Report on the PANalytical User Symposium – 28th/29th April 04

Introduction

The meeting, hosted by PANalytical Ltd., Cambridge, was held at Dunchurch Park, Nr. Rugby – a former manor set in 30 acres of picturesque woodland and grassed areas. The symposium combined a series of technical presentations on the X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) techniques with the UK launch of the Axios XRF Spectrometer.

Meeting welcome and introduction

by Reg Nichols, PANalytical Ltd.

Reg welcomed the 20 delegates and went on to explain the format of the meeting. He explained that PANalytical, formerly Philips Analytical, was acquired in 2002 by Spectris plc, a FTSE 250 company and a holding company for a dozen or so 'analytical measurement' companies which include BTG, Seivomex and Arcom.

X-Pert High Score Plus

by Robin Aird, PANalytical Ltd.

Robin described the new X'Pert Highscore Plus XRD software available from PANalytical. The software is a complete powder pattern analysis tool, covering phase identification, cystallographic analysis and Rietveld calculations. All of the common and many of the less common data formats can be imported into the software and it supports the internationally recognised CIF format for the publication of XRD data. The Reporting interface has MS Word compatibility. Of particular interest to those working in a 'Quality' environment is the capability to create and maintain a 'history' file which records all data manipulations so that the measured data cannot be destroyed.

The **Phase Identification** area covers qualitative phase analysis, semi-quantitative analysis using 'relative sensitivity factors', crystallinity determination and standard pattern treatments like background fitting and Kalpha2 stripping. Multiple scans can also be compared and 3D graphics are available for studying phase transitions with temp. The software also supports PDPDF4, the relational database offered by the ICDD (International Centre for Diffraction Data).

The **Crystallographic area** is used to determine unit cell information. Three classical indexing routines are used - DICVOL, TREOR and ITO which increase the possibility of indexing unknown patterns. These routines determine the unit cell parameters by finding the 'conventional cell' with the highest possible symmetry and greatest density. Cell standardisation and transformation functions are provided.

The **Rietveld calculation** area can be used for both X-ray and Neutron data. Automatic refinement strategies are provided for the novice. Rietveld analysis links the structural data to the Powder Diffraction File (PDF) reference pattern. Automated Processing Procedures (APP) allow Rietveld Analysis to occur following pattern measurement and identification. The software can be used for phase identification (based on structure and/or hkl file), determination of amorphous content, crystal size/strain measurements and calculation of cell distances/angles.

A rapid method for the determination of Arsenic in Soils by transportable EDXRF
by Leain Grimsley, British Geological Survey

Leain explained that XRF equipment has traditionally been large and expensive and not suitable for field work. However, with the advent of cooled detectors and small XRF tubes, XRF equipment is now breaking free of the laboratory.

Leain described her work in the sampling and analysis of soil in the Tavistock district of Devon. The PANalytical MiniPal 2 energy dispersive (ED) XRF instrument was used to measure As and Zn in soil. Results were compared with those obtained from a hand-held Niton XLT 700 ED XRF and a laboratory MAGIX Pro 4kW wavelength dispersive (WD) XRF instrument. The MiniPal showed good accuracy at the 0.1% level. Portable XRF's can analyse up to 40 samples per day whereas the 'hand-held' versions can analyse hundreds of samples per day (some of these come with GPS so that each analysis and its location can be accurately recorded).

The study of 'spintronic' (GaMnAs) materials
by Chris Staddon, Nottingham University

Spintronic materials are at the centre of new electronic semi-conductor devices. They are ferromagnetic semi-conductors which use the magnetic state of the electron to encode and transfer magnetic information. The materials are coating stacks consisting of alternating layers of low temperature and high temperature GaAs and GaMnAs. Chris said that for the devices to be useful the temperature needs to be over 300K. A Materials Research Diffractometer (MRD) is used to obtain reciprocal space maps and to obtain strain measurements. Chris said that strain has been seen to relax as the coating thickness goes above a critical limit. Annealing the coatings produces changes in the XRD pattern which has been attributed to the removal of interstitial Mn through thermal diffusion. Annealing improves the crystal quality.

Identification of steels and other metals from 'rubbings' on diamond coated papers
by Rob Foster, Exposure control section, H&S Laboratories

Rob described the XRF metal rubbing technique in which diamond coated paper is used to obtain specimens from metal surfaces. The technique is non-destructive, can be used on any size of item and does not require the metal item to be taken to the lab. Diamond coated 'lapping paper' discs, 30mm in diameter are used. Rob uses the PW1480 XRF instrument with a Mo/Sc X-ray tube. The 'finite element' option of the SuperQ IQ software is used to analyse data obtained from 15min measurements. For gun-metal rubbings, the 'K' lines from most of the metals are used, in the case of Pb the 'L' line. Blank substraction of trace impurities from the aluminium mask is then carried out before the 'finite thickness' measurement which requires input of the diameter of the sample and the weight of the film. Rob said that 0.003mg of Cr, Ni, Mn and Fe could be determined within 1% of certified values.

Application of Small Angle Scattering (SAXS) in the surfactants industry
by Richard Morris, Huntsman Surface Sciences

Sugar based structured surfactant system is a novel aqueous delivery system that comprises surfactant, carbohydrate and water. This system is formed by the interaction of surfactants with water-soluble carbohydrates acting as a "structurant" pushing the dissolved surfactant out of solution as liquid crystals. Sugar induced 'Lamellar' sheets are formed with a spacing in excess of 500 angstroms. Richard explained how SAXS is used to measure the bi-layer spacing, to 'tune' formulations and to determine thermal stability. Richard showed that a 15% sugar solution produced a 315-angstrom bi-layer whereas a 45% sugar solution was not thermally stable. These systems have an internal yield stress which is high enough to suspend solid particles and low enough to allow the system to flow as a normal liquid. Richard demonstrated this in the clearest possible way by passing around several exhibits. He said that we could make similar solutions by mixing washing up liquid (the cheap stuff), sugar and Listerine mouth wash - give it a go!).

Reducing XRF Running Costs
by Cyril Marchant, PANalytical Ltd.

Cyril explained that instrument breakdowns and performance problems fall mainly into three catogories: vacuum, water and software, with the majority of situations relating to the first two. He went on to describe some basic 'ground rules' to reduce running costs. Ensure that the gas bottles (e.g. He and Ar) don't run completely empty before they are replaced. Following this simple advice can reduce long-term stability problems, improve the quality of results and thus reduce down-time periods. Check gas bottles for leaks at regulators and unions (use soapy water and watch for bubbles). The X-ray tube is a very expensive item but if taken care of its lifetime can be extended. Ramp up the kV and mA when the tube is cold and don't switch it off from high power (ramp it down slowly). Use sleep and dose channels when the instrument is not being used and tube 'breeding' to run up slowly. The water supply needs to be set-up correctly and maintained. The correct water temp is vital since it cools the 'MPPC' and 'HT' tanks. If the temperature is too low then condensation on internal parts occurs. A circulating water system needs to be topped up periodically and external water filters need to be checked and replaced as required. Local operators should be trained in the techniques of sample preparation. Clean samples reduce vacuum faults around the loading area and dry samples prevent loss of vacuum and keep vacuum oil and pump in good condition. For liquid samples make sure the 'cup' or cell is in good condition and use once only – ruptured cells damage internal parts.

The coolest news of the year – new low temperature capabilities of the flexible X'Pert PRO
by Martijn Fransen, PANalytical Ltd.

Martijn began by saying that the non-ambient features of the X'Pert Pro instrument support products from Anton Paar, Huber, MRI and Oxford Cryosystems. Heating attachments include a Pt heating strip (1600 to 2300C) furnace heaters with sample rotation and radiation heaters. Cooling attachments include Peltier cooling and the Oxford Phenix Cryostat (no need for a continuous He supply). Martijn went on to address some issues concerning non-ambient chambers. 1) *How to deal with temp induced sample height variation?* Sample height should be measured before heating and corrected 'on the fly' or afterwards. Parallel beam optics are better than focussing optics since sample height can move over a mm without a change of d-spacing.

2) *What is the real sample temperature?* A d-spacing can be measured as a function of temperature and compared with literature values or a temperature calibration point defined where a known phase transition takes place.

Comparison of Limits of Detection for various XRF's in various matrices
by Philip Russell, PANalytical Ltd.

Philip described an investigation he had carried out concerning the detection limits for specific XRF systems. The instruments are of two main types: Wavelength Dispersive (WD) XRF and Energy Dispersive (ED) XRF. The 'power' of the systems also vary: lab instruments with high and low power, bench-tops and field portable instruments.

WDXRF instruments (broadband excitation and selective detection) provide the best detection limits, generally for light elements especially those lighter than zinc. Detection limits for 'sequential systems' (those that scan elements one at a time) are a function of the total number of elements detected.

EDXRF instruments (selective excitation and broadband detection) have best limit of detection for elements with atomic number >40 (Nb and higher). Practical limit is a function of the complexity of the system – e.g. presence/absence of major elements in the vicinity of the elements of interest.

Theoretical detection limits are [3x[√Background counts]x constant]/Element counts for a given measurement time whereas practical limits are usually 3x this.

For a simple sample the limits of detection can be determined from the slope and intercept of a calibration graph or the spread of intensity values at zero concentration. This method gives a good feel for detection limits. The 'Total Method' is more rigorous and is used for legislative purposes. LOD's for high power (2-4kW) WDXRF (100sec measurements) systems (Axios) are typically below 1ppm, for low power (200W) systems (Venus) below 10ppm and for low power EDXRF systems(MiniPal benchtop spectrometer) 10-100ppm for transition metals. EDXRF(polarised) systems are good for low atomic number elements such as geological samples and organics.

XRD analysis of the hydration states of cement products
by Mark Russell, Queens University

Mark described his work on Portland cements. He uses an Anton Paar Humidity chamber to control the temperature and moisture environment of his cement samples. An X'Celerator X-ray detector is used to typically obtain 150scan at 10mins per scan.The hydration characteristics of new and blended cements are determined which are then used to predict reactions and design new mixes.

Analysis of High Z trace elements in Geo-environmental samples using polarised EDXRF
by Heather Harrison, British Geological Survey

Heather described the use of the Epsilon 5 polarised EDXRF for the measurement of soil samples in the Merseyside and North Wales areas. The principle of EDXRF is that a primary beam excits a polarising target. Target fluorescence then excites the sample. ED(P)XRF produces high energy 'K' lines with fewer overlaps and interference from majors compared with WDXRF. 'L' lines are very weak so poor LLD's. The high excitation voltage gives good results for high Z elements. 300 samples per week are measured and have produced a geographical map containing 35,000 samples!

Axios: The Introduction to the new XRF Spectrometer
by Reg Nichols, PANalytical

Reg explained that the Axios systems have been configured to meet the needs of specific industries both in hardware and software. For example, the Axios-Cement protects itself from dusty environments and dusty samples, reducing wear on critical components. Reg announced the UK launch of the Axios-Advanced spectrometer, an instrument equipped for ultimate precision and demanding light element applications. He said it delivers unmatched performance incorporating numerous cutting-edge technologies such as the SST-Max tube.

Axios: The detail
By Phil Russell, PANalytical

Phil gave specific details about the Axios-Advanced spectrometer. It contains a Rh-anode SST-Max tube which guarantees excellent tube stability all the way up to 160mA improving analytical performance in the light element range. Power settings are 2.4, 3.0 and 4.0keV and it has up to 8 crystals and has duplex detection (3 million counts/sec). There is an integrated sample changer and a choice of loading mechanics which can be used to analyse up to 168 samples at a time. Sample loading can be continuous or direct. It can measure and analyse a variety of samples including solid pieces, pressed and loose powders, fused beads, liquids, foils, granules and thin films. There is also He flushing and a dust collection device. The software includes SuperQ 4, IQ+, Pro-trace, EP-multi, EDS and SPC. The new version of SuperQ4 incorporates an improved user interface for sample handling, multiple languages, refinements in trace analysis and compatibility with FDA reporting. With a minimum of training, most day-to-day operation is a push-button exercise.

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