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Malmqvist, Klas; Johansson, Gerd; Akselsson, Roland

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LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00

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Proton Induced X-rays and Gamma Rays for the Analysis of
Welding Fumes.

K.G. Malmqvist¹, G.I. Johansson¹, and K.R.Akselsson^{1,2}

¹ Department of Nuclear Physics, University of Lund,
Lund, Sweden

² Department of Environmental Health, University of Lund,
Lund, Sweden.

ABSTRACT

Welding aerosols have been sampled in different size fractions using a moving stage cascade impactor. Sampling has been done for different welding methods and for varying welding parameters. The elemental composition of the different size fractions have been determined by Proton Induced X-ray Emission, PIXE, combined with a nuclear method for fluorine analysis.

Results show maximum mass of most elements to be on particles with an aerodynamic diameter in the range of 0.25-1µm.

Varying the welding parameter will affect the size distribution and chemical composition of the aerosols as well as the fume formation rate.

INTRODUCTION

There is a rapid development within metallurgy and welding technology, producing new types of highly tensile steel and welds. This development will affect the hygienic conditions of those working with welding as variations in the concentrations, the elemental composition and the size distribution of the emitted aerosol will occur.

It is important to study the particle size distribution and the elemental composition of different size fractions for several reasons:

This kind of information is a necessity for dose-response curves and thus for more adequate hygienic standards. Also it facilitates the development of effective elimination techniques for the protection of the workers. Further the results from characterization of welding aerosols using different welding parameters may increase the understanding of the particle formation processes. It will then be possible to consider health aspects when developing new methods and materials.

Particle Induced X-ray Emission, PIXE, constitutes a feasible method for trace element analysis in aerosol application.

ANALYTICAL PROCEDURE

PIXE - analysis¹

When irradiating a sample with a beam of protons, the protons will interact with electrons and cause innershell vacancies in the atoms present in the sample (Figure 1). The energies of the X-rays, emitted when the vacancies are filled again, are characteristic of the elements from which they originate and the number of X-rays of a certain energy is proportional to the mass of the corresponding element in the sample.

Due to the bremsstrahlung from decelerating secondary electrons, produced by the incident protons, a continuous X-ray spectrum is produced as well. This background component is low compared to those of electron and X-ray excitation.

In an experimental arrangement for PIXE-analysis (Figure 2) an energy dispersive detector (Si(Li)-detector) is used to detect the X-ray produced. The pulse-height spectrum obtained from the detector is accumulated in a multichannel analyser and then stored on magnetic tape for subsequent computer evaluation. Figure 3 shows a X-ray spectrum obtained when irradiating a welding aerosol sample. For a sample comprising several elements there will be interferences in the spectrum due to overlapping of adjacent peaks. However, the computer programme, used, resolves these peaks, so that 15 to 20 elements may be determined in a single analysis.

The absolute lower limits of detection for elements heavier than phosphorus are in the range of 0.1 - 10 ng and the typical time of analysis is between one and five minutes.

Accuracy and precision are about 10% each, for elements well above their detection limits.

Table 1 shows the most important properties of the PIXE method.

The multielemental capability of PIXE is very favourable in the analysis of work environmental samples, like for instance welding aerosols, which very often contain many different elements. Adding the rapidity of the analytical procedure this will reduce the cost and enable more samples to be processed within the same budget. Another advantage is the capacity of the method to reveal elements not expected in a sample.

The major drawback of the X-ray analysis methods is the restriction in the analysis of lighter elements. The X-rays emitted from these elements have low energy and thus the X-ray intensity in the detector will be too low due to severe absorption losses. However, in contrast to many other X-ray methods, PIXE may be used simultaneously with analytical methods based on nuclear reactions. For instance, by determining the number and energy of the protons which are scattered from the sample it is possible to analyse the elements lighter than phosphorus². This may be done simultaneously with the PIXE-analysis.

Simultaneous fluorine analysis

When welding with electrodes with low hydrogen coatings considerable amounts of fluorine may be emitted, thus constituting a hygienic problem. Fluorine, being an element lighter than phosphorus, is not possible to determine with PIXE-analysis. However, when protons of a suitable energy, e.g. 2.5 MeV, interact with the fluorine nuclei in the sample, nuclear reactions take place in which high energy γ -rays are emitted (see Figure 4). These γ -rays may be detected with a sodium iodide crystal (see Figure 5) using a discriminator to eliminate the contributions from low energy γ -rays.³

The lower limit of detection of this arrangement is in the interval 50-100 ng. The precision is about 5% and the accuracy is depending of the accuracy at the standard foil used in calibrating for absolute amount determinations. Standards of that kind are commercially available within 5% accuracy.

In PIXE-analysis, corrections have to be made for samples thicker than about 1 mg/cm^2 due to slowing down of the protons and due to attenuation of the X-rays in the sample. For the fluorine analysis, however, no corrections have to be made for samples thinner than about 4 mg/cm^2 (see Figure 6). The general properties of the fluorine analysis procedure described is shown in Table 2.³

SAMPLING DEVICES

Among aerosol samplers used in the work environment, two common devices, the membrane filter sampler and the single orifice cascade impactor are well suited for PIXE-analysis. The cascade impactor produces very small and inhomogenous samples distributed over a small area, while the membrane filter collects the particles as a thin homogenous layer on its surface.

As mentioned above it is important to determine the particle size distributions for several reasons. When using the cascade impactor for these purposes there have often been problems to accomplish an adequate chemical analysis of the very small samples collected on each stage. Hence the impaction stages often have been overloaded causing bounce off effects and distorted size

distributions. These problems were avoided as the PIXE-method, having very low absolute detection limits, requires only moderate loading of the stages. For our experiments on welding aerosols we are using a small size 1 liter/minute cascade impactor of Battelle design⁴. This impactor has been modified with a back-up filter and, for the welding aerosol sampling, with moving collection plates⁵. The 50% cut off diameter of the different stages are 0.25, 0.5, 1, 2, 4 and 8 μm for spherical particles of density 1. Particles smaller than 0.25 μm aerodynamic diameter are collected on a Nuclepore back-up filter. The excentrically rotating collection plates are used for the 0.25 and 0.5 μm cut-off diameter stages as they are heavily loaded when sampling welding aerosols. Having the samples distributed over a larger area, will give less risk for bounce-off effects. The samples will also be thinner than 1 mg/cm^2 and well suited for the subsequent PIXE-analysis.

Cascade impactors are often too sophisticated and expensive when monitoring work environments on a routine basis. Filter samplers, with cellulose acetate membrane filters, are the most common devices for this purpose. Precollectors, for instance with a cyclone, may be used to determine the respirable fraction of the aerosol. These membrane filters with only very little impurities have a thickness of about 5 mg/cm^2 and are well suited to the PIXE-analysis. Still better, however, are the Nuclepore filters, as they are thinner (1 mg/cm^2) and therefore will create less background radiation when irradiated.

Another sampling device suitable for PIXE-analysis is the time resolving sequence samplers as developed for outdoor air by Nelson and coworkers at the Florida State University⁶. We are at present developing a small two stage sampler designed for work environment aerosol sampling, using 15 minutes interval sampling on Nuclepore filters.

WELDING AEROSOL CHARACTERIZATION

Our group is at present working with a project on welding aerosol characterization, sponsored by the Swedish Work Environment Fund. The intention is to develop our PIXE-facilities for work

environmental samples and to use PIXE and simultaneous nuclear techniques to determine fume formation rates, the chemical composition of different particle size fractions and their variation with welding parameters as current, voltage and electrode dimensions.

Experimental arrangement

The production and sampling of the aerosols are carried out in a welding technology laboratory. The welding takes place in a hood (see Figure 7) in which the aerosol is collected onto a large filter using a fan. A small fraction of the total emission is isokinetically drawn to the impactor described above. It is also possible to collect samples in this hood onto membrane filters with and without precollector cyclones. When welding, the current and the voltage are recorded.

Results⁷

The fume formation rate per cm^3 of electrode material has been measured for different welding electrode diameters. The process used was shielded metal arc welding (SMAW) with low hydrogen coated electrodes. The result shown in Figure 8, is that the fume formation rate decreases with increasing electrode diameter. For each diameter medium recommended current has been used.

For the same type of electrode, the impactor sampling gives the results shown in Figure 9, where the size distribution of the detected elements are plotted. Using the impactor data it is also possible to calculate the mass median diameter of the different elements. In Figure 10, the mass median diameter of iron is plotted versus the electrode diameter. There is an indication of reduced mass median diameter when reducing the electrode diameter.

As seen in Figure 11 the chemical composition of the aerosol is depending of the applied voltage. At the lower voltage a large fraction of the sampled mass seems to be of electrode coating origin.

In Figure 12 we have plotted the cumulative mass versus the aerodynamic particle diameter as determined by the impactor in a probability diagram. This has been done for the electrode

used above as well as for two others - one stainless steel electrode and one with metal added in the coating.

As seen from the plots all three particle size distributions seem to be close to log-normal distribution for both the elements iron and potassium. The mass median diameter for all three methods are between 0.25 and 0.5 μm . It is also seen that most of the mass of iron and potassium will be on respirable particles. These will be deposited, to a high extend, in the lower parts of the respiratory tract.

Samples have also been collected in the actual work environment. Table 3 shows the results from PIXE-analysis of filter samples collected in a welders breathing zone. It is demonstrated that great variations in the exposure occur, because of changed locations during the welding operations .

ECONOMY

In our laboratory we have analysed thousands of samples delivered from Swedish authorities and industrial hygienists. They have recognized the PIXE-method to be highly competative from an economical and qualitative point of view, when compared to other commercially available methods. When doing our PIXE-analysis we are using an accelerator primarily designed for nuclear research but it is possible to buy a mini-accelerator (see Figure 13) well suited for routine PIXE-applications at a price below 150 000 dollars.

CONCLUSION

Due to the low detection limits and the multielemental capability, PIXE constitutes a powerful method in research and development for work environment purposes. This is further stressed by the possibility to analyse lighter elements simultaneously.

The speed, the low cost per analysis and the multielemental feature will facilitate further extensive industry monitoring programmes and enable the development of new kinds of adequate aerosol samplers.

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(In swedish only)

FIGURE CAPTIONS

1. When the incident particle (A) interacts with a K-shell electron a K-vacancy is created and when this is filled with an electron from a higher shell (C), X-rays of a characteristic energy may be emitted (D).
2. Typical experimental arrangement for PIXE-analysis.
3. Pulse height spectrum obtained when irradiating a welding aerosol sample (low hydrogen SMAW) with 2 MeV protons.
4. When a proton of a few MeV is incident to a fluorine nucleus (a) there is a high probability that the proton reacts with the ^{19}F -nucleus forming a $^{20}\text{Ne}^*$ -nucleus (b) which will immediately decay to ^{16}O and an α -particle and a high energy (6 MeV) γ -quantum will be emitted.
5. Typical experimental arrangement for simultaneous PIXE and fluorine analysis.
6. Welding aerosols from a low hydrogen SMAW process have been sampled on membrane filters. In the diagram the fluorine content as determined by the fluorine analysis method has been plotted versus the total sample content as determined by gravimetric analysis.
7. The experimental arrangement used to collect welding aerosols. When welding under the hood a fan is sucking the air through a large filter in the top. A small portion of the aerosol is sampled isokinetically with an oscillating probe and then collected in a cascade impactor and on membrane filters.
8. Diagram showing the fume formation rate per electrode mass (in diagram expressed as volume) consumed, versus the diameter of the welding electrode. The medium recommended current has been used for each electrode diameter (low hydrogen SMAW)

9. The diagram shows the elemental variation with particle size as determined by the cascade impactor. The arrows are indicating lower limits of detection. (low hydrogen SMAW, medium recommended current)
10. The mass median diameter for iron has been calculated and plotted versus the electrode diameter (low hydrogen SMAW, medium recommended current)
11. Circular diagram showing the variation in elemental composition of the aerosol with the arc voltage.
12. Probability plots for three different welding electrodes with the cumulative mass plotted versus the aerodynamic diameter for potassium and iron. The distributions fit well to log-normal distributions.
13. A schematic drawing of a commercially available compact 2 MeV tandem Van de Graaff accelerator for protons, which could be used for PIXE-applications.

TABLE 1

PROPERTIES OF PIXE

1. Multi-elemental method
2. Low mass detection limits (0.1 - 10 ng)
3. Concentration detection limits in the ppm-range
4. In thick samples only the first few mg/cm^2 are analysed
5. Precision and accuracy $\sim 10\%$
6. Fast (routine analysis in 1-4 minutes)
7. Non-destructive
8. Low cost
9. Quantitative analysis for $Z > 15$
Qualitative analysis for $Z > 12$
10. Possibilities to combine with other methods
for simultaneous detection of low Z elements

TABLE 2

PROPERTIES OF FLUORINE ANALYSIS.

1. Detection limits ~100 ng.
2. Precision and accuracy ~5%.
3. Fast ~5 minutes.
4. No sample preparation required.
5. Non-destructive.
6. Low cost when combined with PIXE.
7. Standards are required for calibration.

TABLE 3.

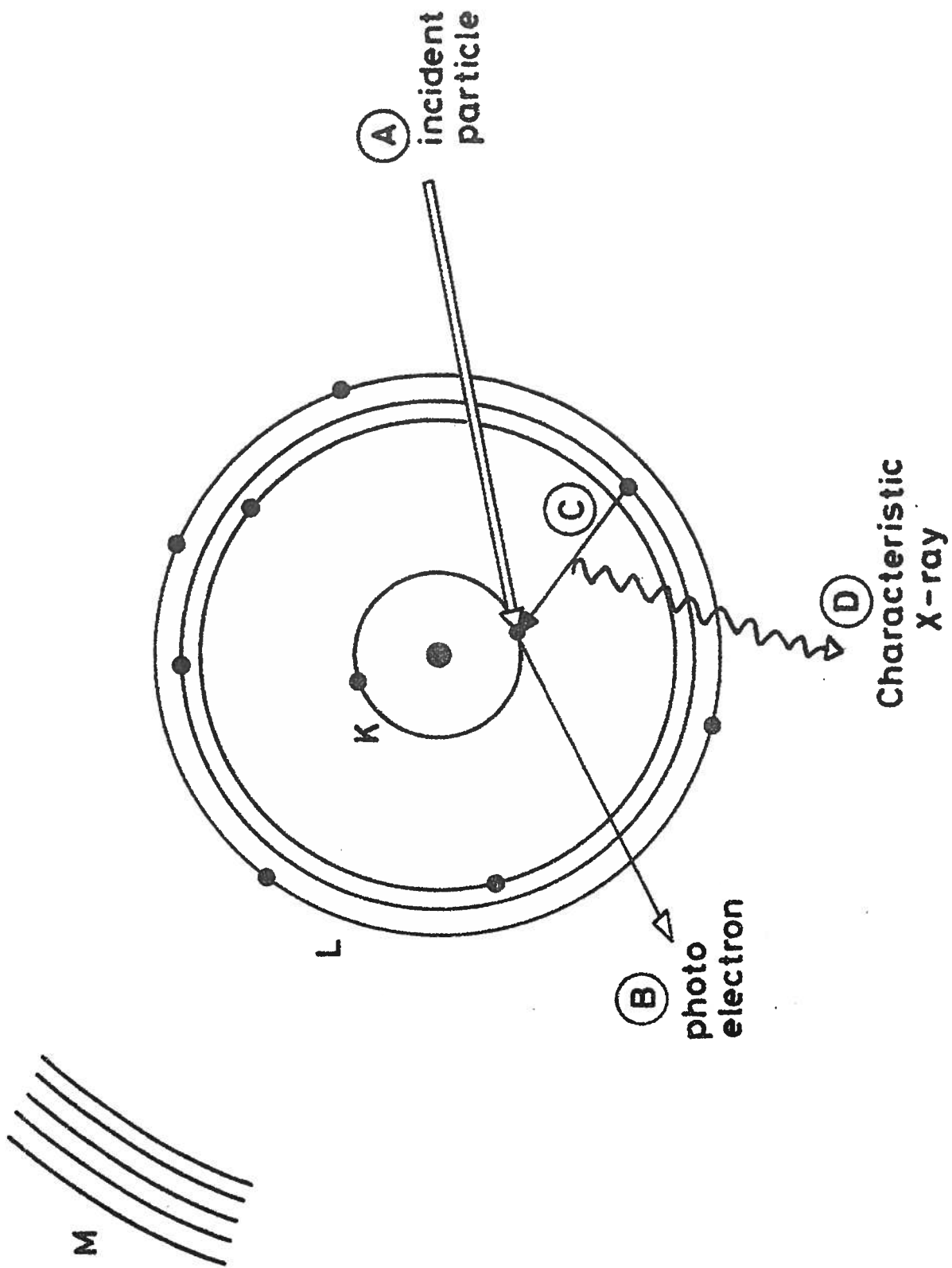
Total filter samples⁺ from a work environment in Sweden. Sample A is from welding in a semiconfined space, and sample B from welding in a confined space. Both sample A and B are collected inside the welding helmet in front of the welder's face. Sample C is a background sample collected in a welding hall far from welding operations. The errors in the elemental analysis are 10%, if not otherwise stated.

	A	B	C
F	4.8	14	0.005
K	5.5	24	0.05 ± 16%
Ca	1.1	9.5	0.02
Ti	0.35	1.0	-
Mn	3.2	5.3	0.02
Fe	15	26	0.19
Zn	0.2	1.1	0.01
sampling time (min)	50	40	285

(mg/m³)

⁺ The filters used were Millipore cellulose acetate filters with a pore diameter of 0.8 µm and a flow rate of 1.0 l/min.

Figure 1



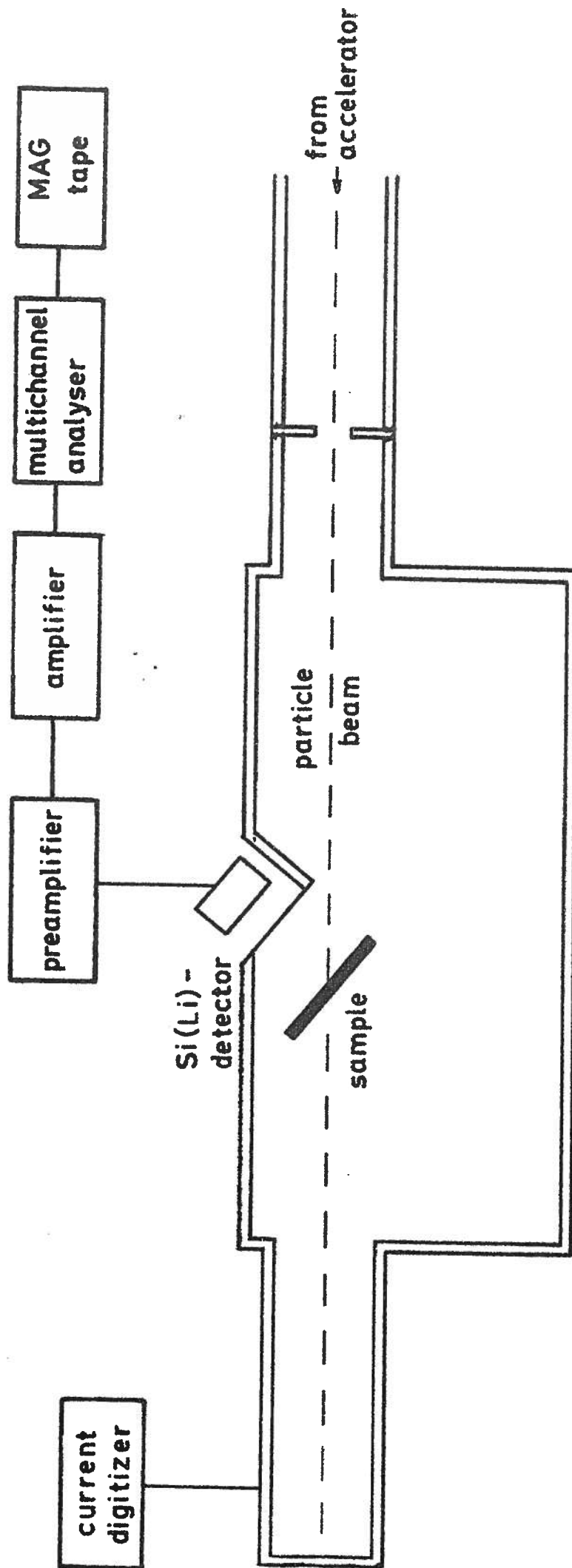


Figure 2.

Figure 3.

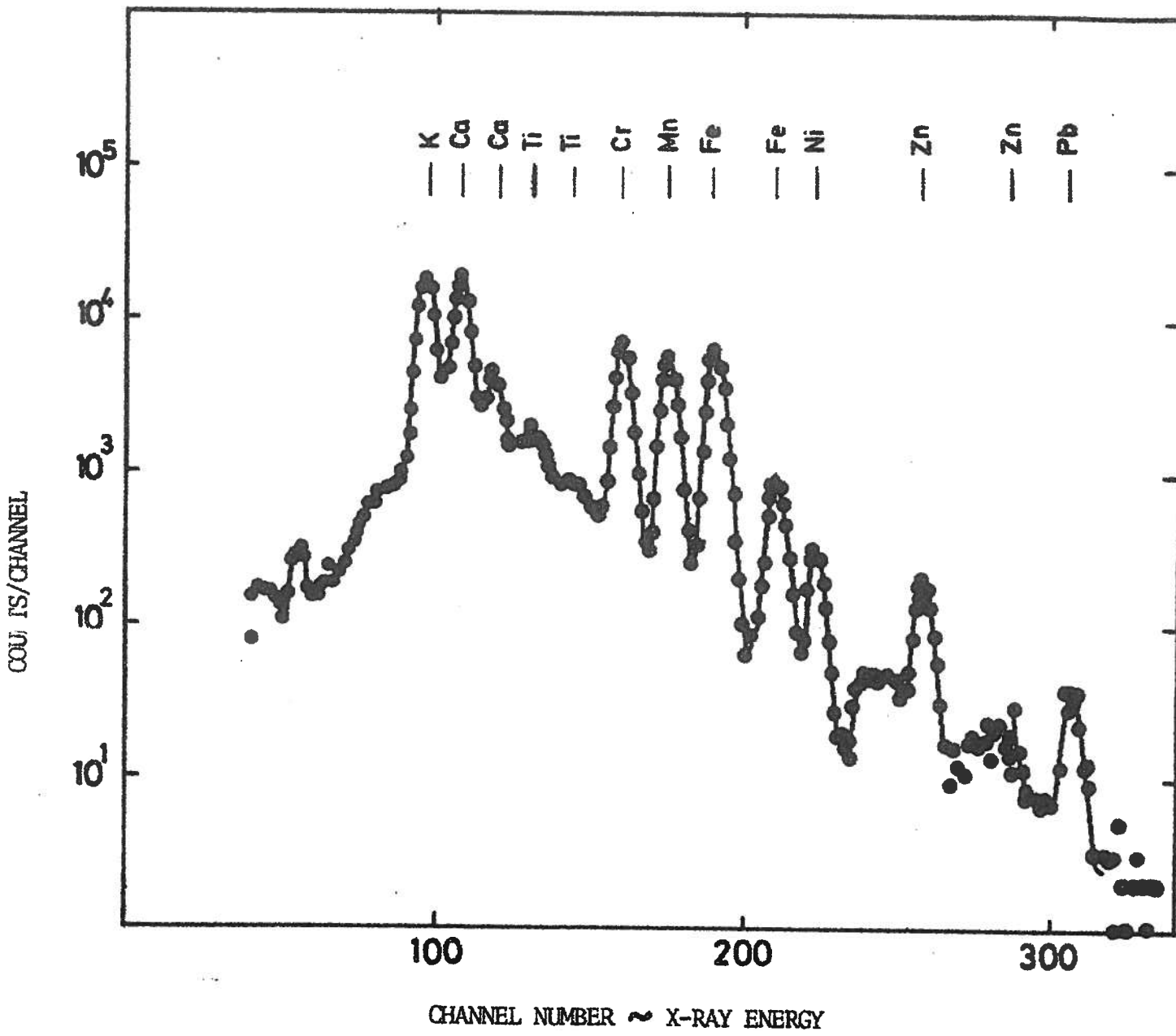
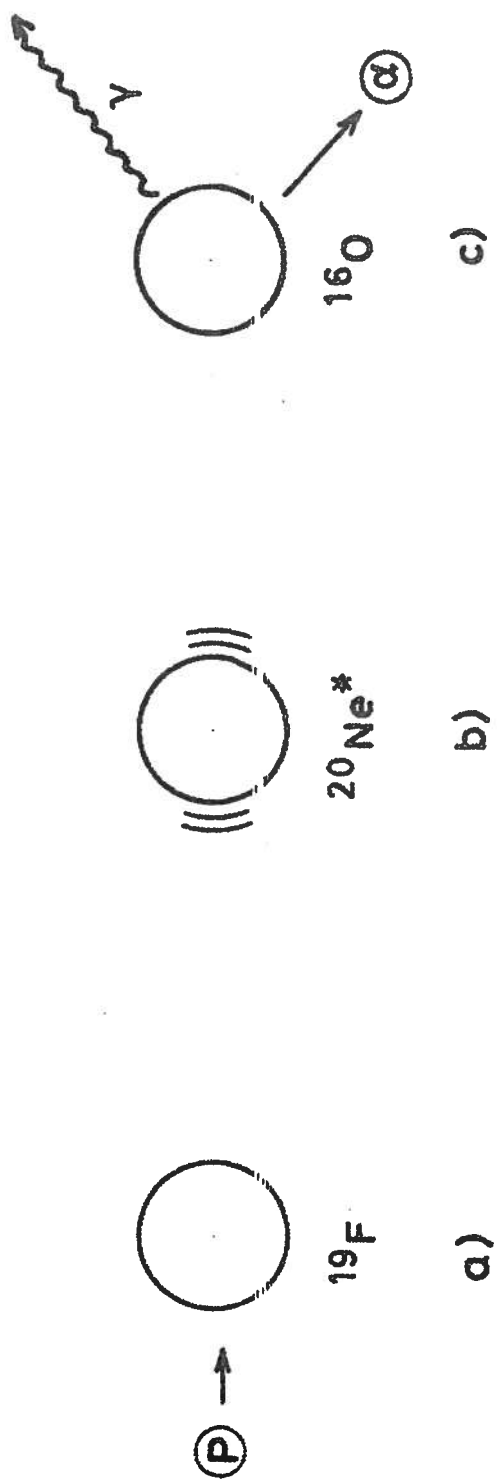


Figure 4



$^{19}\text{F}(p, \alpha)^{16}\text{O}$ - reaction

Figure 5

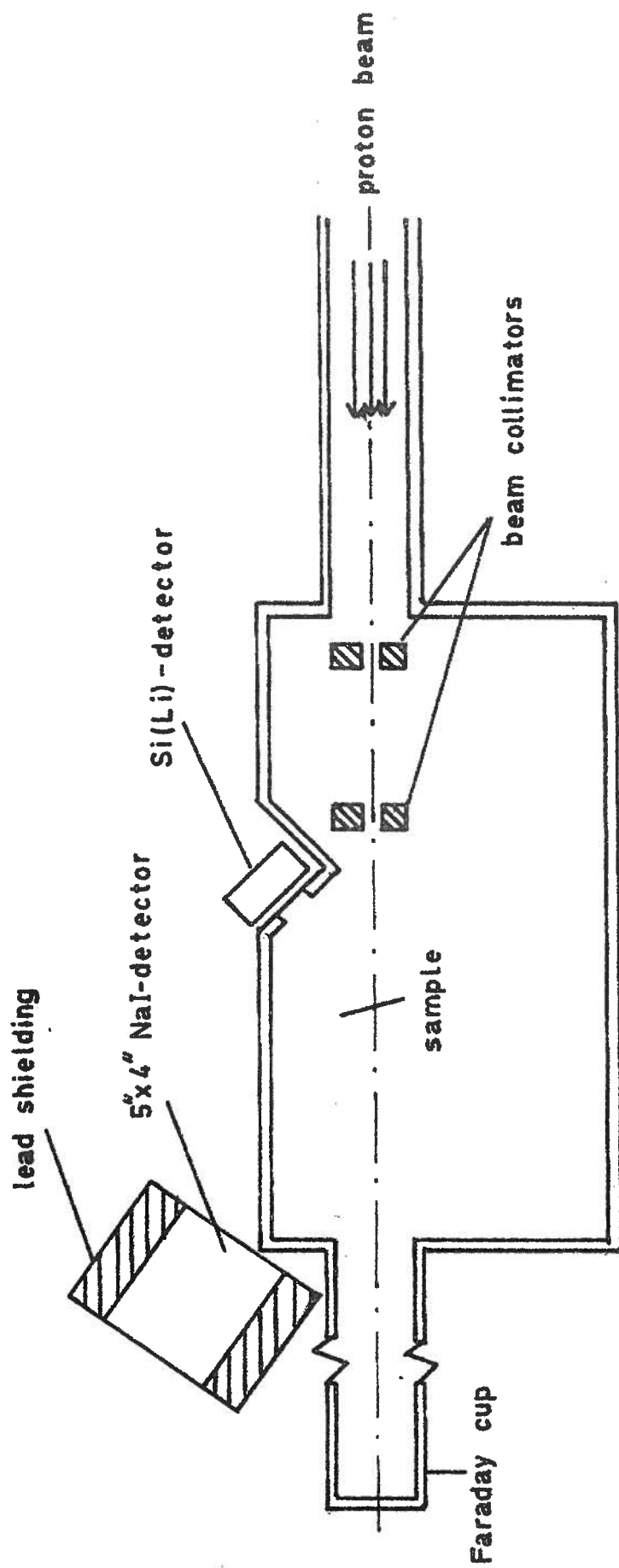


Figure 6

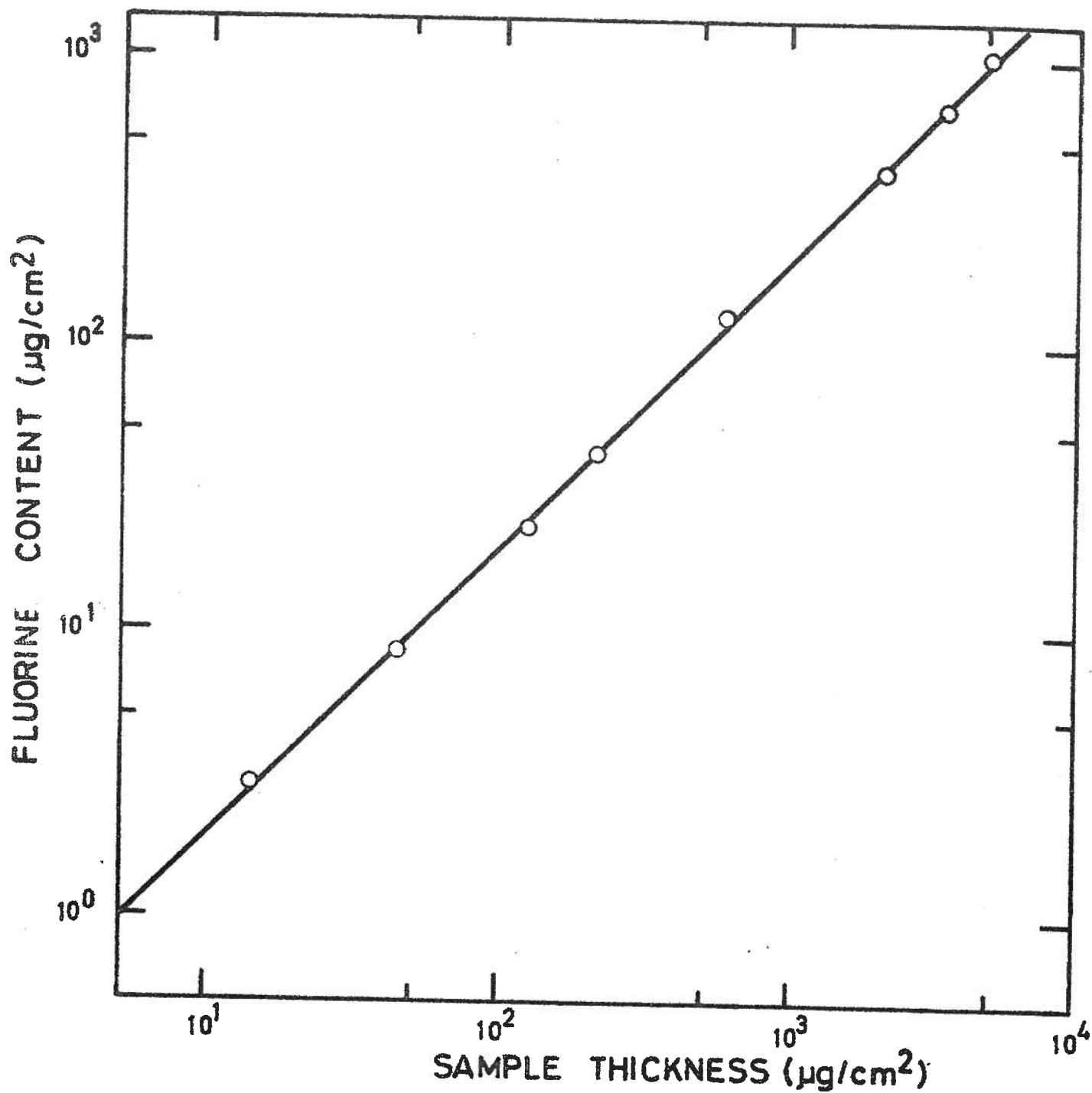


Figure 7

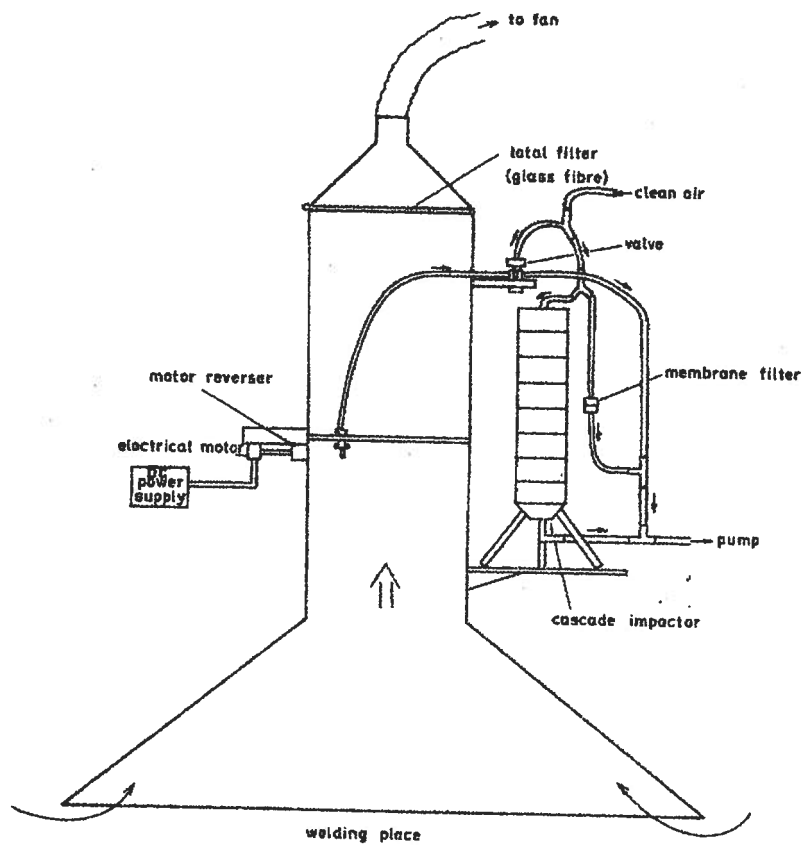


Figure 8.

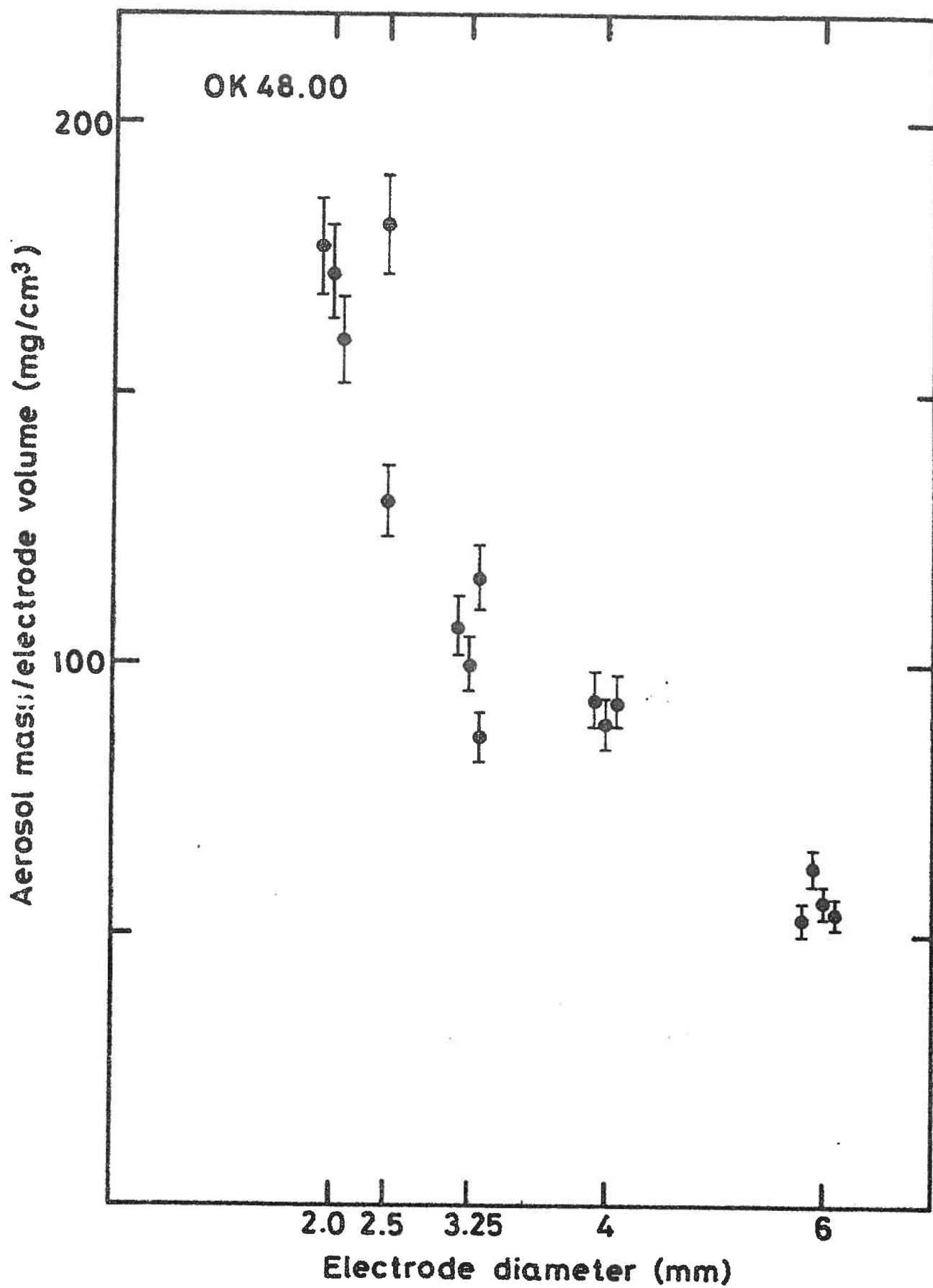


Figure 9.

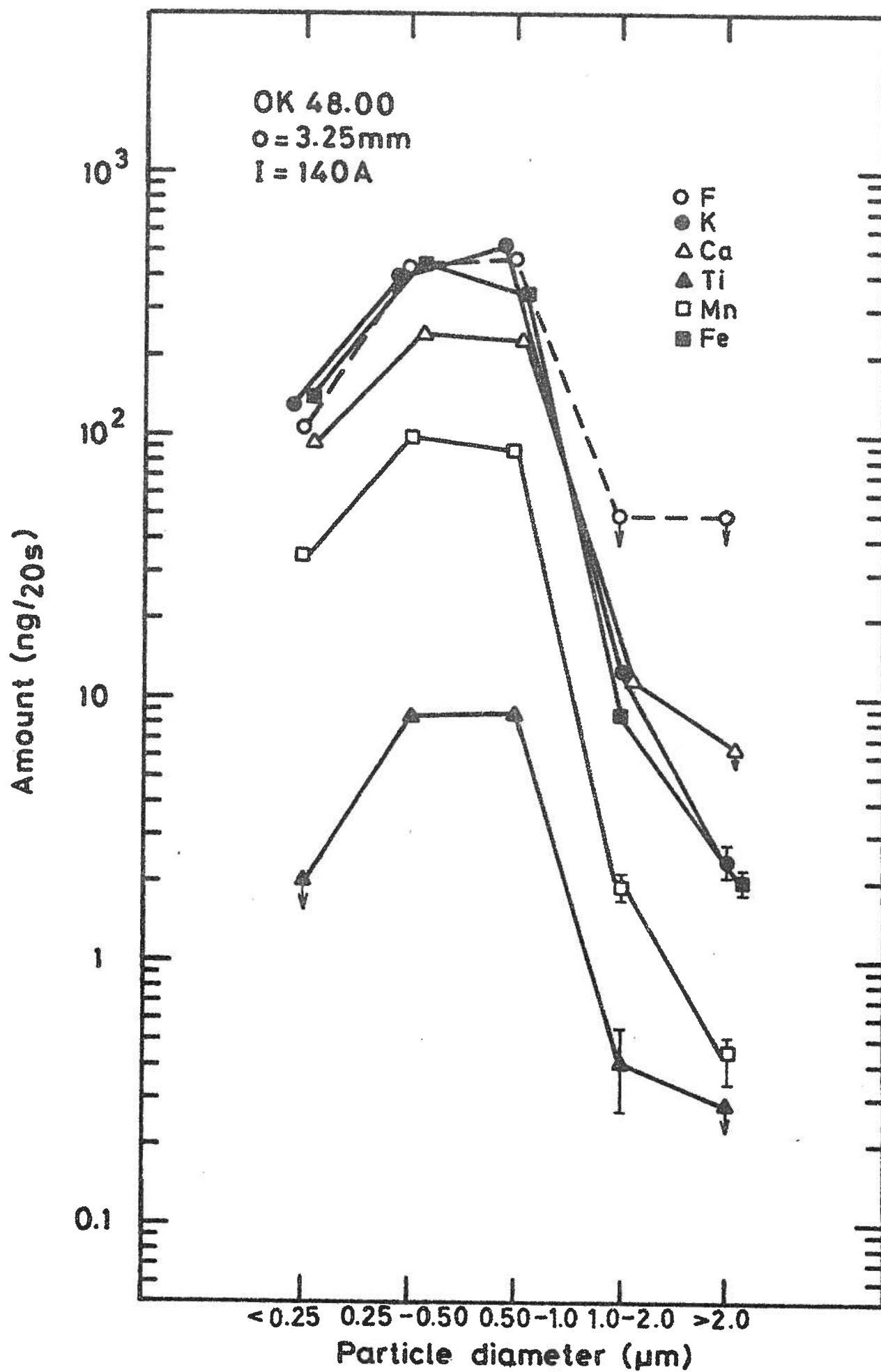


Figure 10.

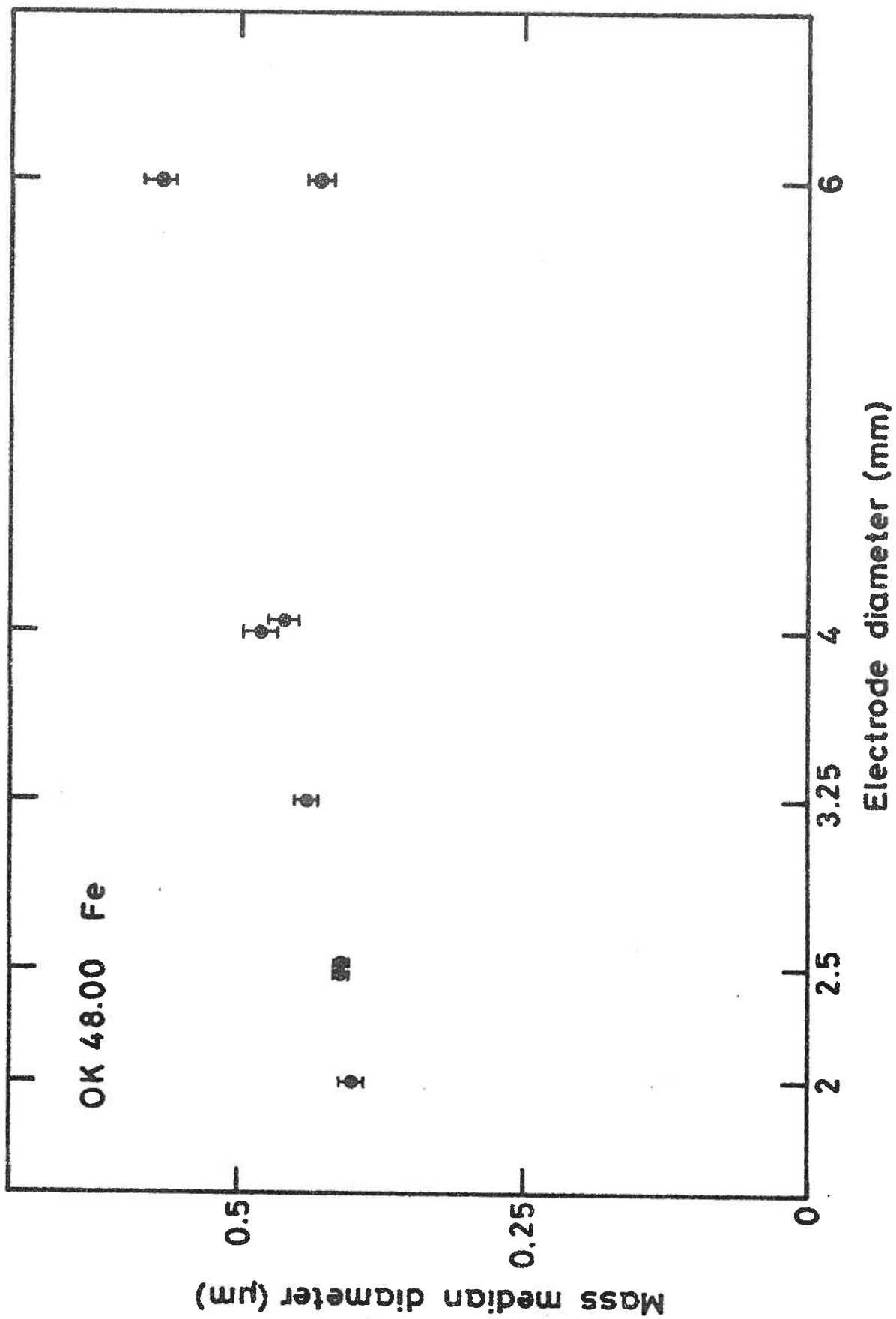


Figure 11.

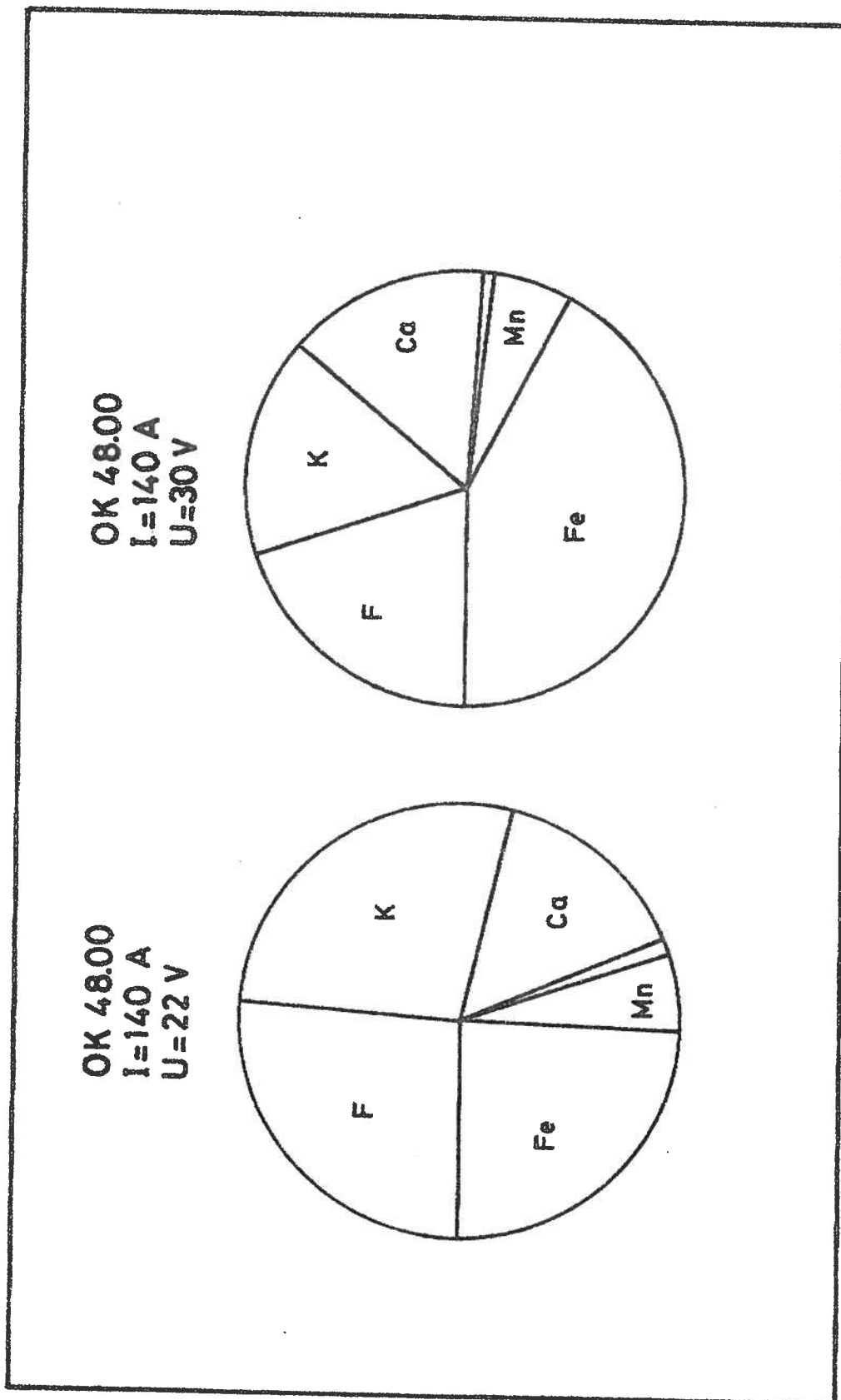


Figure 12

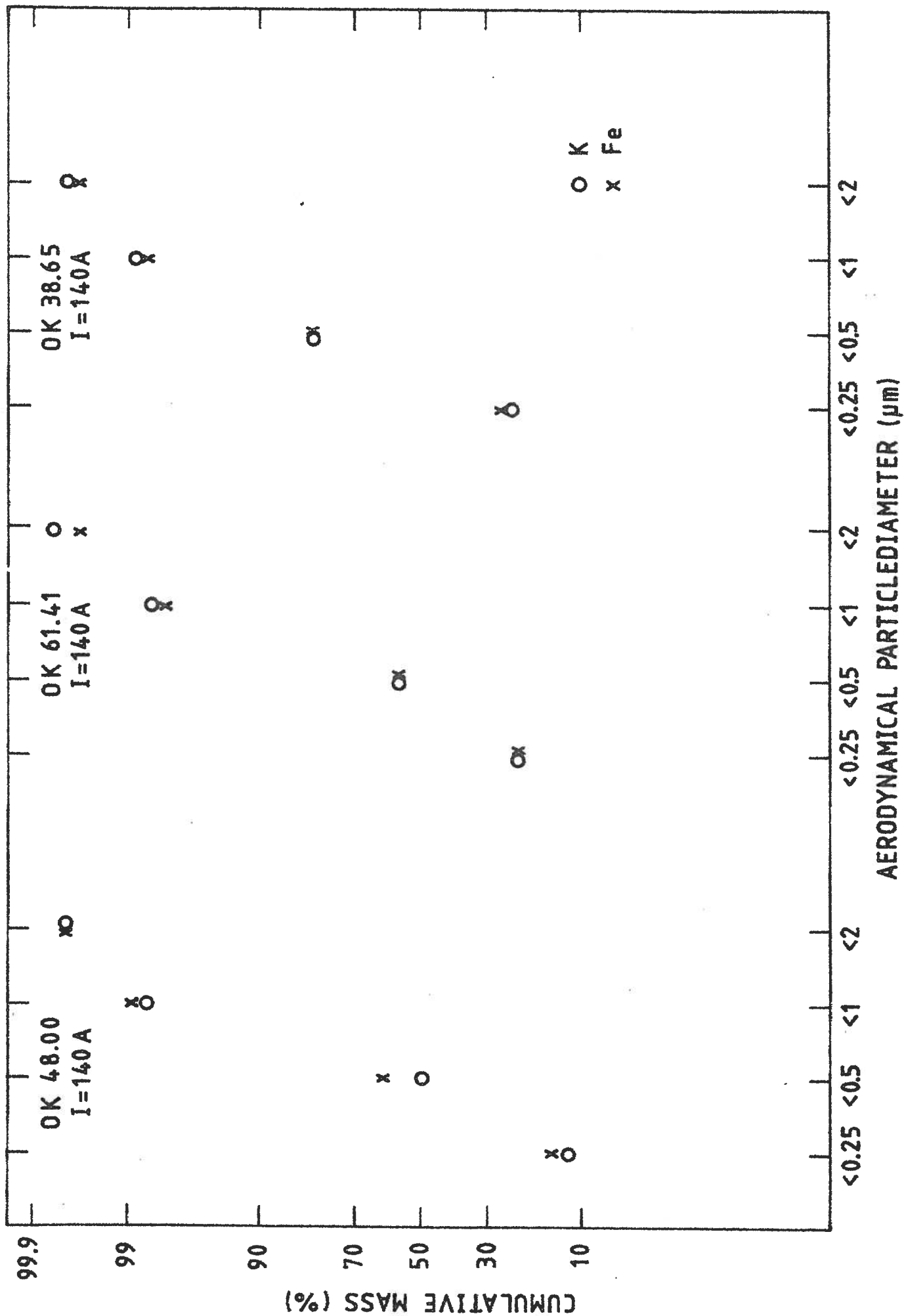
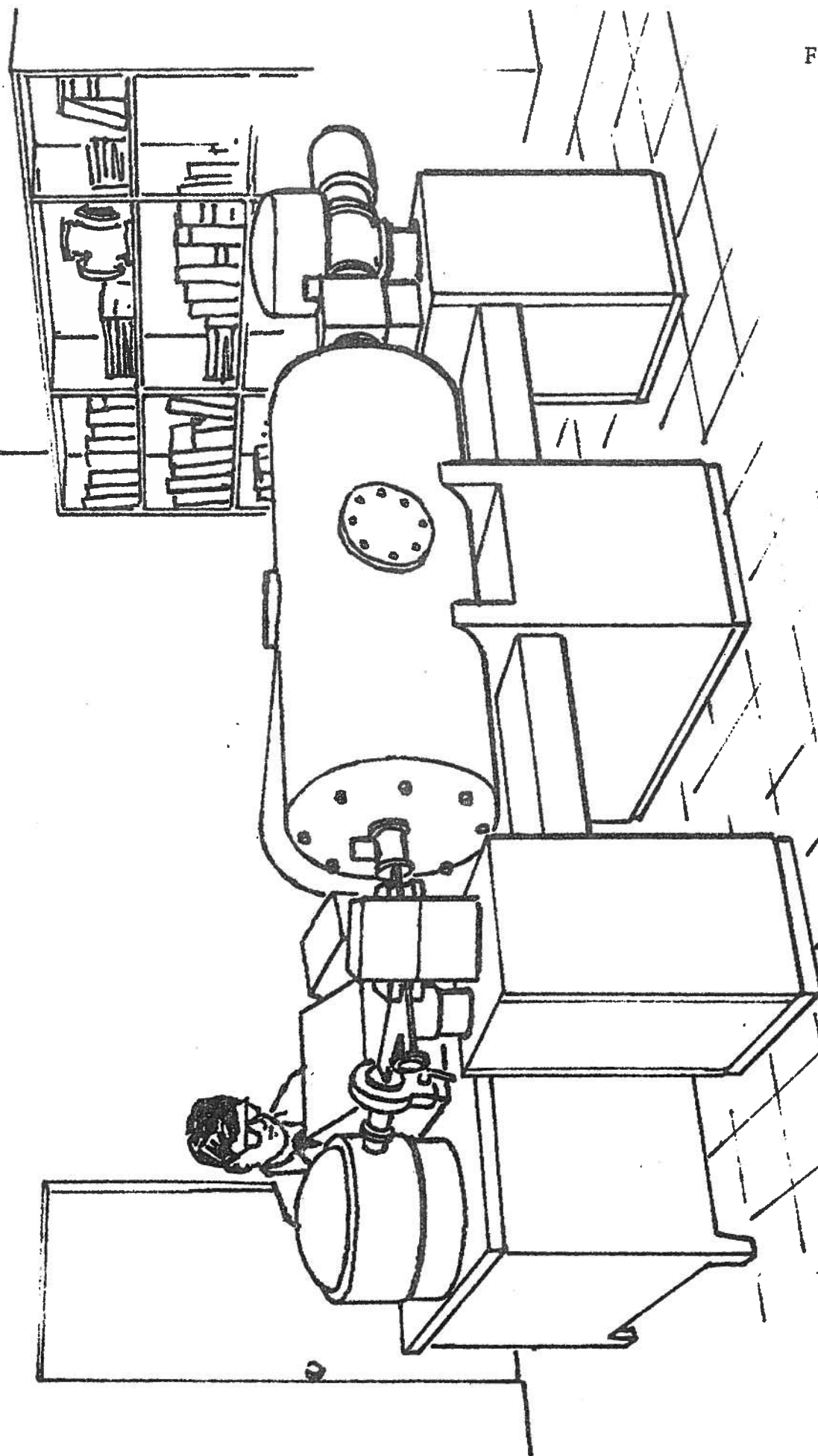


Figure 13



TANDETRON SURFACE ANALYZER
2 MBV TANDEM M. ACCEL. PRATOR