



## Australian X-ray Analytical Association (AXAA)

### AXAA E-Newsletter

Issue 2006/04 September 2006

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#### **CALL FOR TECHNICAL/TUTORIAL NOTES:**

**This edition of the newsletter presents very useful XRF tutorial notes from Ulrich Senff and Ken Turner. Our set of downloadable technical notes, which is available at the AXAA website, continues to grow. Thanks Ulrich and Ken.**

**We invite XRD and XRF practitioners to submit more of these ‘best-practice’ notes, e.g. on matrix corrections in XRF; standards for XRD phase analysis; and quality assurance procedures in x-ray analysis. These are not intended to be original research publications. Articles on other subjects such as methodology, XRF matrix correction in pressed powder samples, etc, would be welcome.**

**We require approximately 1 page of text (tables can be included, but not figures or photographs). We can accept several pages if needed. The web based tutorial version of the article may contain pictures, graphs and illustrations.**

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#### ADVERTISING SECTION

*Australian X-ray Tubes Pty Ltd: X-Ray Solutions for Science and Industry*

*PANalytical: Axios-Minerals Sequential WDXRF Spectrometer*

## 1. MESSAGE FROM THE AXAA PRESIDENT ON THE NAME OF THE ORGANISATION

The July 2008 Newsletter carried a very thoughtful article by Nick Pearson of the WA Branch on the potential opportunities for AXAA from today's extraordinary advances in x-ray related characterisation. Nick spoke of the possibility of changing the name of the organisation as well as expanding its charter. I sense that Nick's sentiments are supported by significant numbers of the membership - particularly our younger AXAA people, and therefore that the issue should be debated by the National Council when it meets in February. I would greatly value any feedback on these matters.

For you information I am reproducing Nicks letter here:

### Is AXAA still the best name for our Association?

Over the years a significant number of x-ray scientists have become increasingly involved in analyses other than laboratory based XRD and XRF - historically the core activities for AXAA members. These 'new' analyses employ specialised techniques that may utilise x-rays generated by advanced sources, or radiations other than x-rays.

I would like to propose that the AXAA National Council and members consider whether the name AXAA should be changed to reflect the broader analytical techniques that our members are working with. Considerations in selecting an alternative name include:

- Maintaining representation for laboratory based XRD and XRF.
- Reflecting the advanced radiation sources and techniques being used (synchrotron x-rays; other parts of the synchrotron spectrum; neutrons and other 'particle' radiations).
- Extension beyond diffraction to scattering techniques more generally (including SAXS and SANS).
- Surface analysis techniques (e.g. XPS).
- Catchy acronym, but avoiding a name that is long and cumbersome when written out in full.

There are various ways such an association could be administered. For example there might be one "umbrella" Association, but allowing members to select areas of interest administered by sub-committees. This would allow members to stay informed regarding techniques, facilities, and developments in areas related to, or complementary to, their primary field of interest.

Such an organisation would benefit not only from increased membership, but from the diversity of members and interaction between disciplines.

Nick Pearson

Brian O'Connor  
AXAA President

## 2. AXAA SEMINARS FOR THE REMAINDER OF THE YEAR

### 3.1 AXAA NSW Branch Christmas Technical Meeting

Date: Tuesday 12<sup>th</sup> December, 2006

Venue: Macquarie University - Building E7A, Room 829. (Go to Building E7A, 8th floor, turn right out of the lift, end room on the right).

A map of Macquarie University may be downloaded from  
[http://www.ofm.mq.edu.au/images/map\\_large.jpg](http://www.ofm.mq.edu.au/images/map_large.jpg)

Parking: Macquarie University - \$6-\$8 (4 minute walk from venue).  
Macquarie Centre – free (7 minute walk from venue).

Program: (Coffee from 10am)

10:30am. Erika Heiden (Macquarie University): “X-ray analysis of metals in water: are thin film evaporites superior to ion exchange?”

11:00am Catherine Kealley (ANSTO): “Small-angle scattering from proteins in the ‘dry state’”

11:30am Damian Gore (Macquarie University): “Preparation and analysis of electrical equipment for RoHS/WEEE assessment”

12:00 AXAA NSW General Meeting – Chairman’s report, AXAA National update, election of NSW Branch committee.

12:30pm Lunch (provided by NSW Branch)

1:30pm Tour of Macquarie University facilities.

RSVP: RSVP (for catering purposes) to Ned Blagojevic (phone 02 9717 3660, e-mail [nbx@ansto.gov.au](mailto:nbx@ansto.gov.au)) by 1<sup>st</sup> December, 2006.

### 3.2 AXAA Victorian Student Seminar Day

Date:	Wednesday, 22 November 2006
Time:	To be advised – see Further Information below
Venue:	RMIT Chemistry – see Further Information below
Parking:	See Further Information below
Program:	To be advised

Further Information: Contact Jorg Metz, Victorian Branch Chair – see Item 6.

## 4. PROGRAM FOR AXAA-2008

Newsletter 2006/03 (July 2006) provided a detailed account of organisation and program planning for the next AXAA National Conference (AXAA-2008) will be held at the Grand Hyatt Hotel in Melbourne from 4 – 8 February 2008.

Substantial progress is being made in developing the program, and a report on progress will be provided in the next edition of the newsletter.

Key planning horizons are:

First brochure	Late October 2006
Program Committee Exec meets to finalise program and to issue formal speaker invitations	Mid-January 2006
Registration brochure	June 2007
Abstract submission	September 2007

Tulips Meetings Management (Principal: Jane Yeaman) is serving as the conference secretariat. Jane’s extensive responsibilities include convening the Exhibits Committee. Each prospective exhibiting company will be invited to nominate a representative for this committee.

Prospective sponsors are being contacted by Jane.

See item 6 for Jane’s contacts

## 5. EVENT REPORTS

### 5.1 AXAA 2006 NSW Student Seminar Day: 19 Sep 2006

#### *Overview*

The AXAA NSW branch held its 2006 Student Seminar Day entitled “A Smattering of Scattering and Diffraction” on the 19<sup>th</sup> September 2006. The event, hosted this year by the School of Chemistry at The University of Sydney, aimed to showcase the impressive scientific research that is being undertaken by young researchers in NSW. This years programme featured both single crystal and powder X-ray and neutron diffraction applied to complex solid state systems including perovskites, clathrates, and nanoporous spin crossover materials.

#### *Participation and Speakers*

5 undergraduate and 3 graduate students were selected from a strong field of applicants. Undergraduate presenters included Benjamin Beccari, Ivanka Barisic, Murad Tayebjee, Scott McKenzie, and Karina Aivazian. Graduate presenters included Natasha Sciortino, Paul Saines, and Neeraj Sharma. A varied audience of over 40 was in attendance.

#### *Organisation and Promotion*

AXAA NSW branch members Vanessa Peterson and Catherine Kealley were the seminar organisers, who extend a special thankyou to this years judges for their time and expertise, Margaret Elcombe, Alison Edwards, Gordon Thorogood, and Ned Blagojevic.

#### *The Winners*

Congratulations to this years winners, Scott McKenzie in the Undergraduate category for his presentation “Cation Substitution Within Aurivillius Phases” and Paul Saines in the Graduate category for his presentation “Valency Transitions and Oxygen Vacancy Ordering in  $Ba_2LnSn_xSb_{1-x}O_6$ ”. This year’s winners received a cash prize in addition to the AXAA newsletter subscription and membership offered to all of this year’s presenters. Post seminar pizza and refreshments were enjoyed by all.

Hope to see everyone back for more next year,

Vanessa Peterson  
Catherine Kealley

### 5.2 AXAA (WA) and WA Society for Microscopy [WASM] Annual Conference, Margaret River, WA. 22–24 Sep 2006

This successful annual event was the 10<sup>th</sup> joint conference of the AXAA (WA Branch) and the WA Society for Electron Microscopy, and, in effect, the 20<sup>th</sup> annual conference for the AXAA (WA Branch). It was held in the delightful town of Margaret River and close to the picturesque vineyards of the region. Sadly, the big technical programme provided only limited opportunities for wine-tasting, but that was set right during two delightful evenings. The event is becoming to some extent a national meeting given that we had about 25% of the registrants from other States including the entire National Council of AXAA.

The quality of the meeting was first rate, there being 55 registrants and 34 technical papers of which 11 were by student presenters.

There were 2 superb talks by our plenary speakers:

Joanne Etteridge, Monash University. *Measuring structure factor phases and amplitudes with 3 beams and a ruler.*

Evan Gray, Griffith University. *In-situ real time synchrotron XRD study of the phase transformation in  $LaNi_5-H_2$ .*

The student talks were all quite excellent which made the selection of best-paper awards challenging. Notwithstanding, the 2 recipients richly deserved their success:

Nigel Chen-Tan, Curtin University. *Studies of local fly-ash for geopolymer production.*  
 Nathan Webster, University of WA. *Structural investigations of highly conductive bismuth oxide based solid electrolytes using x-ray, electron and neutron diffraction*

Our thanks go especially to Rob Hart who almost entirely carried the AXAA part of meeting organisation. The meeting has marked the end of Rob's monumental contribution to the WA Branch. He moves to Melbourne soon, and we hope will continue from there as National Treasurer.

The success of the meeting was enormously enhanced by the support of sponsors and by their presence and also contribution of papers. Our sponsors were:

Platinum Level: nanotechnology Systems, PANalytical, Australian Microscopy and Microanalytical Society, JEOL, Thomson Scientific

Gold Level: Cockburn Cement, ThermoElectron, XRF Scientific

Brian O'Connor

## 6. CALENDAR OF EVENTS

Dates	Event	Location	Further information
25-27 Oct 2006	ICDD Specimen Preparation for XRF Workshop	ICDD headquarters, PA, USA.	<a href="http://www.icdd.com">www.icdd.com</a>
20-23 Nov 2006	Asian Crystallographic Association (AsCA) Conference (AsCA'06)	Tsukuba, Japan	<a href="http://www.realize-at.jp/AsCA2006/AsCA2006-CrSJ.htm">http://www.realize-at.jp/AsCA2006/AsCA2006-CrSJ.htm</a>
29 Nov – 1 Dec 2006	Joint Workshop, Australian Synchrotron and Australian Synchrotron Research Program	Melbourne	<a href="http://www.synchrotron.vic.gov.au/content.asp?Document_ID=4675">http://www.synchrotron.vic.gov.au/content.asp?Document_ID=4675</a>
11-13 Dec 2006	5 <sup>th</sup> Annual AINSE/ANBUG Neutron Scattering Symposium	Lucas Heights (Sydney)	<a href="http://www.ainse.edu.au/conferences/AANSS_registration_abstract.doc">http://www.ainse.edu.au/conferences/AANSS_registration_abstract.doc</a>
12 Dec 2006	AXAA NSW Branch Christmas Technical Meeting	Macquarie University, Sydney	<a href="http://www.axaa.org">http://www.axaa.org</a>
4-8 Feb 2008	AXAA National Schools and Conference (AXAA-2008)	Grand Hyatt Hotel, Melbourne	<a href="http://www.axaa.org">http://www.axaa.org</a>

## 7. AXAA WEBSITE AND CONTACTS

**WEBSITE** <http://www.axaa.org>

**NATIONAL COUNCIL PRESIDENT**

**Brian O'Connor**, Curtin University of Technology, Department of Applied Physics, GPO Box U1987 Perth WA 6845.

Telephone: (08) 9266 7843 and (08) 9291 7067. Facsimile: (08) 9291 7064

e-mail: [B.O'Connor@curtin.edu.au](mailto:B.O'Connor@curtin.edu.au)

**NATIONAL COUNCIL SECRETARY**

**Ned Blagojevic**, ANSTO, PMB 1, Menai NSW 2234

Telephone: (02) 9717 3660. Facsimile: (02) 9717 9286

e-mail: [ned.blagojevic@ansto.gov.au](mailto:ned.blagojevic@ansto.gov.au)

**NATIONAL COUNCIL TREASURER**

**Rob Hart**, Curtin University of Technology, Department of Applied Physics, GPO Box U1987, Perth, WA 6845.

Telephone: (08) 9266 3708. Facsimile: (02) 9266 2377

e-mail: [r.d.hart@exchange.curtin.edu.au](mailto:r.d.hart@exchange.curtin.edu.au)

**AXAA-2008 CONFERENCE SECRETARIAT**

**Jane Yeaman**, Tulips Meetings Management, PO Box 116, Salamander Bay, NSW 2317.

Telephone: (02) 4984 2554. Facsimile: (02) 4984 2755

e-mail: [jane@pco.com.au](mailto:jane@pco.com.au)

**WA BRANCH CHAIR**

**Rob Hart (Interim)**, Curtin University of Technology, Department of Applied Physics, GPO Box U1987, Perth WA 6845.

Telephone: (08) 9266 3708. Facsimile: (02) 9266 2377

e-mail: [r.d.hart@exchange.curtin.edu.au](mailto:r.d.hart@exchange.curtin.edu.au)

**NSW BRANCH CHAIR**

**Ken Turner (Interim)**, Ken Turner Consulting, "Elkin Ridge", Bicton Lane, Cumnock, NSW 2867

Telephone: (02) 6367-7167. Facsimile: (02) 6367-7168

e-mail: [ken.elaine@bigpond.com](mailto:ken.elaine@bigpond.com)

**VICTORIAN BRANCH CHAIR**

**Jorg Metz**, XRF Scientific Ltd, 24/200 Canterbury Road, Bayswater VIC 3153

Telephone: (03) 9720 6339. Facsimile: (03) 9720 6412

e-mail: [jorg@xrfscientific.com](mailto:jorg@xrfscientific.com)

**E-NEWSLETTER EDITOR**

**Tony Raftery**, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001

Telephone: (07) 3864 2271. Facsimile: (07) 3844 8343

e-mail: [a.raftery@qut.edu.au](mailto:a.raftery@qut.edu.au)

## **8. SUBSEQUENT ISSUES OF THE NEWSLETTER AND ADVERTISING**

NEXT ISSUE (2006/5) - TO BE PUBLISHED (LATE) NOVEMBER

Final date for submission of material: 31 October 2006

Material other than company news and advertising to be submitted to the Editor, Tony Raftery: see item 7 for contacts.

Company news and advertising to be submitted to Brian O'Connor: see item 7 for contacts.

Specifications for company news items:

Items to be non-sales focussed, eg staff appointments, product releases. There is no charge for companies which have exhibited at recent AXAA meetings and/or have sponsored recent AXAA events. Limit of 25 lines of 12-point text per company.

Specifications for advertisements

Text only

40 kB limit

Charge per advertisement = \$100/10kB plus GST, based on 1 page per 10 kB.

ISSUES SCHEDULED FOR 2007: FEBRUARY, MAY, JULY, SEPTEMBER,  
NOVEMBER

## X-RAY ANALYSIS TECHNICAL NOTES SECTION

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### **Calibration of Wavelength Dispersive X-Ray Fluorescence Spectrometers: Part 1 – a Few Things to Consider**

Ulrich Senff, Australian X-Ray Tubes, PO Box 249 Terrey Hills, NSW 2084, Australia  
[Ulrich@AXT.com.au](mailto:Ulrich@AXT.com.au)

#### Introduction

This article gives an overview of factors that need to be considered when calibrating a Wavelength Dispersive X-Ray Fluorescence (WDXRF) spectrometer. Areas of the calibration procedure requiring attention that are introduced here will be later treated in more detail. A wider range of contributions from people with different experiences in XRF can only serve to increase the overall knowledge base. Requests for information by XRF analysts who require some input into a particular area could influence the order in which topics are addressed, so that all contributors obtain the best yield from their input.

The general aim of calibrating an XRF spectrometer is to convert measured intensity values of the characteristic x-rays emitted from the components of an irradiated sample into the concentration values of the sample components. These concentrations need to have well defined precision and accuracy values associated with their determination to be of any use to the customer who requires the analytical data.

In order to achieve this objective, the calibrator needs to have a good understanding of what the likely error sources are in their analytical method, how to determine them and the extent to which they contribute to the total analytical error; how the error sources can be controlled and then how to construct a well-defined calibration that satisfies the analytical requirements.

Well-defined calibration does not necessarily mean the best possible calibration with the lowest analytical error bars, but it means having the capability of stating the uncertainty of your results to the limits required by your customer.

When calibrating, people frequently take their best guess at what the required sample preparation is that will ultimately lead to a calibration with minimal error bars i.e. lead to a graph of intensity versus concentration where the points lie very close to the line of best fit.

How good this guess is for a particular material type depends on experience. If the preparation method does not result in a calibration of the required precision, then the whole time-consuming procedure will need to be repeated once the error sources have been identified and minimized. Thus it is worthwhile familiarizing yourself with what the requirements of a sample suitable for XRF analysis are, where typical sources of divergence from such a sample lie and what to do about this. Doing so will increase the probability that your initial guess in preparing a suitable sample will be correct. In addition to this, tests can be carried out on some typical samples to be analysed to see how reproducibly they can be prepared.

### Typical Error Sources in XRF

The ideal XRF calibration assumes your samples are homogeneous, perfectly flat and critically thick (unless you are dealing with thin films). Any deviation from these parameters will lead to errors in a calibration. The extent of these errors will depend on:

- the concentration ranges and material types that are to be covered in the one calibration,
- sampling errors,
- the sample preparation method,
- sample measurement errors,
- errors in the concentration values and
- homogeneity of standards used for calibration
- errors in the mathematical procedures used in converting intensity values into concentration values.

Error sources in XRF analysis include:-

- the sampling error in providing the analyst with a representative sample of the material whose composition needs to be defined (e.g. a shipload of iron ore)
- the sub-sampling error when taking a portion of the provided laboratory sample for analysis (e.g. taking a fraction of iron ore powder from a container to use for making a fused glass disc for analysis)
- sample and flux weighing errors due to the weighing balance, its environment or how the weighing procedure is carried out
- contaminants present in the sample or flux from their preparation
- moisture absorption by the sample from the initial sample taking stage, to the presented laboratory sample and during the weighing of this or a dried sample for fusion; variations in the moisture content of the flux prior to preparing calibration standards or unknowns
- errors in preparing a fused glass disc e.g. incomplete sample dissolution, crystallization of the disc to various extents, air bubbles on the analytical surface, absorption of analyte radiation by the addition of too much releasing agent, line overlaps due to a component of the releasing agent, variations in disc curvature, contamination of the analytical surface with fingers or other foreign material, critical thickness problems for the selected analyte lines
- errors in reproducibly preparing a metal surface e.g. due to smearing effects, where a soft sample component is preferentially distributed over the surface to be analysed, thereby leading to false high intensity values compared to a homogeneous sample, oxidation of the sample surface before analysis, variations in grinding or finishing marks, contamination from the surface preparing material, the effects of micro and macro sample segregation, the sensitivity of the chosen analyte line to some of the factors above, preferential abrasion of softer components from the sample surface
- errors in pressed powder samples due to variations in particle size, mineralogy, contaminants introduced by crushing, milling and by the binding agent, surface effects due to the binding agent when pressing a powder to form a compact pellet, segregation of sample components soluble in a liquid binder which rise to the analyte surface on drying,
- sample measurement errors emanating from the spectrometer used for measurement. These variables are addressed in **Australian Standard 2563-**

**1996** and should be checked at the recommended frequency. Error sources addressed by the standard include correctly accounting for detector counting losses due to detector dead-time, correctly setting the pulse height settings, checking the resolution and position of the pulse height distribution (PHD), measuring an analyte line at the peak position and checking for the reproducibility in setting any moveable spectrometer part. If the standard is followed at the suggested testing frequency, errors due to the instrument will be well known and any error source within the instrument will be found using the systematic checking procedure. It is also useful to determine how long a tube will take to stabilize when powered up from minimum power and how long it takes an instrument to stabilize when powering up from being switched off to pass a certain level of precision e.g. 0.1% by accumulating 1 million counts for each measurement in a series of measurements. Regular servicing of your instrument is recommended. Instrument suppliers usually have their own criteria for determining if your instrument is working to specifications. The advantage of using the Australian Standard to check your instrument is that it is designed to check your instrument at the level of precision required by your particular analytical requirements and that if your laboratory has either NATA or ISO Standard certification, these organizations prefer that Standard Methods are used to ensure the integrity of your process where available.

#### Choice of Instrumental Measuring Conditions

Armed with a knowledge of what your sampling and sample requirements are for the planned calibration and having checked your instrument according to AS2563-1996 to ensure that the pulse height distribution for each line is centered correctly and the energy window is set correctly, the instrument is working to the required level of precision when setting any movable part (such as crystals, angles, masks, filters collimators detectors etc.), plus keeping a copy of all test results for later comparisons, it is time to select your instrumental measuring conditions.

##### *1. The X-Ray Tube*

The choice of X-ray tube target material these days, where the major manufacturers produce end-window XRF spectrometers, is mainly rhodium. A rhodium tube produces K lines for the excitation of the more energetic X-ray lines of heavier elements, has a relatively intense continuum, since the target is a fairly heavy element, for the excitation of energetic lines and produces L lines for the excitation of light elements. As such, Rh tubes are considered a reasonable all purpose tube for the excitation of both heavy and light elements. Since end window tubes cannot be powered to more than 60kV normally (or 75kV in some cases) they are not as effective in exciting the K lines of heavy elements as compared to side window tubes, which can be powered to 100 kV. However, they are the best choice available for the excitation of both heavy and light elements at present.

If you are only interested in the analysis of light elements then a tube with a light element target can be provided by most manufacturers. If you mainly require the determination of trace heavy elements, you could purchase a tube with a heavy element target such as W or Au, for example. Since the tube can only be powered to 60kV or so, the target material cannot perform to its optimum capabilities but it could outperform the Rh tube for certain groups of elements. If this still does not lead to satisfactory detection limits, energy dispersive XRF spectrometers or other

instrumental techniques need to be evaluated. Manufacturers can usually give you a table of detection limits for a range of elements in some common matrices.

## *2. Analyte Lines and Their Measuring Conditions*

If you settle for the standard configuration of a WDXRF spectrometer then the remaining parameters of the spectrometer need to be evaluated and set-up to best suit your analytical needs.

In doing this, the first step is to decide which characteristic X-ray lines to use for analysis and which instrumental parameters to use with this choice.

The  $K\alpha$  lines of an atom are the most intense and energetic and would be the first choice for analysis. Intense means high count rate, which leads to minimal counting times and lowest detection limits and most energetic leads to minimal influence by physical characteristics of the sample surface.

In cases where conditions for the optimal excitation of a particular line, e.g. the  $K\alpha$  line of a heavy element, cannot be met by a spectrometer due to restrictions on the kV the X-ray tube can be powered to, using the  $L\alpha$  line would be the next best choice for obtaining the highest count rate. Various other lines are also available, depending on your needs.

The optimum kV for exciting a particular line is about 4 times the energy of the associated absorption edge (the energy required to eject the K shell electron which will result in the production of  $K\alpha$  radiation, for example). This can be used as a guide for selecting the kV for a line.

The software of modern spectrometers usually suggests which lines and instrumental conditions to use. The suggested conditions are the ones the manufacturer has determined as optimal for their product, taking into consideration variables such as the maximum kV the tube can be operated at, the choice of collimator dictated by the required resolution for a particular line when considering the usual line overlaps, the power settings which will lead to the maximum intensity of a line, the required mask size which will ensure radiation from your sample cup will not pass through your collimator onto the detector and contaminate your readings (having chosen a sample cup with a particular opening size), which crystals and detectors are most suitable in giving the required resolution and maximum intensity for your line, the pulse height settings for the energy (PHD) peak which will best exclude line overlap, crystal fluorescence, double energy peaks and electronic noise from your measurement and the detector dead-time limits to which intensity values need to adhere to.

The one set of instrumental parameters are not always optimal for all analytical situations, since the XRF technique is capable of analyzing from sub-ppm concentration levels to 100%. Thus it is possible that the suggested settings of the manufacturer's software will need to be altered to produce the best combination of instrumental settings for your particular analytical needs.

Equations for *Figures of Merit* (FoM) for the best set of instrumental variables, including tube power, tube filter, collimator, crystal and detector that will result in either the lowest analytical error or best detection limits are available in the usual XRF textbooks. These conditions can also be used when comparing spectrometers from different manufacturers, faced with a decision on which one to purchase and requiring some justification for the choice by management.

For major and minor elements the FoM is based on minimizing the relative percentage error of your analytical result. Relative percentage error means, for example, if you require a sample component usually present at the 2.0% level to be determined to the precision of  $\pm 0.05\%$ , then this relative % error is  $100 \times 0.05 / 2.0 = 2.5\%$ . The absolute error for this measurement is 0.05%.

The relative % error of a measurement can be expressed as:-

$$e\% = (100/\sqrt{T})/[1/(\sqrt{R_p}) - \sqrt{R_b}] \quad \dots (1)$$

where  $e\%$  = relative percentage error,  $T$  = total (peak + background) measuring time (sec),  $R_p$  = peak measured count rate,  $R_b$  = background measured count rate

For the relative percentage error in a measurement at any fixed time to be a minimum, the square root of the peak intensity minus the square root of the background intensity needs to be a maximum, i.e. the highest value you obtain for this subtraction when comparing settings will show your optimal choice.

The above equation can also be rearranged to calculate the required measuring time to achieve a certain level of precision in a concentration value. This total measuring time can then be split between time spent on counting the peak and the background using:

$$T_p/T_b = \sqrt{R_p/R_b}$$

where  $T_p$  and  $R_p$  are peak counting times and count rate and  $T_b$  and  $R_b$  are the corresponding background values.

For trace analysis, the lower limit of detection is expressed as:-

$$LLD = (3/S) \times \sqrt{R_b/T_b} \% \quad \dots (2)$$

where  $S$  = the sensitivity in terms of counts per second per percent,  $R_b$  is the background count rate and  $T_b$  is the time spent counting on the background, which is half the total counting time for trace analyses

From this, the FoM for obtaining the minimum detection limit at a fixed counting time is achieved when  $S/\sqrt{R_b}$  is a maximum.

Another consideration in choosing analytical conditions is the cost of replacing an XRF tube. These items can be very expensive, so frequently a compromise needs to be made when striving for maximal tube life and sample throughput based on minimal % error or lowest detection limits

The use of high mA increases the rate of filament evaporation. This leads to premature filament failure and a reduction in the intensity of some type of tubes by coating the inside of the Be window with tungsten. Using a lower power setting will increase your tube life and (unfortunately) your analysis time.

### Setting-Up the Instrument

Having made the decision as to which instrumental variables are most suitable for your analytical situation, it is time to optimize these settings for your calibration.

#### *1. Wavelength Peak Positions and Pulse Height Energy Windows*

The initial step is to carry out wavelength scans for each of your analyte lines using some typical sample types you intend to analyse with your calibration. You should already have carried out wavelength scans to ensure each analyte was measured at the peak position and the pulse height energy window as checked and set to avoid the normal interferences when optimizing the spectrometer parameters for each line. At this stage you want to ensure your settings are optimal for your specific calibration.

By specific I don't mean that your calibration needs to be for only a particular material type with narrow concentration ranges. Most things work for a situation like that without too much effort. I frequently made wide concentration range calibrations for fused beads. Depending on the material types that could be successfully fused with a particular fusion recipe and the sample components, those calibrations needed to take care of a number of wavelength and energy overlaps and it is those specifics we are trying to find and take care of in our particular calibration.

Measurements of a line need to be made at its peak position so that counts obtained from the measurement can be reproduced with high precision. Carrying out these wavelength scans with a typical sample will clearly show which elements will interfere with the determination of a particular line.

If the peak of a proposed analyte line suffers from too much interference via a line overlap, then it is best to find the peak position of this line with a different sample that does not contain the interference, since the incorrect peak position could be found due to this interfering line. For light elements it is also important to use a sample with a similar matrix to find a peak e.g. metallic Mg will give a different peak position for the Mg-K $\alpha$  line than MgO powder, due to the different energy levels of outer shell electrons involved in bonding. Thus, if trying to peak an angle for a calibration using fused beads, use a bead containing the element under consideration with the addition of a good glass-making compound such as SiO<sub>2</sub> and flux to produce your bead.

The next step is to check the pulse height distribution. When examining the energy peak, a decision needs to be made as to the lower and upper energy limits to set for the energy window. The usual decision is where to set the lower level so that it avoids an electronic noise peak and whether to include the escape peak or not. Normally you try to include the escape peak to obtain maximum intensity for your analyte line. The escape peak has an energy value which is a difference between the energy of the analyte line and the energy of the Ar-K $\alpha$  energy. When this energy difference is small and the escape peak is close to the main peak, the escape peak must be included in your settings. When the energy difference becomes large and the escape peak clearly separated from the main peak and perhaps combining with the electronic noise, it should be excluded. Whatever the situation, don't set an energy lower level which dissects the escape peak. This will lead to instability in your measurements.

At the higher energy end of the plot (towards the right) you will see double peaks come in at high count rates. These are peaks where two photons from the analyte hit the detector at virtually the same time and register as a pulse of double the energy. These pulses should be excluded, as should any peaks which arise from higher order energy interferences from another sample components or crystal fluorescence.

Apart from minimizing interferences, another reason for finding the optimal energy window settings is that your dead-time correction is based on the window setting. For this correction to be most effective, the dead time needs to be determined under the usual settings used.

## *2. Background Determination*

When the wavelength peak has been determined and the pulse height energy window set, it is recommended to re-determine the wavelength peak position if a significant interference has been removed. During this, or the initial wavelength scan, positions can be determined for background measurements.

Background measurements are required when analyzing for trace or minor components, or for all components when constructing a wide concentration range calibration for all sample components.

The idea of measuring backgrounds is to determine what the background level is at the peak position. If this is known then the background can be subtracted from the peak to obtain the correct intensity level due to your analyte line.

Taking a background reading on one or both sides of your peak and interpolating these readings for the peak position are only an approximation to the correct result. Modern software allows the user to select a number of background positions from the wavelength plot so these points will provide a contour of the background which will be better described by a polynomial expression. Such an expression should then lead to a better approximation of the background under the peak, at the expense of additional measurements.

In cases where impurities from the x-ray tube contribute to the background of an element, measuring a number of off peak positions will not help. A background intensity level needs to be found for the contaminant from a blank sample. The intensity obtained from the scattered tube radiation off the sample will depend the sample matrix. If you use a light matrix, the intensity reading will be higher than if you use a heavier matrix. Thus either the blank sample needs to be matrix matched with the calibration samples and intended unknowns, or this intensity needs to be matrix corrected. The manufacturers software needs to take care of this situation or unnecessary errors will occur in determining the concentration levels of trace sample components.

END OF ARTICLE

## **XRF Laboratory Tips I. Sample Preparation**

Ken Turner, Ken Turner Consulting. E-Mail: [ken.elaine@bigpond.com](mailto:ken.elaine@bigpond.com)

### Overview

Many laboratories spend a considerable amount of time and money setting up a XRF laboratory but sometimes fail to realise the full benefits. This is often due to poor sample preparation maintenance practices. Sample preparation equipment tends to be purchased, put into service and then forgotten about. Somehow it is expected to run forever. It is often not until a mill stops running, fused beads shatter repeatedly or the QC samples go out of control that action is taken. I cannot emphasise too strongly that the results obtained from an XRF spectrometer are only as good as the sample presented to it. In this article I would like to look at a number steps in the sample preparation process and suggest some simple maintenance actions that will greatly assist the quality of results.

### Primary Sample Crushing and Splitting

The greatest potential threat to analysis quality at this stage of the operation is sample contamination. This is especially so in automated grinding systems. A strict protocol needs to be in place to ensure that mills and sample dividers are cleaned between samples. For automated systems a maintenance regime that includes ensuring that drains are not blocked, cleaning reservoirs are full and that the cleaning cycle operates correctly are required. Mills and grinding elements should be replaced or refurbished if they become badly pitted (i.e. can retain traces of the previous sample).

### XRF Pressed Powder Pellets

To obtain good XRF results using the pressed powder technique, control of particle size is absolutely critical. Particle size can be controlled by closely controlling grinding time and the mass of sample introduced to the mill. Initially grinding times are determined by experimentally constructing grinding curves. These are plots of XRF intensity versus grinding time. XRF intensity initially rises sharply with grinding time and then tends to plateau. The chosen grinding time should be in the "plateau" region. Grinding time should be set by means of a timer connected to the mill power supply. Control of mass can often be achieved by using scoops of a suitable volume.

In production or when rapid analysis results are needed there is often a temptation to shorten the grinding time. Operators need to be given an understanding of why grinding times must not be altered.

A similar set of operational and maintenance protocols are required as for Primary Crushing to minimise the risk of sample contamination.

### XRF Fusions

XRF bead quality is critical for good XRF results and yet many operators will tolerate poor quality (chipped, scratched, not flat) or cracked beads. Factors that effect bead quality include:

- Fusion temperature
- Mould temperature
- Quality of the platinum ware surface
- Mixing during fusion
- Cooling rate
- Sample flux ratio

- Flux composition
- Sample composition
- Use of a release agent

Assuming that we are dealing with an established fusion method (i.e. sample and flux type and ratio have already been established) then it is essential that the first five items above are maintained. Fusion equipment, especially furnace types, are often treated as “set and forget”. This is a dangerous practice. A regular checking and maintenance program is needed.

- Fusion and mould temperatures can be checked with a thermocouple, optical pyrometer (especially useful with gas fusion equipment) or observing the melting points of specific compounds.
- The mixing action of automated systems should be regularly checked for correct operation.
- Refractory furnace linings should be checked to ensure that they are not spalling. Potentially particles of lining could contaminate the fusion sample.
- Gas burners should be visually inspected to ensure that jets are not blocked.
- On gas systems, gas pressures and flow rates should be maintained within the correct operating range.
- Where forced air cooling of the beads after fusion is used, flow rates must be maintained within the correct operating range.
- Platinum ware, especially moulds, should be in good condition. Crucibles and moulds should be free from pits and scratches, moulds should be flat and should have a high polish. Moulds should be re-polished regularly and crucibles keep in good shape. Moulds that are in poor condition will invariably cause XRF beads to stick to the mould and/or crack. Commercial crucible reshaping tools and polishing equipment is available.

Adherence to the above practices will help ensure that your XRF laboratory operates smoothly and produces quality results. A regular maintenance program is preferable to a sample preparation crisis.

END OF ARTICLE

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