

“Total IBA” – Where Are We?

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The suite of techniques which are available with the small accelerators used for MeV ion beam analysis (IBA) range from broad beams, microbeams or external beams using the various particle and photon spectrometries (including RBS, EBS, ERD, STIM, PIXE, PIGE, NRA and their variants), to tomography and secondary particle spectrometries like MeV-SIMS. These can potentially yield almost everything there is to know about the 3-D elemental composition of types of samples that have always been hard to analyse, given the sensitivity and the spacial resolution of the techniques used. Molecular and chemical information is available in principle with, respectively, MeV-SIMS and high resolution PIXE. However, these techniques separately give only partial information – the secret of “Total IBA” is to find synergies between techniques used simultaneously which efficiently give extra information. We here review how far “Total IBA” can be considered already a reality, and what further needs to be done to realise its full potential.

Keywords: Ion Beam Analysis, Rutherford Backscattering, Particle Induced X-ray Analysis, Thin films, elemental depth profiling, mapping, trace elements, high sensitivity, accurate analysis, uncertainty budget, blind samples, certified reference materials, forensics, SIMS standards

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Glossary of IBA Techniques

"Total IBA" (thin film elemental depth profiling techniques)

- BS** (Elastic) backscattering. Can be either RBS or EBS. Here we use RBS and EBS exclusively although many authors do not distinguish them (calling both "RBS") and RBS can be considered a special case of EBS.
- Channelling:** The scattered ion yield is a very strong function of the relative alignment of a well collimated ion beam and major crystallographic axes in a single crystal. Channelling contrast can be used for the lattice site location of impurities, and the quantification of strain in single crystal heterojunctions and damage in ion implanted single crystals. Can readily be used with PIXE, BS, NRA, and also STIM because the energy loss is a strong function of the position of the ion in the channel. Is always available with MEIS.
- EBS** Elastic (non-Rutherford) backscattering. The scattering cross-section is given by the the elastic scattering channel of the reaction, and depends on the nuclear structure of the two nuclei. The cross-section can be calculated by R-matrix or other methods which have nuclear data (energy levels etc) as input, but the calculations must be informed by direct cross-section measurements. If the Coulomb barrier is not exceeded EBS becomes RBS, but here we use RBS and EBS exclusively. Measurements and evaluations are on the IBANDL website.
- ERD** Elastic recoil detection. Follows the recoiled rather than the scattered ion in the elastic collision. He-ERD is valuable for analysing H isotopes. HI-ERD (heavy ion ERD) typically uses primary beams of ~1 MeV/amu, and ToF (time of flight) or gas detectors for the heavy recoils.
- External beam** Because MeV ion beams are very penetrating it is feasible to bring the beams out into air (through Kapton or silicon nitride windows). This is a powerful method for valuable, delicate, large or wet samples. External beams have been used for Total IBA with PIXE, BS, ERD, PIGE, MeV-SIMS.
- IBA** Ion Beam Analysis. By "Total IBA" we mean MeV thin film elemental depth profiling methods, which include PIXE, BS (RBS or EBS), ERD, NRA, PIGE. STIM is often used with PIXE. MeV-SIMS can be used as a molecular depth profiling technique. PIXE with high energy resolution detectors can be used for chemical state sensitivity. Other MeV IBA techniques (not primarily elemental depth profiling) include AMS, IBIL, IBIC. Other IBA techniques (not MeV) include: MEIS and LEIS, which are lower energy versions of RBS with completely different instrumentation; and SIMS, where commercial SIMS instruments use keV primary beams. NDP is a neutron analogue of IBA. An ion analogue of INAA exists.
- IBANDL** IBA Nuclear Data Library. Website of the IAEA Nuclear Data Section containing extensive scattering and reaction cross-section data and SigmaCalc evaluations relevant to IBA: <http://www-nds.iaea.org/ibandl/>
- MeV-SIMS** Secondary ion mass spectrometry with an MeV primary ion beam. The sputtering mechanism in this case is through the inelastic energy loss, and is significant only for insulating materials.
- Microbeam** Ion beams used for IBA are frequently focussed and used in a scanning mode for imaging (SIM), usually mainly with PIXE since beam currents are limited and PIXE production cross-sections are high.
- NRA** (Inelastic) nuclear reaction analysis. Like EBS, NRA cross-sections can be calculated as well as measured, and a few evaluations are on the IBANDL website together with many measured cross-sections. PIGE, NRP and NDP are special cases of NRA, although NDP is not an IBA technique.
- NRP** Nuclear reaction profiling. NRA using very narrow resonances for ultra-high depth resolution.
- PIGE** Particle induced gamma ray emission. A special case of NRA where a gamma ray results.
- PIXE** Particle induced X-ray emission. The ion analogue of XRF, or EPMA, or SEM-EDS since today PIXE is usually used with a scanning microbeam.
- RBS** Rutherford backscattering spectrometry. Scattering cross-section is analytical, given by the Coulomb potential (with screening). Ion analogue of the BSE signal in SEM. Switches to EBS when the Coulomb barrier is exceeded. Called MEIS for beams near the stopping power maximum (~100 keV for protons), and LEIS for keV beams. Many authors indiscriminately call BS "RBS", but we insist on distinguishing the case where the cross-section is analytical because the traceability of RBS and EBS measurements are different in principle.
- SEM** Secondary electron microscopy. Often used to form an SEM image of the sample when a scanning microbeam is used. Sensitive to topography, which may be of importance since sample roughness can modify IBA spectra.
- SigmaCalc** Website of the IAEA Nuclear Data Section containing evaluations of scattering and reaction cross-section data relevant to IBA: <http://www-nds.iaea.org/sigmacalc/>
- SIM** Scanning ion microscopy (see "Microbeam"). Ion analogue of SEM. Regularly used with PIXE, BS, STIM, channelling, external beam.
- STIM** Scanning transmission ion microscopy. Imaging, using the energy loss of primary scanned microbeam particles transmitted through thin samples, so that it is similar to EELS in the TEM. Can be "on axis" using a low intensity direct beam, or "off axis" where forward scattering reduces the intensity. Off-axis STIM is often used simultaneously with PIXE.

Other related and complementary techniques

- AES** Auger electron spectrometry. Also SAM: scanning Auger microscopy. Electrons ionise the atom, Auger electrons out as the last stage of atomic relaxation: a three-electron process. Same electron spectrometer as XPS, and the same EMFP, thus also a true surface technique. SAM is really SEM in UHV (ultra-high vac-

uum), but looking at the Auger electron energies rather than the number of secondary electrons. Atomic relaxation can result either in the emission of the Auger electron (AES) or a photon (EPMA).

AFM	Atomic force microscopy. One of a number of scanning probe microscopies, including the original STM (scanning tunnelling microscopy).
AMS	Accelerator mass spectrometry. A form of IBA (the accelerator is the same) where the sample goes in the source. Used routinely for ¹⁴ C and similar isotopic analyses.
BSE	Backscattered electron detector. Used in the SEM for Z-contrast. Electron analogue of BS, but gives only qualitative information. Quantitative information would need a Monte Carlo treatment of multiple scattering and is not feasible.
DESI	Desorption electrospray ionisation. As MALDI.
DART	Direct analysis in real time. As MALDI.
EDS	Energy dispersive (X-ray) spectrometry. See SEM and EPMA. PIXE uses the same detectors as SEM-EDS.
EELS	Electron energy loss spectrometry. Often used in the TEM.
EPMA	Electron probe microanalysis: just an SEM specialised for X-ray analysis, generally with one or more WDXs (wavelength dispersive X-ray spectrometers) as well as energy dispersive spectrometers (EDS).
ESCA	Electron spectroscopy for chemical analysis. Synonym for XPS.
FTIR	Fourier transform infra-red spectrometry. One of a large class of emission and absorption spectrometries sensitive, like Raman spectroscopy, to atomic and molecular vibration modes.
IBIC	Ion beam induced charge. The electrical response of semiconductor devices irradiation is measured <i>in situ</i> . IBIC is an IBA technique but usually used alone because of the very low beam current required.
IBIL	Ion beam induced luminescence. The ion analogue of cathodoluminescence (electron-induced) and photoluminescence. IBIL is an IBA technique but is very sensitive to defect structure and has never been used for depth profiling.
ICP-MS	Inductively coupled plasma mass spectrometry. One of a large class of mass spectrometries sensitive to ng/g (and better) where PIXE is only sensitive to mg/kg (at best). But ICP-MS analyses trace elements in bulk samples whose gross composition is known.
INAA	Instrumental neutron activation analysis. A trace element method for bulk samples, using neutron beams from a nuclear reactor.
LEIS	Low energy ion scattering. RBS using keV ion beams. New high sensitivity detectors make this a rapid technique which looks at the outermost layer of the sample. Thus complementary (with higher depth resolution) to XPS.
MALDI	Matrix-assisted laser desorption ionization. An in-air spectrometry sensitive to molecules of high molecular weight. SIMS (with keV ions) must be done in vacuum; also gives molecular ions, but is a much more energetic sputtering technique and fragments the sputtered ions more for larger molecules.
MEIS	Medium energy ion scattering. RBS using ~100 keV ion beams. Gives information on the crystallography and composition of the near-surface region (~100nm).
NDP	Neutron depth profiling. An NRA method using a neutron primary beam (from a research reactor).
SAM	Scanning Auger microscopy. AES in the SEM. Often used with sputtering to give depth profiles.
SEM	Scanning electron microscopy for imaging surface topography, primarily looking at the secondary electron signal. Often comes with EDS (or EDX: energy dispersive X-ray spectrometry) and often has a BSE (backscattered electron) signal too. The X-ray detector is the same as usually used for PIXE. The scanning ion microbeam (SIM) is thus an analogue of SEM-EDS, EDS and BSE being analogues of PIXE and EBS. And often an secondary electron detector is included in an SIM chamber to see the topography directly.
SIMS	Secondary ion mass spectrometry. Another form of IBA using (for example) a 30 keV ion source for sputtering. The secondary (sputtered) ions are mass analysed. One important variant is FIB (focussed ion beam machining) which uses a high intensity (and very bright) nano-focussed liquid metal ion source (usually Ga): another is MeV-SIMS, where the sputtering results from electronic energy loss, not the nuclear collision cascade.
TEM	Transmission electron microscopy for imaging in both real and reciprocal space: always includes SAD (selected area electron diffraction). Also XTEM for cross-sectional TEM, and HR-TEM for high (atomic) resolution TEM. Often has EDS, and an EELS attachment (with variants) which is also sensitive to atomic excitation.
XPS	X-ray photoelectron spectrometry. X-rays in, photoelectrons out: a one electron process. Because the EMFP (electron mean free path) is only a few nm this is a true surface technique, but sputtering is frequently used to give depth profiles. Used to be called ESCA: electron spectroscopy for chemical analysis, because chemical shifts are readily observable allowing chemical valence states to be determined.
XRD	X-ray diffraction for observing crystalline structure. A very wide variety of methods are in use including thin-film variants.
XRF	X-ray fluorescence. Like PIXE and AES with the same physics but excited by X-rays, and looking at the X-ray not the Auger electron resultant. It is therefore a "bulk", not a surface, technique.

Introduction: Scope of Review

This paper is about materials characterisation methods, and necessarily discusses and compares a very large number of techniques involving the systematic use of a veritable soup of acronyms. We refer the reader to the Glossary for the expansion and explanation of these acronyms, also taking the opportunity to explain the connection between the various techniques. Many techniques are rather closely related in ways that are often not sufficiently appreciated.

We review the enhanced power of ion beam analysis (applied to thin film elemental depth profiling) available when the various IBA signals are analysed self-consistently. A probing ion beam striking a target yields a variety of IBA signals. These include nuclear reaction products (NRA, PIGE, RBS, ERD, EBS), and products consequent to the relaxation of the target in response to the energy deposition in it: including atomic effects (photons – PIXE), topography effects (electrons – SEM), and lattice effects (secondary ions – SIMS). The underlying idea of "Total IBA" is that with suitable instrumentation all of these products can be detected simultaneously, and the resulting information interpreted self-consistently. It is the self-consistency of the interpretation that is not routine at present, although the complementary nature of the various signals has been recognised from the earliest days of IBA. We will survey the reasons for this, and show how we now have the tools to start to effectively implement Total IBA.

We will use "Total IBA" to refer to thin film elemental depth profiling using probing ion beams with MeV/nucleon energies. This is because with these energies we have useful signals with a variety of different types. Similar sorts of synergistic "Total" techniques are already well established in electron microscopy. So TEM instruments often have EDS and EELS detectors as well as imaging capability in both direct and reciprocal space, together with confocal methods. The SEM generally also incorporates EDS and BSE detectors. Many IBA analysts already collect multiple signals specifically because their synergy is well understood. But these are rarely analysed self-consistently, partly because suitable software tools have not been available. This review shows how this situation is changing.

The potential field of "Total IBA" is vast, and this brief review will focus on the new synergistic benefits that we believe are now available. We will arbitrarily exclude various important topics just to conveniently limit the scope of the work. IBA is not a deliberately destructive technique (unlike SIMS) but clearly these energetic ion beams must modify the targets, some of which will be more sensitive than others, but this beam damage will not be discussed. Because we are specifically considering IBA primarily as a thin film elemental depth profiling technique we will exclude IBIL and IBIC, since these signals are generated mostly from defects rather than elemental composition. Crystallographic (channelling) methods are of great importance and power for single crystal samples, but are really a large topic of their own and will also be excluded. We also exclude any delayed response of the target to the beam, which occur if nuclear reactions in the target result in its activation. This is an ion analogue of INAA but it is rarely used for depth profiling.

We will concentrate specifically on the self-consistent treatment of particle backscattering (BS, including both RBS and EBS) and particle-induced X-ray emission (PIXE), not because other synergies are not equally available and important (some of which we will note in passing) but because it is for PIXE/BS that suggestive and far-reaching examples have already been worked out in some detail.

The idea of "Total Analysis" was used previously by Bird [1] in the important sense of "the elemental analysis of a sample where the concentrations sum to 100%". He notes

that "the possibility exists for obtaining a total analysis" in a variety of different contexts, and hence on the remarkable versatility of IBA. He also notes that a "self-consistent set of depth profiles can be derived from the data, but only with tedious iteration of spectrum simulation calculations" (this is in 1990), commenting that: "These calculations should be automated to derive the profiles without the need for manual intervention." We shall show that automation and self-consistency are now available. The present idea of "Total IBA" takes Bird's concept of total analysis for granted and emphasises the self-consistent (synergistic) treatment of data from multiple IBA techniques, which was not then available. It hardly needs adding that there is a large literature which makes use of multiple IBA techniques: however, because these manual iteration methods are so difficult where the interpretations of the various spectra are mutually dependent, remarkably little of this literature (which we will cite in the proper places) treats these techniques in an intrinsically self-consistent way.

Introduction: Structure of the Review

This work is wide-ranging, and some comment will be helpful for the reader to appreciate the interconnectedness and purpose of the various sections. We believe that "Total IBA" amounts to a new analytical technique since we will demonstrate that its power is substantially greater than that of the sum of the individual IBA techniques. "Total IBA" is clearly promising, a promise which is presently incompletely realised. But its development presupposes a wider acceptance. We therefore address a series of topics of great importance for a technique expected to be industrially significant.

We start with a sketch of the competitive analytical techniques and continue with a discussion of why MeV-IBA techniques (specifically BS and PIXE) have historically been used separately so frequently up to now if the benefits of their synergistic use are so clear. We then review the issue of the *accuracy* of IBA, concentrating on RBS which is the IBA technique with by far the shortest traceability chain. The absolute (traceable) accuracy of an analytical technique is necessarily one of its essential features, and any general discussion of a technique should start with this.

We continue by pointing out that IBA is regularly used where the sample structure is unknown, that is, it is used to provide a *model-free* analysis. "Total IBA" usually enables a completely unequivocal analysis of "blind" samples, that is, samples of which nothing is known for certain. Other techniques may be ambiguous but can give an unequivocal analysis where the sample structure is known. But, given the limitations on sensitivity and spacial resolution, "Total IBA" is remarkably unambiguous. We give an interesting example (using self-consistent BS and PIXE) which we develop to the point where we can demonstrate the viability for IBA of real elemental tomography of blind samples. This is significant since X-ray tomographic techniques currently give access to the density distribution but not a full 3-D elemental distribution. There are many fields where model-free analysis is particularly valuable, including forensics and cultural heritage.

Industrial applications often involve very large numbers of samples, and a technique must be capable of *mechanisation* to handle these cases. Several examples of different sorts demonstrate that this is now possible. IBA also has the possibility of obtaining *chemical* or chemical state information from samples in addition to elemental spacial distributions, using PIXE detectors with high energy resolution, or MeV-SIMS. Finally, *complementary* techniques are revisited, now from the point of view of how much information obtained by IBA is commensurate with them. The oldest example of "Total IBA", the self-

consistent use of BS with PIXE to determine trace elemental metal content in protein samples to relieve the systematic ambiguity of crystallography, is one of these.

MeV IBA and its competitors

Thin film elemental depth profiling is of critical importance to a wide variety of modern technologies, including the semiconductor, sensor, magnetics, and coatings industries (including both tribology and optics), among others. It is also valuable in many other disparate applications such as cultural heritage, environmental monitoring and forensics. We will mention examples of the use of MeV IBA for depth profiling most of these.

In all these fields the analyst has various standard tools: the electron microscopies and spectroscopies (SEM, TEM, XPS, AES and their variants), the scanning probe microscopies (AFM and variants including the new optical near-field methods), X-ray techniques like XRF and XRD (also with many variants) and optical methods like ellipsometry, Raman, FTIR and other spectroscopies. Elemental depth profiling can be done destructively using sputtering techniques with SIMS (or, frequently, AES). If destructive techniques are considered then bulk methods like ICP-MS and AMS should be mentioned, and there are a wide variety of wet chemical analytical methods. XRF and XRD are frequently applied to "bulk" as well as thin film samples, and other comparable fluorescence techniques are cathodoluminescence or photoluminescence. Molecular imaging can be done in vacuum by SIMS and in air by MALDI, DESI and DART.

Where does IBA fit in this kaleidoscope of techniques? IBA typically uses an accelerator which needs a hall of at least 200m², a footprint well over an order of magnitude larger than any of the other techniques mentioned – it is necessarily a technique with high running costs. What can it do which cannot be done reasonably easily by other techniques? If a materials research organisation (for example, a University) were to set up a central analytical laboratory to service the needs of all its research groups and other collaborators, would IBA be one of the techniques considered "essential"?

Our thesis here is that the old approach of IBA labs, where RBS was mainly on offer in one lab and PIXE mainly in another, is not sustainable in the second decade of the 21st century. RBS is good for heavy elements in a light matrix and typically the mass resolution is not very good, so that only fairly simple things can be said about fairly simple samples. On the other hand, PIXE cannot compete on price against the almost equivalent XRF (for the near-equivalence of PIXE and XRF see [2]), and for half the price of microbeam PIXE equipment would one not be better off investing in a micro-XRF? Why bother with IBA at all?

We believe that if an integrated approach is used, where multiple detectors are used with every analysis beam so that some combination of STIM / PIXE / RBS / EBS / ERD / PIGE / NRA / SIMS is always systematically done, then not only does the range of samples for which IBA is appropriate increase dramatically but also the quality of information about each sample also increases. We will show several cases where neither the backscattered particle signal nor the emitted photon signal by themselves could solve the sample; but where the solution is straightforward when multiple signals are treated self-consistently. And these cases are only examples of very general classes of sample.

Why "Total IBA"?

Why have the laboratories using PIXE and backscattering (BS) historically been so separate (with even a separate "PIXE conference" series)? There are good and bad reasons for

this. Undeniably, for samples where the trace element content is important, BS often adds little useful information; similarly for PIXE where a layer thickness is required. Also, PIXE quantification is rather troublesome, with quite a long traceability chain (see a recent discussion of approximations of ionisation cross-sections [3], and a quantitative comparison between BS and PIXE [4]); so that if accuracy is required for the major elements seen by BS, then PIXE adds no information.

Moreover, because the cross-section for PIXE is large relative to RBS, microbeam maps obtained from the particle detector have a very low number of counts compared to those obtained from the X-ray detector. Do very noisy spectra have negligible information? A Bayesian analysis of a complicated 3-layer mixed Co:Fe silicide [5] emphatically denies this. The structure could easily be resolved from the RBS spectrum with a very small charge solid-angle product of only 0.3 $\mu\text{C}\cdot\text{msr}$ (readily obtained in $\mu\text{beam-PIXE}$). It is very clear that it is completely *false* to assume that the noisy BS spectra obtained in regular $\mu\text{beam-PIXE}$ mapping are effectively information-free: on the contrary, these spectra probably contain crucial information. For example, in such mixed silicides with closely spaced atomic numbers, the absorption of the metal K lines even in relatively thin layers will be significantly different for different layer structures. Recent work has underlined that robust information is available even in the presence of 10% Poisson noise [6].

For PIXE a very common beam to use is 3 MeV H^+ . This is because the production cross-section goes up with beam energy, but beyond this energy nuclear reaction products tend to also decrease the signal to noise ratio. Thus this beam usually gives about the best available sensitivity. However, for this beam the particle scattering is non-Rutherford up to at least Fe [7] [8] [9]. In the last ten years the (non-Rutherford) differential scattering cross-sections for most of these reactions have been measured and evaluated, so that today we can usually do accurate analysis even at sharp resonances [10]. Previously this was unthinkable. So although in the quite recent past it was reasonable to discount the particle spectra on the grounds that they were uninterpretable, today this would be a grave mistake.

Therefore, although even in the quite recent past it was understandable that self-consistent PIXE/BS was often judged to be too problematical to be worth the effort, this is not the case today. We should point out that self-consistent PIXE/BS has been available for a long time [11] [12], and accurate analysis using "Total IBA" has been applied recently to applications in geochemistry (PIXE/BS/ERD, [13]), Alzheimer's disease (mapping STIM/PIXE/BS, [14]), biomedical surfaces (PIXE/BS, [15]), amino-functionalised gate oxides (RBS/ERD, [16]), and multilayer materials (RBS/EBS/PIXE/HR-PIXE, [17]): in the latter case high energy resolution PIXE was also essential.

We should emphasise the obvious fact that every technique, however powerful, has limitations; we have merely mentioned the wide range of complementary (or competing) techniques. This brief article cannot detail the limitations of IBA, but we should point out that most ambiguities are due to the limited energy resolution and sensitivity of the techniques since there are usually ways of using Total IBA methods to determine the structure and composition of the sample without a prior model. However, some ambiguity may be intrinsic; for example, roughness only has a secondary effect on IBA spectra and therefore different models of roughness (or interlayer diffusion or sample inhomogeneity) may be indistinguishable. The analyst should always be aware of these limitations, and know when to use other methods.

IBA for Accurate (Traceable) Analysis

The idea of an Uncertainty Budget [18] to quantify experimental and traceability uncertainties for IBA was published only recently [19]. However, despite the previous interest of national standards institutes in the use of RBS in particular for metrology (for a Ta₂O₅ standard material [20], for a metrology exercise on the native oxide of Si [21], and for the certified reference materials used for fluence in IBA [22] [23]), none of the labs involved (IRRM in Geel, BAM in Berlin, NPL in London) now has IBA capability. The situation is entirely different for XRF, where the PTB has been active in obtaining ISO 17025 certification (see [24] and further references therein) and where EXSA (the European X-ray Spectroscopy Association) are sponsoring a "Fundamental Parameters Initiative", supported by three National Standards Institutes (PTB in Berlin, LNE in Paris and NIST in Gaithersburg, [25]). This FP initiative has as much relevance to PIXE as it has to XRF.

To obtain ISO 17025 certification for IBA, certain requirements must be fulfilled. There should be a laboratory management system of a certain quality. The Surrey IBC has obtained ISO 9001 certification with a Quality Manual that is a model for the SPIRIT consortium [26]. For "Fixed Scope" ISO 17025 certification a specific analysis can be specified for which there should be a method validation document [27]. This should demonstrate the validity of the method in detail and would be expected to cite papers in the academic literature as well as establishing the validity of computer codes used (which is already achieved both for particle scattering [28] and for PIXE [29]). Yet no IBA lab, to our knowledge, has gained such accreditation.

The Surrey IBC makes many SIMS standards by ion implantation, with an implantation fluence accuracy that depends on the integrity of the charge collection apparatus, which is essentially independent of the implant species. Therefore, for our purposes, the qualification of implantation fluence is a very valuable activity, and not only for our own internal quality assurance purposes. We have already demonstrated an absolute accuracy of about 4% (95% confidence) in the determination of implantation fluence [30] [31] [32], where the cited uncertainty was dominated by the uncertainty in the stopping powers used. However, we have demonstrated that for 1.5 MeV He in Si, the SRIM 2003 [33] [34] stopping powers are accurate at 0.8% (1 σ , see Fig.1 in [35]), and therefore the absolute traceable accuracy of RBS should approach 1% (1 σ) if this beam is used with a-Si substrates to determine the actual charge.solid-angle product for a given spectrum. There is no other thin film technique that can match this level of absolute (traceable) accuracy for the determination of quantity of material.

To achieve this accuracy it is necessary to correct properly for pulse pile-up [36] [37] [38], and to correctly determine the electronic gain of the detectors, including the appropriate pulse height defect correction [39]. Incidentally, it is the absence of this PHD correction that accounts for the misfit at the low energy edge of the N signal in Fig.1b of [40] (this is more clearly seen in Fig.6b of [41]): the effect is surprisingly large. The low energy signal in backscattering calculated by the analytical codes usually neglect the deviations from single scattering. These can now be calculated with Monte Carlo codes [42], but reasonable approximations can also be made by analytical codes, both for double scattering [43] [44] and for other low energy effects [45], and these analytical codes can be extraordinarily accurate – see Fig.1 of [79].

A fully self-consistent and convenient PIXE/BS analysis code based on the DataFurnace [46] and DATPIXE [47] codes was introduced in 2006 [48]. This was used to analyse Niepce's heliograph of 1827 [49], a 19th century reproduction of Frans Hals' *La Bohémienne* [50], oxidation of carbon nanotubes [51] and photovoltaic and ferroelectric mate-

rials [52] [53] [54]. The *La Bohémienne* analysis followed a PIXE/BS analysis which was not self-consistent [55], but was itself flawed by an incorrect treatment of the sample roughness. Using a correct analysis of this same data, Molodtsov & Gurbich [56] have shown that gross surface roughness can be treated correctly; moreover, IBA can be used with good sensitivity to determine the average roughness parameters of a sample without any prior model and also without any surface contact! Gross surface roughness is not yet implemented by any IBA code, but mild roughness can be readily simulated [57] [58]; indeed, it turns out that RBS can be sensitive to differences in average interface roughness at the sub-nm level [59]!

A number of different forensics applications are being developed at present [60]: in principle the analysis of samples for forensic purposes should be fully quantitative and non-destructive. The previous discussion makes it clear that IBA can be accurate even for complex samples requiring the use of multiple IBA techniques. Gunshot residue (GSR) analysis by IBA looks very promising: interestingly, current police practice uses exclusively qualitative SEM-EDS as a characterisation technique. Different GSR particles which can be recovered from the crime scene and from suspects can be shown to distinguish the primers for the explosive charge used by different gun manufacturers. Electron-induced EDS (energy dispersive X-ray spectrometry) has poor sensitivity, as well as no depth information. SEM-EDS therefore cannot discriminate many modern primers, limiting its usefulness for forensic evidence. We have already shown that IBA can give very sensitive quantitative information on many types of primer ([61] [62]) thereby giving IBA increased discrimination power over SEM-EDS.

For any sort of accurate IBA, an essential prerequisite is the availability of statistically robust estimates of the uncertainty of the result. Such an estimate is entirely absent in the classical approach to solving RBS spectra where manual simulations are made until a plausible fit is obtained. Such an approach is not adequate to explore the intrinsic ambiguity of the data; this ambiguity is discussed at length in [41]. A fully Bayesian (maximum entropy) approach to this has been made [63] but has not proved to be generally usable. Although astonishingly good results can be achieved, the calculations are very time consuming and the information needed about the system is prohibitively detailed. However, a cruder approach using the DataFurnace code (see [5] [41] [46] [79]), still Bayesian but not using maximum entropy, has proved to be of general use in IBA depth profiling (see [40] [99] for example).

It is worth emphasising that this approach to uncertainty in the DataFurnace code is quite general. It is applied to all the data submitted for self-consistent analysis, currently including PIXE, RBS, EBS, ERD, PIGE, NRA and NDP (neutron depth profiling). The inclusion of PIGE [64] is important as many applications make use of PIGE to detect the important light elements F, Na, Mg which are troublesome for both BS and PIXE. We have already mentioned atmospheric pollution studies: cultural heritage studies [65] and geo-archaeometry [66] are among others that also systematically use PIGE, for which the IAEA has recently announced a Coordinated Research Proposal [67]. "Total IBA" for cultural heritage and similar samples now regularly uses PIXE/BS/PIGE (see [68] for example), although the analysis of the different techniques is not yet usually integrated.

We should point out that for a valid estimate of the total combined uncertainty, an estimate of the database uncertainty is also required. The stopping powers used are usually from a semi-empirical compilation whose uncertainty in any particular case can generally be estimated quite well. But in cases where the stopping power is not known, or not

known well enough, a Bayesian method of extracting the stopping power from thick sample spectra [69] is particularly valuable, since it also gives the uncertainty.

EBS cross-sections on the other hand should properly be obtained using thin film samples, although some evaluations also make use of thick film data inverted to obtain the cross-section [70] [71]. But evaluations of EBS cross-sections (see [7]) do not as yet include any reliable estimate of the uncertainty since these are very complicated to calculate correctly. Clearly this is a major problem for accurate (traceable) analysis that needs evaluated EBS cross-sections. We believe that one useful approach to determining such uncertainties could include uncertainties obtained from benchmark measurements which use this Bayesian method [72]. But this approach is still to be properly developed.

IBA for Blind Samples

One great strength of IBA is in the unequivocal information that can be obtained for samples about which little is certain. For example, neutron reflectometry is systematically used in polymer chemistry to determine details of reaction kinetics at remarkably good spatial resolution, but NR spectra are multiply ambiguous and need a fairly tightly constrained model, such as can be provided by IBA (see [73] for one recent example of many), before they can be interpreted.

Protein crystallography is another important example where IBA is used to interpret another technique: in this case the bound metal ions or co-factors cannot be uniquely determined by X-ray or NMR methods. PIXE has the sensitivity to detect the metals, which are usually in trace concentrations, and uncertainty is avoided by the use of the intrinsic protein S content as an internal standard for normalisation. The critical feature of this method, on which its accuracy depends, is the use of the BS spectrum for an internally consistent absorption correction [74] (and see [75] for a recent example).

Another interesting example is of the so-called Darwin glasses [76] which are impact glasses resulting from a meteor strike 800,000 years ago near Mt. Darwin in Tasmania. The geologist subsequently used one of these glass samples as an amorphous standard for setting up his XRD kit, and was astonished to see the diffraction spots of quartz. These crystals – unexpected in a glass – turned out to be inside *inclusions* in the glass. But the nature of these inclusions was entirely unknown. IBA analysis demonstrated them unequivocally to be carbonaceous, a result that initially baffled the geologists, for whom such a sample was unprecedented. Moreover, not only did the microbeam PIXE/BS determine the main constituents and demonstrate the great heterogeneity of the samples (both laterally and in depth: see Fig.1), but the IBA data could be completely quantitatively analysed without any presupposed model despite the heterogeneity (see Fig.1 and [76]).

This sort of mapping microbeam data is effectively a 3-D (three-dimensional) data cube, with 128x128 pixels and a PIXE and BS spectrum pair for each pixel. The data cube, intractable as it stands, can be analysed into its principal components (7 in this case) by using a multivariate image analysis program such as AXSIA (Automated eXpert Spectral Image Analysis [77]). These principal components are determined in the spatial domain [78] each giving a pair of PIXE/BS spectra characteristic for a given area of the map as seen in Fig.2, and which can be directly interpreted by DataFurnace [79]. Selected results of such an analysis are shown in Fig.3 for all 7 components. In principle, the depth profile at each pixel can be reconstructed from a linear combination of the principal components, and therefore the 3-D structure of the sample is completely solved.

This last example points towards tomography. X-ray tomography (XR-T) is already established [80] [81] [82], and STIM-T is an almost equivalent (and solved) problem [83]. Great strides have also been made towards a PIXE-T [84], which is qualitatively much more complex than STIM-T (or, equivalently, XR-T). We have shown that in principle IBA-T (that is, using the BS signals as well as the PIXE signals) is already achievable in principle, and should be significantly more efficient (and therefore much faster) than pure PIXE-T since a single slice already has (nearly) complete 3-D information. This is important since tomography is rather slow, and its importance is increased since it seems that beam damage limits the use of a pure PIXE-T for important classes of samples [85]. In principle, using the depth information available explicitly in IBA-T (from the particle signals) must be quicker than unfolding the depth information available only implicitly (and at much lower resolution) in the PIXE signals.

Another interesting feature of these Darwin glass data is that the heterogeneities are radical, that is, there are precipitates of one material (quartz) in another (the carbonaceous matrix). On the face of it, one does not expect to be able, by IBA, to distinguish a material with precipitates, from a material with a uniform (average) composition. But Stoquert & Szörenyi [86] demonstrated that in fact the density variation in a material will measurably affect the straggling of the probe ion beam as it penetrates the sample. And we can use sharp non-Rutherford resonances in the elastic scattering cross-section as markers for the straggle as a function of depth. This was used by Tosaki [87] to distinguish different forms of carbon, and also used to demonstrate that the DataFurnace code was correctly simulating sharp EBS resonances [88]. It is the behaviour of the EBS resonance for $^{12}\text{C}(\text{p,p})^{12}\text{C}$ at 1734 keV that allows us to prove the presence of SiO_2 precipitates in these inclusions, independently of the XRD.

IBA for Large Datasets

The introduction in 1997 of a usable automatic global minimisation code for RBS (see [46]) has enabled the detailed analysis of large quantities of data that would have been considered intractable in the past. As examples: Milosavljević *et al* have made systematic RBS studies of mixing in binary systems using this tool from 1998 [89] to date [90]; also, the characterisation of plasma-facing components in nuclear fusion experiments is complicated and requires IBA of many samples [91] [92].

Another important application of Total IBA that is already providing a significant funding stream to more than one laboratory is the systematic measurement of air pollution. IBA including PIXE, PIGE and ERD is usual for these measurements, and is usually combined with other techniques such as spectral optical thickness and ion chromatography [93] or a battery of techniques including organic and total carbon analysis, proton NMR spectroscopy, and ion chromatography among others [94]. It should be mentioned that XRF is not an effective competitor technique for IBA in the measurement of aerosols (*pace* [2]) considering that an IBA measurement of a few minutes is really "total", that is, it measures up to 80% of the total mass of the sample (using PIGE for light elements, BS for C & O and ERD for H) where XRF is only partial (and takes much longer). Moreover, the accuracy of benchtop XRF is intrinsically limited by the difficulty of characterising the spectrum of the X-ray tube, but IBA can easily be run at ~2% precision (see [30] [31]).

There is a new approach to IBA which may prove remarkably valuable. Artificial neural networks (ANNs) can be constructed capable of effectively analysing classes of IBA data (see [6]) and are now being used to handle real-time data obtained to determine the detailed annealing kinetics of various systems [95]. Much intervening work has shown that

ANNs can be trained to handle multiple spectra, or multiple techniques; and it is clear that any sort of IBA can be implemented in an ANN for which a valid training set can be defined.

The point here is that once the ANN has been trained [96], a solution of a spectrum is obtained completely automatically and effectively instantaneously. This solution is itself remarkably accurate, and provided the ANN training is adequate, will be qualitatively correct. Such a solution can be given back to the analytical codes for post-processing to automatically obtain the best possible solution, together with robust estimates of the uncertainty. Thus, the qualitative recognition of a set of spectra by an ANN can be used as the basis of an automatic and fully quantitative machine analysis of the dataset. To check whether individual spectra are actually validly analysed by the ANN (based on the sampling space of its training set), prior to passing them to it, an additional ANN can be trained that classifies spectra as "acceptable" or "not acceptable" (see [96]). Thus, the ANN can not only recognise a given spectrum, but can also recognise whether or not it has been trained to recognise it.

The aim is a push-button (or turnkey) system suitable for non-experts ("IBA without Humans" [97]), similar to the systems already available for SEM-EDS, EPMA, XRF, or AMS. Such IBA systems would be essential for a more general industrial acceptance of the technique, and seem to be feasible.

Chemical Analysis with IBA

BS/ERD/NRA, being based on nuclear excitation, strictly contains only elemental information. But Butler long ago pointed out that data interpretation should take chemical constraints into account; he gave the example of a metal alloy sample treated in an oxidising environment ([98], and see [41] for a full discussion). We take it for granted in Total IBA that data are interpreted using valid chemical assumptions, that is, that the depth profiles are given in terms of the natural molecules of the system. For example, analysing an anti-reflection coating of a zirconia/silica multilayer on glass, the three natural molecules to be used would be ZrO_2 (with its Hf contamination), SiO_2 , and the glass composition [99].

However, PIXE is an atomic excitation mode, and there is increasing interest in chemical information obtained directly using high resolution PIXE systems. High resolution also allows much better elemental detection limits in the many cases of characteristic line overlap [100]. But in principle there should be effects similar in PIXE as have been exploited in XPS (and XRF and other techniques) for the last several decades. The chemical shift between the oxide, nitride and carbide of the Si $K\alpha$ line were measured at 0.2, 0.4 and 0.55eV respectively with a wavelength dispersive system [101], the S $K\alpha$ line shifts over 1 eV for sulphates [102], and the Ni K-line absorption-edge energy was found to shift to higher values by about 1.5 eV per unit change in valency of nickel [103]; chemical shifts for $K\beta$ [104] [105] are up to 2 eV per unit change in valency, and those for L lines are similar. For example, about 1 eV/valency was observed by sy-XAFS for Ti $L\alpha$ lines [106].

Recently, high resolution microcalorimeter detectors have been introduced which allow energy dispersive spectra to be collected at high resolution over a wide energy range, which has a dramatic effect on the applicability of this sort of data: we have already cited the use of such data in a Total IBA study (see [17]). The only trouble is that high resolution spectrometry reveals a very large number of lines that are usually ignored, that have complicated chemical state and beam energy (excitation mode) dependencies, and are not yet well understood to the extent that they may conceal new physics [107]. Other exam-

ples of these complications include L sub-shell ionisation cross-section dependency on incident particle energy (proton-PIXE in this case) [108], and the complications can begin to be appreciated by studying the review by de Groot [109].

The comparison here with synchrotron XRF is instructive. With a tunable X-ray energy, sy-XRF has an exquisite sensitivity to the chemistry of the sample that PIXE cannot possibly match. But the excitation giving the PIXE signal also gives (at least) a backscattered particle signal, which contains direct information on the elemental depth profile of the sample that XRF cannot match. All techniques have limitations, and IBA is superior to XRF both for layered (and especially unknown complex layered) samples, for mapping, and (usually) for absolute quantitation.

There is another approach to chemical information by IBA. MeV-SIMS, that is, SIMS using a primary beam of MeV heavy ions, can mass-analyse large molecules (>>1 kDaltons) that have been ionised and ejected from the surfaces of insulating (usually organic) materials [110]. The mechanism depends on the electronic energy loss in the material, and is different from regular SIMS which depends on the nuclear displacement cascade. Moreover, Fig.4 makes it clear that the yield of sputtered high mass molecular ions for heavy swift ions is at least comparable to that for keV-SIMS, and may be greater [111] [112]. MeV-SIMS has already been used to suggest that doped fingerprints (that is, using hand cream) deposited above ink on paper documents can be distinguished from prints that are below the ink, an application of some forensic importance [113], and it is clear that Total IBA is possible: the ability to collect molecular information, which can be directly quantified for blind samples (unlike regular SIMS) by simultaneously collected PIXE/RBS information, is of great interest [114].

Importantly, MeV-SIMS uses a fast primary ion beam which (again, unlike regular keV-SIMS) can be brought out into air, so that analysis can be made (together with PIXE/RBS) in ambient conditions. This allows the analysis of organic features of large, delicate and valuable (such as paintings or manuscripts), or wet biological samples [115], without the need for subsampling. Secondary ion mass spectrometers are already available for work in air, in MALDI (matrix-assisted laser desorption ionization [116]) and DESI (desorption electrospray ionisation [117]) applications, neither of which have the possibility of the simultaneous complementary techniques giving quantification and depth sensitivity.

IBA with Complementary Techniques

We have already mentioned the unexpected detection of quartz by XRD in the Darwin glasses that led to the Total IBA of these fascinating objects. Materials science has many characterisation techniques, and the analyst must always be alive to the strengths and weaknesses of each technique. Good science depends on the complementary use of all appropriate techniques. This section is making the further observation, that some complementary techniques give similar ("commensurate") information from a different point of view that can significantly improve the analysis.

Total IBA ought naturally to be able to incorporate such commensurate data. Ellipsometry is an extraordinarily sensitive non-contacting and entirely non-destructive method for obtaining layer thicknesses. It has been used in reference work as complementary to IBA (see [21]). But as with neutron reflectometry (see above, and [73]) VASE (variable angle spectroscopic ellipsometry) is multiply ambiguous, and IBA could be a complementary technique valuable for constraining the solutions. A Bayesian approach to VASE data [118] could be very easily integrated with IBA.

IBA depth profiling is frequently compared with SIMS, which is vastly more sensitive but not usually quantitative. It is now possible to interpret IBA data self-consistently with SIMS depth profiles [119], which are treated as a qualitative constraint on the structure of the depth profile. If microbeam PIXE maps are available of a cross-section of the sample, thus giving direct access to the depth profile, such profiles are treated as quantitative constraints.

XRF and PIXE give very similar spectra, and use almost identical databases to evaluate them. A portable XRF/PIXE has been reported [120], but in this work the XRF and PIXE data were handled separately. It is only quite recently that any sustained attempt has been made to integrate them [121] [122]. In this rather special case of the Mars Rovers, the data themselves are a mixture of XRF and PIXE because of the mixed radioactive source being used. The handling of the XRF/PIXE data in this case is an analytical *tour de force* that has established the presence of hydrated minerals on Mars, an extraordinarily important result [123]. In principle, more mundanely, IBA codes could incorporate XRF data, which would be (for example) very useful for determining substrate compositions in many external beam applications on layered samples where the thickness of the top (perhaps painted or laquered) layer may be $\sim 20 \mu\text{m}$ or more. This is thick enough to dominate the PIXE spectrum for most analysis beams, but the information depth for XRF is much larger (for the higher energy X-ray lines).

Summary

IBA is a powerful technique of a very wide applicability comparable to XRF, SEM or SIMS, which should be considered essential for a well-found materials characterisation laboratory. In different configurations it is suitable for accurate (traceable) depth profiling, perhaps for QA (quality assurance) purposes; damage measurements on thin-film samples (with channelling); accurate, sensitive and non-destructive analysis of forensics samples; in-air characterisation of cultural heritage samples; and full 3-D tomography of small samples ($\sim 10\mu\text{m}$). It is also capable of scaling up for accurate routine (turnkey) analysis of very large batches of complex spectra from samples out of reasonably well-defined processes. IBA can extract model-free depth profiles for unknown samples, where the depth profiles can include detailed information about interface roughness and the average size of precipitates. In principle IBA is sensitive to gross roughness, and model-free parameters can be extracted from the data to characterise this roughness.

The establishment of important niche applications to provide support for IBA laboratories at a reasonable level will be important for the survival of this technique. We believe that these initial applications will include accurate and certificated analyses for QA purposes (such as certified materials standards for SIMS) and analyses of forensics samples of a quality sufficient to present in court.

We expect future applications to include various integrated self-consistent analysis methods, such as IBA/ellipsometry, IBA/XRF or IBA/SIMS; and also high volume applications such as air pollution measurement campaigns where the quality and sensitivity of the data analysis is of high importance. Future challenges will include the development of much more user-friendly data handling (software) methods. Present tools allow very sophisticated data manipulations, but still require expert handling. Perhaps the extension of artificial neural network methods will enable the same turnkey approach to IBA that is already standard in XRF and EPMA?

Conclusions

Where are we? "Total IBA" is clearly a present reality in at least a limited sense, being very clearly demonstrated in a number of recent examples of PIXE/BS. The self-consistent use of all combinations of PIXE, BS, ERD, NRA is currently feasible; in fact, examples of all of these have already been published.

"Total IBA" is not a totally satisfactory name since it is premised on the availability of an unambiguous and self-consistent analysis of simultaneously collected IBA signals of *all* available types. But in many cases an unambiguous analysis depends on a self-consistent treatment of several sequentially-collected and partial datasets which may individually be of single types (e.g. NRP + He-RBS + H-PIXE or He-RBS + H-EBS), and may even include non-IBA techniques (we have given specific examples of IBA + protein crystallography, and IBA + neutron reflectometry). But what is important is not the name of the analysis but that it is valid and unequivocal, and for that two things are crucial : a *self-consistent* analysis and the *usability* of any relevant IBA signal. The main barrier until recently was that PIXE could not be handled self-consistently with the nuclear IBA techniques.

Nevertheless, we have demonstrated the power of self-consistent IBA. At present, fully exploiting this power is often quite difficult even where the experimental hardware for collecting multiple signals is available : the software tools are still rather clumsy and underdeveloped, and many databases are quite incomplete. But the more analysts realise the potential of IBA the sooner these difficulties will be overcome.

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Figures

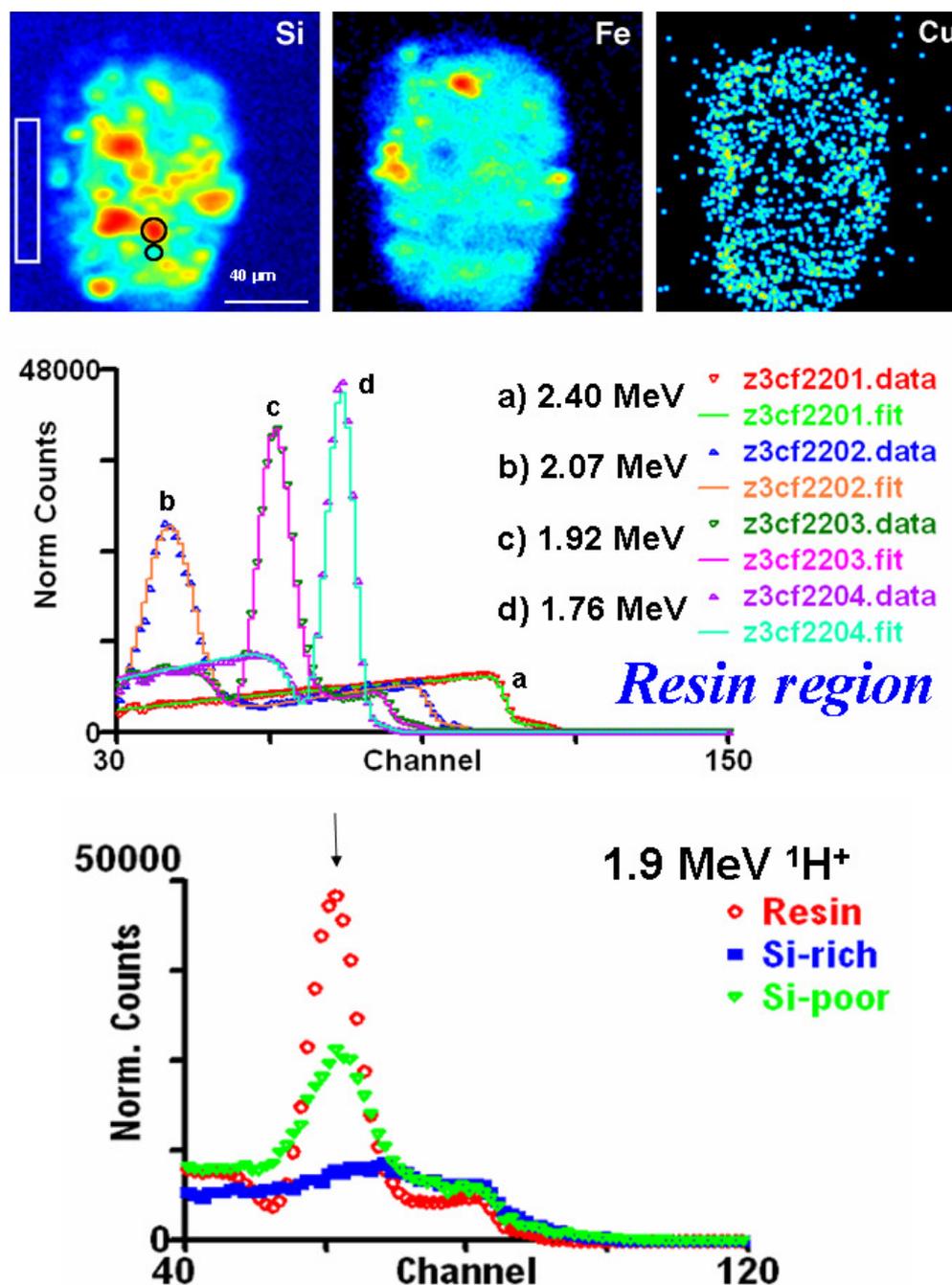


Figure 1. "Total IBA" of an inclusion in a Darwin Glass (see text). *Above*: selected PIXE maps of the inclusion in a resin mount, showing distribution of Si, Fe, Cu; *Centre*: EBS spectra at varying proton beam energies of the resin region showing the $^{12}\text{C}(p,p_0)^{12}\text{C}$ resonance at 1734 keV; *Below*: EBS spectra at 1.9 MeV for three areas marked on the Si PIXE map (above, left). (See Bailey *et al*, *Nucl. Instrum. Methods B*, **267**, 2009, 2219 [76]).

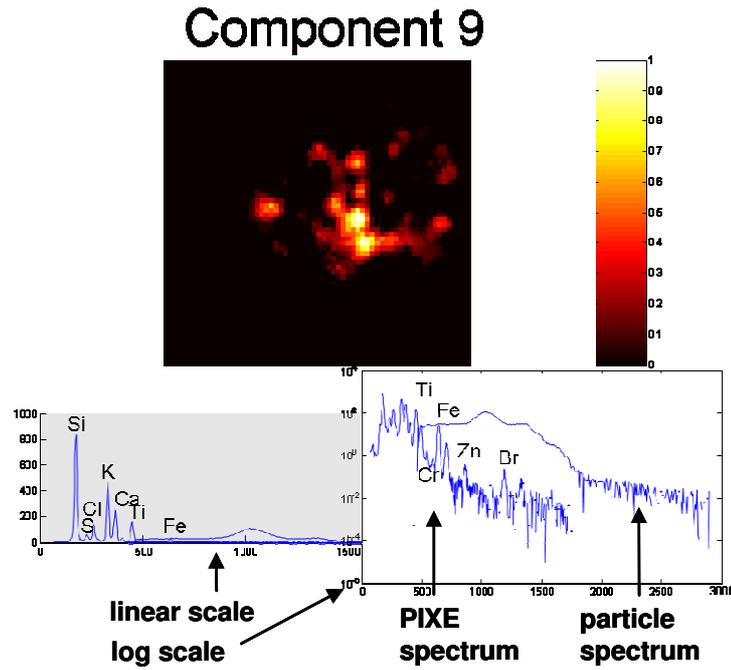


Figure 2. One component from the principal component decomposition of the data cube of Fig.1 using AXSIA (see Doyle *et al*, *Nucl. Instrum. Methods B*, **249**, 2006, 828 [77]). This component is one of the several Si-rich components.

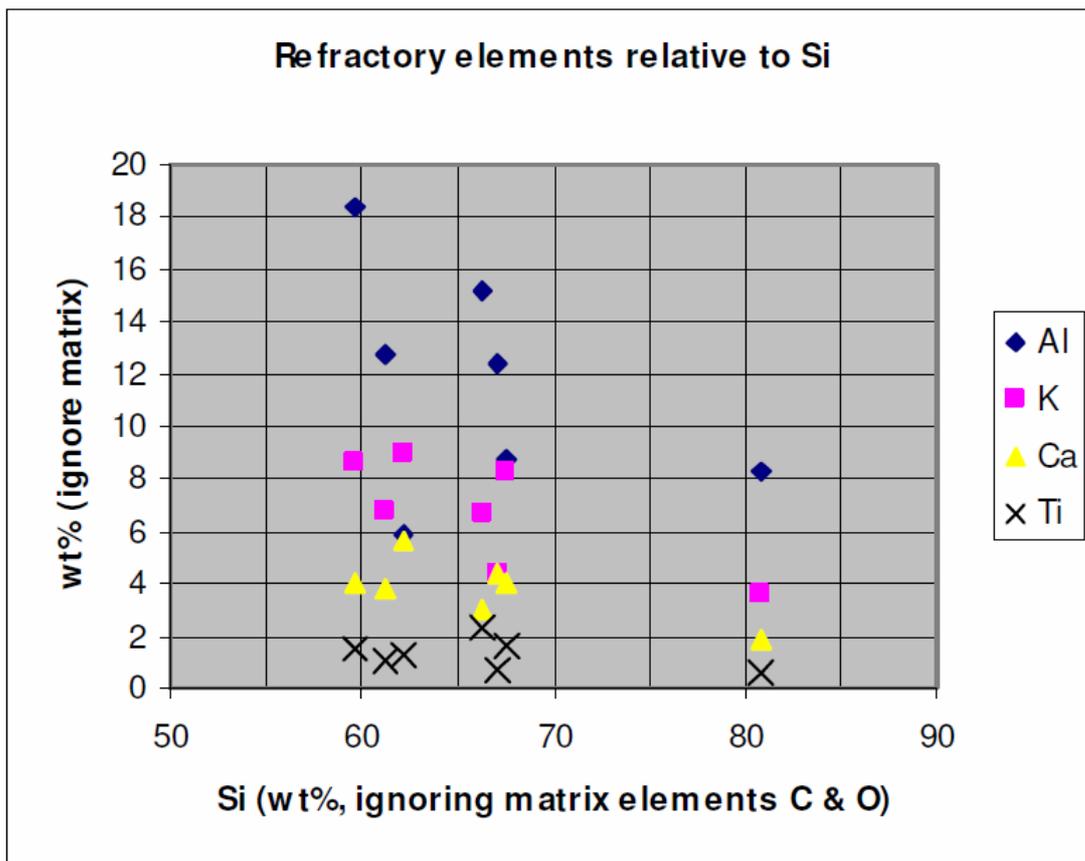


Fig.3. Composition plot of the relative abundance of minor elements relative to silicon in seven regions from a mapped carbonaceous inclusion of a Darwin glass sample (Bailey *et al*, *Nucl.Instrum.Methods B* **267** (2009) 2219; [76]), analysed by DataFurnace from a decomposition of the data cube by AXSIA (Doyle *et al*, *Nucl.Instrum.Methods B* **249** (2006) 828; [77]) see text.

The Secondary Ion Mass Spectra of Angiotensin II using various primary ions and energies

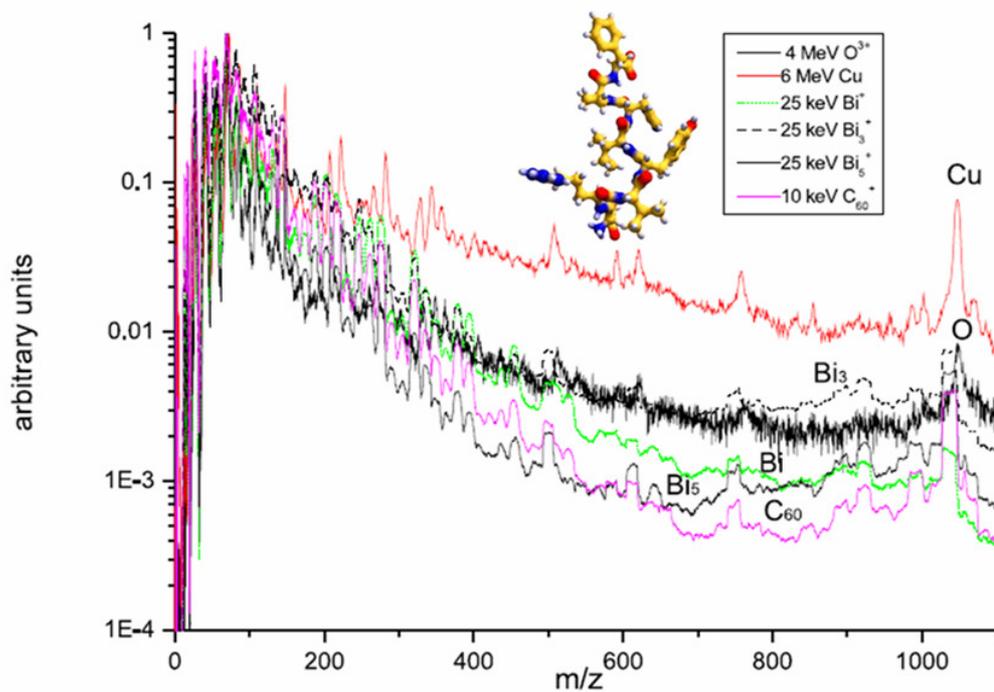


Fig.4. Comparison of MeV-SIMS of an organic sample with keV cluster SIMS (see text, and Fig.4 of Jones *et al*, *Surf. Interface Anal.*, **43** (2011) 249 [111] for more details; the lack of yield in this Figure for 4 MeV O³⁺ at m/z~1050u proved to be an experimental artefact). MeV-SIMS has orders of magnitude higher yield for larger molecules.

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