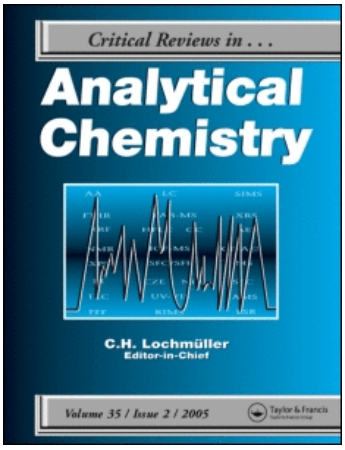

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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To cite this Article Khan, Md. Rashiduzzaman , Crumpton, Dennis and Johansson, Sven(1981) 'Proton-Induced X-Ray Emission Analysis', Critical Reviews in Analytical Chemistry, 11: 3, 161 — 193
To link to this Article: DOI: 10.1080/10408348108542731
URL: http://dx.doi.org/10.1080/10408348108542731

PROTON-INDUCED X-RAY EMISSION ANALYSIS:* PART II**

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TABLE OF CONTENTS

VII. Limitations and Improvements
- A. Background Radiation
  - 1. Bremsstrahlung
  - 2. Compton Scattering of Gamma Rays from Nuclear Reactions
  - 3. Environmental Background
  - 4. Background Due to Charge Build-Up
- B. X-Ray Detection — Limitations
  - 1. Detector Resolution
  - 2. Detector Efficiency
- C. Backing Materials

VIII. Applications
- A. Materials and Solid State Studies
- B. Geology
- C. Archaeology
- D. Liquids
- E. Biomedical
- F. Environmental Pollution
- G. Depth Profile Measurements
- H. Positional Analysis

IX. Comparison of PIXE With Other Analytical Techniques

X. Conclusions

Acknowledgments

References

* Part I appeared in Volume 11, Issue 2.

** Based in part on an earlier review by M. R. Khan. Atomic Energy Organization of Iran. Technical Report AEOI-58, NRC-76-37, 1976.

VII. LIMITATIONS AND IMPROVEMENTS

As discussed previously, the minimum detectable limit (MDL) and the efficiency of PIXE analysis depends on the characteristic X-ray peak to background ratio and the capabilities of the X-ray detecting system. Any discussion of the limitations and possible improvements for PIXE analysis must be based on a full understanding of these factors.

A. Background Radiation

The background radiation associated with X-ray production consists of:

1. Bremsstrahlung radiation
2. Compton scattering of gamma rays produced in nuclear reactions
3. Environmental background
4. Background due to charge build-up in the sample

1. Bremsstrahlung

A charged particle can produce bremsstrahlung when passing through matter, directly when accelerated in the Coulomb field of the nucleus or, indirectly, by secondary electrons produced by ionization. Since the energy loss by radiation for a charged particle in passing through matter is proportional to $(1/\text{mass})$,[2] it is expected that the electron contribution will be quite significant. Experimentally, one finds that the bremsstrahlung intensity is very high at the low energies and decreases rapidly as the energy of the radiation approaches T_m, the maximum energy a projectile can transfer to a free electron. For a 3 MeV proton, T_m is approximately given by $T_m = E/460 = 6.5$ keV, as discussed earlier. The radiations produced at the lower end of the bremsstrahlung spectrum are mainly the contribution of the secondary electrons, whereas their contribution is small at radiation energies greater than T_m. The higher energy bremsstrahlung is produced when the projectile experiences a large acceleration in a close encounter with a nucleus. The differential cross section for the production of bremsstrahlung photons of energy E_r by the projectile (A_1, E_1, Z_1) on a target (A_2, Z_2) is given by Alder et al.[148] as,

$$\frac{d\sigma_r^B}{dE_r} = C \cdot \frac{A_1 Z_1^2 Z_2^2}{E_1 E_r}\left[\frac{Z_1}{A_1} - \frac{Z_2}{A_2}\right] + \text{higher multipolarities} \quad (1)$$

The term $\left[\frac{Z_1}{A_1} - \frac{Z_2}{A_2}\right]$ arises from the interference between the radiation of the projectile and the recoiling nucleus. This implies that one can make the electric dipole radiation vanish by a suitable choice of projectile target configuration $\left[\text{i.e., when } \frac{A_1}{Z_1} = \frac{A_2}{Z_2}\right]$. In these cases, high multipolarities become important, but, according to Folkmann et al.[99] are of much less intensity.

Folkmann et al.[99] calculated the production of bremsstrahlung for indirect processes in two stages. First, the binary encounter approximation was used to calculate the probability that a projectile with energy E_1 will produce an electron of energy E in the energy range E_e to $E_e + dE_e$. Then they calculated the cross section for an electron of energy E to produce a photon of energy E_r to $E_r + dE_r$. Combining these two stages and integrating over all possible energy exchanges, they found that the cross section for the

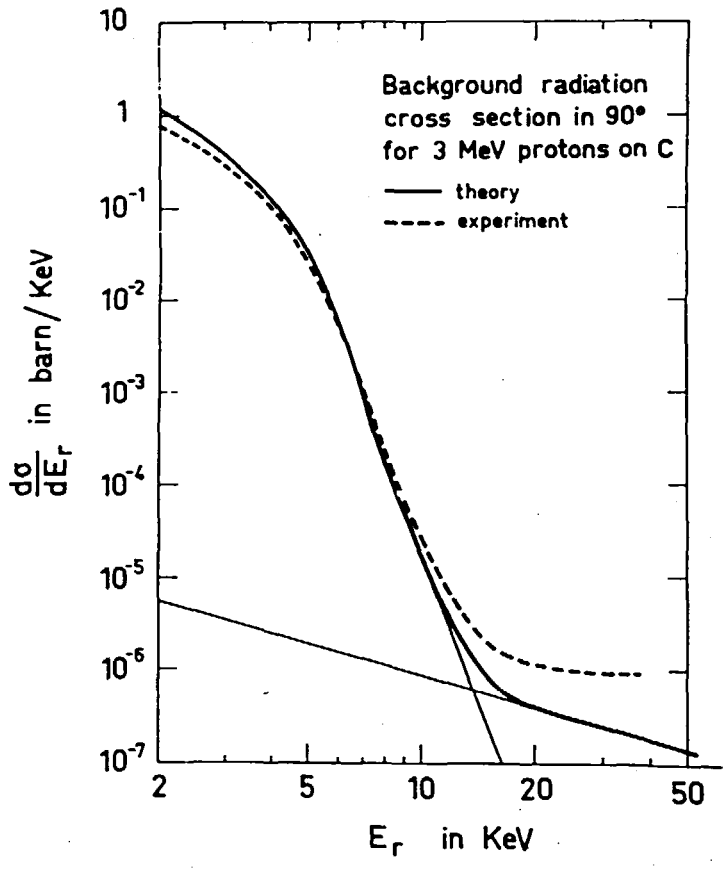

FIGURE 29. Experimental and theoretical background radiation cross sections for a thin sample. (From Folkmann, F., Gaarde, C., Huus, T., and Kemp, K., *Nucl. Instrum. Methods*, 116, 487 (1974). With permission.)

production of bremsstrahlung by the indirect process is proportional to E_i^4 and decreases as E_r^{-8}. Hence, the probability for the production of high energy photons by an indirect process is negligible. In contrast, the probability for the direct production of bremsstrahlung radiation varies as E_i^{-1} and E_r^{-1}, making the contribution of higher energy radiation along the spectrum very flat. The graph in Figure 29, reproduced from Folkmann et al.,[99] illustrates these points. In addition, it was found that for all practical purposes, the emission of bremsstrahlung photons is isotropic. Subsequent studies by Ishii et al.[100] have shown that the emission is anisotropic, as discussed in Chapter 4. The Auger electrons produced in the process of inner-shell excitation and de-excitation may also produce bremsstrahlung photons. However, the energies of these photons are very low and consequently do not offer a serious problem.

From the foregoing discussion, it is clear that the background level can to a certain extent be minimized. For example, if thin samples are employed, then the secondary electrons, which contribute the most to the bremsstrahlung spectrum, escape from the target — making very little contribution to the background. In addition, one endeavors to choose the projectile energy in such a way that the X-ray of interest of energy E_x is greater than T_m so that the large bremsstrahlung background from secondary electrons is again avoided. Finally, optimizing the angular position of the detector affords a useful decrease in the background.

2. Compton Scattering of Gamma Rays From Nuclear Reactions

If the sample matrix is such that the energetic protons induce excited nuclear states, then high energy gamma rays will be produced. Compton scattering of these gamma rays by the surrounding materials and in the detector itself produces a low-energy continuous background in the X-ray energy region. Fortunately, even for a low Z matrix, the production of nuclear excited gamma rays is small. However, one should be careful about the presence in the matrix of elements like ^{19}F, ^{23}Na, and ^{27}Al which exhibit large resonance reaction cross sections for protons of energy less than 3 MeV. In these cases, Compton-scattered gamma rays may be a serious source of background.

3. Environmental Background

Environmental background may arise from radioactive sources in a laboratory, from cosmic rays, natural radioactivity in the building materials, nuclear fallout, etc. Provided normal laboratory procedures are adhered to, the environmental contribution to the background can be assumed negligible except in extremely unusual conditions.

4. Background Due to Charge Build-Up

In the case of nonconducting samples, background arising from charge accumulation in the sample can be a serious problem. For thick samples, the charging is due to the protons which are brought to rest within the sample, thus producing a net in-balance of charge. When the protons pass through thin samples, the secondary electrons produced escape from the sample, thus leaving a net positive charge. The discharge of the samples produces bremsstrahlung photons of energies extending up to a few tens of keV of high intensity. This results in a drastic decrease of the peak-to-background ratio and a corresponding increase in the minimum detection limit. Moreover, due to the limited count rate of the detecting system, the increase in background counting rate restricts the use of beam currents to a few nA, and the accumulation time must be increased in order to obtain meaningful statistics on the required X-ray peaks.

A number of possibilities exist to reduce or eliminate this problem. One approach is to evaporate a small quantity of ultrapure, low-atomic-number-conducting material such as aluminum onto the surface of the sample to make a conducting layer. Papper et al.[61] successfully employed this approach to reduce the charging of their thick samples of compressed freeze-dried blood. They evaporated 200° A of pure carbon onto the surface, which resulted in a considerable reduction in background, affording an enhanced sensitivity (clearly shown in Figure 30). The authors suggest that any carbon impurities can be identified by analyzing a similar layer of carbon simultaneously evaporated onto a polymer backing.

Two other methods are described by Ahlberg et al.[145] In the first of these, an electron gun was employed with a commercial carbon filament. The filament was fastened to Plexiglas®, and electrical connections were made through the Plexiglas® to the filament. The filament was placed close to the sample and a bias of 7 V applied to give a filament current of 0.25 mA, which was found satisfactory to neutralize the charge produced on the sample by a 50 nA, 2 MeV proton beam. A perforated cap at + 100 V was placed over the filament to prevent the positive impurity ions reaching the sample. Similar arrangements with tungsten filaments were found to contaminate the sample severely with tungsten ions. In the second method, the pressure in the sample chamber was increased to about 10 μm when charging by 2 MeV protons ceased. Increased pressure in the chamber, however, produces additional uncertainties in terms of beam energy and contamination.

A novel approach has recently been reported by Mingay and Barnard,[149] which would seem to reduce the probability of sample contamination associated with the previous

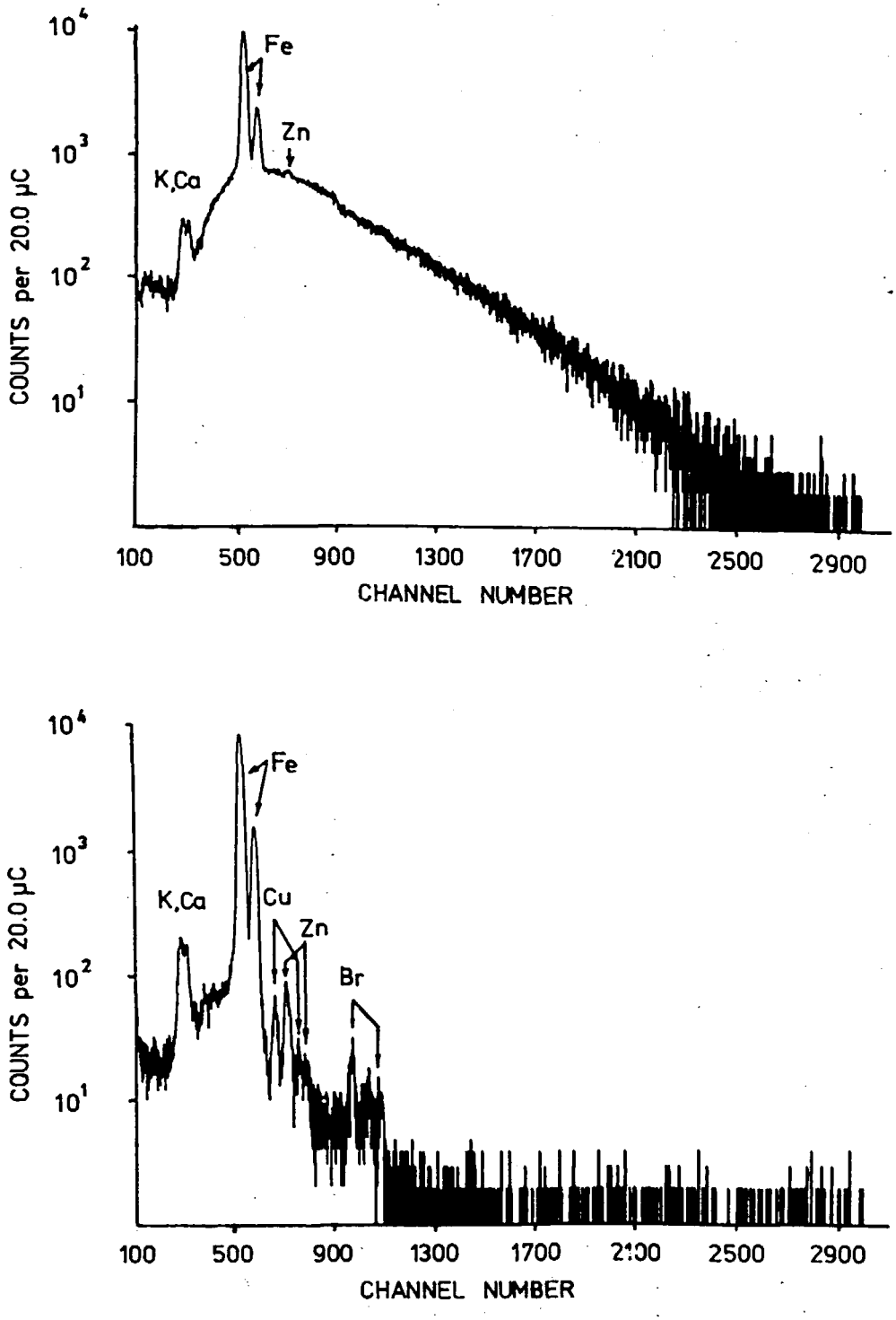

FIGURE 30. PIXE spectrum of thick whole blood showing the effect of charging, upper spectrum, and reduction in background obtained by coating the sample with carbon, lower spectrum. (From Papper, C. S., Chaudhri, M. A., and Rous, J. L., *Nucl. Instrum. Methods,* 154, 219 (1978). With permission.)

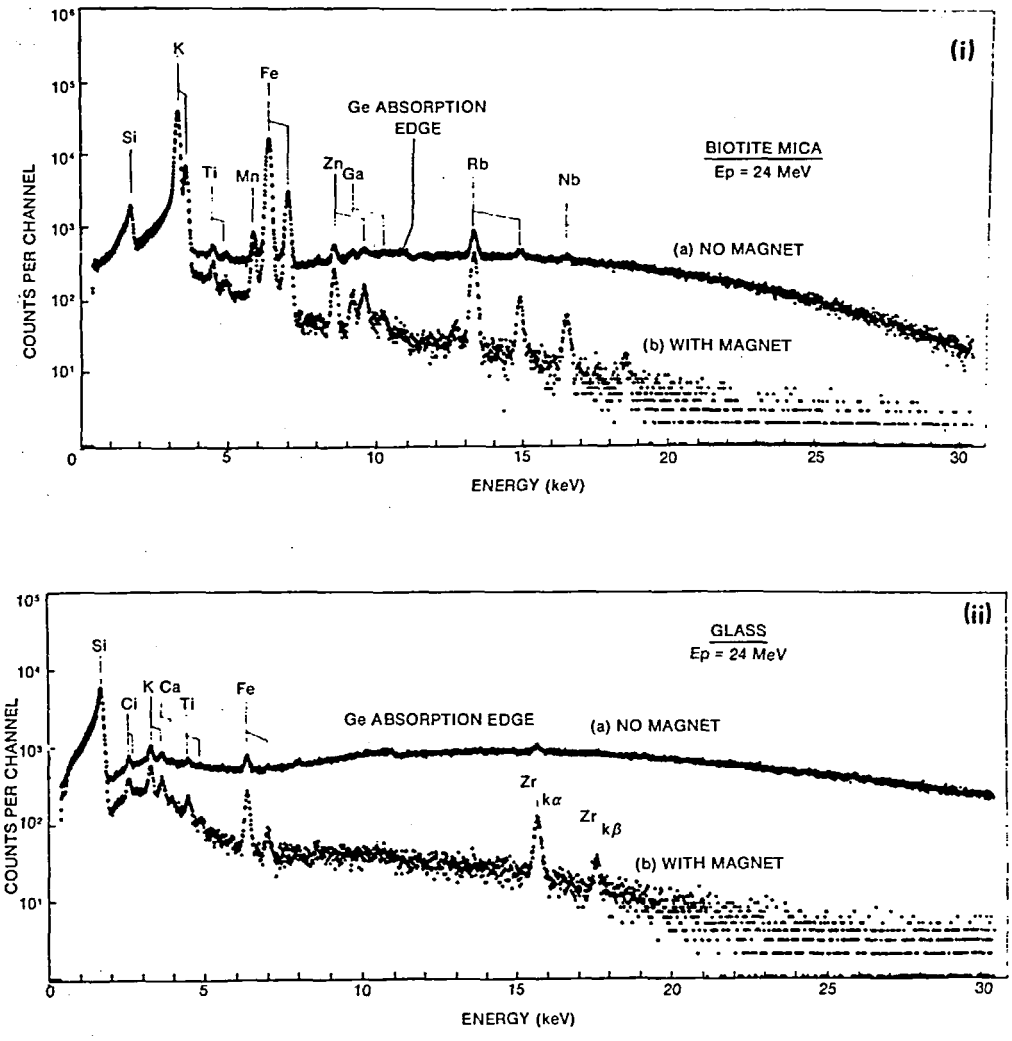

FIGURE 31. Spectra from the analyses of thick insulating samples showing the reduction in the continuous background obtained with magnetic suppression. (From Mingay, D. W. and Barnard, E., *Nucl. Instrum. Methods*, 157, 537 (1978). With permission.)

methods. In this application, a transverse magnetic field of some 0.03 T is provided in the plane of the target extending out to the target holder. Secondary electrons are thus returned to the target without being fully accelerated by the potential developed between the sample beam spot and earth. Spectra obtained using this system for thick samples are shown in Figure 31. A comparison was made between the magnetic suppression and electron flood gun suppression and it was found that very similar reductions in background were achieved.

B. X-Ray Detection — Limitations

The main limitations to the detection system are the resolution afforded by state of the art Si(Li) detectors, their efficiency, and the limited count-rate capability of the detector electronics. This later limitation has in part been circumvented by the use of on-demand beam pulsing.

1. Detector Resolution

Although the current interest in the use of PIXE for trace element analysis is due in part to the availability of high resolution Si(Li) detectors, the resolution is one of the main limitations of the detecting system. Detectors currently offer resolutions of about 150 eV to 200 eV at 5.9 keV X-ray energy, depending on the size of the detector and the price one is prepared to pay. Resolutions of this order do not allow the K X-ray peaks of the neighboring elements around sodium to be separated unless there are exceptionally favorable circumstances. There is an additional limitation due to the overlapping of some of the L X-rays of the heavy elements with the X-rays of the light elements. For example, the barium L_α X-rays at 4.47 keV are unresolvable from the K X-rays of titanium at 4.51 keV. Additional information in terms of K_α/K_β or L_α/L_β intensity ratios or the presence of the L_γ line of barium is required to distinguish between titanium and barium. The exploded view of the spectra from different elements shown in Figure 2 shows the overlap of the K and L spectra. The use of a crystal spectrometer, together with a Si(Li)/Ge(Li) spectrometer, has been demonstrated by Willis et al.[150] and Watson et al.[151] as a possible approach to solving these difficulties. These limitations, however, often are less serious that one would expect at first sight due to the fact that these elements are not often found present together in the same sample. A more frequent problem is the overlapping of the K_α and K_β radiation of neighboring elements. This problem can be resolved sufficiently by knowing the K_α/K_β ratios which are invariant to the energy and mode of excitation, values of which can be found in the literature.[124-131]

On the other hand, $L_\alpha/L_\beta/L_\gamma$ intensity ratios depend both on the excitation mode and the projectile energy. Theoretical calculations may be made from the tables of Choi et al.[46] for the plane wave born approximation, McGuire[152] for the binary encounter approximation, and Hansen[50] for the constrained binary encounter approximation. A number of experimental ratios at different projectile energies have been reported in the literature: Khan,[153] Tawara et al.,[154] Close et al.,[155] Shabason et al.,[156] Akselsson and Johansson,[129] and Abrath and Gray.[157]

2. Detector Efficiency

The X-ray detector efficiency also imposes limitations on the detectability of X-rays and the overall efficiency of the system. The efficiency curve, Figure 10, clearly shows the fall in efficiency of a typical Si(Li) detector above 20 keV and below 5 keV. The fall in efficiency at low X-ray energies is due to the increased absorption of the soft X-rays in the thin detector window and dead layer. Coupled with this, the absorption of low energy X-rays in the exit window of the sample chamber, which separates the detector from the chamber vacuum, makes it increasingly difficult to detect X-rays arising from elements below atomic number $Z = 11$. To overcome this limitation, detectors can be obtained, the fabrication of which is such that they can be used inside the vacuum chamber. The use of so-called "windowless' detectors then becomes a real possibility and has long been advocated. In both cases, however, protons backscattered from the sample into the detector can swamp the electronics and be a real nuisance. The successful use of windowless detectors for the detection of oxygen K X-rays has been reported by Musket and Bauer.[158] The main hindrance to the use of windowless detectors is that the vacuum system must be extremely clean, which can be very difficult to achieve in many instances due to the nature of the samples.

The problem of low efficiency at high energy may be solved by the use of an intrinsic detector or a planar Ge(Li) detector. Both have good efficiency up to 100 keV and possess good resolution. The efficiency curve for a 5 mm Ge(Li) detector is shown in Figure 32. Note the discontinuity at the Ge K absorption edge at 11.1 keV, which is produced by significant absorption in the germanium dead layer near the entrance window.

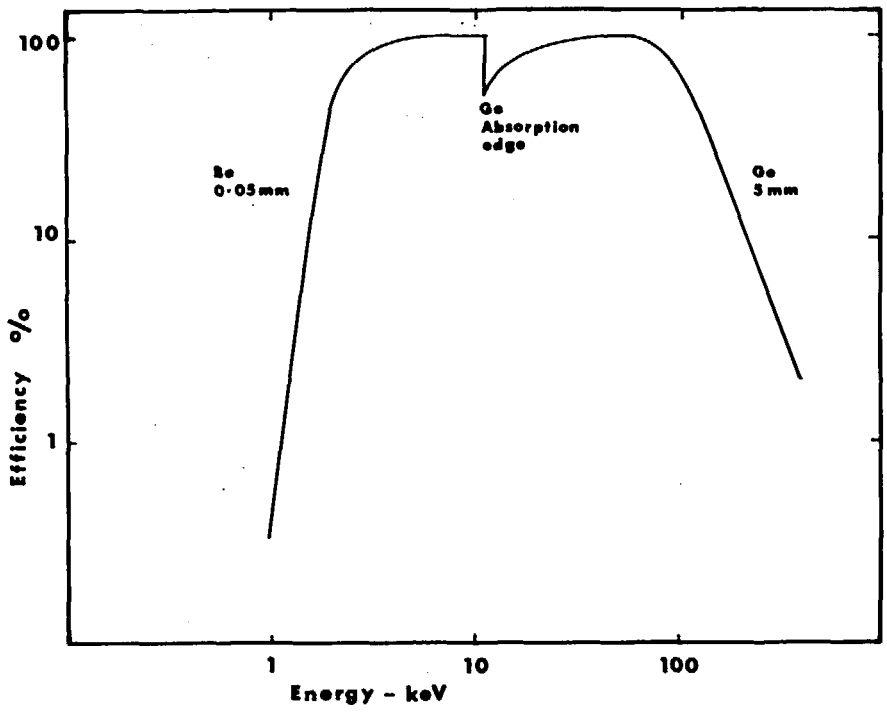

FIGURE 32. The variation of efficiency of a Ge(Li) detector with X-ray energy for a 5 mm thick crystal with a 0.05 mm thick beryllium window.

C. Backing Materials

In order to facilitate the analysis of thin samples, a supporting backing material is required. Materials suitable for use as a backing support should, as far as possible, have the following characteristics:

1. Low atomic number, Z
2. Relatively inert to chemical solutions containing samples
3. High purity
4. High mechanical strength
5. Good electrical and thermal conductivity

The backing material must be of a low atomic number so as not to produce X-ray lines which may interfere with the X-rays from the elements of interest. The X-rays from the backing material which contribute to the general background must be of low intensity to give optimum peak-to-background, and hence sensitivity, so as not to contribute significantly to the count-rate capability of the detector. It must be relatively chemically inert since many of the samples are deposited from solutions which are strong acids or bases. High mechanical strength is important to facilitate ease of handling and high purity so that the best analytical results can be obtained.

For greater efficiency of analysis, one generally aims to use a maximum beam current to obtain maximum X-ray yield in a minimum of time. The sample heating, due to the energy loss of the protons in the sample, often sets severe limitations on the use of high currents. Since the samples are in a vacuum, evaporation takes place at much lower temperatures than at normal pressures; consequently, sample heating may result in the differential evaporation of elements from the sample. In extreme cases, total evaporation

of the sample and deformation of the backing material results. Any attempt to increase the backing material thickness to act as a heat sink meets with little success since the background signal increases almost linearly with the thickness of the backing material.[12] Moreover, as the thickness is increased, impurities in the backing materials increasingly interfere with the signal from the sample. Finally, good electrical conductivity is important to prevent charge build-up in the sample, as discussed earlier.

There are two types of backing material currently in use, ultrapure foils like carbon and aluminum, and commercially available plastic materials. Carbon foils of thickness 20 to 50 $\mu g/cm^2$ are the most widely used backing materials onto which thin samples are deposited, either for elemental analysis or for cross-section measurements. For measurements requiring high sensitivity, 20 $\mu g/cm^2$ carbon foils have been used by Johansson et al.,[1,2] Gordon and Kraner,[159] and Herman et al.[160] Herman et al.[160] have made a comparison between commercially available carbon materials. Thin films of carbon were prepared by vacuum evaporating them onto microscope slides covered with a thin layer of detergent material. The carbon foils were then floated off the slides on immersing in warm distilled water. Foils produced in this manner were collected onto suitable frames and analyzed. The study showed that the main impurities were iron, copper, and zinc with traces of nickel, and that great care must be taken in the preparation so as to avoid contamination. They concluded that by careful choice of backing foil, the sensitivity for certain elements could be enhanced considerably.

Aluminum foils have good electrical and thermal conductivity, but, at the thicknesses required, lack mechanical strength. They are available commercially in ultra high purity form, but only in limited sizes. In addition, being a higher Z material compared to other backing materials, aluminum produced significantly more bremsstrahlung. Its own characteristic radiation may also be a nuisance. Commercially available plastics are widely used as a backing material for routine analysis. They are much thicker than carbon foils and are nonconductors of heat and electricity. They have very good mechanical strength and are obtainable in high purity form. Due to charge build-up and heating problems, use of them is limited to beam currents of a few nanoamperes.

A wide range of different backing materials, including carbon, aluminum, graphite, mylar, kapton, millipore, formvar, and several other polystyrene and plastic materials, have been studied by several workers: Thomas et al.,[15] Mangelson et al.,[10] Gordon and Kraner,[159] Valkovic et al.,[63] Flocchini et al.,[12] Barns et al.,[16] Folkmann et al.,[99] and Walter and Willis.[13] Gordon and Kraner[159] studied the suitability of 50 $\mu g/cm^2$ carbon foil, aluminum foil, thick reactor grade graphite, mylar, and kapton foil, and recommended carbon foil as the most suitable. Flocchini et al.[12] studied the sensitivity of alpha particle-induced X-ray analysis for different backing materials, using 700 and 800 $\mu g/cm^2$ mylar, kapton, and Teflon®, using a 30 nA beam of 50 MeV alpha particles. They found that for the same thickness, mylar and kapton produce similar backgrounds, while Teflon® gives a more intense background.

Walter and Willis[13] have compared different organic foils, including cellulose acetate, polystyrene, mylar, millipore, nuclepore, and formvar. Though formvar was found to produce the least bremsstrahlung (Figure 33), they recommended Nucleopore® as the best material overall. Bearse et al.[111] reached the same conclusion in a similar study. In addition to its low background Nucleopore® was found to have low impurities, was easy to handle, and was heat resistant. Formvar is fragile and difficult to handle, and its use was recommended only in cases where extreme sensitivity is required.

Valkovic et al.[63] have demonstrated that the strength of plastic materials can be combined with the thermal and electrical conductivity of aluminum to make a satisfactory target which possesses all the desired properties. The technique involves producing a thin, 50 $\mu g/cm^2$ film of formvar onto which is evaporated a 100 $\mu g/cm^2$ high-purity aluminum film. The resulting material possesses good mechanical and thermal

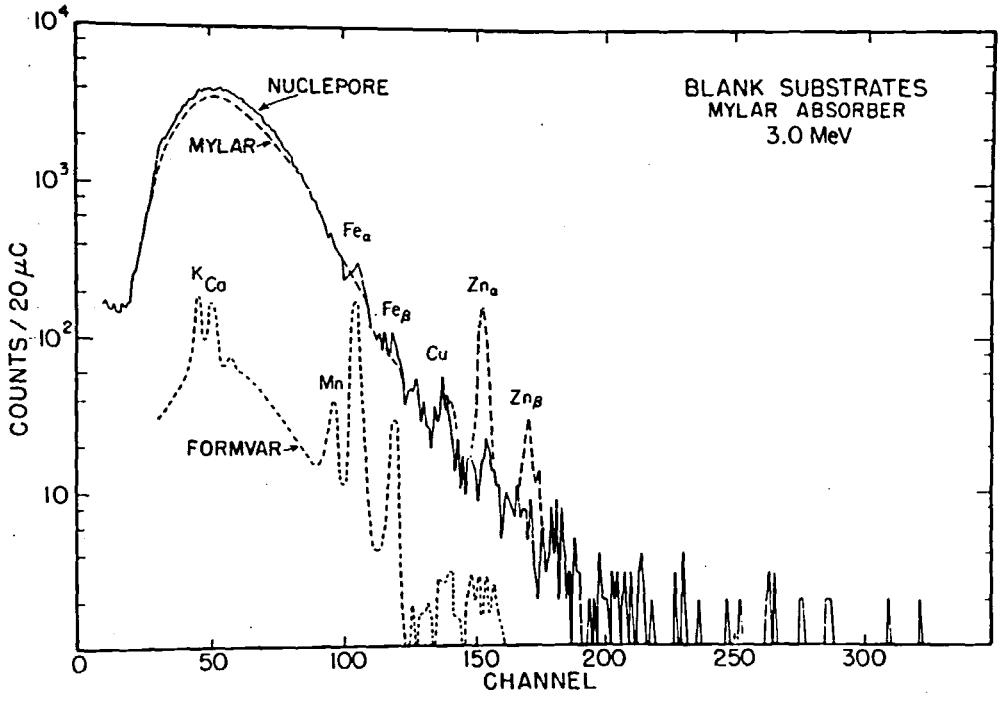

FIGURE 33. Comparison of spectra obtained from three different blank substrate materials. (Reprinted with permission from *Analytical Chemistry*, 46, 843, 1974. Copyright by the American Chemical Society.)

properties, in addition to being relatively thin and of low atomic number. A similar approach has been used with success by Jolly et al.;[66] they employed carbon-impregnated polycarbonate backings which withstood several microamps of beam.

The choice of backing material obviously depends on the application, as discussed by Campbell,[101] but the polycarbonate backings seem to have been most widely adopted. The interesting development evaluated by Jolly et al.[66] would appear to remove the current limitations normally associated with these backings and make them even more universally acceptable, provided that the carbon does not significantly increase the impurity background.

VIII. APPLICATIONS

The importance of PIXE as a simultaneous multielemental analytical technique of high sensitivity is illustrated by the diversity and range of applications which can be found in the literature, of which a representative selection is presented below.

A. Materials and Solid State Studies

Chemin et al.[161] analyzed implants of S and P in a Ge crystal using 500 keV protons and reported a sensitivity in excess of 10^{14} atoms/cm^2, while Thomas et al.[15] studied thin films of glass with 1 MeV protons with a sensitivity of the order of 0.1 μg/cm^2 for the elements S, Ge, As, and Te. Boron films were also examined using a 2 MeV beam.

Gray et al.[162] have measured Zn implanted in GaAsP using a 1.4 MeV proton beam. Detection limits of 10^{11} atoms/cm^2 for Zn and 10^{13} atoms/cm^2 for As in silicon were achieved. Cairns[163] measured the boron concentration profile implanted in silicon using 100 keV protons, and also reported[164] the use of a crystal spectrometer and a 200 keV beam to detect 14 ppm boron in nickel based alloys. The concentration of Zn in a thin

epitaxial layer of InSb has been determined by Pabst and Schmid[165] using 1.3 MeV protons. In order to observe the zinc K_α and K_β lines, it was found necessary to selectively reduce the intensity of the indium and antimony L X-rays from the sample, using a Nb absorber foil. The zinc concentration was obtained by reference to a bulk zinc sample, a zinc-silica film, and the In and Sb K lines of the epilayer, and found to be 0.70, 0.60, and 0.74%, respectively.

Trace elements present in synthetic glass have been determined by Garten et al.[166] in a detailed study of thick sample analysis. Samples were analyzed with a 20 nA beam of 2.5 MeV protons, with a beam spot size of $150 \times 150\ \mu m^2$. The distribution of the elements in the samples was also obtained with a resolution of 1 mm and found to be homogeneous with a standard deviation of 2%. The sensitivity for the lanthanides was compared directly with that obtained using the scanning electron microscope and electron probe microanalyzer and found to be much higher,[167] resulting in a lower detection limit for the experimental conditions employed. Studies of the migration of Si, Ga, Cl, and Fe impurities in graphite specimens when heated to 3800° C have been made by Shroy et al.[168] using a proton microprobe. The beam was brought out into the air through a 25 μm pinhole and traveled 3 mm before encountering the sample, which had been suitably heat treated. The sensitivity was obtained by analyzing graphite samples of known impurity concentrations and dried salts on filter papers. Sensitivities of $\leqslant 5$ ppm were obtained for elements of atomic number greater than 12 with a 2-min irradiation. These migration studies are of importance in relation to safety studies of high-temperature, gas-cooled reactors. The results indicate that the impurities migrate from the hotter regions to the cooler regions accompanied by vaporization and discrete condensation. The authors report that the work is to be extended to include the important fission fragments, and their behavior.

B. Geology

The zirconium to hafnium ratios in zircon extracted from different rocks has been studied by Van Grieken et al.[169] The material was powdered, from which samples of less than 1 mg were prepared by gluing the powder onto a polyethylene backing. These samples were analyzed and the Zr to Hf ratio established to within 6%. Annegarn et al.[170] have employed PIXE successfully to study single grains of separated mineral phases. Single grains of gold, zircon, and chromite, obtained from horizons in the Klerksdorp and East Rand goldfields, were mounted onto 2.5 μm mylar with starch solution. These were then irradiated with a 2 mm uniform beam of 3 nA. The nature of the samples, which are essentially thick for 3 MeV protons, was such that no problems relating to charge build-up were observed. A typical emission spectrum from a single zircon of diameter 100 μm and from 20 grains of zircon is shown in Figure 34. It should be noted that the Hf L_α and L_β lines fall in the same region as the Cu K_α and K_β and can give rise to interference problems. This study has shown that the elemental ratios commonly employed as geochemical indicators can be determined with precision using PIXE and that results enable different horizons to be distinguished.

PIXE analysis has been applied by Kirchner et al.[171] to the determination of sulfur in ferromanganese nodules found on the deep ocean floor. These nodules are considered a potential source of mineral reserve containing copper, nickel, cobalt, and molybdenum. For these complex matrices containing sulfur present in low concentrations, ~0.1 and 0.2%, normal techniques such as photoelectron spectroscopy have proved inadequate. Heterogeneous fragments of the nodules were bombarded with a 1 MeV proton beam covering 5 mm^2 area of the surface. The use of a low-energy proton beam, together with a carbon diffuser foil reduced the bremsstrahlung background considerably. It was found that when fragments containing pale yellow embedded granules were analyzed, the relative Si/S ratio obtained was almost the reciprocal of that normally obtained; in

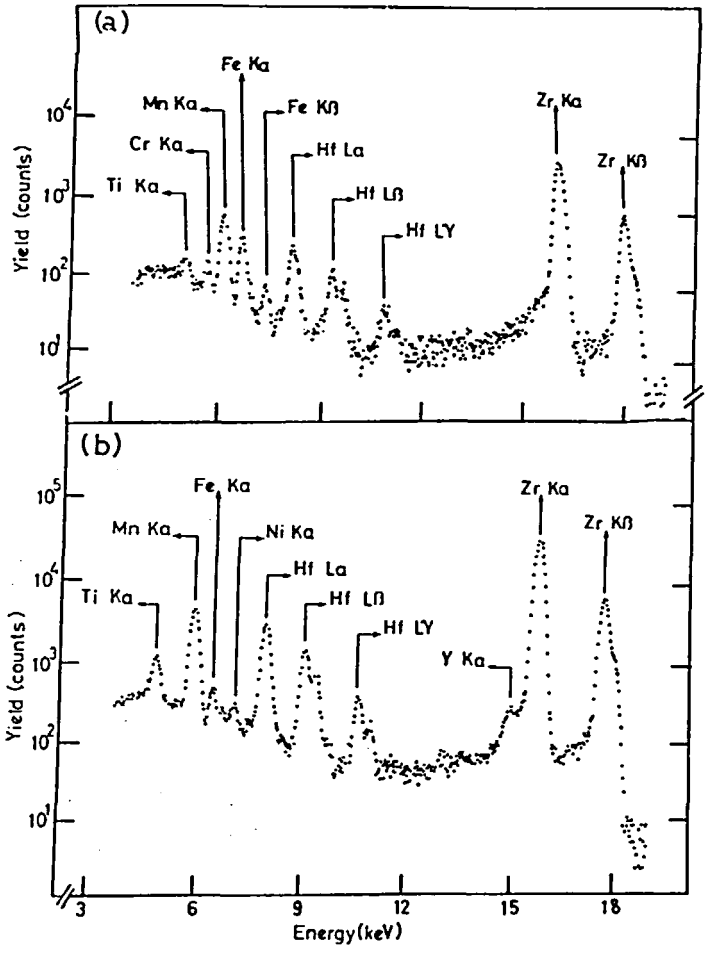

FIGURE 34. Proton-induced X-ray emission spectra of a single zircon of diameter ≃ 100 μm (a), and a bulk zircon sample of 20 grains (b), obtained using a 2 nA, 3 MeV, proton beam and an irradiation time of 15 min. (From Annegarn, H. J., Keddy, R. J., Madiba, C. C. P., Renan, M. J., and Sellschop, J. P. F., *Adv. X-Ray Anal.*, 21, 245 (1977). With permission.)

addition, the major cations Mn and Fe were not evident. The authors concluded that the sulfur is present in the elemental form rather than as an anionic species, contrary to previously accepted views. Verification of this unexpected result was obtained by examining the X-ray photoelectron spectra from the sample and samples of iron sulfate, sulfide, and elemental sulfur.

Raith et al.,[67] in collaboration with the Institute of Mineralogy of the Ruhr-Universitat, Bochum, have analyzed a variety of quartzes. Thick samples of 20 to 30 μm were analyzed with 2 MeV protons, and a number of trace elements with atomic number less than 30 were identified.

C. Archaeology

The wedge-shaped pendants from the bronze age, in the custody of the Historical Museum at the University of Lund, have been analyzed by PIXE for their elemental concentration by Ahlberg et al.[172] The presence of significant amounts of gold and silver

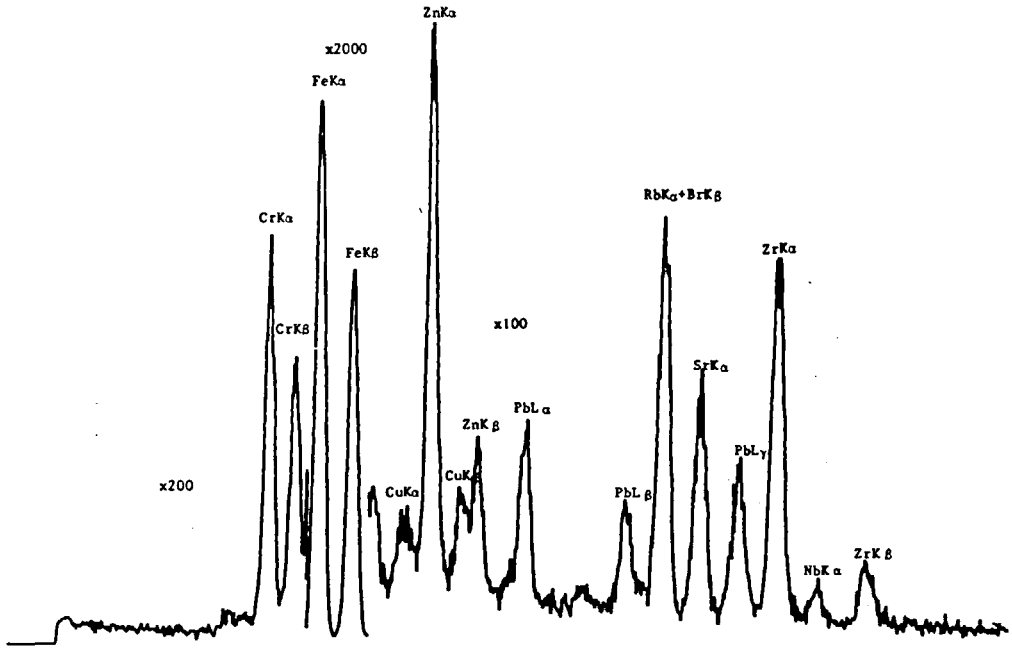

FIGURE 35. Spectrum obtained by bombardment of fourth century pottery in a helium atmosphere (From Baijot-Stroobants, J. and Bodart, F., *Nucl. Instrum. Methods*, 142, 293 (1977). With permission.)

suggests that these pendants could have been employed as touchstones for these precious metals. Gordon and Kraner[159] have detected chromium and manganese in the presence of significant quantities of iron in an archeological sample using the critical absorber technique.

Baijot-Stroobants and Bodart[173] have employed PIXE combined with Mössbauer spectroscopy to examine ancient pottery from different archeological sites in the Namur region of Belgium. Two sample techniques were employed. In the first, glazing and clay powder were compressed into thick homogeneous samples and irradiated in a vacuum. In the second, the pottery was analyzed nondestructively by bringing the beam into a helium atmosphere containing the pottery and irradiating it directly. Elements ranging from iron to zirconium were detected (Figure 35) and the concentrations determined by comparison with a standard of known composition analyzed under the same experimental conditions. The usefulness of the analysis in the helium atmosphere was limited by local elemental variations in the pottery. Statistical evaluation of the results of the analysis in vacuum indicated that their was no significant difference in the elemental composition, at the 60% confidence level, of the clay and the glazing of different centuries, with the exception of Pb, as can be seen from the results presented in Table 9. The Mössbauer measurements were made to establish the oxidation states of the iron present in the glazing which can be related to the firing conditions.

D. Liquids

The analysis of water for its trace elemental concentrations is of importance for a variety of reasons including biomedical, environmental, and industrial. Peisach et al.[174] analyzed a drop of water which was placed on a carbon foil and allowed to evaporate. Subsequently, metals were extracted from a known quantity of water by forming chelated complexes with 2% ammonium pyrrolidine dithiocarbonate and extracted with isobutyl ketone at ph 4. An extraction efficiency of 80 to 90% was obtained for the

Table 9
ABSOLUTE CONCENTRATIONS (ppm) OF DIFFERENT ELEMENTS IN GLAZING AND CLAYS FROM DIFFERENT CENTURIES

	Second century	Fourth century		Sixth century
Element	Clay	Glazing	Clay	Clay
Fe	219×10^2	$(940 \pm 94) \times 10^2$	$(950 \pm 95) \times 10^2$	$(1060 \pm 106) \times 10^2$
Zn	57.4	167 ± 50.1	96 ± 30.76	221 ± 115.8
Pb	0.27	2.05 ± 0.8	0.72 ± 0.253	0.57 ± 0.047
Rb	72.7	62.8 ± 8.6	78 ± 5	72.8 ± 7.43
Sr	68.7	69.3 ± 8.2	83.6 ± 5.8	90.7 ± 10.5

From Baijot-Stroobants, J. and Bodart, F., *Nucl. Instrum. Methods*, 142, 293 (1977). With permission.

elements Cr, Fe, Co, Zn, Cd, and Pb. Lien et al.[88] analyzed 0.01 mℓ of water deposited directly on formvar foil, allowed to dry before analysis with 80 nA of 2.25 MeV protons. They detected eight elements at concentrations ranging from 0.079 ppm for Cu to 42.7 ppm for Ca and determined the detectability limits for ten other elements. To obtain the precision of the analysis, 15 samples were prepared from the same water sample and analyzed. The potential application of PIXE to water analysis has also been demonstrated by Sioshansi et al.,[175] who analyzed some 30 samples, doped with selenium oxide, and deposited onto kapton foils using a nebulizer.

A detailed study of the analysis of drinking water, using PIXE, has been made by Simms and Rickey.[120] Samples were prepared using a novel vacuum filtration system developed at Purdue University, as discussed earlier, which provides a significant concentration of the sample. Of the group, 76 elements heavier than aluminum were detected, the majority with a sensitivity of 0.1 to 100 ppb. In order to reduce the absorption of the light elements in the samples, samples were employed which had been prepared from 1 mℓ of water for the analysis of elements from sulfur through calcium, instead of the normal 30 mℓ samples. The overall precision of the measurements was determined to be of the order 10%, as revealed by a study of replicate measurements of samples prepared from standard solutions. The authors estimate that they could achieve a throughput of some 20,000 samples per year at a cost of about $20 per sample, and point out that this could be further reduced and sensitivity improved if the high quantity of calcium and sodium in the water could be reduced before the vapor filtration stage of sample preparation.

An alternative approach has been employed by Deconninck,[176] who analyzed liquid drops and jets at atmospheric pressure, thus reducing the uncertainties and problems associated with the evaporation of liquids from carbon foils and membranes. A 50 nA proton beam, of energy 2.5 MeV, was brought into the air by passing through a 2.3 mg/cm^2 aluminum window and traveled a few millimeters in air before encountering the liquid sample. The sensitivity was established by studying the response to standard solutions at concentrations of 500 ppm, and normalization was achieved using As as an internal standard. A sensitivity of 2 ppm was achieved for elements for Mn and Zn with an analysis time of 1 min. For the single-drop analysis, a rotation system reduced the loss of material due to boiling effects. The author employed the technique to successfully analyze biological liquids and pollutants in plant extracts such as Fern Oil. Lin et al.[23] also report the use of an external beam for liquid analysis and have made a detailed study of the change in sensitivity due to matrix effects. Their experimental arrangement is shown in Figure 36. A typical spectrum obtained from a prepared liquid sample

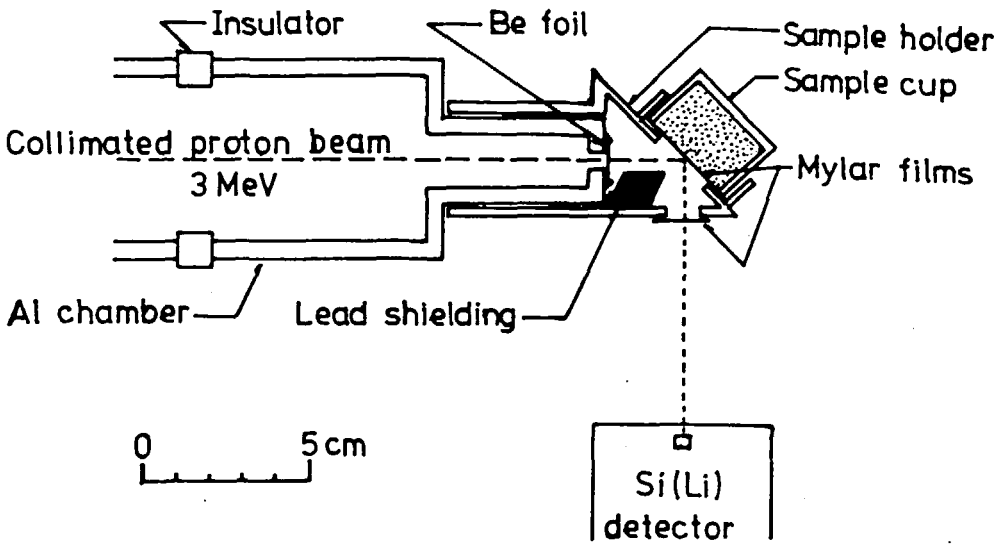

FIGURE 36. *Schematic diagram of a PIXE external beam facility. (From Lin, T. S., Luo, C. S., and Chou, J. C., Nucl. Instrum. Methods, 159, 387 (1979). With permission.)*

containing 100 ppm Ni and Sc, 150 ppm Cr, and 200 ppm Co is shown in Figure 37. It was found necessary to flush-dry nitrogen through the volume contained between the beam exit window and the sample to avoid troublesome Ar X-rays which result if this volume is air-filled. The Ca and Zn present in the spectrum is attributed to impurities in the mylar film covering the plastic sample holder.

Campbell et al.[177] have shown that the multielemental nature of PIXE makes it ideally suited to the determination of trace elements in wine. Samples were prepared from European and California wines by spotting a droplet of the wine, doped with 421 ppm of Cd and 71.6 ppm of Sr as internal standards, onto carbon foils. These were then analyzed with a 200 nA beam of protons of energy 2.3 MeV. Measurements on ten elements confirmed that the levels were below the maximum acceptable levels and that residues due to pesticides were well below the maximum allowed levels.

E. Biomedical

The multielemental nature of PIXE coupled with the small sample size requirements makes the technique ideally suited to biomedical sample analysis, and its potential has been demonstrated by a variety of authors using a wide range of samples. Kemp et al.[106] measured elemental concentrations in freeze-dried animal liver tissue, and detected 16 elements including As, Se, and Pb with a sensitivity of a few parts per million. Barnes et al.[16] compared the elemental concentrations in blood from malaria-infected mice to that from an uninfected control group. Statistically significant differences were observed. Bearse et al.[178] studied elemental variations in whole blood of gamma-radiation injured mice. Six elements were studied in 0.1 mℓ samples of whole blood which were ashed in a plasma asher, dissolved in acid solution, and placed on formvar foils to dry. To establish the reliability and precision of the method, 27 samples were analyzed with 150 nA proton beam of 3.75 MeV energy. A detailed study was then made of 90 samples obtained during an irradiation experiment. Results indicated that the concentration of K, Fe, and Rb vary with the red blood cell count. The Fe concentration, contrary to expectation, did not decrease to the same extent as the red blood cell count.

Boro and Cipolla[179] analyzed whole blood for K and Fe concentration with a 250 keV

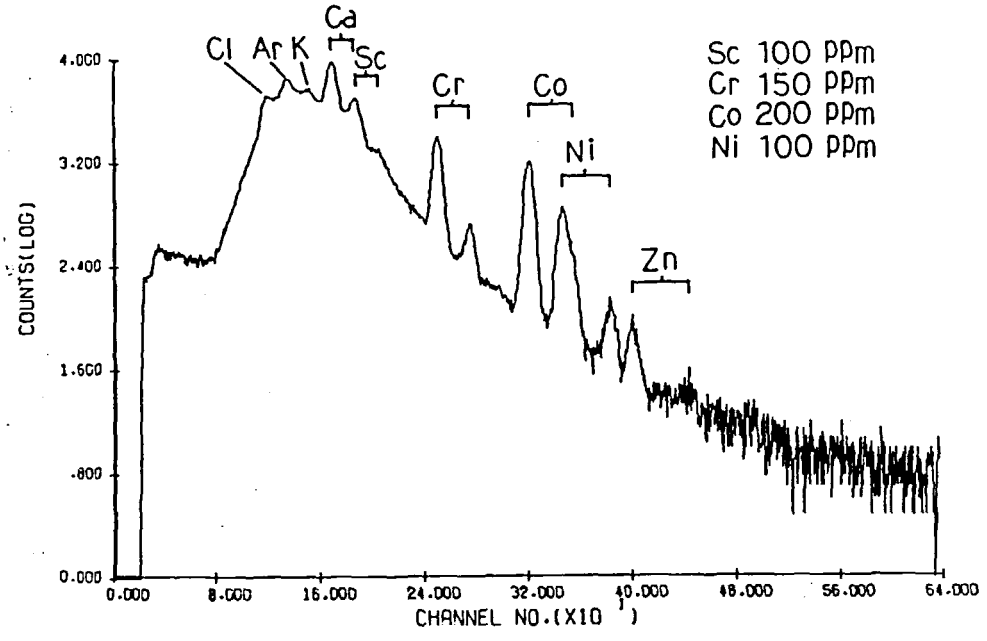

FIGURE 37. PIXE spectrum of a prepared liquid sample obtained with an external beam. (From Lin, T. S., Luo, C. S., and Chou, J. C., *Nucl. Instrum. Methods*, 159, 387 (1979). With permission.)

proton beam using a standard addition technique. Vis et al.[180] also employed the standard addition technique and investigated matrix absorption and enhancement effects in their study of sera of nephritic patients. Hasselman et al.[91] analyzed rat liver in their investigation into correlations between nutritional trace elemental input and liver concentrations. Walter et al.[114] discuss the application of PIXE to bioenvironmental samples and have studied samples which include human lung, organ sections, muscle, hair, whole blood, urine, and serum. Huda[24] analyzed thick plasma samples under both vacuum and atmosphere conditions. Dried and ashed plasma samples were pressed into a pellet and irradiated with a 10 nA, 2 MeV proton beam. For elements above Fe, the detection limit in air was found to be <1 ppm mass concentration. Absorption in the air prevented the observation of X-rays from elements below Fe.

Valkovic[181] discusses the application of PIXE analysis to the determination of the essential trace elements for higher animals and points out that of the 14 essential trace elements, the majority can be determined by this technique. Important correlations are found to exist between these trace elements in different tissues and blood with disease activity, and hence PIXE could fulfill an important role in this context.

A very careful investigation into the absolute concentration of elements in blood serum has been made by Barrette et al.[182] with a view to obtaining a maximum precision and reproducibility. The ease of obtaining small samples of blood and blood serum from patients makes it an ideal material for analysis, particularly as it is now established that Cu elemental levels in blood serum are correlated with certain cancers.[183,184] Forty samples were prepared from blood serum, doped with yttrium as an internal standard by depositing a small drop onto a mylar or formvar backing, and freeze-drying. These were then analyzed with a 20 to 30 nA beam of 3 MeV protons. The interelemental calibration was achieved by bombarding a range of standard solutions for 16 elements, and the relative yield was determined to be better than 2% for X-rays above the low energy

region. The mean elemental concentration of Fe, Cu, Zn, and Br were determined and compared with the Biology Data Book.[185] Problems were experienced with the zinc determination in the case of the mylar backings since they contain traces of zinc. A study of the sensitivity revealed that the only other elements capable of measurement were Ni, As, Rb, and Zr, and concentration limits were determined for these elements. The Ni concentration was determined to be <0.019 mg/ℓ and was barely visible in the spectrum. The authors draw attention to the work of Valkovic et al.,[63] who detected 0.27 mg/ℓ of Ni under similar experimental conditions. The sensitivities reported could be improved if enrichment of the trace elements was accomplished by the use of an alternative sample preparation technique such as ashing. Simpson and Dyson[186] have measured the concentration of Fe, Cu, Zn, and Pb in thick samples of human blood which are in reasonable agreement with accepted values, and also report[187] the study of Cu, Zn, and Fe in liver autopsy specimens.

Van Rinsvelt et al.[188] report on a comprehensive study aimed at correlating human diseases with trace element in-balance: 1500 autopsy samples from up to 15 different organs have been investigated with PIXE. Specimens were ashed at high temperature and samples prepared by mounting the residue between two formvar backings. The elemental data from this study, some 20,000 concentrations, have been stored in a computer file so that an automatic screening and correlation study can be executed. Initial data indicates that concentrations of Fe, Cu, Zn, Ca, and Cd varies with age in the kidney. Detailed programs under investigation include a study of Zn deficiency in children, arteriosclerosis, and molybdenosis.

Mangelson et al.[189] report a similar detailed study of tissue samples, taken at autopsy from Southwest Indians of the Pima Tribe. Tissue samples, including liver, spleen, aorta, kidney medulla, kidney cortex, abdominal fat, pancreas, and hair were ashed to reduce mass and eliminate inhomogeneities. The ash was dissolved in nitric acid and deposited on Nucleopore® filters for analysis. The accuracy of the sample preparation technique and analysis was confirmed by the analysis of NBS Standard Reference Material bovine liver and by atomic absorption spectroscopy. Although samples prepared from 500 mg of tissue showed inhomogeneities, differences in the elemental concentration of tissue types and individuals was established.

Cookson and Pilling[190] have exploited the potential of the Harwell microprobe to investigate the elemental distribution in hair. A 3 MeV proton beam 7×15 μm was scanned across the cross section of individual hairs and the X-ray yield from elements of interest determined. A somewhat larger probe, 100 μm, has been employed by Grodzins et al.[191] to determine the elemental concentrations along the length of a strand of hair with a lateral resolution of 150 μm. As pointed out by Campbell[192] in his discussion of progress in biological applications, relating trace elements in hair to medical conditions is very controversial due to surface contamination problems.

F. Environmental Pollution

It is in the field of environmental studies that the full potential of PIXE analysis has been exploited. The realization of the serious problems caused to the environment and to health by widespread pollution has prompted a series of extensive programs to monitor the environment on a regular basis. The first reported air pollution study using PIXE was made by Johansson et al.,[1] who detected 13 elements at the nanogram and subnanogram level on a carbon foil which had been exposed to the outdoor atmosphere for 24 hr. A 2.5 μA beam was employed and the irradiation time was 1 hr. Johansson et al.[86] have also made a careful study of their analysis system and the precision of their elemental analysis.

Mangelson et al.[10] have studied air particulates in samples collected from a copper smelter, and soils, plants, rodent tissue and air particulates collected from two specific regions to obtain details for an ecological baseline of the regions. The air particulates

were collected over 2-week periods using an Anderson minisampler. The backup Nucleopore® filter was used directly as a sample, and the particulates collected on the four impaction stages were transferred to a Nucleopore® filter for analysis. Nelson et al.[193] have used PIXE in conjunction with neutron activation analysis and proton scattering to determine quantitatively the elements found in air particulate matter. Samples obtained by filtering and impaction were analyzed with a 10 nA beam of 4 MeV protons. In the 12-hr size fractioned impactor samples, 15 elements above aluminum were observed. Time variations of these same elements were obtained with the 2-hr total filter samples. Akselsson and Johansson[34] are investigating the long-range transport component of aerosols in Sweden. Samples are collected on a single orifice cascade impactor allowing a size distribution with cutoff diameters 0.25, 0.5, 1.0, 2.0, 4.0, and 8.0 μm. Elemental analysis of the samples for 10 to 15 elements has established a data bank of 10,000 mass concentration values. Low Z elements are detected using the backscattered particles and fluorine using the (p,$\alpha\gamma$) reaction.

By far the most comprehensive and ambitious program is that of Cahill,[80] University of California, based on a 190 cm isochronous cyclotron employing 18 MeV alpha particles. In this program, 102 targets can be handled at any one time, mounted on 35 mm slide frames and introduced into the beam under computer control. Standards, blanks, and previously run samples are often included with the samples so as to verify the performance of the system. Between 600 and 1000 samples can be analyzed in a run of a normal day at a cost of approximately $10 per sample,[194] irrespective of the number of elements analyzed. Barfoot et al.[195] report on the air particulate pollution studies undertaken by Central Bureau for Nuclear Measurements (CBNM) and the University of Surrey. PIXE is used in conjunction with neutron activation analysis and Rutherford backscattering to determine elements present in time-resolved air particulate deposits. Minimum detection limits were determined to be typically 10 ng/m^3 of air sampled with a beam of 2 to 3 nA at 2 MeV and an analysis time of 25 min.

G. Depth Profile Measurements

In addition to identifying the trace elements present in a sample, it is sometimes of paramount importance to establish their position in the microstructure. For many of the light elements, nuclear (p,γ), or (p,$\alpha\gamma$), resonances can be exploited to probe the depth of the sample, as reported by a number of workers.[196,197] The possibility of employing PIXE to measure the depth distribution has been studied by several workers, but the smooth variation of cross section with energy suggests that extracting a unique estimate of the depth profile from the yield measurements may not be possible. With (p,γ) resonances, the technique is to vary the incident proton energy to obtain the depth distribution, and this was the approach proposed by Reuter and Smith[198] and Musket and Bauer[158] for PIXE. Reuter and Smith[198] showed that only one or two elementary distributions could be determined. An alternative approach reported by Pabst[19] and Feldman et al.[21] involves the variation of the target angle to reveal the concentration profile. Pabst[20] found strong oscillations in the depth profile which he overcame to some extent by comparing the experimental yields as a function of target angle with theoretical yields, and including angles close to zero. Ahlberg[199] reports depth profile measurements on the basis of the changes that occur in the K_α / K_β and L_α / L_β ratios, due to differences in their respective attenuation coefficients.

Kropf[200] has calculated the normalized yield v's proton energy for uniform copper layers and AgCuAg sandwiches. The similarity of the results underlies the difficulty of obtaining any useful information, other than the thickness of one layer, as reported by Benka et al.[201] Végh et al.[202] have studied the concentration profile of Zn in aluminum specimens containing the same Mg and Zn concentration (~1%) but annealed for different time periods up to a maximum of 65 hr. The zinc X-ray yield was determined as

a function of proton energy, from 0.8 to 2.8 MeV, from which the zinc profiles were obtained with an estimated precision of 15%, using an iterative algorithm procedure. The depth resolution achieved, 1.5 μm, is, however, significantly worse than can be achieved employing alternative methods such as Rutherford backscatter analysis and nuclear reaction analysis.

From the foregoing examples it is clear the PIXE has only limited application in determining depth concentration profiles in materials.

H. Positional Analysis

In contrast to the difficulty of obtaining depth distribution information, PIXE is ideally suited to the measurement of the trace element distribution across the surface of a sample with high spatial resolution, i.e., positional analysis. This results from the extremely small quantities detectable using PIXE analysis. This, together with a proton beam of very small dimensions, facilitates the highly sensitive elemental analysis of a number of positions on a sample in a reasonably acceptable analysis time. Proton beams of micrometer dimensions used in this manner are thus highly sensitive probes of microscopic structures.

Proton beams of microprobe dimensions can be obtained either by the collimation of the proton beam from an accelerator (Horowitz and Grodzins[203]) or by the use of quadrupole lenses suitably located along the beam line (Cookson et al.,[204] Nobiling et al.,[205] and Brune et al.[206]) Cookson[207] discusses in detail the production of MeV ion microprobes down to 2 μm in his recent comprehensive review article on nuclear microprobes and their use for analysis. In addition, a detailed summary is given of the work reported by a number of laboratories employing microprobes in conjunction with particle-induced X-ray emission analysis. This summary is reproduced in Table 10 together with the addition of a few recently reported applications. The advantageous characteristics of PIXE analysis, when combined with a microbeam facility, clearly produce a very versatile analytical technique which has already found wide application.

IX. COMPARISON OF PIXE WITH OTHER ANALYTICAL TECHNIQUES

Studies by several authors, including Johansson et al.,[1,2] Umbarger et al.,[234] Duggan et al.,[3] Watson et al.,[235] and Flocchini et al.[12] clearly show that alpha and proton-induced X-ray analysis have tremendous potential as rapid and efficient tools for multielemental trace analysis with sensitivities in the 10^{-9} to 10^{-12} g range. Johansson et al.[1] in their studies with 1.5 MeV protons evaluated the minimum detection limit (MDL) appropriate to their particular experimental configuration by determining the number of atoms, and hence the mass, which would produce 100 counts in the appropriate X-ray peak in the spectrum. For an incident beam of 5 μA and an accumulation time of 30 min, they found that the MDL was in the range 10^{-13} to 10^{-11} g for elements ranging from phosphorous to lead. It was further suggested that a MDL in the region of 10^{-15} g could possibly be obtained by the use of ultrapure backing materials coupled with improvements in the measurement technique.

The MDL clearly depends on the X-ray production cross section and the background against which the measurement has to be made. The use of multiple charged heavy ions, with their significantly larger X-ray production cross sections and reduced particle bremsstrahlung compared with protons, seems, at first sight, to be an obvious way of improving the sensitivity of the technique. This has been investigated in detail by Herman et al.[236] and Folkmann et al.[4] Herman et al.[236] made a systematic study using H^+ ions, 2 to 10 MeV; $^4He^{2+}$, 6 to 25 MeV; and $^{16}O^{5+}$, 6 to 40 MeV. Beam currents employed were 1.5 μA, 0.4 μA, and 0.05 μA, respectively. The reduction in beam current for the heavy

Table 10
APPLICATIONS OF PARTICLE-INDUCED X-RAY EMISSION ANALYSIS USING A MICROPROBE[207]

Specimens	Main elements	Resolution (μm)	Comments	Ref.
Biological				
Human hairs	As, Pb, etc.	7	Linear scanning across diameters	190, 208
Hamster cell	Si, P, S, Cl, K	≈2	Continuous linear scanning in air	209
Rose petal	$Z \leqslant 20$		Continuous scanning bright-up maps	210
Sections of human lung	Al	>25	Bright-up area maps and linear scans in air	191
Rat's eye and kidney	S, Cl, K, Ca	100		211
Human hairs	Cl, Ca, Fe, Zn, As, Hg	100—150	Scans along length	191, 211
Wheat leaves and seeds	Many from Si to Pb	10	Computer-produced area maps	212
Ant's head	Ca, Fe	10		213
Chick embryo section	K, Ca, Cr, Cu, Zn	<100	Step-by-step profile	214
Cataractous lenses of guinea pigs	S, Cl, K, Ca	200	Distribution along line through anterior and posterior poles.	215
Oyster shell	Mg, S, Fe, Zn, Sr, Br	75 or 150	Spectra from different sections sampled in air preliminary studies	216
Metallurgical				
Steels	Cr, Fe, Ni		Linear scans compared with C^a	217
Ceramic nuclear fuel	U		Linear scan compared with O^a	218
Steels	Fe, Cr		Bright-up maps compared with C^a, N^a, and O^a	219
Steels	Ti, Cr	13	Linear and area scans compared with C^a and N^a	220
Alloys	Ti, Cr, Fe, Ni, Cu, Mo	4	Linear and area scans compared with Li^a, Be^a, B^a, C^a, N^a, and Si^a	221
Amorphous alloys	Fe/Ni ratio trace elements	75 to 150	Preliminary studies in air	216
Geological				
Copper pyrites	Si, S, K, Fe, Cu	5	Spectra from different regions	222
Sphalerite	Ca, Fe, Zn	>25	Bright-up maps	203
Zircon crystals	Hf, Zr, Tl, Pb	15	Linear scans compared with U autoradiograph	223, 224
Monazite from "Giant Halo"	Superheavy elements?	~30	Peaks seen from several specimens	225, 226
Monazite from "Giant Halo"	No superheavy element seen	10 × 15	One of the above specimens	227
Monazite from "Halo"	No superheavy elements			228, 229
Perthite	K, Fe, Ga, Sr, Rb, Pb	~11	Linear scan; few ppm sensitivity	228, 229

Table 10 (continued)
APPLICATIONS OF PARTICLE-INDUCED X-RAY EMISSION ANALYSIS USING A MICROPROBE[207]

Specimens	Main elements	Resolution (μm)	Comments	Ref.
Microtektites	K, Ca, Ti, Cr, Mn, Fe, Rb, Sr, Zr	75 or 150	Preliminary compositional studies of samples <1 mm diameter	216
Archaeological				
Fragments of pottery 2200—2600 B.C.	K, Ca, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Y, Zr	75 or 150	Spectra from different sections sampled in air, preliminary studies	216
Miscellaneous				
Furnace slag	Si, Fe, Cu, Zn, Pb	5	Bright-up maps	204
Electronic component	Si, Ge	5	Linear scans	230
Corrosion layers	Fe, Cr	5 × 30	Depth profiles on taper sections compared with D^a, C^a, N^a, and O^a	231, 232
Soot	V, Fe, Ni	10 × 15	Linear scans	233
MgO doped with Al	P, Ti, Cr, Fe	140	Area map	191
Fe implanted in C	Fe	30	Area map	228
Graphite	Si, S, Cl, Ca, Fe, Mn, Cr	~40	Area maps, positional scans in air	168

[a] Measured by nuclear reactions.

From Cookson, J. A., *Nucl. Instrum. Methods,* 165, 477 (1979). With permission.

ions was necessary to maintain target integrity, and consequently offsets to some extent the larger cross sections of the heavier ions. It was observed experimentally that the H^+ beam at 2.2 MeV resulted in a significantly higher peak to background ratio than all other energies and ions, and therefore represents the most favorable choice.

Folkmann et al.[4] studied the sensitivity achievable using H^+, $^4He^{++}$ and $^{16}O^{7+or8+}$ ions with energies of 3 and 5 MeV/u. The K and L X-ray emission cross sections were measured for each ion for six elements in the range $29 \leqslant Z \leqslant 82$ and the background spectrum from typical matrices investigated using a pure Ge detector. The background radiation from a thin plastic foil for the three projectiles is shown in Figure 38. The enhanced background above 20 keV, due to nuclear gamma ray production and subsequently Compton scatter, is clearly seen. From these measurements, the sensitivity as a function of Z was obtained for the three projectiles (Figure 39), based on the criterion that the X-ray peak must be at least equal to the background for MDL. In agreement with Herman et al.,[236] they concluded that protons give a better sensitivity than the alphas or the ^{16}O ions, and, in addition, the lower energies favor the lighter elements.

In a study of the analysis of freeze-dried blood serum, Barrette et al.[182] compared the sensitivity obtained with protons with that of alphas. The energies of the protons employed was 2.25, 3, and 6 MeV, and of the alpha particles 6, 9, 12, and 16 MeV. Although the relative sensitivities at various bombarding energies could not be evaluated with precision, due to problems of beam location and sample nonuniformity, the authors were able to conclude that the best sensitivity was obtained with protons of energy 2 to 3 MeV.

Clearly protons of 2 to 3 MeV yield the highest sensitivity, but in making a choice of which particle to employ, ultimate sensitivity is not the only criterion. Other factors —

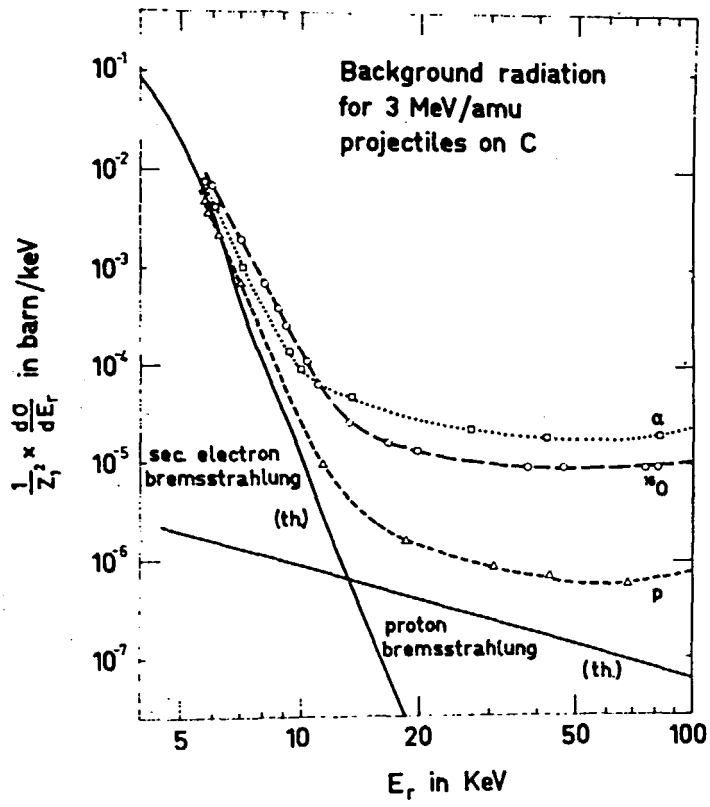

FIGURE 38. Experimental and theoretical background cross section for a thin plastic foil for different projectiles. (From Folkmann, F., Borggreen, J., and Kjeldgaard, A., *Nucl. Instrum. Methods*, 119, 117 (1974). With permission.)

such as the aims of the analysis, the cost, the convenience, and the availability of an accelerator — have to be considered. Ions other than protons have been used with great success and will continue to play an important role in the field of analysis. Bauer et al.,[237] for example, report the use of 30 MeV alpha particles for the general analysis of thick samples. They find the alphas more suited to this application than low energy ions since the stopping power and X-ray production cross sections are more precisely known at these energies. Hommsen et al.[147] have extended this work and determined the sensitivity for bulk analysis using 30 MeV alphas, obtaining a value of <100 ppm for elements with $Z > 20$. For bulk analysis of steel samples, Ahlberg et al.[145] also report a sensitivity of below 100 ppm, but using protons of energy 1 to 2.5 MeV.

The analytical capability of photon-induced X-ray analysis compared with particle-induced X-ray analysis has been studied by a number of authors including Cooper,[5] Perry and Brady,[6] Gilfrich et al.,[238] Goulding and Jaklevic,[239] Sheer et al.,[240] and Ahlberg and Adams.[8] Cooper[5] in a detailed study established the relative and absolute sensitivities for the analysis of trace elements in environmental samples employing alpha particles, protons, transmission tube X-rays, and 100 mCi radioisotope sources. Several standard environmental samples were analyzed using the different excitation modes, and a comparison of the signal to noise ratio of the X-ray peaks was made. For particle excitation the sensitivity was found to improve as the particle energy decreases, the optimum sensitivity being obtained with protons of energy 2 to 4 MeV, in agreement with other studies. The sensitivities obtained with photon excitation was found to be superior

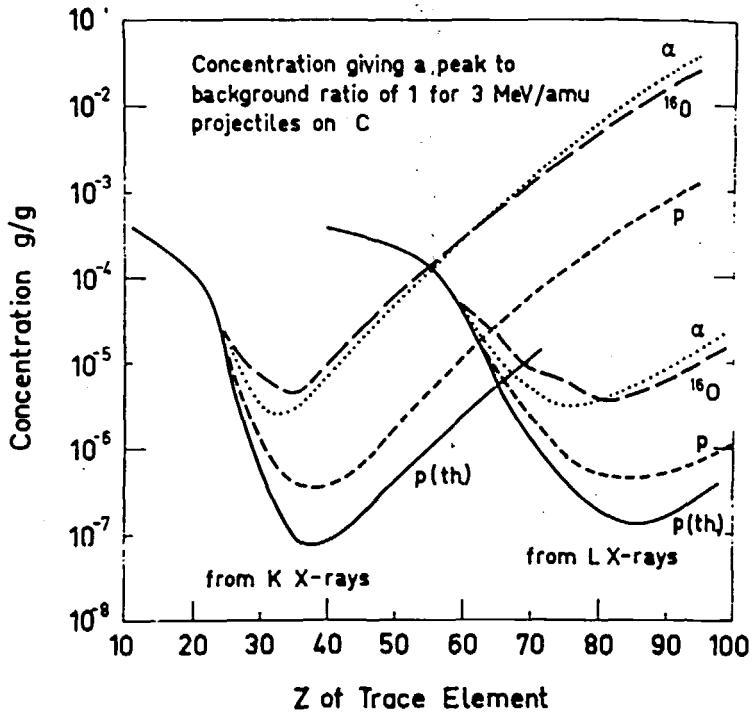

FIGURE 39. Minimum concentration of trace elements detectable for different projectiles on a thin carbon matrix, based on a signal to noise ratio of one. (From Folkmann, F., Borggreen, J., and Kjeldgaard, A., *Nucl. Instrum. Methods*, 119, 117 (1974). With permission.)

to those obtained with high-energy alpha particles, in agreement with the finding of Perry and Brady.[6] For proton excitation, Cooper found sensitivities similar to those obtained using photons — that is, about 1 to 5 ppm in environmental samples for elements V through to Mo. He concluded that the practical advantages associated with photon excitation such as cost, availability, and versatility make photon excitation a more attractive analytical technique. It should be noted, however, that Cooper did not attempt to optimize the system for maximum sensitivity and indeed commented that making valid comparisons between the techniques was a major difficulty since the normal sample requirements for the two techniques are so different. Photon measurements are usually made on large samples ($>$g) in air, while proton work is most suited to very small samples ($\leqslant$mg) on thin backing materials analyzed in vacuum.

Gilfrich et al.,[238] in their detailed study of the comparison of excitation sources for particulate air pollution, investigated the detection limits achievable (for K, Cu, Br, and Au,) using X-ray tubes, radioisotopes, 5 MeV protons, and alpha particles. Using optimum excitation conditions and energy dispersive spectrometry, they found the proton sensitivities two orders of magnitude better than other excitation techniques. Goulding and Jaklevic[239] have also compared the sensitivities of particle and photon excitation. The application considered was the analysis of some 30,000 air particulate samples per year, thus restricting the analysis time to 10 min. The comparison was made between protons of energy 2 and 4 MeV and Ti K_α, Mo K_α, and Sm K_α characteristic X-rays excited by the tungsten radiation from a pulsed X-ray tube. Both systems were found to yield detection limits around 1 ppm, with the sensitivity for protons being somewhat better under ideal conditions for this type of sample. They also observed an unknown source of background radiation in the photon case, removal of which would

improve the sensitivity. The dependence of the sensitivity on the sample matrix for proton and photon excitation has been studied by Scheer et al.[240] Sensitivity calculations based on measured backgrounds from 500 $\mu g/cm^2$ blank Höstaphan foils indicate that the sensitivity for PIXE is an order of magnitude greater than for XRF for the majority of elements, as is shown in Figure 40. However, analysis of samples containing about 30% KCl was found to produce a significant increase in the PIXE background, particularly from 9 keV to 12 keV and below 5 keV, reducing the sensitivity to the same order of magnitude as XRF. The higher background is reported to be due to Compton scattered radiation, higher energy bremsstrahlung from heavier matrix elements, and pulse pileup. The authors conclude that XRF should be considered as a complementary technique, which for certain matrices has more favorable sensitivities for $Z < 20$, and similar sensitivities $Z > 20$, provided the sample area is large enough.

The situation regarding the appropriate choice of excitation source specifically for the light elements has been investigated by Moriya et al.[241] Adopting a similar approach to Folkmann, calculations were made of the background radiation to be expected from thin samples of Be, C, and Al, using 150 keV and 2 MeV protons. From these calculations and a knowledge of the X-ray emission cross sections, the concentrations of the elements giving a peak to background ratio of one were calculated. The results of these calculations are shown in Figure 41. For $Z \leqslant 18$, the sensitivities are significantly higher in the case of the 150 keV protons than for 2 MeV protons. As noted by the authors, the presence of a significant X-ray line of slightly higher energy than the trace element sought will reduce the sensitivity because of the low energy tail in the spectrum. Similar calculations relating to characteristic Mn K X-rays based on measured backgrounds for Be and C matrices indicate a poorer sensitivity for photons. Confirmation of these calculations were obtained by comparing the spectra obtained for NBS standard orchard leaf with the various excitation modes. The authors conclude that for relatively large samples and high-intensity radioactive sources, XRF is competitive with PIXE, but for small samples proton excitation is more sensitive.

Ahlberg and Adams[8] have studied the sensitivity obtainable for air particulate matter using 2.3 and 5 MeV protons, and K radiation photons from Ti and Mo, obtained as secondary fluorescence radiation using appropriate secondary fluorescors and a tungsten anode X-ray set. Three large area filter samples were analyzed, which had sampled between 15 and 1700 m^3 of air, and one mylar foil, 0.35 mg/cm^2 thick and 0.7 mm diameter, which had sampled 1 to 3m^3 of air. In the case of the filters, it was found that protons and photons yield comparable results, but for the small mylar foil sample, the sensitivity with protons is 30 times that obtained with photons. The authors conclude that for the larger samples, photons are the more convenient for general elemental analysis, while protons are more suitable for small samples and for determining spatial distributions.

It is clear from the foregoing studies that the sensitivity achievable depends to a large extent on the nature of the sample and the methods employed for the basis of the comparisons. What does emerge from the latest studies is that protons give somewhat lower detection limits than photons, but their use may not always be as convenient. It should be noted, however, that in the case of small samples, photon-induced X-ray emission analysis cannot in any way compete in terms of sensitivity with PIXE. With photons as the exciting source, the maximum sensitivity can be obtained only for samples above a certain minimum weight. One of the main characteristics of PIXE is that its high sensitivity can be maintained even for extremely small samples.

The situation regarding comparison of proton and electron excitation has been studied by Folkmann et al.,[99] Cairns et al.,[242] and Reuter and Lurio.[146] The accelerating voltages nominally available in electron microscopes are typically in the range 20 to 50 kV, which gives rise to K-shell ionization cross sections very roughly the same order of

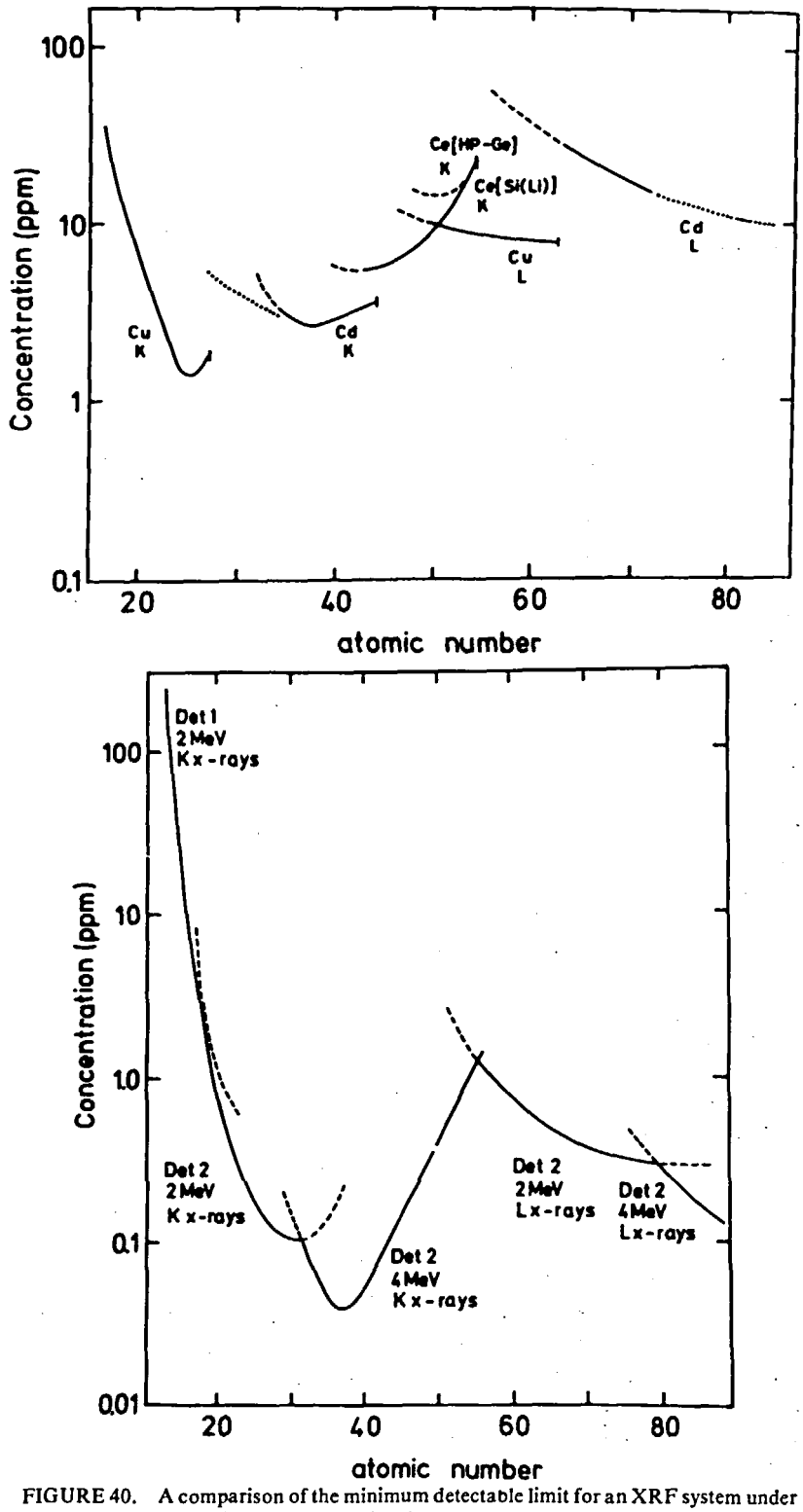

FIGURE 40. A comparison of the minimum detectable limit for an XRF system under standard running conditions using Cu, Cd, Ce as secondary fluorescers, upper curve, and a PIXE system under standard running conditions. (From Scheer, J., Voet, L., Wätjen, U., Koenig, W., Richter, F. W., and Steiner, U., *Nucl. Instrum. Methods*, 142, 333 (1977). With permission.)

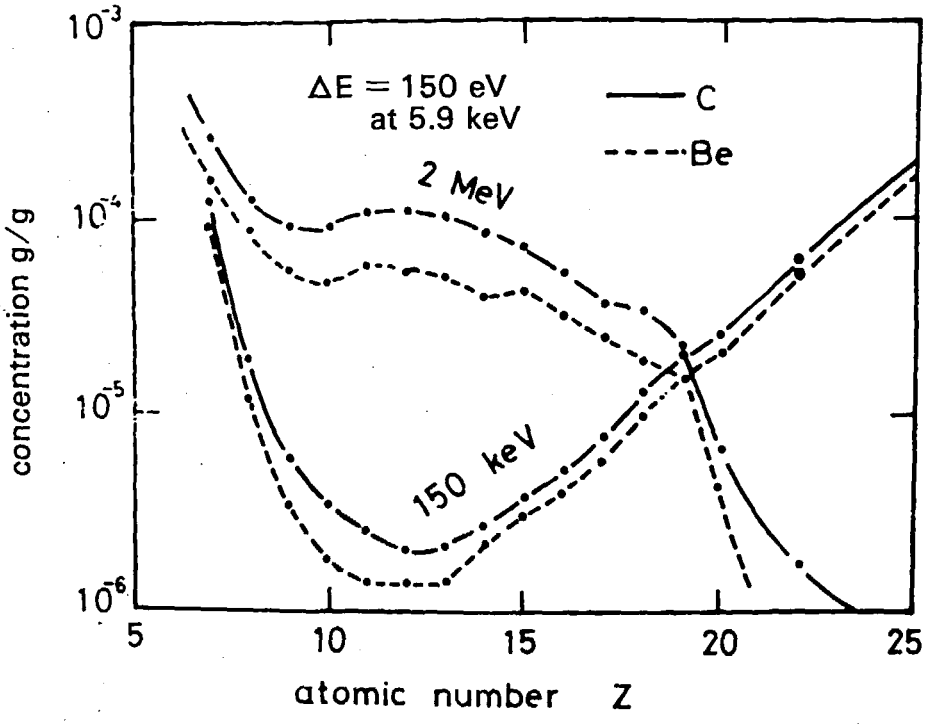

FIGURE 41. Minimum concentration of trace elements detectable on a thin carbon and beryllium matrix for protons of 150 keV and 2 MeV, based on a signal to noise ratio of one. (From Moriya, Y., Ato, Y., and Miyagawa, S., *Nucl. Instrum. Methods*, 150, 523 (1978). With permission.)

magnitude as those for protons of energy 2 to 4 MeV. The magnitude of the continuous bremsstrahlung background radiation, however, is significantly higher in the electron case due to the difference in their masses. This results in an improved signal to noise ratio in the proton case giving rise to an improved sensitivity. Folkmann et al.,[99] using the electron cross sections for K-shell ionization given by Gryzinsky,[243] have computed the concentration of trace element required in a thin sample to give a signal to noise ratio of one, and compared this with the corresponding concentration obtained for protons. They conclude that under optimal conditions, where the energy of the X-ray of interest is greater than 1.4 T_m, the detection limits are three orders of magnitude better for protons than electrons, in agreement with the estimates given by Cairns et al.[242]

The situation regarding thick samples has been investigated experimentally by Reuter and Lurio,[146] who determined the minimum detectable limit of nine elements, Z = 14 to 29, in NBS low alloy steel standard 461, using both electrons and protons. The electron microprobe analyzer employed an electron beam of 25 keV energy and the ion accelerator a proton beam energy of 2.4 MeV. The sensitivity of both techniques was found to be reasonably independent of the atomic number of the alloy constituents, with the protons giving a sensitivity only a factor two better than the electron excitation case. In view of the results of the computations of Folkmann et al.[99] for thin samples, one might expect a greater difference between the two techniques for thick samples. However, the detection limits achieved by Reuter and Lurio[146] for thick samples are in good agreement with those obtained by Ahlberg et al.[145]

X. CONCLUSIONS

From the applications reviewed, it is clearly evident that PIXE as a multielemental analysis technique of high sensitivity has been very successful in contributing significantly to the solution of problems from a wide range of disciplines. In part, at least for the major studies reported, this has been due to the development of fully automated, computerized PIXE analysis systems. Such systems obviously make good economic sense. It should be borne in mind, however, that analysis problems encountered are not always suited to automation and computer-evaluated data analysis, due to the nature of the samples, the problem, and/or the number of samples involved. Limitations imposed by X-ray detector pulse-pileup have now largely been removed by the technique of on-demand beam pulsing. Correct and careful sample preparation is a prerequisite for a successful analysis, and most of the problems relating to this, although widely spread through the literature, are reasonably well documented. Regarding the analysis of thick targets, X-ray enhancement by the matrix is an obvious difficulty, the solution of which often requires considerable computation, as each problem has to be assessed and evaluated individually.

It is now well established that relatively little information can be obtained directly concerning the depth distribution of the elements present in a sample. The deployment of a proton beam in the form of a microprobe, however, does enable lateral distributions to be determined, and — if a sample can be sectioned — depth distributions can be obtained in this manner. PIXE analysis, when combined with a microbeam facility, has been demonstrated to be a very powerful and versatile technique. As microbeam facilities become more universally available, we shall see a considerable growth in this area of activity.

Analytical problems to which solutions are sought are invariably complex problems and cannot always be solved using the information obtained from a single analytical technique. As a consequence of this, one must bring a variety of complementary techniques to bear upon the problem. Therefore, in addition to dedicated PIXE analysis systems, we shall witness the development of comprehensive multipurpose systems capable of exploiting the majority of the accelerator based analytical techniques as required, without the need to transfer from one dedicated accelerator beam line to another.

One problem that still exists, however, is one that is common to all comparatively new and developing analytical techniques — namely, that of bringing it the attention of those who could exploit its potential and capabilities to help solve their specific analytical problem. This is especially so in the case of PIXE analysis, since PIXE systems are not available from the manufacturers of analytical instruments, and hence the technique does not enjoy the benefits of commercial advertising. The onus thus falls on those currently engaged in the PIXE analysis field to give it the widest possible publicity.

ACKNOWLEDGMENTS

We would like to thank colleagues and staff at the Nuclear Research Centre, Tehran, and the Physics Department of the University of Aston for their continued interest and encouragement in the preparation of this manuscript. In addition, we would like to express our thanks to the support staff, especially the typists, for their invaluable assistance with the manuscript.

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