Analysis of Medium and Heavy Elements by Means of K X-Ray Fluorescence
Induced by 20-50 MeV Protons

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ABSTRACT

The technique of K x-ray fluorescence induced by 20-50 MeV protons appears to be well suited for use in trace element analysis of medium and heavy elements as the K x-ray yield is high at these proton energies. The separation in energy between K x-rays from adjacent heavy elements in the periodic table is such that spectra taken with a suitable Ge(Li) detector are readily analysed, and individual elements identified. Because of the high energy of the K x-rays, self absorption in the sample is greatly reduced over L x-rays from the same element - in some cases by several orders of magnitude. With thin samples, the effects of self-absorption are usually negligible, and beam energy loss in the sample is small. Some problems of targetry are discussed.

In such fields as environmental toxicology, medicine and biology, the need often arises to determine the concentration of various elements in a sample. If the atoms of the sample can be caused to emit x-rays, then the energy of the characteristic x-rays identifies the elements and the number of counts in the peaks determines the amount of each element present. Such methods of analysis using x-rays have been in use for many years, often in the form of x-ray fluorescence sets that use x-rays to induce the fluorescence. These, however, tend to be relatively slow (up to hours per sample) and are non-local (It is not possible, for example, to examine how concentration of a given element varies with position on the sample).

X-ray emission induced by charged particles offers many advantages as an analytical tool[†]. Particle induced x-ray emission (PIXE) is fast, (minutes per sample) highly sensitive and is capable of covering almost the whole periodic table in a single measurement. Further, through the use of a microbeam, a region of the sample as small as 10μm in diameter can be analysed. Such a microbeam facility is being investigated for the University of Manitoba[2].

In spite of the well established advantages of PIXE techniques, it is only lately that much work has been done using protons of cyclotron energies. As recently as the last Cyclotron Conference in Zurich (1975) it was suggested that there was no significant advantage in studying x-ray fluorescence at energies greater than a few MeV[3]. This was apparently due to a widely held belief that Compton scattering would produce a high enough background to obscure the x-rays. This is however, not the case. Much clean PIXE work has been done at the University of Manitoba Cyclotron Laboratory using protons in the 20-50 MeV energy range and detecting the x-rays with a Ge(Li) detector without Compton suppression[4,5,6,7,8]. Recently, by varying the energy of protons incident on a variety of targets, it has been possible to produce several self-consistent sets of relative K-shell ionization cross sections covering the region from below to above the velocity matching peak[††]. Figure 1 shows the data scaled for comparison with the Plane Wave Born Approximation (PWBA)[9,10].

The above work is of interest mainly for the fundamental physics involved. Later work has been more of an applied nature, currently concentrating on development of a rapid elemental analysis facility. It is felt that a system based on K x-rays excited by protons in our energy range is well suited to analysis of medium and heavy elements. There are several reasons for this.

[†]See the comprehensive review of Johansson and Johansson[1].

[††]so called because it corresponds to an incident proton velocity equal to the orbital velocity of the K electron.
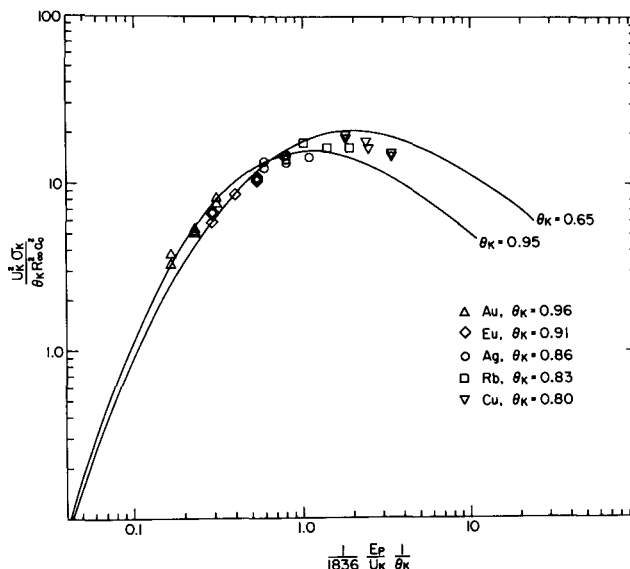

Fig. 1 K-shell ionization cross sections plotted on the "universal curve". The axes are dimensionless. U_k is the actual K-ionization energy, θ_k the K shell screening parameter equal to the ratio of actual to hydrogenic ionization energies, R_∞ the Rydberg constant, a_0 the Bohr radius, E_p the proton energy and 1836 the ratio of proton mass to electron mass (In convenient units, $R_\infty^2 a_0^2 = 5179$ keV^2 barns). Solid lines are PWBA results[10].

(a) The cross section for K x-ray production is high - the cross section maximum for medium Z elements occurs in the 20-50 MeV range (see Fig. 1).

(b) K x-rays from adjacent elements in the periodic table are well separated and are easily resolved by a suitable Ge(Li) detector.

(c) The efficiency of a Ge(Li) detector is high for the K x-rays of interest.

(d) Self absorption of K x-rays is small. For typical targets it is negligible, whereas self absorption of L x-rays may be significant. For example, a gold target thin enough to transmit 95% of gold K x-rays will only transmit 10% of the L x-rays.

(e) Proton energy loss in the target is small.

There are some potential difficulties associated with the use of fast protons. Inelastic scattering or nuclear reactions may give rise to nuclear gamma rays. These may result in increased Compton background and in some cases gamma peaks superimposed on the x-ray spectra. It is also found[6] that satellite peaks may result from de-excitation by internal conversion of residual nuclei from (p,xn) reactions. Compton background is not serious and it can be reduced even further by equipping the detector with a Compton suppression unit. Such a unit has been ordered and will be put into operation shortly. Satellite peaks are handled by including them in the standard shapes used in analysis. This is done with the computer code KOCAKIZ developed by Teoh[11]. In this way, full advantage is taken of the benefits of using K x-rays induced by 20-50 MeV protons.

In addition to problems peculiar to higher energy bombardment, there are certain inherent problems which tend to degrade the quality of data and the detection sensitivity in all PIXE work. These include energy lost by the protons while traversing the target material, Bremsstrahlung, pile-up, self-absorption, charge build-up, etc. These have been treated in detail in the literature and will not be discussed here except to say that these problems can be substantially reduced by using thin targets on very thin backings, using specially designed filters to reduce copious radiation, and by keeping the counting rate reasonably low.

In the present work, targets are prepared by gluing a piece of pre-cleaned mylar (thickness 480 μ g/cm^2) over a 1.8cm diameter hole in a target holder measuring 2.5cm x 6cm x 0.08cm. The target material is dissolved in a suitable solvent prior to use. A known volume of this solution (usually 20$\mu\ell$) is put on the centre of the mylar film, and is allowed to dry in a clean dessicator under an infra-red lamp. A set of up to 10 targets can be made, loaded on a ladder and bombarded sequentially in the PIXE chamber. An ORTEC 5mm planar Ge(Li) detector is used for the detection of x-rays. The amplified signal is fed into one of the eight Northern Scientific ADCs interfaced to a PDP-15/20 computer. A computer program, code named MIRAD, together with an ADC handler, is used for data acquisition. At the conclusion of each run, the accumulated data is stored on DEC tape for off line analysis.

Data analysis is carried out using the computer programme KOCAKIZ mentioned earlier. KOCAKIZ is designed for x-ray emission spectroscopy. The analysis is done off-line on a PDP-15/40 computer operated under B/F monitor. Essentially, KOCAKIZ performs a least squares fit to the data using a set of standard shapes and background stored on disk. The area under the characteristic x-rays of each element of interest is determined and converted to abundance (in μg) and to concentration (in ppm) if the sample weight is known. Figure 2 shows the x-ray spectrum of silver. The target is prepared by depositing 50 μgm of Ag (in the form of silver nitrate solution) as discussed previously. The fitted spectrum, including the background, is indicated by the continuous line. From the area of the x-ray peaks, KOCAKIZ determines the abundance to be 47.2 μg, which is well within the experimental accuracy. The same program is routinely used for water analysis by the XRF technique. By way of example, Figure 3 shows the KOCAKIZ analysis of a water sample from an old electric kettle. The presence of lead is unmistakable. The result of the analysis as printed by KOCAKIZ is shown in table I.

Good targets are important to accurate PIXE analysis. If the droplet evaporation method described earlier is used, proton beam illumination must be uniform for repeatable results. If it is not then the x-ray counts produced for a given total charge will be
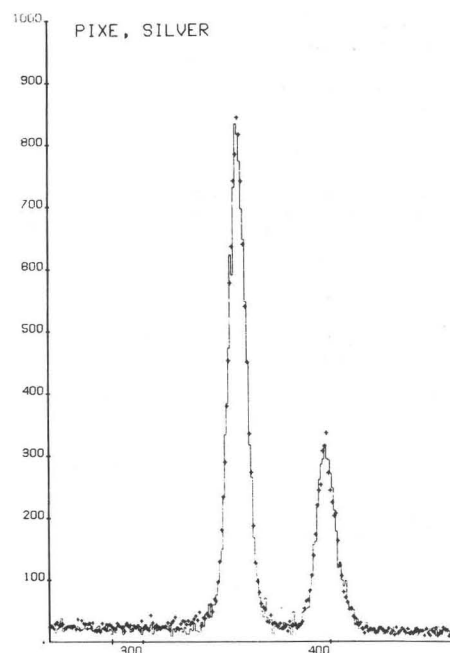

Fig. 2 X-ray spectrum from 27 MeV protons on silver. The crosses are data points and solid line the KOCAKIZ fit.
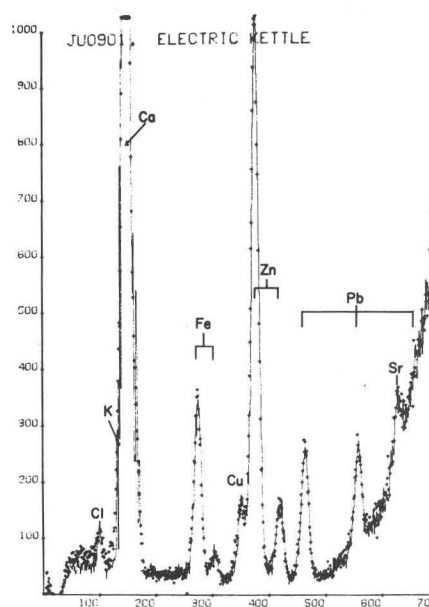

Fig. 3 XRF data from old kettle water. Solid line is the KOCAKIZ fit.

different for a different position of the sample in the proton beam. This problem can be overcome by applying the sample as a uniform spray over the entire target backing, but then it is difficult to determine the target thickness accurately. Both problems can be solved by use of a "dopant". In this method, some element not found in the sample to be analysed is introduced in accurately known concentration. The results are then normalized relative to this dopant. A further problem may arise when samples containing volatile elements such as mercury must be analysed. In such cases, if the target is placed in a vacuum, the concentration of the volatile element is found to decrease with time indicating it is being evaporated.

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..FILENAME......    JU0901BIN
.....      OLD,OLD ELECTRIC KETTLE, MAY CONTAIN LEAD
..ANALYSE FROM   40  TO   750
..TIME.....   24.250   HRS
..SAMPLE WEIGHT.....  100.000   MG


         .. RESULT OF ANALYSIS ..

  ELEMENT     AREA      MASS      CONC

    Cl       0.034     0.530    5.300  PPM
    K        0.031     0.158    1.581  PPM
    Ca       1.405     4.290   42.901  PPM
    Ti    LT 0.017 LT 0.023 LT 0.225  PPM  DET LIM
    Mn    LT 0.019 LT 0.008 LT 0.081  PPM  DET LIM
    Fe       0.215     0.068    0.685  PPM  EXTRAPOLATED
    Co    LT 0.019 LT 0.005 LT 0.050  PPM  DET LIM
    Cu       0.095     0.018    0.178  PPM  EXTRAPOLATED
    Zn       0.630     0.089    0.890  PPM  EXTRAPOLATED
    Br    LT 0.035 LT 0.001 LT 0.014  PPM  DET LIM
    Sr       0.083     0.004    0.044  PPM  EXTRAPOLATED
    Hg    LT 0.057 LT 0.005 LT 0.045  PPM  DET LIM
    Pb       0.326     0.029    0.291  PPM  EXTRAPOLATED


..FITTED SPEC, YES OR NO
YES
..FILE NAME FOR FITTED SPECTRUM

UJ0901BIN
DIS NOT READY
"R..FILE   UJ0901BIN   COMPLETED
..ANY MORE

NO
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Table I Results of the analysis of Fig. 3

In such cases the target may be placed in a gas cell containing Helium under about 100 Torr pressure and the beam current kept low to minimize heating.

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