examples in archaeological chemistry of the use of analytical results in decisions on, for example, the provenance of an article is enormous. In this regard, it is felt that XPS can be used successfully if all that is required is a mapping of major elements. Fig. 4 shows wide-scan spectra from samples of Palestinian pottery and clay slip from Egyptian pottery. Note the presence of fluorine and chlorine in the latter. Again, XPS can be applied, with little or no sample preparation, where general comparisons are required with speed. With some ingenuity the technique can be non-destructive, in that the sample could be replaced on the artefact intact.
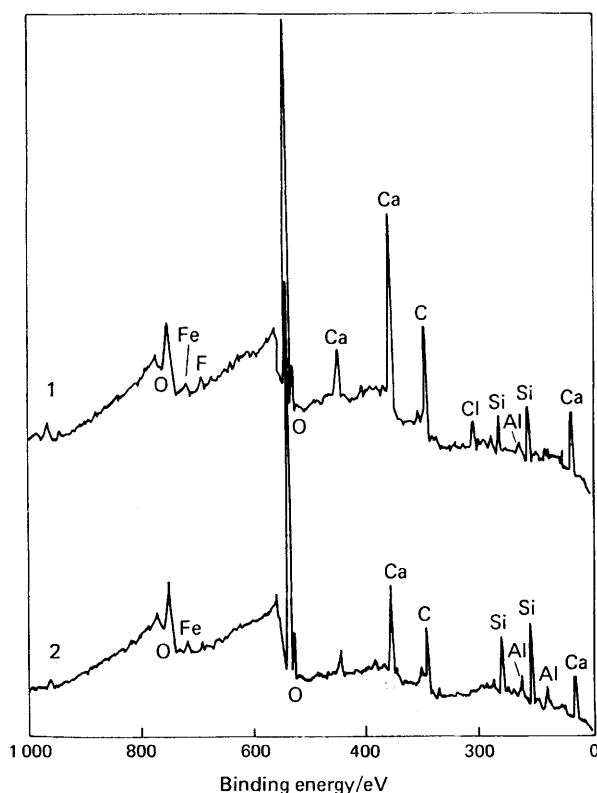

Fig. 4. XPS spectra of samples of pottery material: 1, Egyptian clay slip; 2, Palestinian pottery.

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Particle-induced X-ray Emission: A Useful Analytical Method

G. Johansson,* R. Akselsson,* M. Bohgard, L. E. Carlsson, H. C. Hansson, H. Lannefors and K. Malmqvist

Department of Nuclear Physics, Lund Institute of Technology, Lund, Sweden

In 1970, it was shown experimentally by Johansson *et al.*[1] that the excitation of atoms by charged particles, *e.g.*, protons, and the subsequent detection of the induced X-rays by an energy-dispersive detector constitutes a non-destructive multi-elemental method with low detection limits and several other properties desirable in an analytical method. Since then, many investigations have been performed and the method, known as particle-induced X-ray emission (PIXE), has been developed further. The development of suitable methods of pre-treating samples for PIXE analysis has also been intensively pursued. In the Proceedings of the International Conference of Particle-induced X-ray Emission,[2] the method and its applications are thoroughly reviewed. Two reviews have also recently been published.[3,4]

In this summary, the principles and properties of PIXE are discussed. Possible areas of application are briefly discussed, and limits of detection of elements in blood plasma are considered.

Principles of PIXE

When a beam of protons, alpha-particles or other heavy ions bombards a sample, X-rays are emitted, the energy of which is characteristic of the elements from which they originate. The number of X-rays of a certain energy emitted is proportional to the mass of the corresponding element in the sample.

In addition to the characteristic X-rays, a continuous X-ray spectrum is also created, mostly due to bremsstrahlung from decelerating electrons, which have been accelerated by the bombarding particles. However, in comparison with electron excitation and X-ray excitation, the continuous components are of low intensity in particle excitation.

By using an energy-dispersive X-ray detector, *e.g.*, a lithium-drifted silicon detector, a multi-element method for simultaneously identifying and assaying the elements in the sample is obtained. From the detector a pulse-height spectrum is obtained from which the elements present in the sample and their masses can be calculated, preferably with a computer.

K X-rays are normally used for measuring elements lighter than barium and L X-rays for those which are heavier. The simultaneous occurrence of both light and heavy elements may cause problems with interferences, but often a good computer program is able to detect small differences in energy and provide information even about minor peaks. Although their efficiencies are low, wavelength-dispersive detectors can also be used to resolve interferences, as they have a superior energy resolution in the low-energy end of the X-ray spectrum.

Properties of PIXE

In particle excitation, the probability per particle of inducing characteristic X-rays is high and, in most instances, there is no problem in obtaining adequate intensities of the particles. Also, as mentioned above, the non-informative radiation components are relatively small. Thus, the detection limits are low and are normally set by the data-taking capacity of the detection system. A useful feature of the detection limits is that they vary smoothly and not very rapidly with the atomic number of the element and particle energy. Absorbers

* Also Department of Environmental Health, University of Lund, Lund, Sweden.

inserted between the sample and the detector attenuate mostly low-energy X-rays, giving an opportunity of increasing the intensity of the bombarding particles without increasing the total intensity of the X-rays reaching the detector. Thus, it is possible to optimise the sensitivity to suit the particular kind of information the analyst wants. Another method of optimisation is to change the particle energy, because the relative excitation probabilities vary with incident particle energy.

For an element with a low atomic number, the sensitivity decreases owing to absorption in the materials between the sample and the detector. Also, absorption of these low-energy X-rays in the sample itself requires a correction that may be uncertain. Thus, for most applications, the PIXE method is quantitative only for elements heavier than phosphorus.

In combination with other methods, PIXE offers a number of unique possibilities of obtaining information about elements with low atomic numbers. Thus, Malmqvist *et al.*[5] reported the possibility of using a nuclear method for simultaneous measurements on fluorine. Another means of obtaining quantitative information about most low atomic number elements is to detect the back-scattered particles.

Mass calibration is easy owing to the known behaviour of the physical parameters involved in PIXE analysis. Once the calibration has been made, only rapid periodic control runs with a suitable standard have to be performed in order to check that no changes in the experimental arrangement have occurred. For routine analysis, the accuracy is about 10% for elements well above their limits of detection.

The most common types of sample analysed by PIXE are thin, solid samples. By "thin" in this context, we mean samples in which both the slowing down of the bombarding particles and the attenuation of the characteristic X-rays are negligible. Of course, this definition of "thin" depends critically on which particles are used, their energies and which X-rays are detected. Usually, however, samples thinner than about 1 mg cm^{-2} can be considered to be thin.

A considerable advantage of PIXE is its low detection limits in very small samples (1 μg–1 mg). In a routine analysis lasting 1–4 min, the limit of detection varies between 0.1 and 10 ng.

Often, it is either impractical or impossible to obtain representative thin samples. If sufficient material is available, a homogeneous pellet with a smooth surface can be prepared and analysed. It is just the first few milligrams per square centimetre of the surface layer that contribute to the yield of X-rays.

As such a small volume is analysed, the concentration detection limits are moderate and are typically in the range from 1 to 100 p.p.m.

Thus, when PIXE is used for thick samples, it is because of its speed, the straightforward pre-treatment possible and its multi-element capability rather than because of its limits of detection. Also, it may be pointed out that it is often of minor advantage to be able to prepare thin samples, if it is easier or more convenient to make homogeneous pellets.

Arrangements for PIXE in Lund

At the University of Lund, a 3-MV tandem Pelletron is used, protons up to 6 MeV being available. In the routine analyses performed, 2.5-MeV protons are used and the beam is made homogeneous by letting it pass through a 6 μm thick aluminium foil. The number of protons striking the sample is measured by a charge integrator coupled to the experimental chamber. An electron suppressor at -50 V is used to prevent low-energy electrons passing between the Pelletron transport tube and the irradiation chamber. To avoid charging of the sample, an electron gun is used for discharging.

For routine analyses, an automatic sample changer with a capacity of 40 samples is available. Two standards are usually loaded in each sample tray, one at the beginning and the other at the end.

Applications

In the characterisation of air pollution, size-distribution information is often essential. A sorting tool often used is the cascade impactor. For both convenience and the impaction of

small particles, it is feasible to use small impactors. The function of impactors at high loadings is, however, questionable owing to bounce-off effects. Thus, the samples obtained are usually very small and this is a case where PIXE is a very favourable method. Many PIXE investigations of atmospheric air pollution have been carried out, and the number of samples to be analysed in such investigations is usually very high. With the PIXE method, it has become feasible to perform large-scale investigations with good size resolution and/or good time resolution.

Filter samples of airborne particulates are also suitable in many instances for PIXE analysis owing to its speed and multi-element capability.

The use of PIXE for trace-element analysis in water is of increasing interest and different methods of obtaining suitable samples have been used. By employing evaporation[6,7] or chelating techniques,[8,9] limits of detection in the parts per billion range for elements of medium atomic number are obtained.

For samples of biological material, pre-treatment is usually performed, *e.g.*, wet ashing, low-temperature ashing, freeze-drying or grinding have been employed both at Lund and elsewhere.[10] For plasma samples, we have found freeze-drying to be suitable and Fig. 1 shows the lower limits of detection. Table I lists the elements that normally occur in plasma above and at the limits of detection. Owing to similarities in the compositions of biological material, the diagram is also valid for other biological material if dry-mass measuring is used. Tooth and bone samples can be bombarded directly but damage due to heating sometimes constitutes a problem. For this and other reasons, some laboratories have constructed facilities for optional analysis in air or a gas at atmospheric pressure.
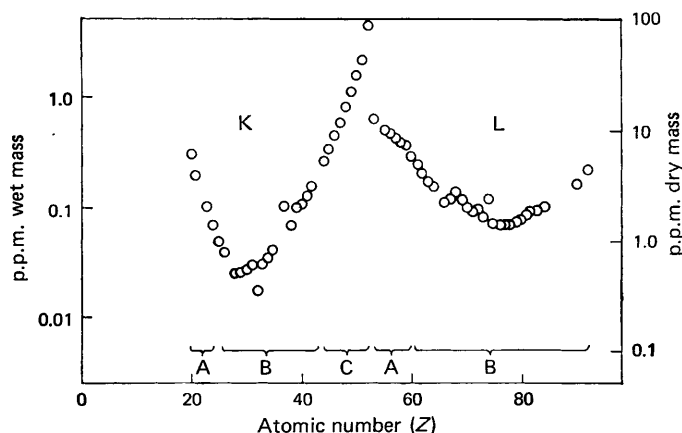

Fig. 1. Experimental detection limits for elements in plasma (with atomic number between 20 and 92) calculated as those concentrations which give a peak three times the square root of the number of pulses in the background in the peak region. Due to interferences, β-peaks have been used in some instances and, in addition, some elements have been excluded (those with atomic numbers $Z = 27, 36, 43, 54, 69, 72, 85-89$ and 91). The limits of detection are calculated for an analysis time of 5 min and a count rate of 2 000 counts s^{-1} using three different absorbers. About the same limits of detection could be obtained in a single analysis by using absorbers with three different foil thicknesses. Absorbers: A, 50 μm; B, 920 μm; and C, 2 000 μm.

Although further development of PIXE can be foreseen, *e.g.*, especially concerning the speed of analysis and an extension of the range of elements analysed by either using more than one detector or using complementary methods simultaneously, we consider that major progress, at least in the near future, will be made in the pre-treatment of samples.

TABLE I

ELEMENTS IN BLOOD PLASMA WITH NORMAL LEVELS ABOVE OR AROUND THE
DETECTION LIMITS

	Elements above detection limit								
	P	S	Cl	K	Ca	Fe	Cu	Zn	Br	Rb
Level, p.p.m. wet mass[11]	132	1 220	3 950	170	99	1.14	1.12	1.6	3.9	1.2

	Elements around detection limit						
	Ti	Ni	Ge	As	Se	Pt	Pb
Level, p.p.m. wet mass[11]	<0.04	0.042	<0.03	0.040	0.11	<0.04	0.043

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