ACCELERATOR BASED ANALYTICAL TECHNIQUES FOR ANALYSIS OF AEROSOL FILTERS.

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Abstract

The ion beam analysis techniques, Particle Induced X-ray Emission (PIXE), Particle Induced Gamma-ray Emission (PIGME), Particle Elastic Scattering Analysis (PESA) and Rutherford Backscattering Spectrometry (RBS) for 2.6 MeV protons, have been developed to operate simultaneously on a 3 MV Van de Graaff accelerator to analyse aerosol filter papers.

PESA is used in the forward scattering mode at 30° to determine the total H content. RBS at 169° is used to determine C, N and O content of the thin filter papers. PIGME is used to determine light elements such as F and Na and PIXE is used for all elements above Al. The system has high sensitivities, is non destructive and can analyse 12 samples/hour. Comparisons of these IBA techniques with neutron activation analysis (NAA) and ion chromatography (IC) will be made.

Introduction

Two mechanisms, diffusion and settling determine the size distribution of fine particles in the size range less than 100 µm diameter which occur in the atmosphere. For the courser particles, generated mainly by mechanical means, such as soil and wind blown sea spray the removal rates from the atmosphere increase with particle size. However, for gases and very fine particles these removal rates decrease with particle size up to a few micrometers in size. Today many of these fine particles and gases are man-made for example, SO_2, NO_x, O_3, and fine particulates such as K from wood burning and Pb and Br from motor vehicles. These two removal mechanisms produce a bimodal distribution of aerosol particle sizes in the atmosphere, the fine mode peaking around 0.1 to 1 µm with a minimum at 2.5 µm is known as the accumulation mode, since it grows from smaller particles. While the size range above 2.5 µm is called the mechanical mode, as it is mostly mechanically generated.

Aerosol particles in the size range less than 2.5µm play an important role in pollution studies. They are small enough to lodge in lungs and cause health problems, they impair visibility and the public's perception of pollution and they are capable of being transported over large distances as they do not settle out readily. In Australia we have established a large area fine particle network consisting of 25 cyclone sampling units covering 80,000 square kilometres of the state of New South Wales. The network called **ASP** -Air Sampling Program - collects particles on 25mm stretched Teflon filter papers which are ideal targets for accelerator based Ion Beam Analysis (IBA). We will discuss the four IBA techniques, PIXE, PIGME, PESA and RBS used simultaneously on the 3 MV Van De Graafff accelerator at Ansto and present some of the early results from this research program.

Methods

At **ANSTO** we have several particle accelerators including an 8MV Tandem and a 3MV Van de Graaff accelerator, as well as two research reactors. This provides us with a variety of nuclear techniques for analysis of Teflon filter papers obtained from the network. To date we have used mainly ion beam analysis techniques based on the

3MV Van de Graaff accelerator together with about 10% of samples being analysed by neutron activation analysis (NAA) for about 12 elements in the larger of our two research reactors and some ion chromatography (IC) for sulphate, chloride and fluoride ions as part of our quality assurance program.

The accelerator based IBA techniques used at **ANSTO** are discussed below:

Particle Induced X-ray Emission (PIXE)

Particle Induced X-ray Emission or PIXE became popular in the mid 1970's following an excellent review on analytical applications of PIXE by Johansson and Johansson/1/.The technique has been adequately reviewed over the years /2,3 and 4/ and will not be treated again here. It suffices to say that PIXE provides the bulk of the analytical information since it is applicable to elements from aluminium to uranium. The X-ray spectra are especially free from background emission as shown in Figure 1 and this allows lower detection limits typically less than 10 ngm^{-3} of air for input proton energies of between 2 and 3 MeV. Typical proton beam currents are less than 1 nA/ mm^{2} for beam diameters of around 8 mm. Thin standard Micromatter foils of Al, Si, Cl, Ca, Fe and Sr are used to calibrate the PIXE detection system from 1.4 keV to 20 keV. Over the past 18 months the calibration has been reproducible to better than $\pm$3%.

Particle Induced Gamma Ray Emission (PIGME)

Particle Induced Gamma Ray Emission or PIGME is produced when the input ion or in our case proton interacts with the target nucleus producing high energy photons or gamma rays. These gamma rays are characteristic of the target nucleus struck and their number is proportional to the amount of this target isotope present in the target. We use PIGME to measure sodium and fluorine only. It has higher minimum detectable limits than PIXE being typical around 150 ngm^{-3} of air for sodium and 60 ngm^{-3} for fluorine for a few minutes of beam time using 2 - 3 MeV protons. A typical PIGME spectrum is shown in Figure 2. Standard thin Micromatter foils of calcium and strontium fluoride and sodium chloride are used to calibrate the PIGME system for these elements. The PIGME technique is run simultaneously with the PIXE technique on the same sample although count rates into the PIGME spectra are somewhat lower than into the PIXE spectrum since PIGME is a nuclear reaction while PIXE is an atomic one.

Particle Elastic Scattering (PESA)

Hydrogen is a difficult species to measure accurately, in our system we acquire total hydrogen measurements on the filter using the proton elastic scattering (PESA) or forward scattering technique /5,6/ at 30 degs The spectrum signature from hydrogen being the lightest element is well separated from the heavier elements as shown in Figure 3 and enables use obtain minimum detection limits around 15 ngm^{-3} for a typical 3 μC run. A standard thin 6 μm Mylar foil is used to calibrated the PESA detection system for hydrogen analysis. The PESA technique can clearly only be used with a thin filter paper target where the ion only losses a small fraction of its total input energy.

Rutherford Backscattering (RBS)

Rutherford Backscattering is similar in nature to PESA except the detection is in the backward direction. In our case we use a reaction angle of 169 degs to detect total carbon nitrogen and oxygen on the filter. Standard thin Mylar and Kapton foils are used to calibrate the detection yields since the reaction cross sections for these light elements are non - Rutherford. Detection limits for nitrogen and oxygen are around 200 ngm^{-3} for typical 3 μC run while minimum detection limits for carbon are much higher at around 500 ngm^{-3} since we have to subtract the effects of carbon in the Teflon filter itself. A typical RBS spectrum for a 3 μC run on a thin stretched Teflon filter paper is shown in Figure 4.

Results

All 25 **ASP** cyclone sampling units in the network have now been operational since 1 March 1992. The collection efficiency for more than 3000 samples from the network in the first year was greater than 96%.The network currently produces 250 Teflon filter papers / month which are analysed for H, C, N, O, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, and Pb using IBA techniques. The PIXAN package developed at ANSTO /7/ is used to analyse the PIXE spectra using the site supercomputer. Fits similar to the solid line shown in Figure 1 are typical. In house spectrum fitting routines have been written to analyse the PIGME, PESA and RBS data obtained simultaneously with the PIXE data. Typically we run 2.6 MeV protons for 3 to 5 mins using a 10 nA, 8 mm diameter beam and the solid angles for each of the 4 detection channels are adjusted so that the count rates produce roughly similar deadtimes in the PC data acquisition system

The results from the IBA analysis have been compared with ion chromatography (IC) on 50 samples and several different chemical species and with neutron activation analysis (NAA) on 100 samples and 15 elements the results are displayed in Figures 5 and 6 respectively and where the techniques do not reach their lower detection limits they all show satisfactory agreement with the IBA methods.

References

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/2/ S.A.E. Johansson and J.L. Campbell, "A Novel Technique for Elemental Analysis", Wiley, New York 1988.

/3/ D.D. Cohen and E.J. Clayton, "PIXE", Chapter 5 in Ion Beams for Materials Analysis, Academic Press, New York 1989. Eds. J.R. Bird and J.S. Williams.

/4/ W. Maenhaut, Control and Fate of Atmospheric Trace Metals, Academic Press, NY, 1989, eds. J.M. Pacyna and B. Ottar.

/5/ D.D. Cohen, "Ion Beam Analysis Techniques in Aerosol Analysis", Clean Air, 26 (1992)113.

/6/ B. Kusko, T.A. Cahill and R.A. Eldred, "Non destructive light element analysis by forward ion scattering techniques", Proc. of 81st Annual Meeting of Air Pollution Control Association, Dallas, Texas, 19-24 June 1988.

/7/ E.J. Clayton, PIXAN Package, ANSTO, AAEC/M113, Sydney, Australia, November, 1986.

Figure captions

Figure 1 : A typical PIXE spectra for Mascot - ASP23 a heavy industrial site, and Oberon ASP13, a rural site, taken on the same day 24 June 1992. The solid curve is the PIXAN fit to the data (the dashed curve).

Figure 2 : A typical PIGME spectrum for Cape Grim - ASP25, a seaside location showing the Na 440 keV gamma ray peak and the 197 keV and 6.129 MeV F gamma rays from Teflon.

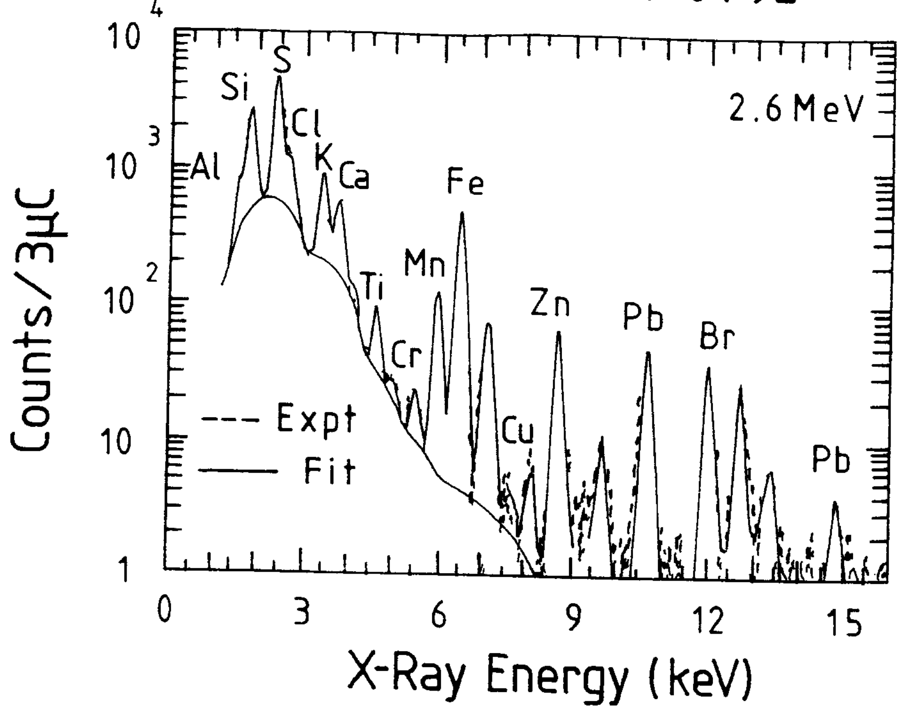
Figure 3 : Comparison of typical PESA spectra for a heavy industrial site - Mascot ASP23 and for Cape Grim ASP25 taken the same day 24 June 1992. These spectra were accumulated simultaneously with the PIXE spectra of Figure 3.

Figure 4 : A typical proton RBS spectrum for a thin stretched Teflon filter paper. The C, O and F peaks are clearly seen. The N peak is small and lies between the C and O peaks.

Figure 5 : (a) Comparison of ASP sulphur levels as measured by PIXE with the SO_4^{2-} ion level as measured by ion chromatography (IC). (b) Comparison of ASP chlorine levels as measured by PIXE with Cl^- ion level as measured by IC. The blank filter concentrations for SO_4 and Cl^- were 140 and 90 ng/m^3 respectively.

Figure 6 : A comparison of PIXE analysis and NAA analysis on the same 100 filter papers for up to 15 different elements.

MASCOT ASP23 29-04-92



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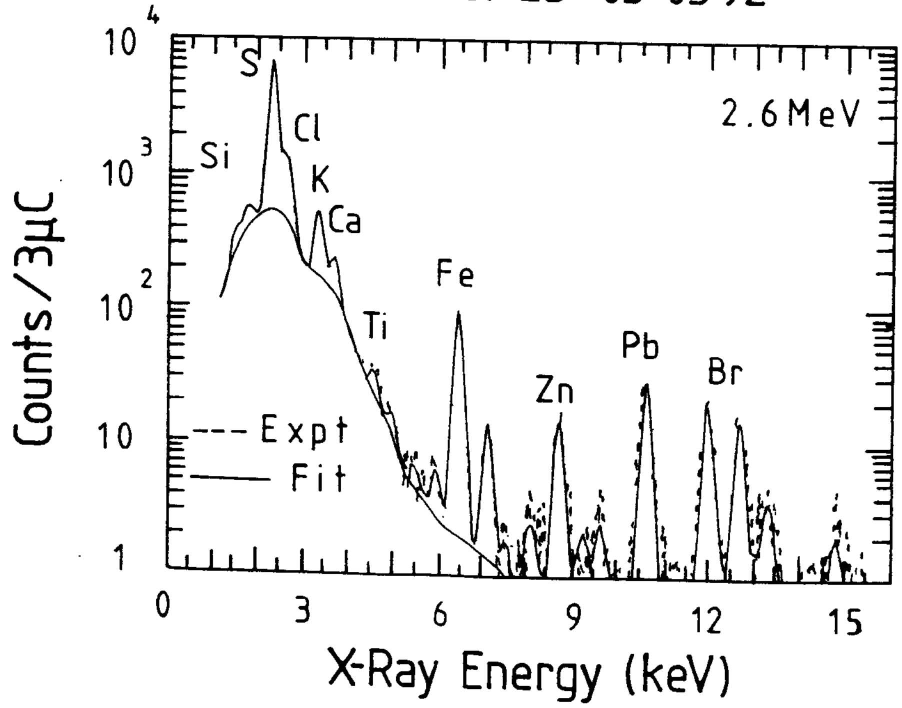
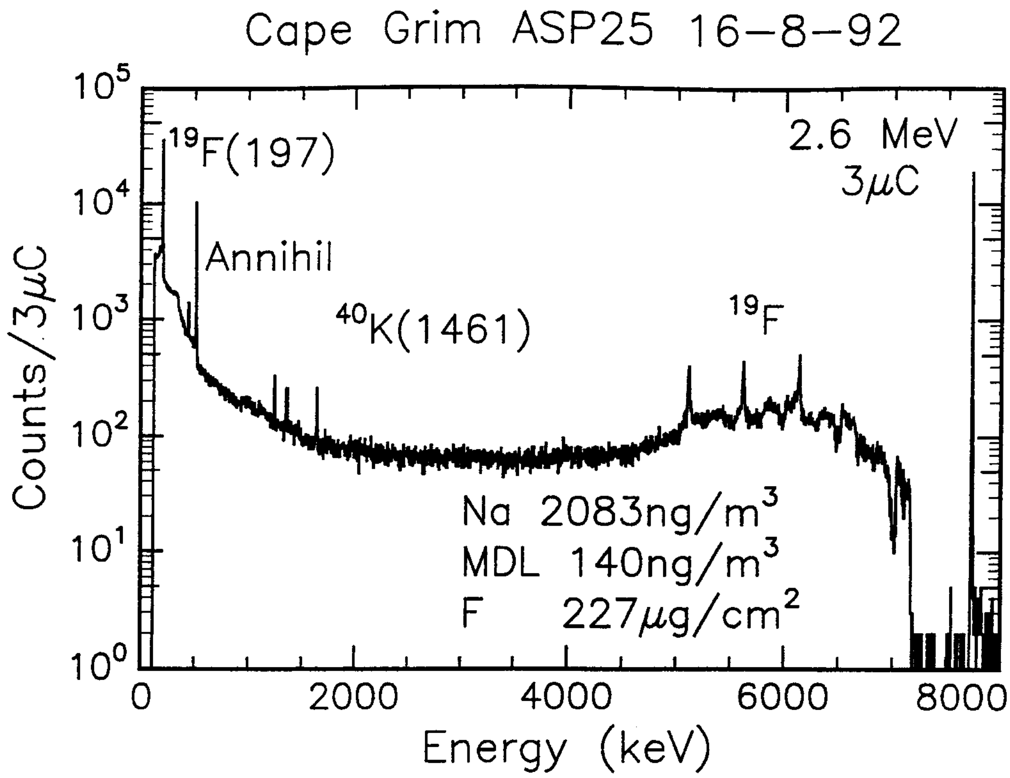
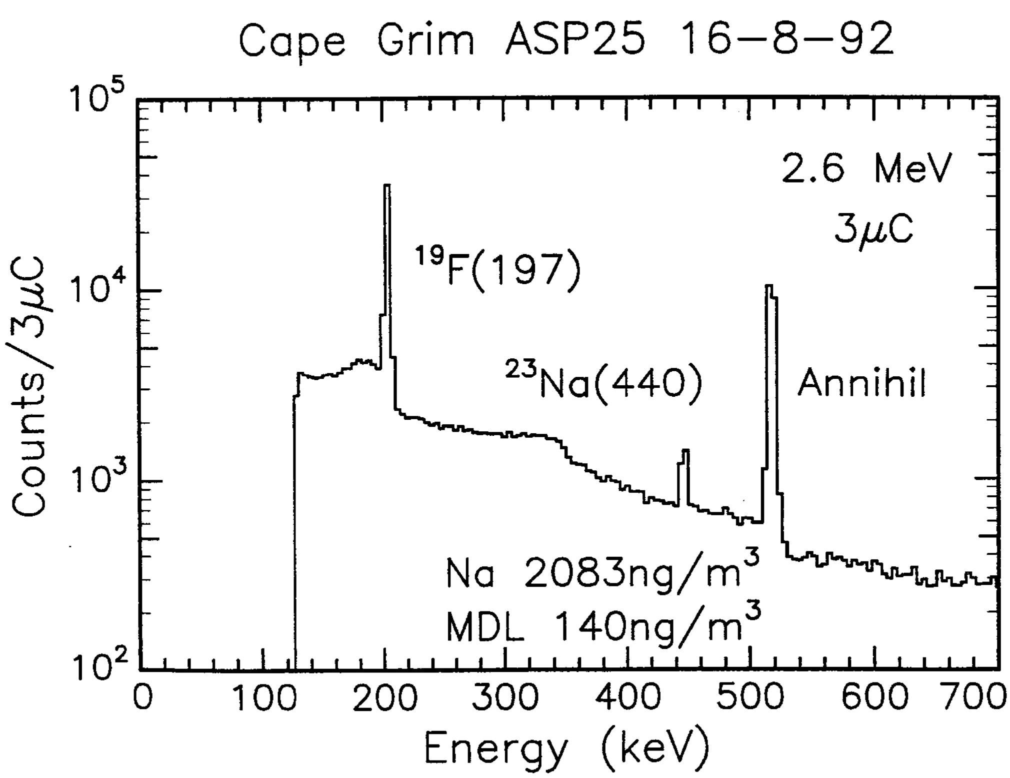


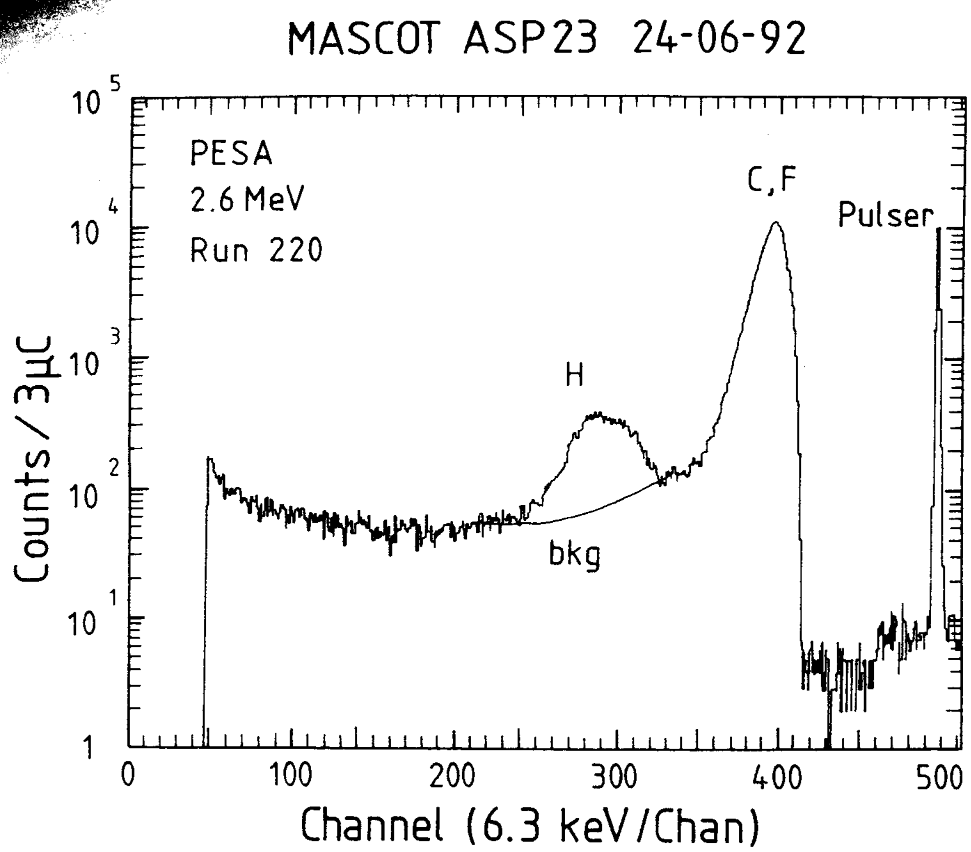


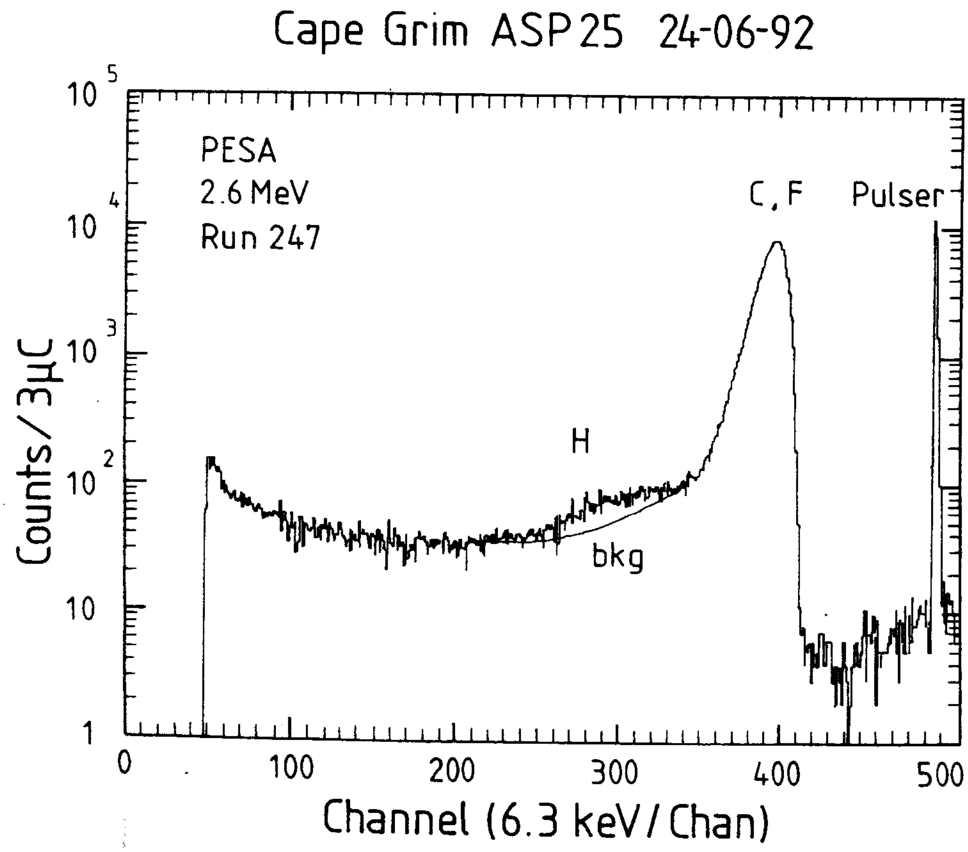
Cape Grim ASP25 16-8-92
^{19}F(197)
2.6 MeV
3μC
Annihil
^{40}K(1461)
^{19}F
Na 2083ng/m^3
MDL 140ng/m^3
F 227μg/cm^2
Counts/3μC
Energy (keV)

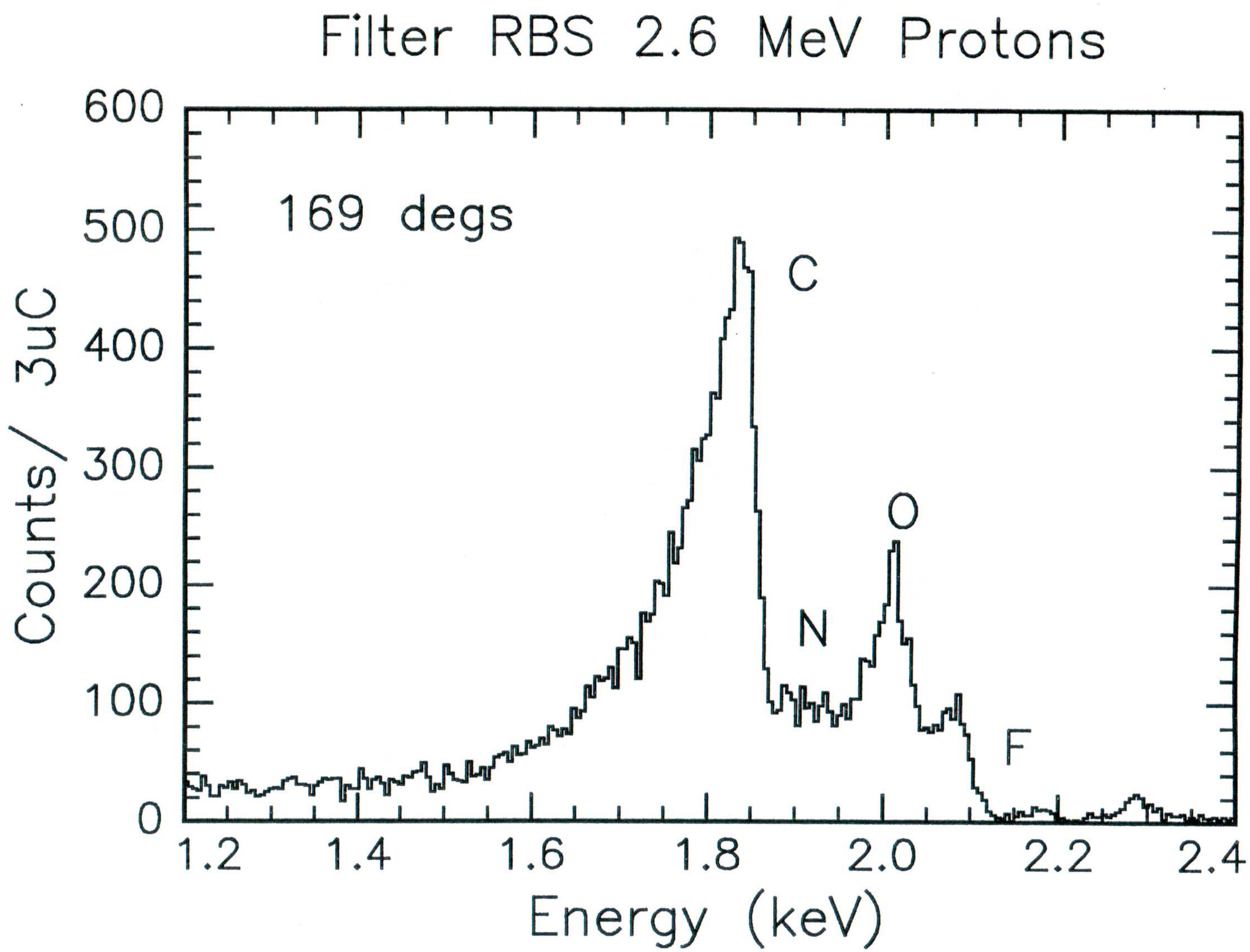


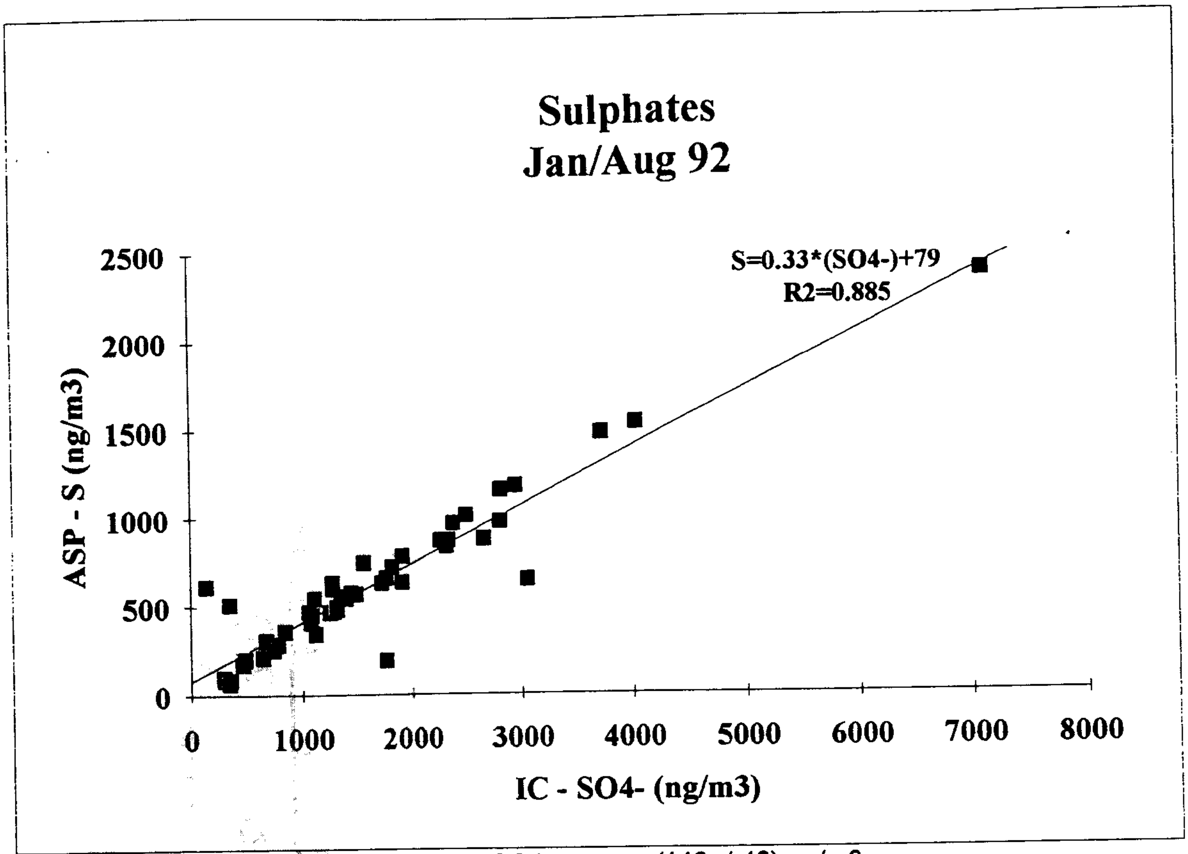
Cape Grim ASP25 16-8-92
2.6 MeV
3μC
^{19}F(197)
^{23}Na(440)
Annihil
Na 2083ng/m^3
MDL 140ng/m^3
Counts/3μC
Energy (keV)

2

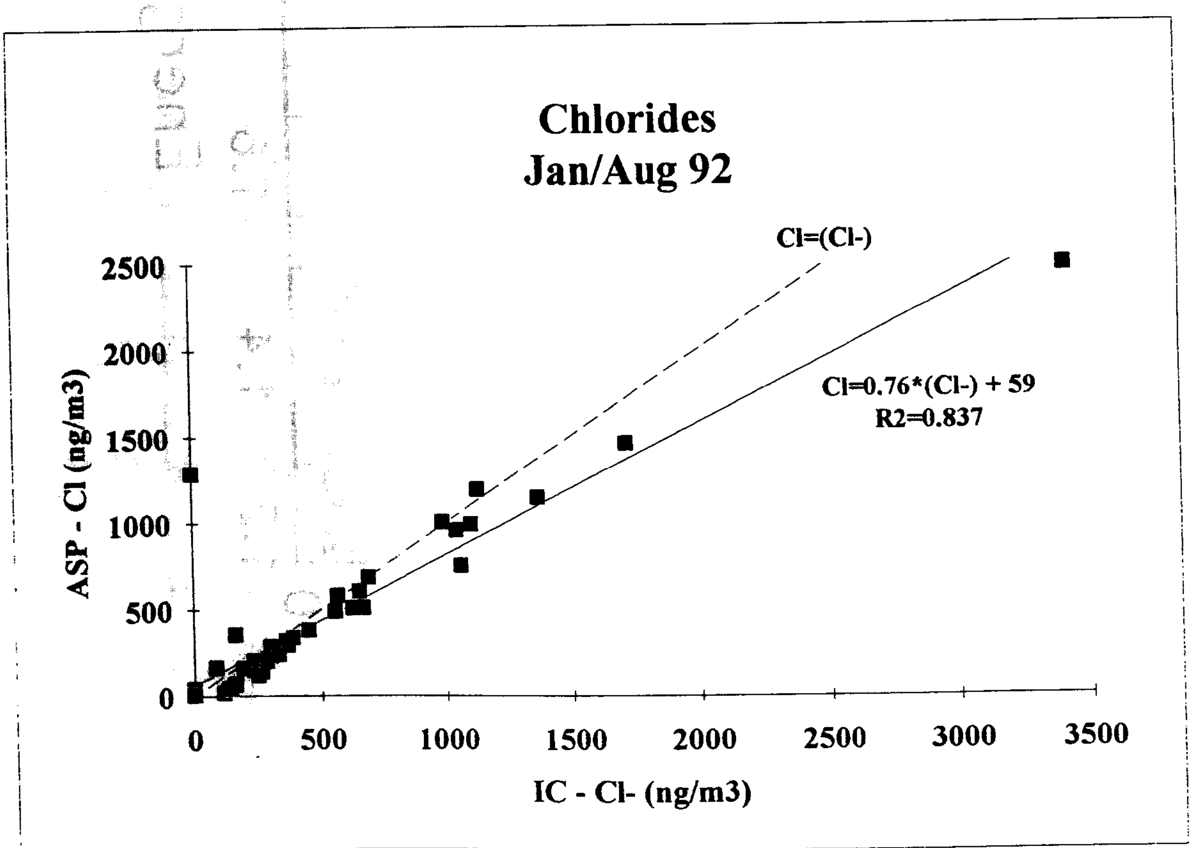

MASCOT ASP23 24-06-92
PESA
2.6 MeV
Run 220
C,F
Pulser
H
bkg
Counts / 3μC
Channel (6.3 keV/Chan)


Cape Grim ASP25 24-06-92
PESA
2.6 MeV
Run 247
C, F
Pulser
H
bkg
Counts / 3μC
Channel (6.3 keV / Chan)


Filter RBS 2.6 MeV Protons
169 degs
C
N
O
F
Counts/ 3uC
0
100
200
300
400
500
600
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Energy (keV)



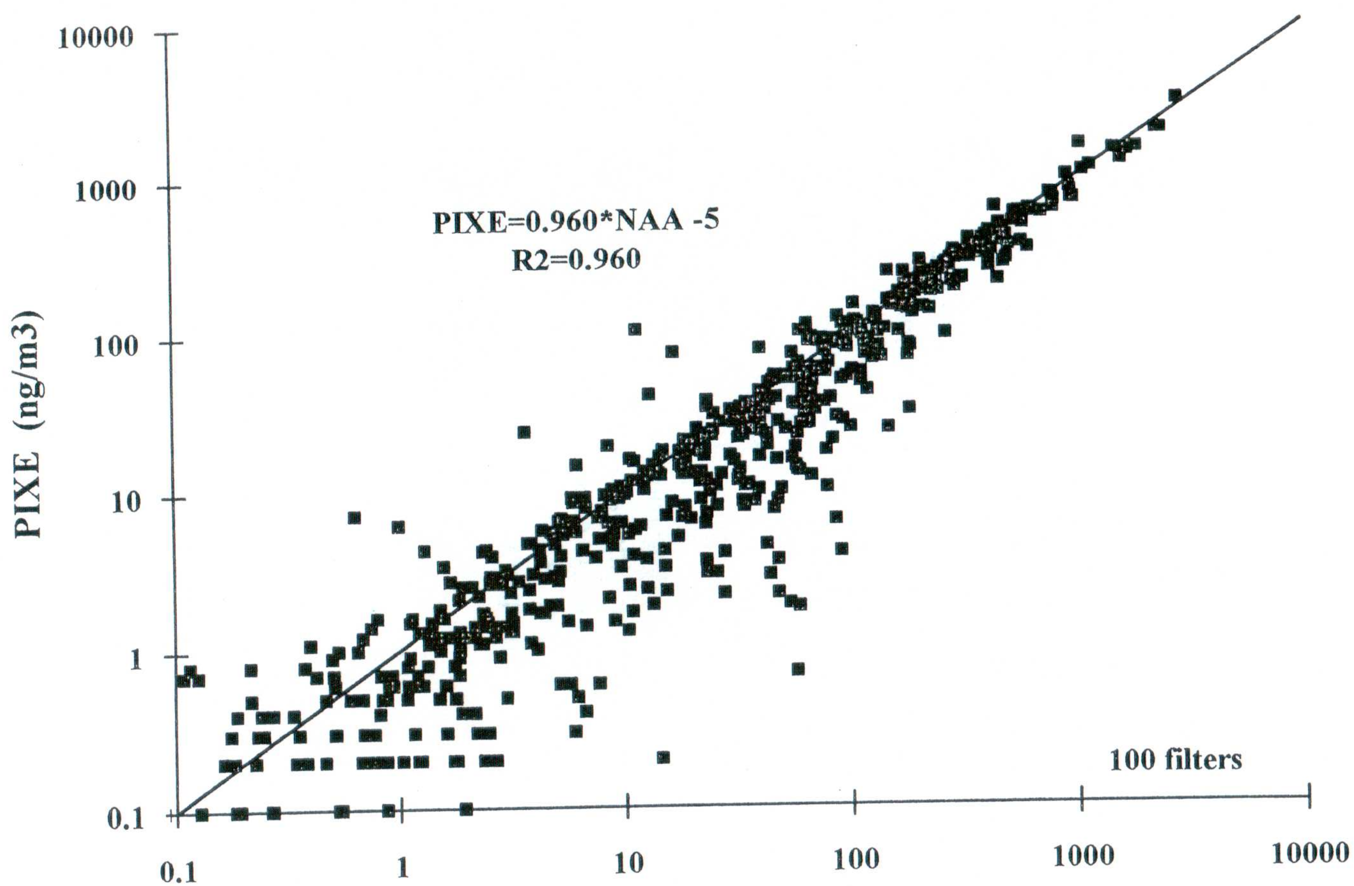
Mean Blank Filter SO4- conc. = (140+/-40) ng/m3



Mean Blank Filter Cl- conc. = (90+/-30) ng/m3

PIXENAA.XLC

All Elements - Feb/Jul 92



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