BCA I G/ RSC XRF Meeting Report - May 2006, BGS, Keyworth.

Morning Session

Welcome - *Dave Taylor, BCA Industrial Group*

Dave provided the welcome for the day from the Industrial Group of the BCA for this first joint XRF meeting with the RSC Atomic Spectroscopy Group. He thanked all the sponsors for their kind contributions. Dave then commented that the aim of bringing together an independent UK forum for XRF appeared to be bearing fruit with 70 delegates registered for the meeting.

Introduction & tour of BGS
Charles Gowling, British Geological Survey.

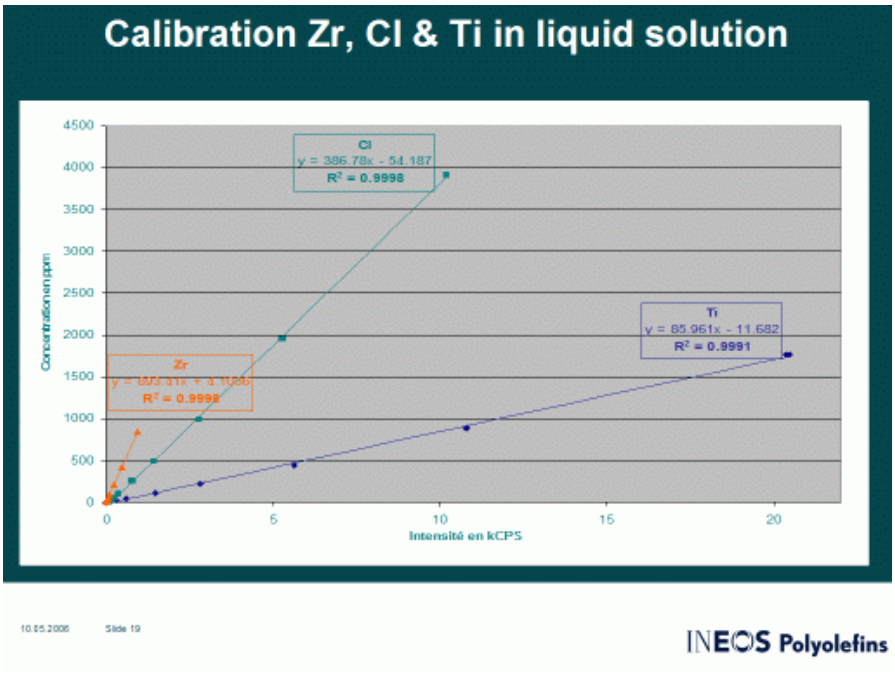
Owing to Mark Ingham having lost his voice, Charles Gowing kindly stepped in to the breach by providing the introduction. He ran through the usual formalities of safety and continued with a review of the day's agenda.
The whole group then split into two for a tour of the British Geological Survey XRF facilities. The laboratory itself was well equipped with PANalytical XRF instrumentation. In daily use are 3 WDXRF instruments - a PW2400, a MagixPro and a new Axios. On the EDXRF side was an Epsilon 5, used when Rh excitation becomes limited e.g. for Sb analysis etc. Outside in the sunshine we were given a tour round the BGS's newly converted mobile laboratory. It is equipped with both a bench top and handheld EDXRF systems. So far the lab has been successfully trialled locally but has not been put to full use in the field. We all returned to the meeting room for the remainder of the day.

Chair, Morning Session
Andy Scothern, RSC.

Andy took the opportunity to inform the delegates of the 13th Biennial National Atomic Spectroscopy Symposium being held at Glasgow Caledonian University from 10th to 12th July organised by the Atomic Spectroscopy Group of the RSC. He then introduced the keynote speaker Dany Doyen.

Keynote Lecture - From Catalyst to Final Product: An overview of XRF analytical and sample preparation techniques in a leading European R&D polymer laboratory.
Dany Doyen, INEOS Polyolefins, Belgium.
E-mail: dany.doyen@innovene.com

Dany began his talk with a brief history of INEOS Polyolefins plus an overview of the company as it is today.
INEOS have a range of analytical techniques that are available in the business so why choose XRF. It is a robust and reliable technique with pros and cons.



A wide range of sample types are analysed at INEOS. These include catalysts, additives, polymers, deposits and defaults (problems). As the majority of the samples are polymeric a 1kW Bruker system with a He atmosphere is used otherwise both standards and samples would be destroyed by the beam. Difficulties arise for the analysis of P, S, Cl and Si, which migrate to the surface of hot pressed films. INEOS get around this by cutting away the surface prior to measurement in their XRF.
A range of sample preparation techniques are employed. Catalysts are measured in solution. Additives such as TiO2 are analysed for their Ti content as pressed pellets and sometimes, especially for pure TiO_2, fused beads are used with $Li_2B_4O_7$ as flux. Dany then covered a range of INEOS specific applications and solutions.
Validation of their XRF is carried out twice weekly and monitored using a control chart. Using these data decisions are taken as to when drift correction is required. Also, every quarter, these data are shared between the different control labs around the INEOS facilities to monitor the company agreement.
Dany concluded that WDXRF provides a rapid analysis for a competitive price.

A Discussion on the Estimation of Uncertainties in XRF Measurements
Ros Schwarz, London & Scandinavian Metallurgical Co Ltd.

Ros introduced her talk by explaining that she is not an expert in statistics but believes it is important for the analytical community to have an understanding and apply it as appropriate.
At London & Scandinavian Metallurgical Co Ltd (LSM) the range of sample types is vast and Ros would like to be able to estimate the uncertainty associated with an XRF measurement so that she can optimise her analysis parameters without spending a vast amount of time running through repeatability/reproducibility exercises. Her aim is to find a simple way to calculate an uncertainty estimate of any element in any matrix.
Documentation Ros has referred to has been the Eurachem/Citac guide and BS EN ISO 12677:2003.

Chemical analysis of refractory products by XRF - fused cast bead method.
For her initial work Ros has assumed that instrument uncertainty and sample preparation uncertainty are not correlated. The factors she is concentrating on are instrumental variance, the detector and counting error/statistics. She is then using this for modelling for changing counting rates. Ros then asked for feedback on her ideas to date and any suggestions on how to apply this idea to matrix corrections which led to useful discussion.

Alison Burke
Huntsman Pigments

Speakers, Chairs and Guides. From left to right: Front row - Sharon Fraser, Heather Harrison (tour guide), Ann Townend, Ros Schwarz, Margaret West (PM chair). Back row - Andy Smith, Daniel Capon, David Beveridge, Dany Doyen, Andy Scothern (AM chair) Charles Gowing (tour guide).

Afternoon Session

Chair, Afternoon Session
Margaret West.

How Corus Group Share Best Practice
Ann Townend , Corus plc. Scunthorpe

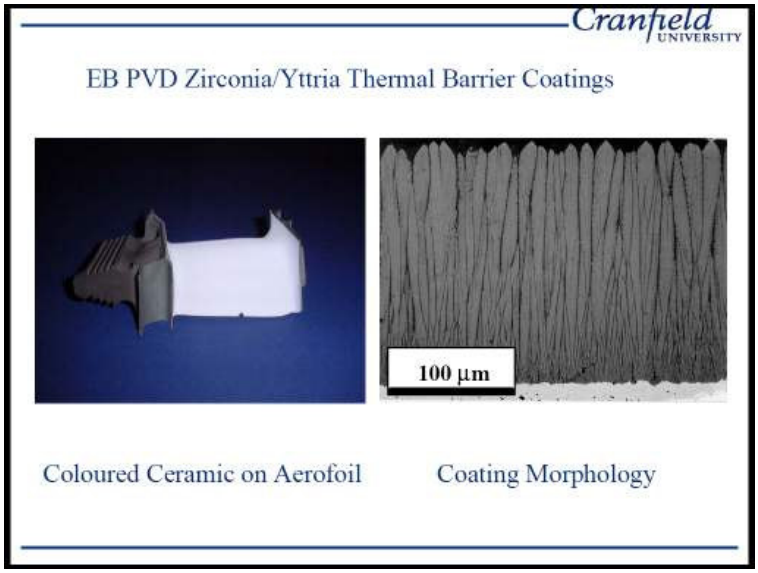
Corus is an international metals company which provides steel and aluminium products to customers worldwide. Ann gave a revealing account of what happened when analysts from the four Corus sites (Scunthorpe, Teesside, Stocksbridge and IJmuiden in the Nederlands) were gathered to pool their knowledge in an exchange of best practices. The XRF analytical group found that completely different techniques had been adopted in site laboratories; sometimes fusion techniques were being used and sometimes pressed pellets for the same analysis. Even when the same techniques had been used, the conditions used were different. To complicate matters, all were using different sample preparation equipment and different XRF instrumentation.

Two years on now, consistency of methods is being achieved. The same fusion equipment is now used at all four sites. Round Robin exercises in the analysis of test samples are showing convergence of the results obtained for the different sites. There have been some spin-offs: for instance, by adopting one site's method, using 8g rather than 10g of flux as used at other sites, £3200 per annum is potentially saved by the company. However, the main gain has been in the exchange of ideas between the analysts of the company's laboratories. Future co-operative plans include joint development of wide range calibrations and the pooling of resources in producing calibration standards.

XRF and Coating Processes at Cranfield University

K. J. Lawson.
E mail: K.J.Lawson@Cranfield.ac.uk

Ken summarised some of the major coatings activity in the National High Temperature and Surface Engineering Centre at Cranfield University. He demonstrated the value of XRF in analysing and monitoring the application of surface coatings, using spectra obtained from a Bruker S2 Ranger multisample XRFS system. He illustrated his talk with applications relating to coatings used on aerospace gas turbine components. Such coatings are applied to give either heat, oxidation or abrasion resistance using specialist processes such as electron beam physical vapour deposition, plasma spraying, metal sputtering and multilayer deposition. They included, amongst others, zirconia-based ceramics used for thermal barrier coatings, superalloys and bond coats. Particular emphasis was placed on the analysis of trace elements in the materials, the concentrations of rare earth oxide dopants and their importance in thermal barrier coating technology.



Silver Determination in Photographic Emulsion by EDXRF

David Beveridge, Harman Technology Ltd - IlfordPHOTO
E-mail: david.beveridge@harmantechnology.com David described his frustrating quest to provide a simple XRF determination of silver in photographic emulsions (suspensions of silver chloride, bromide and iodide in gelatin solutions) as an alternative to the traditional determination -titration with thioacetamide - a relatively toxic reagent.

Since the emulsions tend slowly to settle out, direct determination in a liquid cell was not an option. So he attempted to obtain a clear solution by dissolution of the silver halides. His first thought was to start with a reagent similar to photographic fixers, solutions of ammonium thiosulphate and acetic acid. He added strontium nitrate as an inert heavy absorber, to nullify changes in X-ray ray absorption coefficient of the sample solution due to the variable composition of the emulsions and to decrease critical depth to less than that of the liquid cells. Unfortunately, this resulted in a cloudy suspension solution. He believes this must have been due to the formation of strontium sulphite by reaction with sulphite impurities in the ammonium thiosulphate supply. When he substituted sodium thiosulphate, which could be obtained in a purer form, the required clear solution was obtained. Now, he became concerned that the combination of the strontium nitrate with thiosulphate could potentially prove explosive if it dried out. So

Comparison of ED and WD XRF Emulsion Silvers

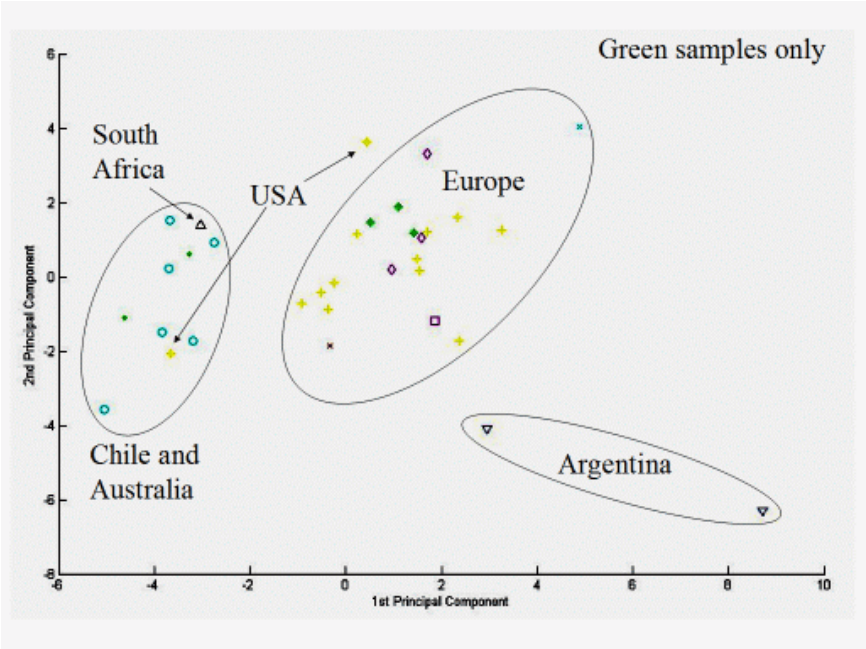
WDXRF	EDXRF	ED/WD
121.3	120.4	99.3 %
120.1	118.3	98.5 %
158.3	155.4	98.1 %
146.9	144.7	98.5 %
165.4	161.0	97.4 %
73.9	73.9	100 %
87.8	87.4	99.5 %
37.9	38.8	102.4 %
	Average	99.2 %

he substituted strontium acetate for the nitrate. As final flourish he added a little acetic acid to the solution to the "strontium fix" to lower the pH and to assist in the dissolution of the gelatin of the emulsions.

He now had an XRF method, which he was able to demonstrate gives, the same result (±1%) as the titration method as shown in the slide above. However, his company has yet to approve a change.

Archaeology of the present?
***Sharon Fraser*[1]**, *Dave Polya*[1], *Paul Lythgoe*[1] *and Tim Insoll*[2]
1. School of Earth, Atmospheric and Environmental Sciences, The University of Manchester
2. School of Arts, Histories and Cultures, The University of Manchester

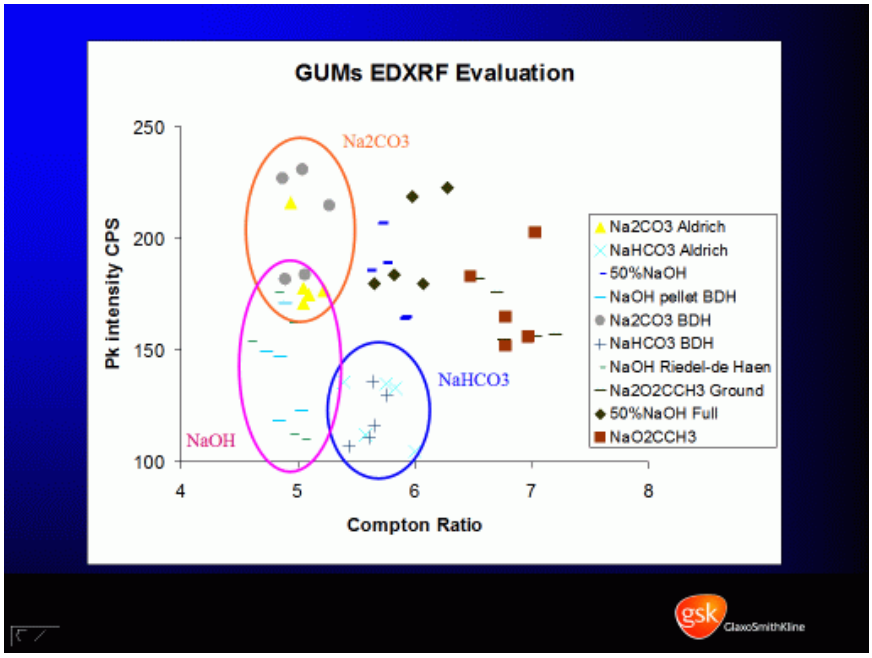
Sharon explained that as a prelude to carrying out a project into the feasibility of provenancing ancient glassware finds on the basis of their XRF analysis of trace elements, she wanted to establish the best XRF analytical methods using less precious artifacts i.e. wine bottles from the local bottle bank. The technique she used was to finely grind the glass before analysing it as a powder. Using a PANalytical Axios WDXRF spectrometer with Protrace software, she was able to determine 44 elements from Cl to U of concentrations down to 2 ppm. Using Principal Component Analysis -a statistical three dimensional breakdown of patterns of elemental concentration - she attempted to identify clusters of data corresponding to different provenances for the glass bottle. She was able to show that it was possible to distinguish between green glass of bottles of European and South American or of Australian origin. However, it was not possible to distinguish a similar pattern of clusters corresponding to different origins for wine bottles made of clear glass. Nevertheless, having proved the potential value of the technique, she now proposes to advance her project attempting to establish the provenance of glass artifacts of Islamic age found in Bahrain and Syria.



A different use for ED-XRF within the Pharmaceutical Industry"
Andy Smith, GlaxoSmithKline R&D. (Stevenage) *and Martin Teasdale, GlaxoSmithKline R&D.(Tonbridge)*

Andy described his attempts to use XRF as a rapid technique to confirm the identity of inorganic compounds used as starting materials in manufacture of pharmaceuticals in pilot plants. Identification of such "General Use Materials" (GUMs) is required by "Good Manufacturing Practice" (GMP) procedures even on small scale production of clinical grade "Active Pharmaceutical Ingredients" (APIs). These inorganic compounds are currently identified using relatively complicated and time-consuming tests involving techniques such as titration and ion chromatography.

He used a PANalytical Minipal4 EDXRF spectrometer. This instrument is simple, low cost and small enough to fit on a standard laboratory bench top. The XRF technique - basically loose filling liquid cells with the powders - is simple and quick. In many cases, a simple matching of XRF spectra with library spectra could be used. However, to distinguish some anion salts of metals, it was necessary to take into account the relative ratios of elemental peaks and Rayleigh and Compton scattering peaks. Using principal component analysis, compounds as similar as sodium carbonate and sodium bicarbonate could then be distinguished.



The work is very promising. GSK propose working with PANalytical towards putting together a suitable software package for general use in the pharmaceutical industry. This method should be suitable for relatively inexperienced operators with very little need to interpret the spectra.

"XRF in the glass industry"
Daniel Capon *and M Marshall, Glass Technology Services 9 Churchill Way, Chapeltown, Sheffield S35 2PY.*

Daniel gave a rapid overview of the tricks used by the glass industry to obtain the required colours of glasses. These were interesting, not especially for an account of the metals which produce the different colours, cobalt -blue etc, but for the different additives which could be used to make the glass appear colourless. These included oxidising agents, added to change the valency state of ferrous iron - the main contaminant giving glass a green colouration - to the ferric state, giving it a less noticeable yellowish tint. Another trick is to introduce a metal salt giving a complementary colour to that due to the contaminants, so cancelling it out, though this tended to produce glass with a greyish tint. With greater use of recycled glass these techniques were coming more into play and depended heavily on the rapid analysis of the glass melts to determine corrective actions. XRF was an ideal technique for this purpose. Andy said that GTS was developing methods for analysing the majority of trace colouring elements commonly found in glass in order to help customers solve problems. Allied with this is the development of specialist drift correction glasses containing detectable quantities of multiple elements, for use with XRF spectrometers.

Margaret West closed the meeting by thanking all the speakers for the work that went into their presentations. She also thanked the staff at the venue for helping to make the meeting a success and an excellent lunch. She closed the meeting by thanking the delegates for sparing valuable time to attend and gave a reminder of the next meeting in Canterbury in April 2007.

Rob Foster
Health and Safety Laboratory