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An external-beam charged-particle (alpha) activation system for direct trace element analysis in liquids

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Abstract. An external-beam system based on charged-particle activation analysis for determination of trace elements in liquids has been developed at the Variable Energy Cyclotron Centre, Calcutta. The system developed is direct, instrumental, non-destructive, simple and suitable for both aqueous and non-aqueous samples. This paper gives the construction details of the system and its standardization for quantitative estimation of transition metals. Medium-energy alpha particles were used. As part of the standardization process the beam energy, beam current, observed interferences, minimum detection limits, system linearity, reproducibility and precision are discussed. We have mainly used aqueous and crude oil samples during this work. A novel method for calibrating the target position with respect to the beam is reported.

1. Introduction

The field of trace element analysis has grown over the years into a major interdisciplinary field [1]. Many analytical techniques have evolved since the earlier chemical methods to the present-day instrumental techniques based on atomic or nuclear processes. The advantages of each technique would vary mostly according to the element of interest, the required sensitivity and the type of sample to be analysed. While some techniques might be multielemental in nature, others might be more suitable for single-element analysis. Further, while most techniques would require some form of sample preparation, nuclear techniques have been able to offer non-destructive means of analysis with minimal or no sample preparation.

Among nuclear techniques neutron activation analysis (NAA) provides a method for multielemental, non-destructive analysis over a large range of samples and elements. Among some of the limitations of this technique are the low (n, γ) cross section for most of the transition elements, thereby requiring elaborate radiochemical separation to avoid interference and attain the required sensitivities, and the high pressure build-up during long hours of irradiation of non-aqueous samples.

Conventional ion-beam-based analysis generally performed in a vacuum rules out the possibility of direct liquid analysis. A recent innovation which has drawn wide attention to these techniques is the extraction of the particle beam from the accelerator vacuum into the atmosphere [2–7]. The advantages of external-beam systems are well established [8–13]. While external-beam proton-induced x-ray (PIXE) and γ-ray (PIGE) emission received wide attention, not much seems to have been done on the standardization and use of any ion-beam technique based on external-beam charged-particle activation analysis (CPAA). External-beam PIXE, though widely used, fails to provide direct analysis for such samples as it has certain inherent problems associated with sample preparation, sample mounting, backing material background, etc [14, 15]. On the other hand external-beam PIGE is found to be more sensitive in the low-Z region [3]. The large number of reactions for most of the transition elements for medium-energy alpha particles along with the advantages of external-beam systems could provide a highly selective direct method of analysis in CPAA.

The aim of the present study was to investigate the feasibility and subsequent optimization of an external-beam system in alpha-induced activation analysis for direct non-destructive quantitative determination of trace elements, in particular for transition metals in liquid samples. The validation of the quantitative results was carried out using crude oil standards from NIST, USA.

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2. Experimental arrangement

The irradiations were carried out at the 224 cm Variable Energy Cyclotron at Calcutta. The irradiation set-up is shown in figure 1. An alpha beam at the 0° port was collimated through two 5 mm adjustable collimators (placed 16 cm apart) and then extracted into air through a Havar foil (thickness 25.4 μm, Goodfellow metals, UK). Eight samples were mounted on the target holder simultaneously. The samples and the exit foil were cooled with a constant flow of water. The target was electrically isolated from the beam tube and the total charge deposited on the sample during irradiation was measured through a current integrator; this value was used for spectrum normalization. High-purity aluminium cans of about 3 ml capacity with precisely known thicknesses were used for holding the samples. Cans of different thicknesses were used to degrade the beam energy to required values without disturbing the incident beam energy, thereby saving a considerable amount of beam time.

To ascertain the precise position of the beam on the target a simple method has been used, where two to three minutes' irradiation of a high-density transparent fluid (silicone oil) was performed in the same geometry as that of the samples. Figure 2 shows the resultant distinct mark of two dark spots corresponding to two different irradiations. This simple inexpensive method helps in positioning the beam spot directly on the sample unlike using a beam viewer at any intermediate point in the beam tube. This has also been helpful in setting the beam transportation parameters. During irradiation the samples were monitored by a closed-circuit TV network.

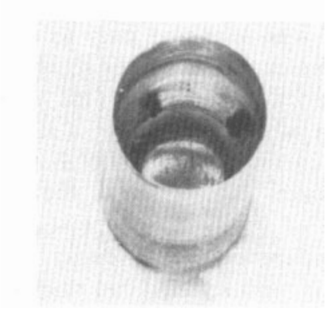

Figure 2. Photograph showing the two dark spots inside the silicone irradiated sample can for two different irradiations.

3. Measurement and results

3.1. Measurement

It was observed that isotopes with half-lives less than 6–8 h were not useful for measurements in the case of liquid samples. This was due to the high count rate of 511 keV γ-rays originating from the positron-emitting nuclei produced from the matrix (mainly C, N and O).

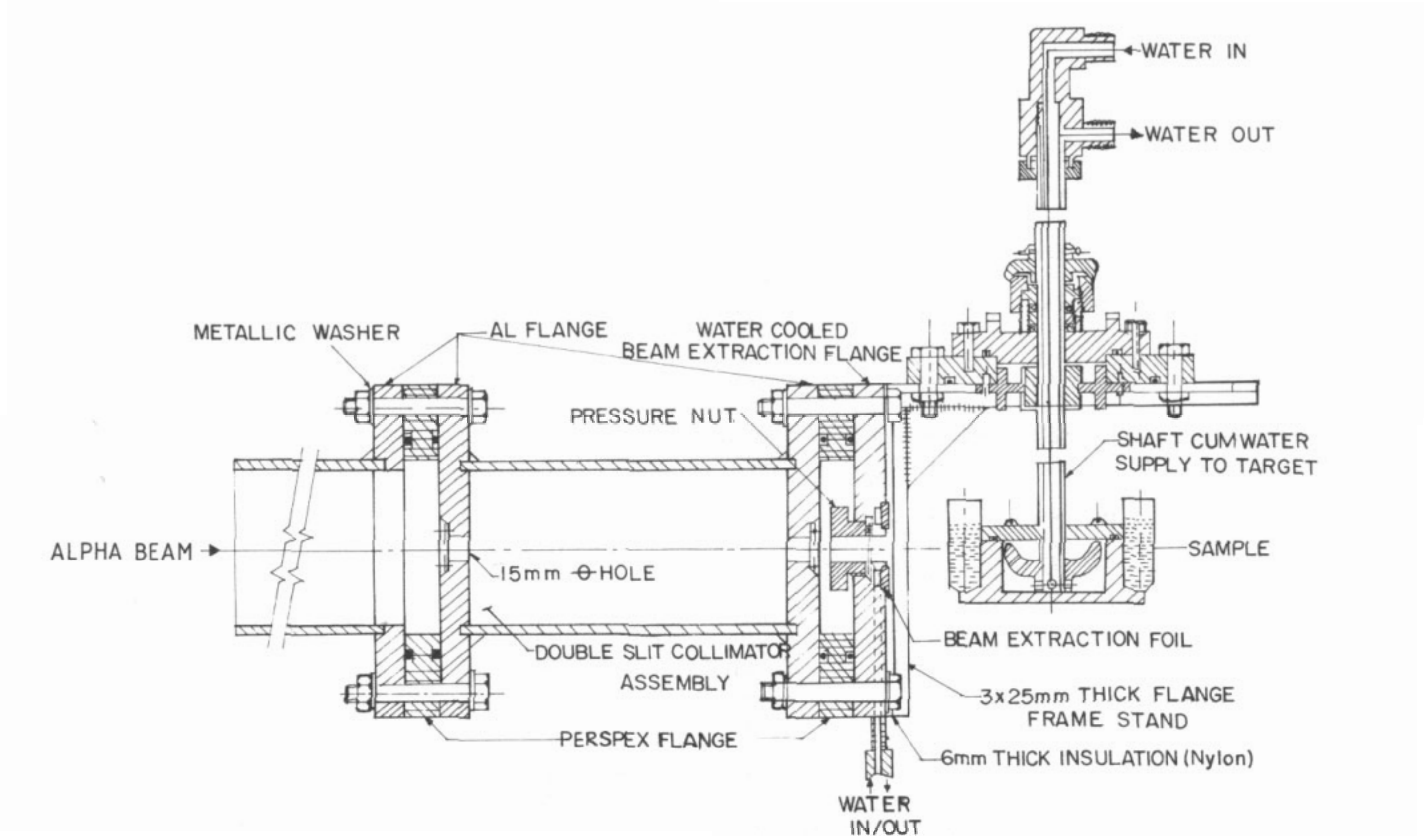

Figure 1. Cross section of the external-beam irradiation system.

Thus the study was restricted only to isotopes which had half-lives greater than a day or so, thereby allowing the 511 keV activity to decay off. This limitation, however, became an advantage in that a large number of samples could be irradiated at a stretch and analysed at a later convenience. Table 1 shows the most sensitive reactions identified (both in the presence and in the absence of interference), their decay characteristics, irradiation energy with selected can thickness, principal γ-rays with intensity and the observed minimum detection limits (MDL). The irradiated samples were transferred to glass containers after cooling for about 6–8 h and counted on a 110 cm^3 HPGe detector (resolution 1.8 keV at 1332 keV, efficiency 15%) coupled to a Series 88 Canberra MCA. 4 K memory spectra were collected at selected time intervals to follow the half-lives of product isotopes and stored on magnetic tape for subsequent analysis. The choice of a reaction for analytical purpose was primarily decided by the natural isotopic abundance, interferences, reaction cross section and product half-life. For quantification, the method of average cross section [16] was used. The concentration N (atoms/g) of an element is given by

$$N_x = \frac{A_x \Phi_s S_s N_s R_s}{A_s \Phi_x S_x R_x}$$

where subscripts x and s are for sample and standard, respectively, A is normalized counts/s at the end of irradiation, Φ is intensity in α-particles/s, R is the range of α-particles and S is the saturation factor ($= 1 - \exp(0.693t/T_{1/2})$), where t and $T_{1/2}$ are the duration of irradiation and the product half-life, respectively.

The range and stopping power data required in quantification and beam energy loss calculations were taken from reference [17]. In the case of exit foil and air (both being composite mixtures) Bragg's formula for the addition of stopping power was used.

3.2. Beam energy

The opening of various reaction channels at high energies results in a complex situation, where a direct one-to-one

Table 1. Nuclear reactions with their decay characteristics.

		Half-life (days)	Can thickness (μm)	γ-ray (keV)	MDL[a] (ppm)
Element	Reaction	Threshold (MeV)	Final energy on target (MeV)	Abundance (%)	Interfering elements
In absence of interfering elements (irradiation energy = 40 MeV)					
V	^{51}V(α,n)^{54}Mn	312.2	200	834.8	32
		2.5	30	99.9	
Cr	^{50}Cr(α,pn)^{52}Mn	5.7	200	744.2	9
		13.5	30	85	
Mn	^{55}Mn(α,n)^{58}Co	70.8	200	810.6	5
		3.8	30	99.4	
Fe	^{56}Fe(α,pn)^{58}Co	70.8	200	810.6	5
		14.7	30	99.4	
Ni	^{58}Ni(α,3pn)^{58}Co	70.8	200	810.6	9
		29.8	30	99.4	
Zn[b]	^{68}Zn(α,3n)^{69}Ge	1.6	200	1106.5	4
		26.1	30	26	
Cu[c]	^{65}Cu(α,2n)^{67}Ga	3.26	200	300.2	0.06
		15.0	30	15	
Ga	^{69}Ga(α,2n)^{71}As	2.67	200	174.8	4
		16	30	93.0	
In presence of interfering elements (irradiation energy = 35 MeV)					
V	^{51}V(α,n)^{54}Mn	312.2	400	834.8	28
		2.5	14	99.9	Cr, Fe
Cr	^{50}Cr(α,pn)^{52}Mn	5.7	150	744.2	90
		13.5	25	85	V
Mn	^{55}Mn(α,n)^{58}Co	70.8	400	810.6	14
		3.8	14	99.4	Fe
Fe	^{54}Fe(α,n)^{57}Ni	1.5	400	1377.6	15
		6.2	14	84.9	Ni
Ni	^{64}Ni(α,p)^{67}Cu	2.58	400	184.6	158
		5.0	14	45	Cu
Ga	^{71}Ga(α,n)^{74}As	17.7	300	595.5	17
		5.0	19	59.5	As

[a] MDL values are for irradiations of 2 h at selected energies with average beam currents of 120 nA in absence and 250 nA in presence of interfering elements. The errors in MDL are within 10%.

[b] ^{66}Zn(α,n)^{69}Ge and ^{67}Zn(α,2n)^{69}Ge also contribute under these irradiation conditions.

[c] ^{63}Cu(α,γ)^{67}Ga also contributes in these irradiation conditions.

assignment of the products to the parent element or isotope can be difficult. Under these circumstances the selection of irradiation energy is important in an ion-beam-based analysis. When a single isotope could result from two or three different elements, the irradiation energy was selected after studying the reaction thresholds. As an illustration, table 2 shows the reactions that can be used, in principle, for determination of V using ^{54}Mn or ^{52}Mn along with the interfering reactions. As shown in table 1, ^{54}Mn has been used for estimation of V, and to do this a target irradiation energy (E_t) of 14 MeV has been chosen. Irradiating at this energy the contribution from Cr via (α, pn) is cut off. From table 1 it is also apparent that in the presence of interfering elements V, Mn, Fe and Ni can be determined simultaneously in real samples by irradiating at 14 MeV (E_t).

When the sample matrix was not multielemental in nature the irradiation energy was chosen primarily on the basis of the shape of the excitation function so as to fully cover the region of maxima. For elements such as Cr, where the required excitation functions were not available, a separate study to generate these was undertaken by the standard stacked foil technique.

The uncertainty in E_t was mainly due to the uncertainty in the can thickness (maximum ~ ±25 μm). This could introduce an energy spread of about ±1 MeV in E_t for an incident beam of 35–40 MeV. This value has been ignored for all practical purposes.

3.3. Beam intensity

Unlike conventional CPAA irradiation using beam currents in the microampere range the optimum beam current found in our case was about 250 nA and 300–400 nA for aqueous and non-aqueous samples (such as crude oil), respectively. The use of a nanoampere level beam current kept the heat energy transmitted to the sample in the milliwatt range, thus reducing the evaporation losses considerably. The value of the integrated charge falling on the target was cross checked by irradiating a pure copper foil. The ^{67}Ga activity produced by the reaction ^{65}Cu(α,2n)^{67}Ga was measured. The intensity value calculated from the measured ^{67}Ga activity compared well with the experimental recorded value to within 5%. The cross section data for this reaction was taken from reference [18]. The stability of the beam intensity was within 5%.

Table 2. Nuclear reactions for the measurement of vanadium with interfering reactions. The values in the brackets correspond to the reaction thresholds in MeV.

Nuclear reaction	Interfering reaction
^{50}V(α,2n)^{52}Mn(13.2)	^{50}Cr(α,pn)^{52}Mn(13.5) ^{52}Cr(α,p3n)^{52}Mn(36.4) ^{51}V(α,3n)^{52}Mn(25.1)
^{51}V(α,n)^{54}Mn(2.5)	^{52}Cr(α,pn)^{54}Mn(13.8) ^{53}Cr(α,p2n)^{54}Mn(22.3) ^{54}Cr(α,p3n)^{54}Mn(32.7) ^{54}Fe(α,3pn)^{54}Mn(30.3)

3.4. Minimum detection limits

The MDL value in this experimental arrangement has been defined as the concentration in ppm which will yield a photo peak with an intensity at least three times the background. MDL values for single-element analysis in typical working conditions were, except for vanadium, of the order of a few ppm. This limit could be further improved by increasing the irradiation time. MDL values under elemental interfering conditions were also determined to simulate actual sample analytical conditions. This was done by irradiating multielemental aqueous standards (which included the element of interest and the corresponding interfering elements), while in the non-interference cases they were obtained by irradiating single-element aqueous standards. The irradiation time in both the cases was 2 h with beam currents of about 250 nA and 120 nA in the presence and absence of interfering elements, respectively. Owing to the strong dependence of MDL on the matrix, beam intensity and time of irradiation for one set of irradiation parameters, the increase in irradiation time could certainly bring down the MDL value. The high MDL values observed for Cr and Ni in the interfering cases are due to the low natural abundance of the parent isotopes. As for V, Cr and Mn, the same reactions were used in both the interfering and non-interfering cases, at different irradiation energies.

3.5. Linearity

Irradiation of different concentrations of a single element was done for one set of irradiation parameters. Figure 3

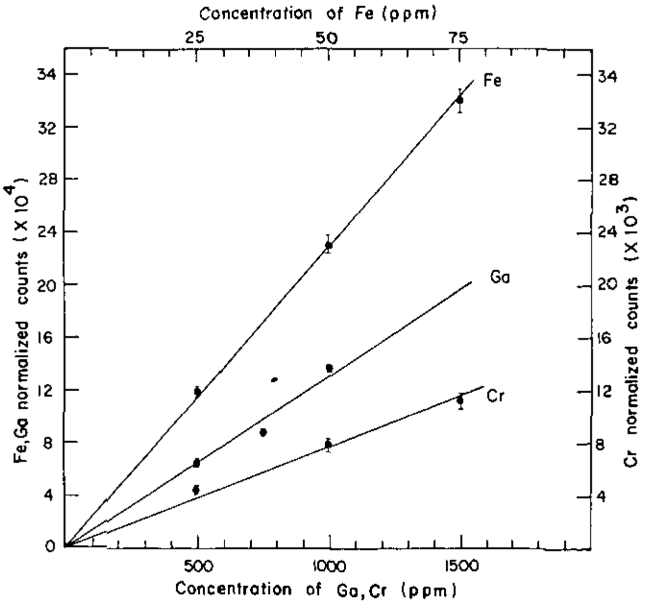

Figure 3. Linearity plot of the system for selected elements.

shows the observed linearity plot for a few selected elements. Different concentrations of V, Cr and Fe standards of crude oil required in this study were made by spiking the oil with corresponding organometallic salts. The linearity study plays an important role in system standardization since it is observed that sometimes the plot of count/μC versus the total accumulated charge shows a constant behaviour [19]. To ascertain the linearity of the system, samples with concentrations over a wide range were analysed.

3.6. Reproducibility and precision

System reproducibility and precision were determined by multiple irradiations of NIST standards using a single set of irradiation parameters. SRM No 8505 (vanadium in crude oil) was used for measuring V in interference-free conditions. To validate the irradiation conditions in the presence of the interfering elements SRM No 1634b (trace elements in fuel oils) was used, where the certified values of V, Fe and Mn are well above our detection limits. Vanadium was estimated in SRM 1634b by considering it as an unknown sample and using SRM 8505 as a standard for comparison. The results obtained for V are shown in table 3. The experimental errors were within 15%. The coefficient of variation was about 8.6%.

3.7. Interferences

The interferences encountered in our study can be broadly divided into two types: (i) product nuclei used for quantitative estimation of the elements of interest are also produced from neighbouring elements, and (ii) interference from background γ-rays. Of the two, the former was more prominent. The check for irradiation energy for interference-free measurement in the presence of interfering elements was done by irradiating vacuum-deposited foils of the metal and its corresponding interfering element on aluminium foils. The mere presence or absence of the required peaks in these irradiations confirmed the validity of the selected beam energy. As an illustration, Cr has been found to interfere in the estimation of V via ^{54}Mn. In fact iron also interferes above 30 MeV (E_t), but as its threshold value is well above the selected E_t it has not been included in the discussion. The contribution from Cr was cut off by choosing an irradiation energy of 14 MeV (E_t), the lowest of the threshold values among the interfering reactions. The absence of the 834.8 keV peak from the Cr spectrum confirms the selected irradiation parameters (figure 4). The total charge deposited on the foils during irradiation (μC) is also shown in the figure. Similar checks were performed for all other cases of interference.

In cases of interference from the background γ-rays, complex mathematical treatment of the spectrum was avoided by using any other suitable γ-ray of the same isotope.

4. Conclusion

The investigation shows that external beam CPAA in the easily available range of cyclotron energy can be effectively used for direct trace-level quantitative estimation of transition metals in liquids. The system developed here offers a non-destructive routine means of analysis in the ppm range. The system, though optimized primarily for transition elements, can be extended to other

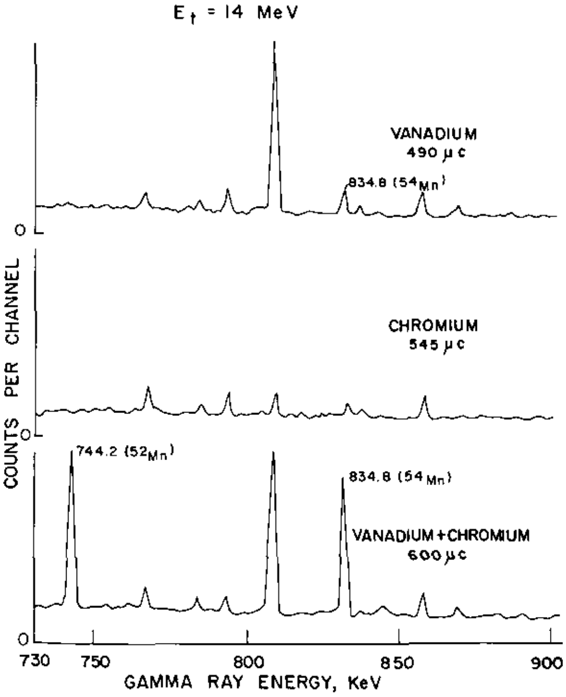

Figure 4. Selected parts of γ-ray spectra of V, Cr and V+Cr to check selection of irradiation energy for interference-free quantitization.

Table 3. Results obtained for vanadium in the analysis of NIST standards.

SRM no	Certified value (ppm)	Obtained value (ppm)	Average (ppm)	Coefficient of variation (%)
8505	390±10	404±34 356±30 355±30 420±36	384±32	8.6
1634b	55.4±1.1	55.1±4.5		

elements too. The large linearity range of the system provides a wide dynamic range for analysis. Some of the important positive features of the system include the utilization of the off-line counting method, use of different thicknesses of sample cans to alter the final energy on the target, small sample changing time, a novel and effective method of positioning the beam spot on the target, minimum sample preparation and subsequent lower handling contamination. These would further contribute to the economic viability of the system.

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References

[1] Laitinen H A 1988 History of trace analysis *J. Res. NBS* **93** 175

[2] Willams E T 1984 PIXE analysis with external beams: systems and applications *Nucl. Instrum. Methods* B **3** 211

[3] Räisänen J 1989 Elemental analysis with external beam methods *Nucl. Instrum. Methods* B **40/41** 638

[4] Räisänen J 1984 An external proton beam for PIGE analysis *Nucl. Instrum. Methods* B **3** 220

[5] Sommer F, Barbier Y, Frachon M and Chartoire M Y 1983 Establishing PIXE analysis conditions for sweat analysis *Nucl. Instrum. Methods* **205** 555

[6] Anttila A, Räisänen J and Lappalainen R 1985 On the optimization of an external PIXE arrangement *Nucl. Instrum. Methods* B **12** 245

[7] Fischbeck H J, Engel M H, Ruffel A V and Weaver B L 1987 Application of an external beam PIXE method for determining the distribution of trace metals in degraded and nondegraded crude oils *Nucl. Instrum. Methods* B **24/25** 655

[8] Seaman G G and Shane K C 1975 Trace-element analysis by x-ray fluorescence with an external proton beam *Nucl. Instrum. Methods* **126** 473

[9] Katsanos A, Xenoulis A, Hadjiantoniou A and Fink R W 1976 An external beam technique for PIXE analysis *Nucl. Instrum Methods* **137** 119

[10] Katsanos A and Hadjiantoniou A 1978 Sensitivity of the external beam PIXE elemental analysis method *Nucl. Instrum. Methods* **149** 469

[11] Deconninck G and Bodart F 1978 New developments in non-vacuum analysis *Nucl. Instrum. Methods* **149** 609

[12] Huda W 1979 Proton induced x-ray fluorescence of thick samples in air for trace elemental analysis *Nucl. Instrum. Methods* **158** 587

[13] Raith B, Wilde H R, Roth M, Stratmann A and Gonsior B 1980 Trace element detection sensitivity in PIXE analysis by means of an external proton beam *Nucl. Instrum. Methods* **168** 251

[14] Johansson S A E and Johansson T B 1976 Analytical application of Particle Induced X-ray Emission *Nucl. Instrum. Methods* **137** 473

[15] Wilk S F J, McKee J S C and Randell C P 1977 PIXE work at University of Manitoba *Nucl. Instrum. Methods* **142** 33

[16] Ricci E and Hahn R L 1967 Sensitivities of activation analysis of 15 light elements with 18 MeV helium-3 particles *Anal. Chem.* **39** 794

[17] Northcliffe L C and Schilling R F 1970 Range and stopping power tables for heavy ions *Nucl. Data Tables Sec.* A **7** 233

[18] Graf H P and Münzel H 1974 Excitation functions for alpha particle reactions with Molybdenum isotopes *J. Inorg. Nucl. Chem.* **36** 3647

[19] Khan A H, Khaliquzzaman M, Husain M, Abdullah M and Katsanos A A 1979 Elemental analysis of liquids by external beam PIXE down to ppb level *Nucl. Instrum. Methods* **165** 253