

iBAT: A new ion beam batch analysis tool for thin samples

Rainer Siegele^{*}, David D. Cohen

Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC NSW 2232, Australia

ARTICLE INFO

Keywords:

IBA
Ion Beam analysis
PIXE
RBS
PIGE

ABSTRACT

We present a new analysis tool and user interface for batch analysis of PIXE, PIGE, RBS and PESA spectra of thin samples. IBA analysis techniques are ideally suited for aerosol filter analysis, because of their high sensitivity and because the layer of aerosol material deposited on the filters is very thin. The analysis tool provides an easy interface for the MS-DOS executable of the GUPIX package, combined with newly developed software for Proton Induced Gamma Emission (PIGE), Rutherford Back Scattering (RBS) and Proton Elastic Scattering Analysis (PESA). For PIGE and PESA background subtraction techniques are applied to extract the gamma and hydrogen recoil peaks and calculate concentrations using suitable calibrations standards. For RBS a similar technique is applied to extract estimates for C, N and O. The results of this new analysis tool will be compared with results obtained from the PIXAN package used previously. The data will also be checked for internal consistencies within aerosol data sets using source apportionment techniques.

1. Introduction

For the past 30 years, we have been using the PIXAN [1] analysis package at ANSTO. In order to run it more efficiently it was bundled with a GUI interface [2]. This GUI facilitates the automated analysis of reference standards producing a graphical comparison of the results with the reference values.

The GUI also included sections for Proton Induced Gamma Emission (PIGE) analysis and in the case of thin samples a simple Proton Induced Elastic Scattering Analysis (PESA) and Rutherford Backscattering Analysis (RBS). Since the original PIXAN package was written in FORTRAN using libraries written at ANSTO it became more and more difficult to maintain.

Therefore we developed a new software package for IBA analysis called iBAT (IBA Batch Analysis Tool). This new package uses GUPIX for the PIXE analysis, while the PIGE, PESA and RBS sections were completely rewritten. Similar to our previous software package, this package also automatically finds any Standard Reference Materials (SRM), that are part of a particular measurement and uses them for calibration.

While the main focus of the program was to replace the GUI, currently used for thin sample aerosol filter analysis, it also allows PIGE and PIXE analysis of thick samples. The thick sample analysis does not extend to PESA and RBS, because the assumptions that can be applied to thin samples don't work in the case of thick samples.

The overall package consists of a number of individual Awk scripts, one for each of the analysis techniques and graphical user interface written in Tcl/Tk tying the individual parts together. The package relies extensively on Gnuplot [3] for plotting and fitting.

As an example spectra for thin sample aerosol analysis are shown in this paper. All 4 spectra of a sample were taken simultaneously, using a 2.54 MeV proton beam. This beam energy was chosen to optimise the PIGE yield for Na analysis, which is an important element in aerosol analysis.

2. GUI

The GUI interface (see Fig. 1) is divided into six sections, four for the individual analysis techniques, plus one for general setup and one for combining the concentration results of the four techniques into a single output file. This last section is mainly for aerosol analysis, for which an output containing the results of the four techniques is generated. It also converts the IBA analysis outputs, which are given in $\mu\text{g}/\text{cm}^2$ into ng/m^3 , which is the output required for the aerosol analysis, using the filter database, that contains the air sampling volumes for each of the analysed filters.

3. Automation & calibration

During the measurement the spectra for each technique are

^{*} Corresponding author.

E-mail address: rns@ansto.gov.au (R. Siegele).

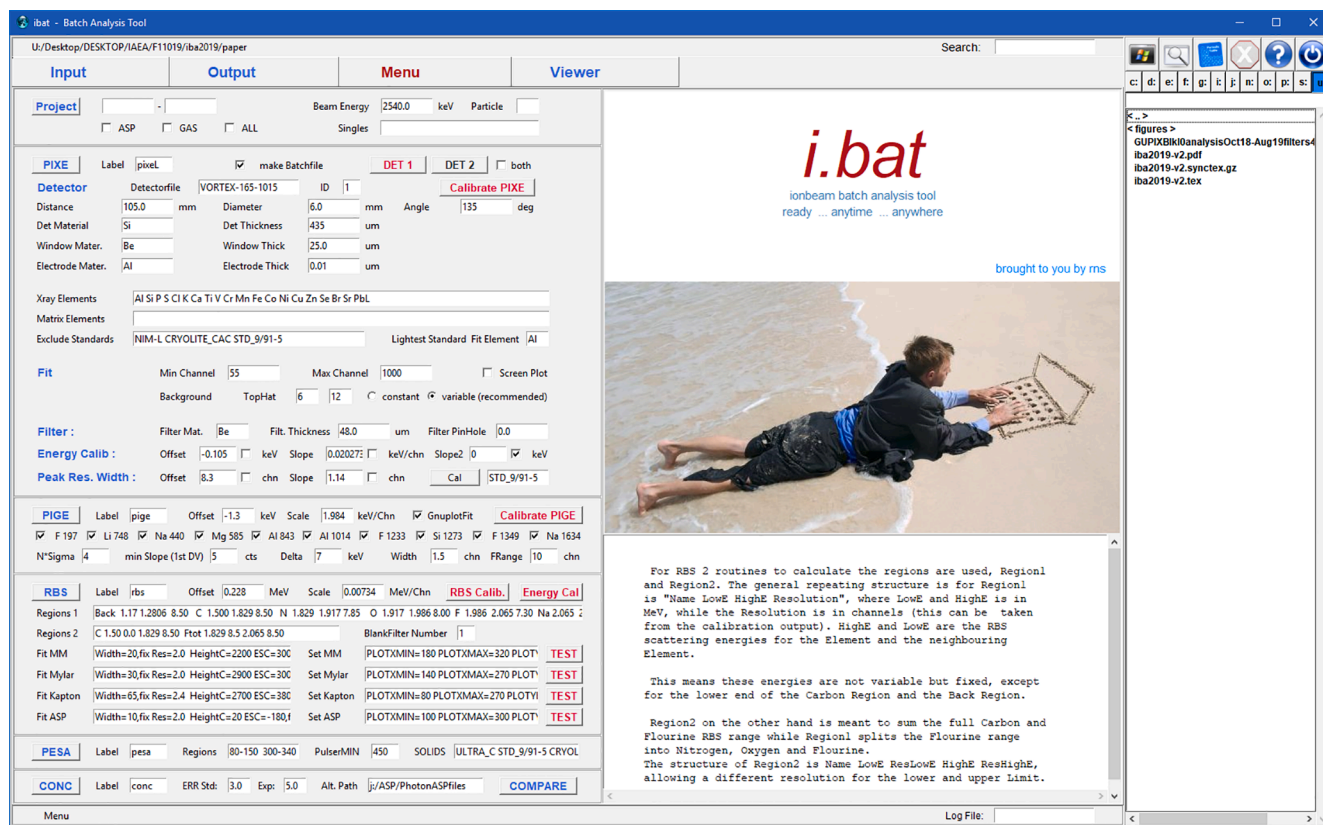


Fig. 1. The figure shows the GUI, which is divided into six section, the top with the general setup is followed by four sections for PIXE, PIGE, RBS and PESA, with the CONC, producing a summary sheet combining all 4 techniques and converting areal density result from the IBA techniques into volume densities for the aerosol filter measurements.

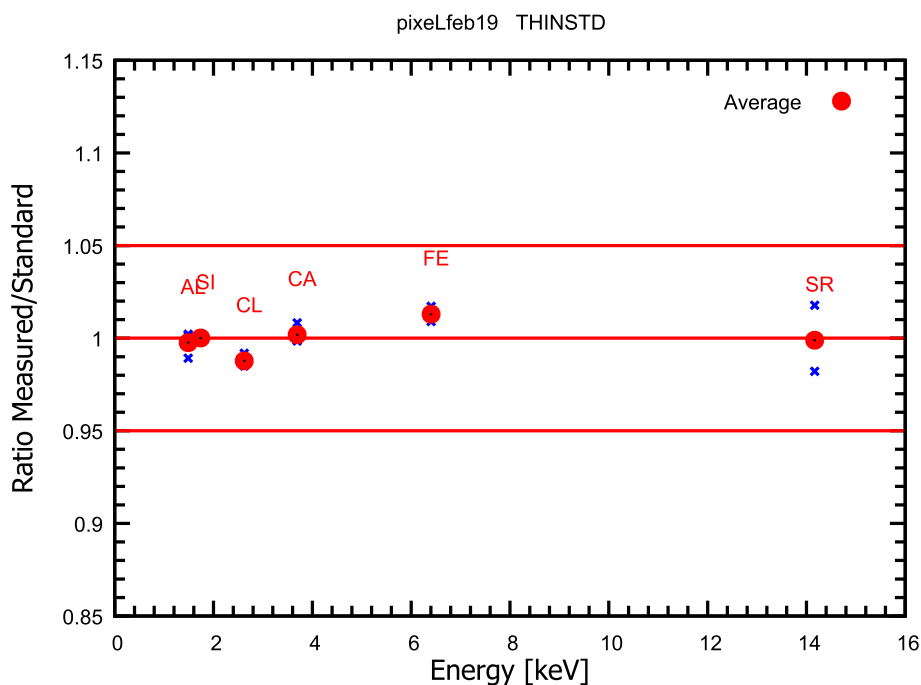


Fig. 2. The figure shows the ratios of measured to certified values for the Standard Reference Materials in the analysis.

transferred to a network drive and catenated into a single file. Each spectra contains the sample name and the total charge.

Generally a run consists of measurements of a number unknown samples as well as known SRM. During the aerosol analysis Kapton

(C₂₂N₂O₅H₁₀) and Mylar (C₁₀O₄H₈) foils as well as a unexposed Teflon (C₂F₄) filter, the so called blank filter (BF), are analysed on each sample stick. The thickness of the filters is typically 200 μg/cm². These are used for the calibration of PESA and RBS. The aerosol filters themselves fall

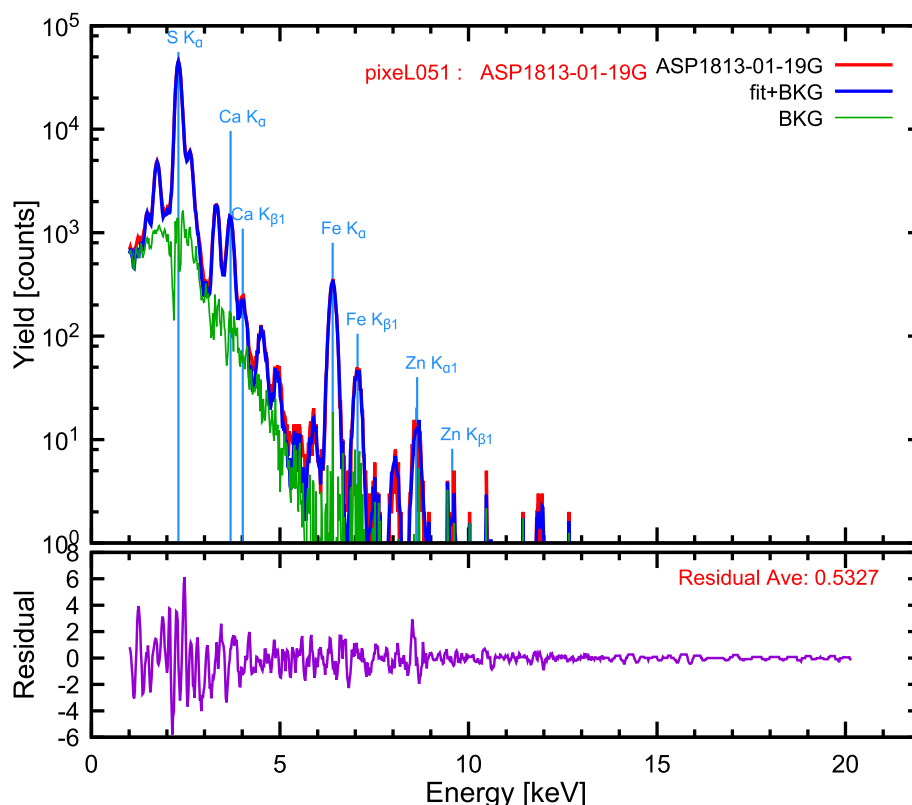


Fig. 3. The figure shows a typical PIXE spectrum for an exposed aerosol filter, together with the GUPIX fit and the background function calculated using the two and the variance output from GUPIX. The lower graph show the variance of the fit, with the average value displayed in the top right corner of the graph.

into two categories, Teflon filters and polycarbonate or Nuclepore filters, in the following labeled ASP and GAS filters, respectively. RBS and PESA spectra are only taken on the ASP filters, because GAS filters are polycarbonate filters, which makes it more difficult to measure the organics deposited on them.

The total charge and sample names are automatically extracted for each spectrum. The sample names are compared with the names in the SRM data base and a list of SRM measurements is generated. Separate lists are also generated for the Kapton, Mylar and BF measurements, as well as for all measurements of ASP and GAS filters.

These lists are used either for calibration or quality assurance, depending on the technique.

For PIXE the measurements of the SRMs are analysed separately and the results are summarised and displayed in graphical form (see Fig. 2) showing the ratio of the measured value to the certified values. In this case six MicroMatter SRMs were measured three times during the analysis run. The red dots show the ratio of the average result for each element to the reference value, while the blue crosses, show the ratios for each individual measurement. The red horizontal lines indicate the $\pm 5\%$ deviation of the measurement from the certified value.

If thin and thick SRMs are measured during the same analysis, separate graphs are generated for each type. For thick SRMs the sample matrix is taken from the SRM database and then used in the GUPIX analysis.

4. PIXE

The PIXE analysis utilises the GUPIX[4] executable pixwin.exe from the GUPIX package. Therefore an input file is generated using the input parameters entered in the GUI interface and subsequently the executable is run. Afterwards the GUPIX output files are used to generate a plot of the fit and to create a list summarising the results for all the unknown samples. All unknowns are analysed for the same trace elements and in

the case of thick samples the same sample matrix provided is used in the analysis.

Fig. 3 shows a typical PIXE spectrum together with the GUPIX fit and its background, in the top graph. The GUPIX output provides only the spectrum, fit and residual and therefore the background is calculated from these two. The bottom graph of the figure shows the GUPIX residuals. The average residual value is printed in the top right corner of the graph.

5. PIGE

The concentration of light elements, such as Li, F, Na, Mg, Si and Al can be measured by PIGE. The PIGE analysis is used as a calibration technique, where the spectra of the SRMs are analysed prior to the main analysis and their known concentrations are used for calibration. The calibration values are compared with the long term average values and the comparison is displayed.

To analyse the PIGE spectrum a peak finding routine is run across the spectrum. This routine is controlled by a minimum values for peak area above background ($N \cdot \text{Sigma}$) and the minimum slope of the 1st derivative of the spectrum. $N \cdot \text{Sigma}$ is the multiple of the peak area compared with the standard deviation of the background area under the peak.

During the development of the other analysis techniques, beside PIXE, alternative solutions were developed, in order to find the best solution. In PIGE, this alternative is to additionally fit the peaks using a Gauss function and a linear background. This fitting is controlled by initial peak width (Width) and the fitting range (FRange). The results from both techniques were found to agree within the error and there was no systematic difference between the two results. However, the fitting routine significantly increases the running time, and therefore the option to turn off the fitting was included.

Currently ten (p, p') reactions are included in the program, however,

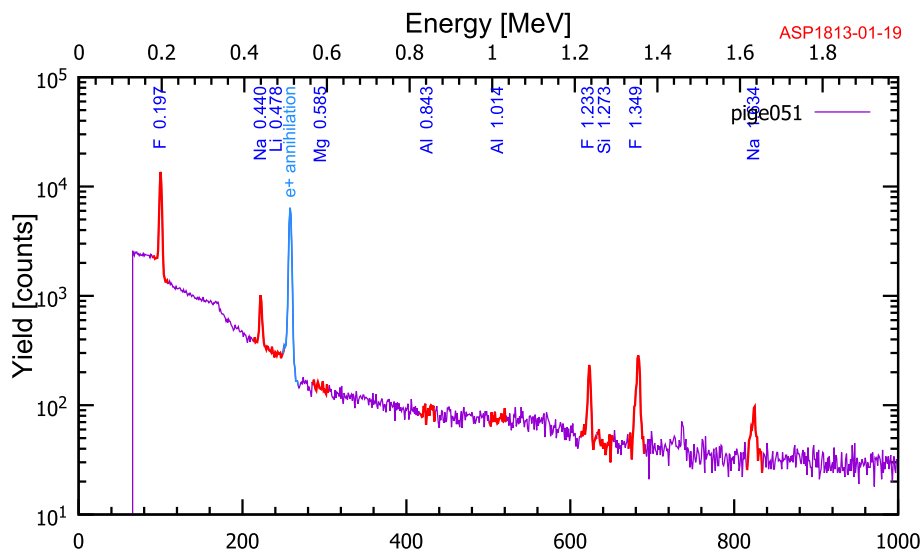


Fig. 4. The figure shows a typical PIGE spectrum for an exposed aerosol filter.

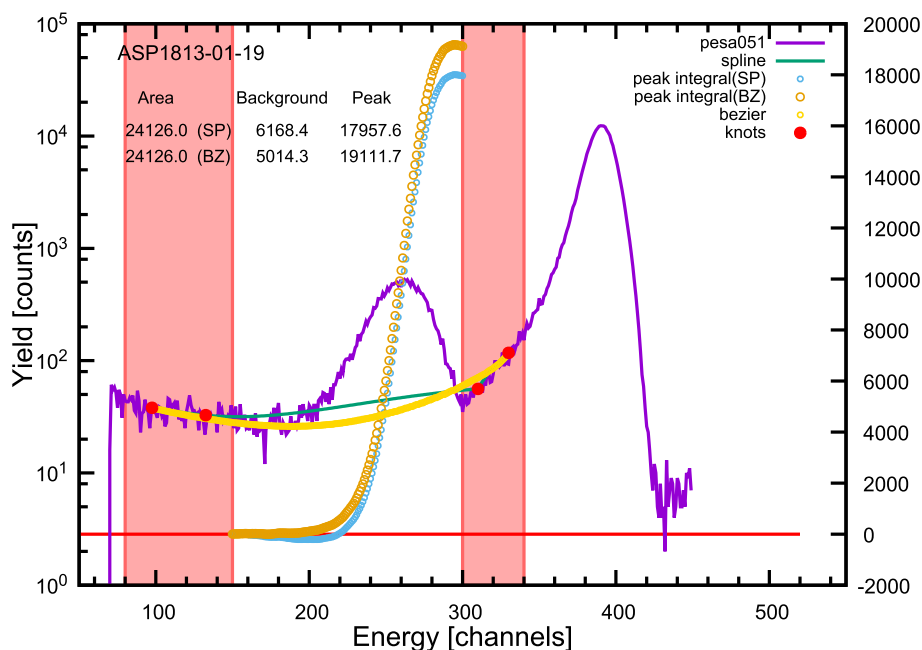


Fig. 5. The figure shows a typical PESA spectrum of an exposed aerosol filter.

new lines can easily be added via the configuration file. Fig. 4 shows a typical PIGE spectrum and the summary of the PIGE analysis. The energies for the ten PIGE lines are marked in the spectrum with the energy and the element indicated at the top of the graph. If a particular line is found in the peak finding routine and peak fitting is selected this section of the spectrum, together with the fit and background is shown in a small figure below the main graph.

6. PESA

In contrast to PIXE and PIGE, RBS and PESA analysis is currently limited to the analysis of our aerosol filters. In general the two routines only work on thin samples. During this analysis an unexposed Teflon filter (blank filter) as well as thin Mylar and Kapton foils were measured on each sample stick. For PESA energy spectra of particles in a 45° forward direction are taken. A thin Mylar foil in front of the detector stops the heavy mass low energy recoils, allowing only the scattered and

recoiled hydrogen ions to pass through to the detector.

The spectrum in Fig. 5 shows a PESA spectrum. The small peak to the left is due to both H projectiles scattered on H as well as the H recoils from the sample. Because the projectile and target have the same mass and both being hydrogen, recoils and scattered projectiles will have the same energy. The broader peak further to the right is due to H projectiles being scattered off all heavy elements including C.

By extracting the area under the left most peak and applying a calibration value, derived from the Kapton and Mylar foils, the H content in thin filters can be calculated.

In contrast to PIXE and PIGE, PESA and RBS are scattering techniques. As such PESA and RBS require different reference materials, in this case the thin Mylar and Kapton foils.

In order for the PESA program to extract the hydrogen peak from the spectrum, regions below and above the peak are selected. These are used to define anchor points or knots for the background calculation, using a spline function. Using these two regions alternative backgrounds are

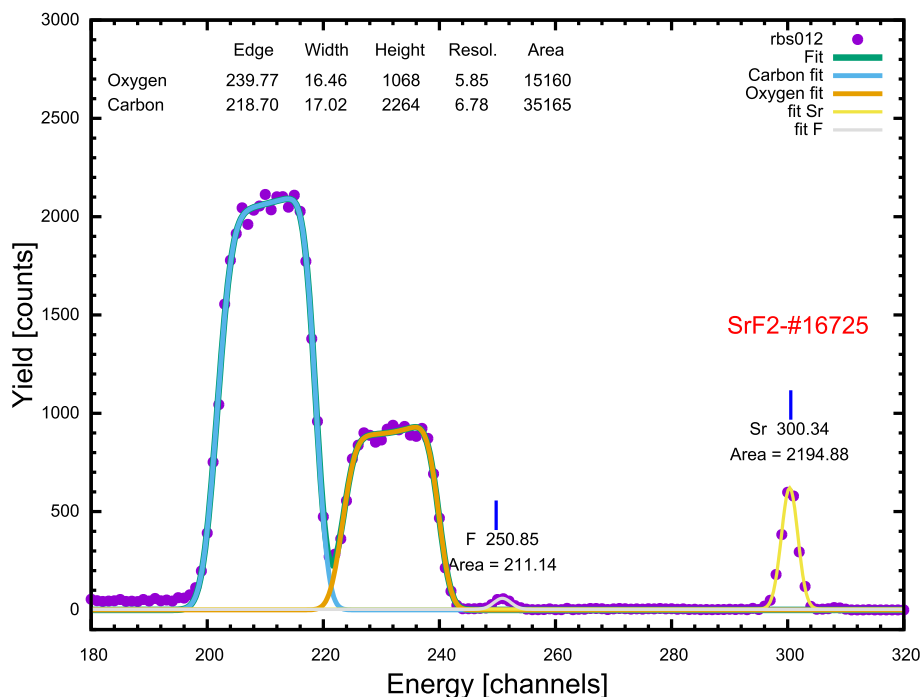


Fig. 6. The figure shows a the spectrum of the SrF_2 MicroMatter (MM) reference material, together with the fit.

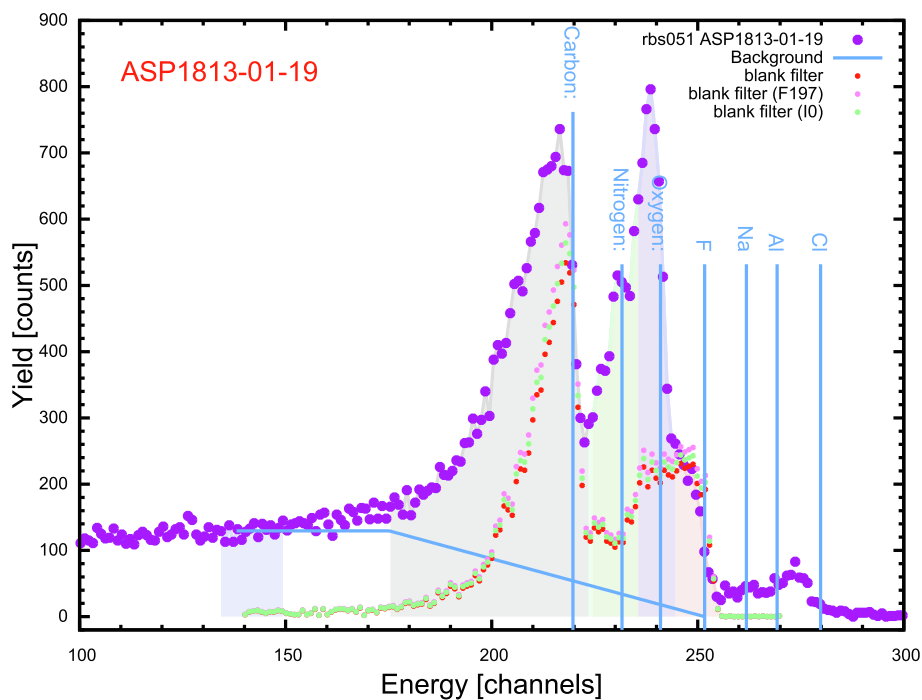


Fig. 7. The figure shows a typical RBS spectrum of an exposed aerosol filter, together with a blank filter spectrum. The energy regions for the scattered C, N, O and F are marked together with the surface energies of a number of elements.

also calculated with a spline (SP) and Bezier (BZ) function. When the hydrogen peak is very small, the lower region will be too far away from the peak and the calculated background can cut through the peak making the total peak area negative. To correct for this the lower region will be automatically moved closer, when the total sum turns negative during the summing.

The Fig. 5 shows the example for the peak analysis. The green line and the bright yellow dot show the spline and the Bezier function. The brown and blue circles show the peak totals using the the spline and

Bezier background, respectively.

The comparison shows that in most cases the Bezier function, more closely represents the background function, with the Bezier result generally about 5% larger. Therefore, the Bezier background result is used in the PESA analysis.

7. RBS

RBS is the most complicated of the four technique and a generalised

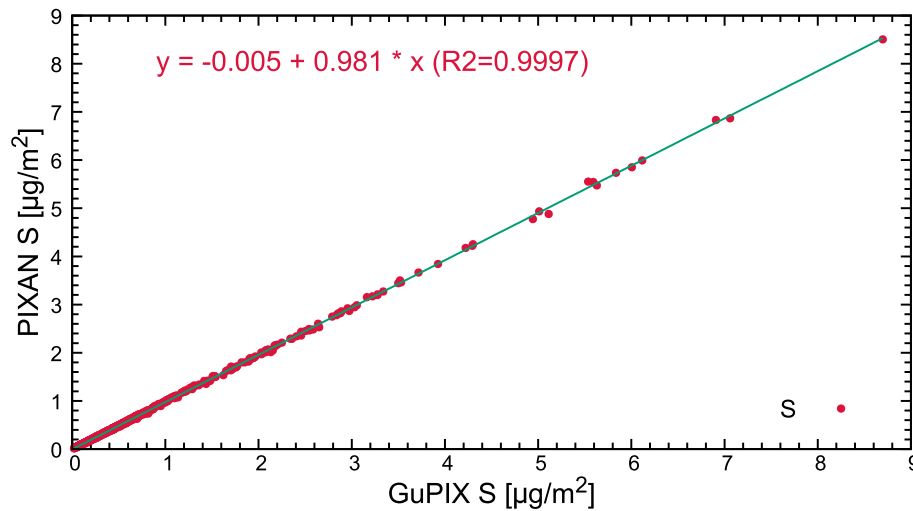


Fig. 8. The graph shows a the comparison of the PIXAN and GUPIX results for Sulphur. The graph show the PIXAN values as a function of GUPIX results. Included in the graph is a fit using the data which shows, the difference between the two techniques is slightly less than 2%, while the R^2 of the fit is very good.

solution is almost impossible to implement. The approach chosen here, is simply to select energy regions representing backscattering from carbon, nitrogen and oxygen. These regions are then used to determine the total scattering count for these elements. Setting these regions accurately, requires an accurate energy calibration, which is obtained by fitting the thin SRMs used in PIXE. These SRMs, supplied by MicroMatter (MM), consist of thin layers of material deposited on a Mylar foil. They are supplemented by thin Mylar and Kapton foils, for which the thickness has been determined by weighting. All these foils are fitted using step functions for each of the elements. Fig. 6 shows the spectrum of the SrF_2 MM reference material together with the fits for each element. The fitted surface edges for all the foils as well as the peaks of the deposited materials are then used to calculate an accurate energy calibration. This energy calibration is used to set sum regions for C, N and O in the filter analysis.

Fig. 7 shows a typical sample spectrum generated by the analysis program. The figure shows the spectrum with the regions marked in different colours, while the surface energy is marked by a blue marker in the graph.

The RBS yield for each element is corrected for multiple scattering, using a linearly increasing background function starting at the F edge and extending to the flat section at low energies. The purple region in the

low energy tail of the spectrum marks the end point to which this multiple scattering background is calculated to.

Besides the deposited material the spectrum also includes scattering from the Teflon filter itself, which also has to be subtracted. The filters are made of Teflon (CF_2) fibre weave structure, which results in a variation of the areal density across the surface of the filter. This leads to a typical filter spectrum, where the peaks for carbon and fluorine have long tails. The spectrum of an unexposed filter taken during the experiment is used to subtract this filter contribution. The spectrum of the unexposed (blank) filter used is included in the figure indicated by the red dots.

Since, the individual filters can vary significantly in thickness this filter contribution has to be adjusted by the actual thickness of each filter. Fortunately, our analysis provides two independent ways to determine the filter thickness. One is the fluorine measurement from PIGE. Since the filter is made of Teflon, CF_2 , and the contribution of the deposited aerosol material to the fluorine content is negligible, the total filter thickness can directly be calculated from the total fluorine and the chemical composition.

Additionally to the IBA analysis all filters are analysed using our MABI [5,6] instrument, which measures the light absorption for 7 different wave length. This measurement is used to determine the Black

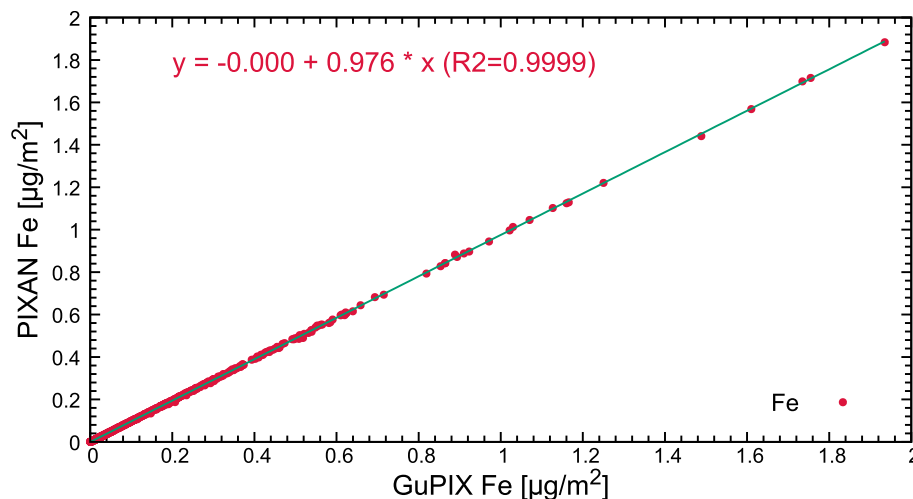


Fig. 9. The graph shows a the comparison of the PIXAN and GUPIX results for Iron. The graph show the PIXAN values as a function of GUPIX results. Again the fit between the two analysis is included with the difference being slightly above 2%.

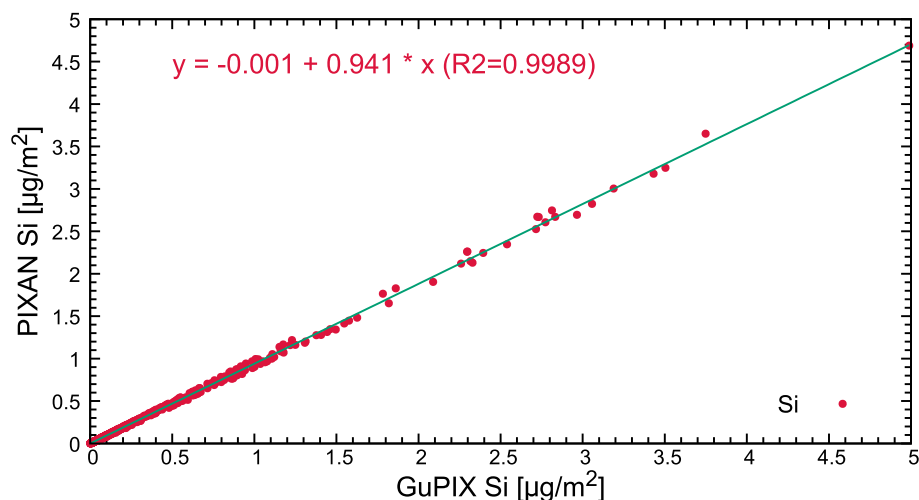


Fig. 10. The graph shows a the comparison of the PIXAN and GUPIX results for Silicon. The graph show the PIXAN values as a function of GUPIX results.

Carbon content in the filters, which requires each filter to be measured before and after exposure, providing a light transmission intensities I_0 and I , respectively. These I_0 measurements are used to determine the thickness of each filter, using a calibration curve, which was developed by accurately measuring the weight and light absorption I_0 of a number of filters over a range of thicknesses.

The filter contribution, derived from the blank filter spectrum (red dots), corrected for thickness using both fluorine PIGE and I_0 are also shown in the graph as pink and green dots, respectively. This demonstrates, how the filter contribution is adjusted for the actual filter thickness, and how this lowers or increases the contribution. The graph shows that this correction is slightly different for the PIGE or I_0 correction.

8. Results and discussions

In order to test the new analysis tool, results of the new iBAT analysis tool were compared with previous results from our PIXAN analysis. To get a better impression of how the results compare we have reanalysed, a complete year of our aerosol project using this new tool. Fig. 8–10 show this comparison for a number of representative PIXE elements (Si, S and Fe). The comparison shows a very good agreement between the two analysis techniques. A fit of between the two measurement, gives a correlation close two unity and the R^2 of the fit being better than 0.99.

However, there is a systematic difference between the two results, with the PIXAN being systematically lower. This difference is quite small for elements, present at medium to high concentrations such as sulphur, for which this difference is smaller than 2%. For iron this difference is a bit larger at just over 2%, while for other elements it can be 5% or more as the example of silicon shows.

The comparison shows that for PIXE, PIGE and PESA analysis the two methods mostly agree within 1–3%, with the GUPIX results generally being higher. Some of the notable difference, being Si and Ca, where the difference is 6% or 8%, respectively. For Si, the larger difference can be explained by the fact, that Si is at the low energy end of the spectrum, where fitting the background can be quite challenging.

The overall difference can probably be attributed to the fact, that the GUPIX and PIXAN calculations are based on different data bases, while the larger deviation for small concentrations is most likely due to the different background subtraction techniques.

For the PIGE analysis of sodium the overall difference between PIXAN and iBAT, is again quite small, with the iBAT results approximately 3% larger than the PIXAN. The overall variation between the two methods is bit larger compared to the PIXE. In this case R^2 is about 0.995 compared to PIXE, for which the R^2 is around 0.999 for elements present at high concentration. However, it compares quite well with elements present at lower concentrations, such as Si or Fe (see Fig. 10, 9). This is reasonable, given the fact that the count rate for Na generally is low,

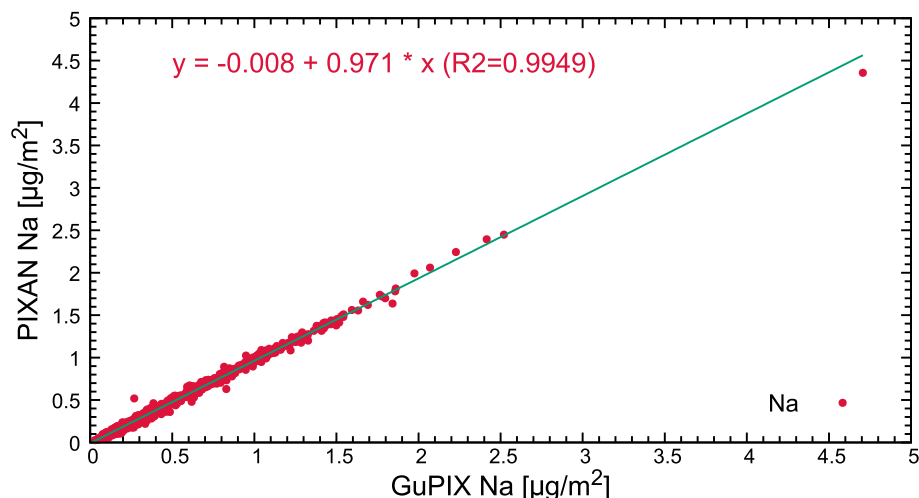


Fig. 11. The graph shows a the comparison of the PIXAN and iBAT results for Sodium. The graph show the PIXAN values as a function of iBAT results.

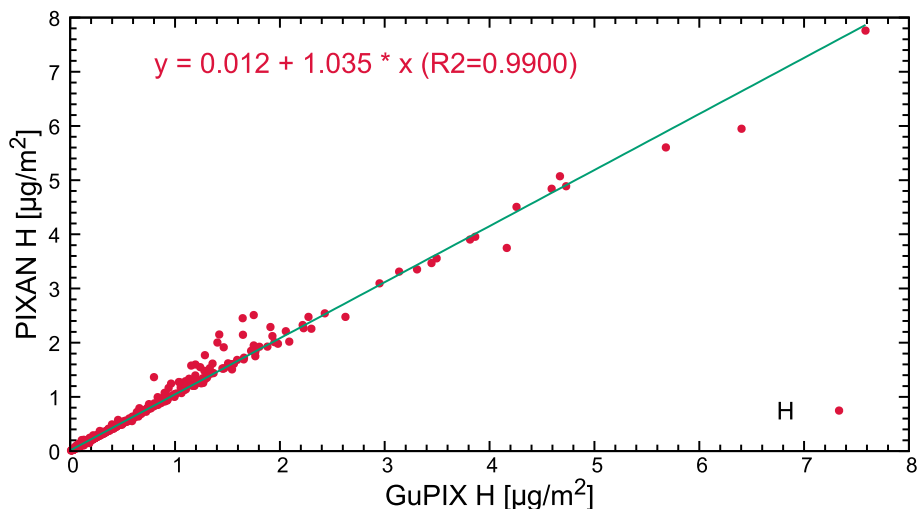


Fig. 12. The graph shows a the comparison of the PIXAN and iBAT results for hydrogen. The graph show the PIXAN values as a function of iBAT results.

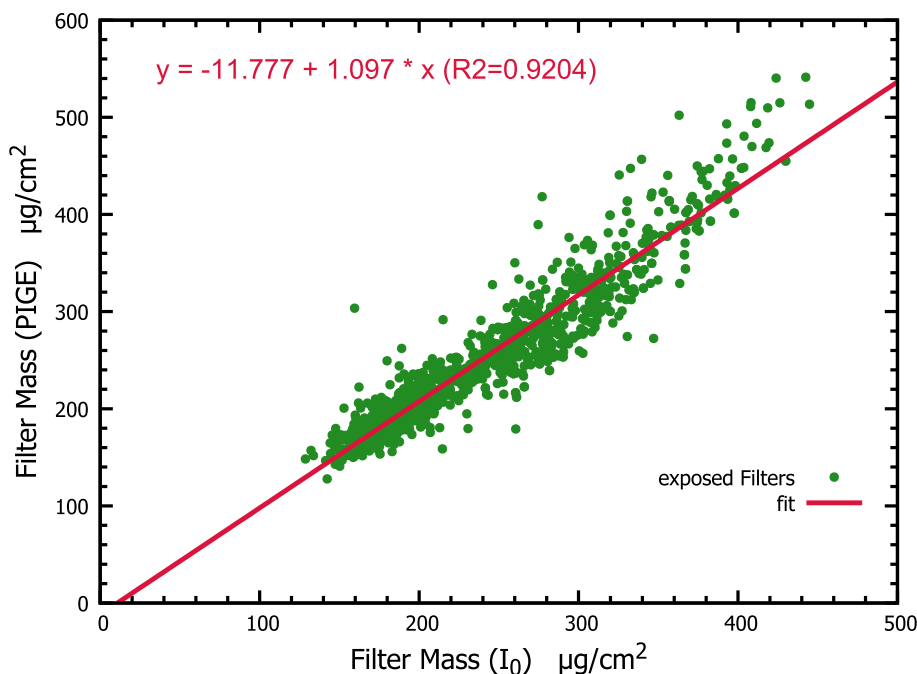


Fig. 13. The filter weight from the PIGE fluorine measurement as a function of the filter weight determined from the MABI light absorption measurement.

compared with S for instance.

The PESA results, for comparison are approximately 5% smaller for iBAT compared with PIXAN. Compared with PIXE and even the PIGE, the variations between the two techniques are significantly larger. This is due to the fact, that the hydrogen peak is quite broad and the width can vary significantly from spectrum to spectrum, which makes it quite difficult to model the background. While both analysis techniques have weaknesses in their approach, our new technique is a significant improvement, especially with the possibility to automatically move the lower region for background determination closer to the peak. In the PIXAN analysis this fixed lower background limits the way to determine the background, which resulted in the wrong background for some measurements. This also explains the larger difference between the two techniques, both of which can lead to less than perfect results in individual spectra (see Fig. 11 and 12).

The RBS analysis on the other hand, was revised with the aim to improve the results. One of the shortcomings of the previous analysis

was that the regions for oxygen, nitrogen and carbon were selected visually, which made the analysis vulnerable to the bias of the operator. Another shortcoming was that calculating the thin foil calibration overestimated the carbon content in the blank filters.

Hence the blank filters themselves are analysed to calibrate RBS. One of the possible explanations for this overestimation is the structure of Teflon filter, which is composed of a mesh of Teflon fibres. This results in wide thickness distribution across the filter, which makes it difficult to determine the cutoff point for the carbon thickness and also makes it more difficult to set the end point for the straggling estimate. Hence, we chose the blank filter spectrum to calibrate the carbon in the RBS, in order to account for the sample structure.

Actually determining the stretched Teflon filter thickness is problematic, the total filter weight is dominated by a thick plastic ring, which provides support and mechanical stability. To overcome this the central stretched Teflon weave portion of several filters were removed from their support rings, weighed separately and their areal mass in $\mu\text{g}/\text{cm}^2$

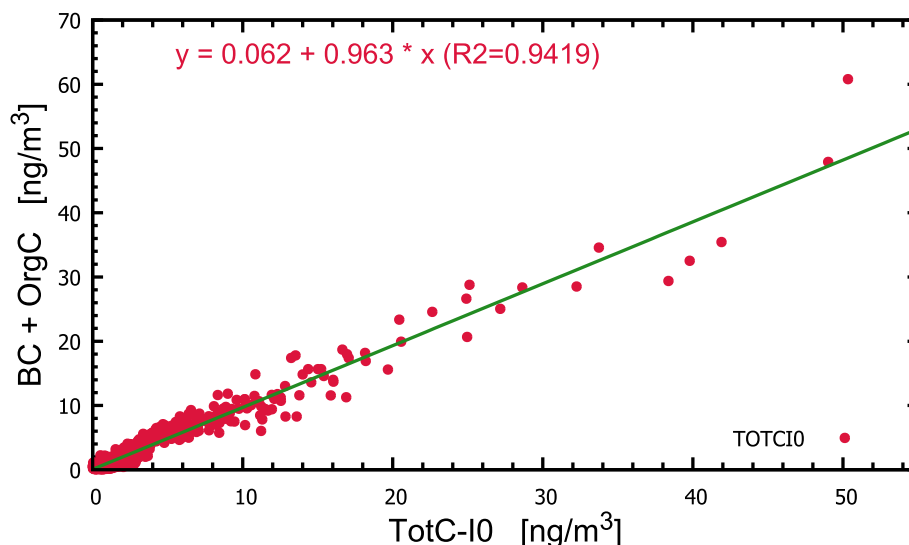


Fig. 14. The graph above shows the sum of BC + OrgC versus the totC, the total C extracted from the RBS spectra.

determined. This areal mass was also correlated with the pre-exposed MABI light absorption measurement for each filter before its central weave was removed. This enabled an absolute filter gravimetric mass to be correlated with the MABI (IO) mass in a similar way to that shown and discussed in Fig. 13 for the PIGE fluorine results. Both measurements are in good agreement with each other and therefore suitable to calibrate the carbon RBS. Fig. 13 show the filter thickness from the fluorine measurement as a function of the filter thickness from the MABI light absorption measurement.

Using this calibration the total carbon in the aerosol material deposited on the filter can be calculated by taking the total carbon count, subtracting the filter and multiple scattering contribution and then applying the calibration. To evaluate this new method, we compare the carbon content resulting from RBS measurement, with the so called Black Carbon (BC) content from the MABI measurement. The MABI measurement estimates total black carbon (BC) only, this generally does not include carbon in organic matter (OrgC). Malm et al. [7] assume the average organic particle is approximately 9% hydrogen, 21% oxygen and 70% carbon. Their estimate of organic matter is obtained by assuming the total hydrogen (H), measured by PESA is the sum of hydrogen in ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ and hydrogen in organics (9%). Hence their organic matter estimate $\text{OMH} = 11(\text{H}-0.25\text{S})$. We then assume the carbon fraction of organic matter $\text{OrgC} = 0.7\text{OMH}$ and that our RBS measurement of the total carbon on the filter (excluding the carbon in Teflon) $\text{TOTC} = \text{OrgC} + \text{BC}$. The good correlation of the data displayed in Fig. 14 shows that these are reasonable assumptions to make.

9. Summary

A new software tool that combines four IBA analysis techniques has been designed and tested. The results of the analysis program have been compared with our previous analysis program and the results agree for

most measurements to within 3–5%. We have also improved the RBS analysis for carbon resulting in a much better agreement of the carbon measurement, with the Black Carbon measurement from the light absorption measurement.

The iBAT package was written for use under MS-Windows consisting of a number of Awk, Gnuplot and Tcl/Tk scripts. Since Awk, Gnuplot and Tcl/Tk are native to most Unix platforms and also available on MacOS the package can easily be ported to any of the platforms, provided a ported version of MS-DOS executable of GUIX is available.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge National Collaborative Research Infrastructure Strategies (NCRIS) for funding of the Centre for Accelerator Science (CAS)

References

- [1] E. Clayton, PIXAN, The Lucas Heights PIXE Analysis Computer Package, AAEC/M113(1986).
- [2] R. Siegele, D. Cohen, M. Ionescu, doiba Manual, Using PIXE and PIGE to their full potential with doiba. ANSTO E765, Apr 2008, ISBN 1921 268 042.
- [3] Gnuplot Homepage (www.gnuplot.info).
- [4] J.A. Maxwell, J.L., Campbell, W.J., Teesdale, Nucl. Instr. and Meth. B43 (1989) 218.
- [5] M. Madhuram, A. Attanacio et al. to be published.
- [6] Multi-wavelength absorption black carbon instrument (www.ansto.gov.au/multi-wavelength-absorption-black-carbon-instrument).
- [7] W.C. Malm, J.F. Sisler, D. Huffman, R.A. Eldred, T.A. Cahill, J. Geophys. Res. 99 (1994) 1347–1370.