FUSIONS – HOW TO IMPROVE THROUGHPUT AND CONCENTRATION RANGE OF ANALYSIS BY ELIMINATING THE LOSS ON IGNITION PROCESS STEP, USING DIFFERENT DILUTION RATIOS AND MAINTAINING ACCURACY AND PRECISION OF RESULTS

Laura Oelofse

Rigaku Americas Corporation, The Woodlands, TX, USA and Yoshijiro Yamada-Rigaku Corporation, Osaka

Email: Laura.Oelofse@rigaku.com

The use of fusions for XRF in industrial process monitoring is common practice and there are several time consuming steps to complete in order to render a sample fusion ready. This paper details a method that would eliminate the need to carry out the Loss on Ignition, Gain on Ignition step thus eliminating 2 hours from the preparation time and it also details the ability to use different dilution ratios of sample and flux for materials on the same calibration curve in order to increase the scope of materials that can be included in a universal calibration curve using both naturally sourced certified reference materials and synthetic pure chemicals as calibration standards.

EXPANDING THE APPLICATION RANGE OF XRF IN GEOLOGY AND MINING

F. Portala, K. Behrens, D. Porta,

Bruker AXS, Karlsruhe Germany

E-mail: Frank.Portala@bruker-axs.de

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is very common for the control of mining operations and determining the final product grade. Benefits are its unique ease of use and the advanced analytical performance of modern instruments. EDXRF instruments are typically very compact in benchtop size and offering low cost of ownership which makes them attractive for dedicated analytical tasks. Up to now the performance for light elements such as sodium and magnesium was very limited. A thick detector window in conventional EDXRF spectrometers absorbed nearly all radiation of light elements. Thanks to the recent developments on modern silicon drift detectors (SDD) combined with high power direct excitation and a thin stabilized entrance window allows the presented EDXRF system to expand its application range beyond other systems. Also the wavelength dispersive X-ray fluorescence spectrometry (WDXRF) profits from the newest technological developments. These WDXRF spectrometers are offering very flexible and compact beam paths, X-ray tubes with improved performance and new multi-layer analyzer crystals. The instruments are able to achieve higher analytical speed and accuracy and offer a high degree of analytical flexibility even for future demands. Examples of geology and mining applications for one EDXRF and one WDXRF system are shown to demonstrate the analytical performance of modern state-of-the-art XRF systems. Both systems are compared to give directions for the use of the best suitable analytical strategy.
XRF MEASUREMENT ON LIQUID SAMPLES AT XSTRATA NIKKELVERK

Helene Trøite, Torkild Eivindson

Xstrata Nikkelverk, Norway

Email: HTroite@xstratanickel.no

This paper presents an XRF method made for analyzing process liquid for the Xstrata Nikkelverk in Kristiansand, Norway.
The method is calibrated for 19 elements. The calibration model uses interelement corrections (alpha-corrections) and the water as a balance component.
The calibration is useful for a wide variation in composition.
The paper also presents a solution to the problem of bubble forming during XRF analysis on liquid samples.
This problem is known to cause poor precession.

ADVANCE APPLICATION XRF IN GEOCHEMICAL AND MINING ANALYSIS

Chris Shaffer, Didier Bonvin and Kurt Juchli

Thermo Fisher Scientific, Switzerland

Email: chris.shaffer@thermofisher.com

In the world of minerals and mining, in-homogeneity is the way of life for nature. Materials are deposited sporadically of millions of years, creating condensed layers or vanes of certain compounds. These formations are typically visible by color and texture differences within a rock body.

Normally in X-ray fluorescence, samples containing these features are seen as potential problems and must be homogenized as much as possible. The sample would need to be crushed small enough so that a representative sample could be taken for further processing. The additional processing typically includes sample grinding and powder homogenization. Finally, the sample is either briquetting or fusion for presentation to the XRF instrument. This method is an ideal way of obtaining the overall composition of the ore body; however the individual lay and vane compositions are completely lost.

In this presentation, we will explore the combination of tradition WDXRF analysis along with the method of small spot and mapping in order to create a more complete profile of the mineralogy for geochemical and mining samples.
TRACE ELEMENT ANALYSIS IN GEOLOGICAL SAMPLES, COAL, AND COKE USING EDXRF

Dirk Wissmann,
SPECTRO Analytical Instruments GmbH, Germany

E-mail: Dirk.Wissmann@ametek.com

Historically the major focus of using ED XRF spectrometers was qualitative screening for simple quality control applications. The introduction of new detector technology and optimized excitation has led to powerful and versatile spectrometers that can be used for a broad range of applications.

Specific applications, like the analysis of trace element content in geological, coal and coke samples, require improved analytical performance more than great versatility. A careful selection of components, along with their optimization, can help to fulfil some typical requirements which were limited, or impossible, for (ED) XRF spectrometers in the past.

RECX – A NEW NORWEGIAN NATIONAL CENTRE FOR X-RAY SCATTERING AND IMAGING

Julian Tolchard
NTNU, Norway

Email: julian.tolchard@material.ntnu.no

RECX is a new national centre for X-ray diffraction, scattering and imaging which brings together laboratories from the Dept of Chemistry at the University of Oslo and the Natural Sciences faculty at NTNU. Jointly funded by Forskningsrådet, NTNU and UiO it is to be a highly equipped national resource which combines and coordinates laboratories and expertise from NTNU and UiO with the goal of providing long term development of skills and methodology in the fields of X-ray scattering and imaging. Importantly, its status as a national centre ensures full access for all areas of the Norwegian X-ray user community, the intention being that it function as a hub, serving and bringing together users from across research, education, public and private sectors.

This presentation will provide an introduction to RECX, giving an overview of the structure and capabilities of the centre, presenting the key people and detailing how to gain access and make use of its facilities. By way of an introduction to our capabilities, some of the recent high temperature diffraction work from the NTNU powder diffraction lab will be presented in the form of “case studies”. These will include both academically and industrially interesting samples, ranging from catalyst nano-materials to metals and electroceramics.
HIGH TEMPERATURE X-RAY DIFFRACTION: SOME APPLICATIONS IN ACADEMIA AND INDUSTRY

Anita Fossdal,
Sintef Materials and Chemistry, Norway
E-mail: anita.fossdal@sintef.no

High temperature X-ray diffraction is a powerful tool for investigating crystal structure, thermal expansion and phase evolution as a function of temperature and atmosphere. Results and experiences from investigation of LaFeO3 and SiO2 (Quartz) are presented.

TEST PORTION GRINDING FINENESS AND XRD DIFFRACTOGRAM QUALITY IN Rietveld PHASE QUANTIFICATION

Lorentz Petter Lossius,
Hydro Aluminium, Norway
E-mail: Lorentz.Petter.Lossius@Hydro.com

Aluminium smelter operation needs analysis of process streams for monitoring the stability of chemical properties. X-ray diffraction is used both for routine monitoring, and for research purposes on these materials. Some of the materials such as smelter grade alumina and anode cover material are complex with components of very different hardness. The presentation gives example of quantitative analysis with focus on grinding and grain size distribution. Tests have been run with different samples (bath electrolyte, anode cover material, smelter grade alumina) on several grinders (swing mill, mortar, McCrone Micronizer) to obtain optimum grain size. The underlying critical issue is that the actual scanned volume of the test portion is small; e.g. with aluminium electrolyte the penetration depth of the x-ray beam is less than 2 mm and the quantitative analysis improves with correct counting statistics. For a diffractogram the optimum grain size is 5-10 µm.
SAMPLE PREPARATION AND CALIBRATIONS: GETTING THE BEST RESULTS USING XRF

Chris Shaffer, Didier Bonvin and Kurt Juchli

Thermo Fisher Scientific, Switzerland

Email: chris.shaffer@thermofisher.com

For standard linear regression analysis using WDXRF, the two most important areas of concern are sample preparation and creation of the calibrations. These fields not only influence the accuracy on unknown measurements but also attribute to the overall instrumentation precision. Improper sample preparation and incorrect calibration settings account for the majority of errors in XRF analysis.

In this presentation, we will explore a variety of sample preparation techniques and discuss the “Pros” and “Cons” of the different methods. We will then examine several instrumentation parameters and condition needed to overcome certain analytical difficulties for better results.

PRACTICAL USE OF NEW VERSION OF ISO 12677:2011 - CHEMICAL ANALYSIS OF REFRactories PRODUCTS BY XRF

Rainer Schramm,

Fluxana, Germany

Email: rschramm@fluxana.de

End of 2011 a new version of ISO 12677 - Chemical analysis of refractory products by X-ray fluorescence (XRF) - Fused cast-bead method was published. The method gives a deep description of the analysis of different refractory materials using the fused bead method. In the authors laboratory the new method was performed for two typical refractory materials: high alumina and Magnesia/chromic oxide. The calibrations were built from primary oxides and verified by certified reference materials. The measurement program of a WDXRF instrument was optimized to meet the performance data of the method. Finally control samples were produced to check the fusion precision and the accuracy. The presentation gives a summary of all important aspects.
PRODUCTION OF PRE-FUSED FLUXES AND PRE-FUSED FLUXES WITH INTERNAL STANDARD

Michel Davidts,
Socachim, Belgium

E-mail: mdavidts@socachim.com

Historically the first fusion flux was the borax, a sodium tetraborate decahydrate. This material is associated with other alkalis such calcium, magnesium. The loss of ignition is too variable and this component is not suitable for accurate XRF analysis.

To obtain better product for this purpose the best way is to produce synthetic flux with very pure raw material. The reaction between pure boric acid and lithium carbonate or sodium carbonate of high purity gives pure lithium and sodium borate on a very fine fluffy powder form. The variable proportion of these reagent permits the production of tetraborate, metaborate or various mixes. To avoid this very light and hygroscopic powder the final product is fused in a platinum crucible to obtain a glassy material anhydrous.

An interesting property of the fusion flux is the obtaining of very homogeneous mix. Therefore very homogeneous flux with dispersion of pure oxide could be used successfully as flux with internal standard. The advantage is obvious the concentration of the unknown component is calculated directly by comparison of the internal line Kalpha or Kbeta of the internal standard. An interesting application is the determination of Nickel with Thulium flux and determination of Iron with terbium flux.

SMALL SPOT ANALYSIS AND MAPPING ON TRADITIONAL WD–XRF

Chris Shaffer, Didier Bonvin and Kurt Juchli

Thermo Fisher Scientific, Switzerland

Email: chris.shaffer@thermofisher.com

While traditionally WDXRF technique has always demanded homogeneous samples, the latest developments in WDXRF have permit analysis of small spots down to 0.5mm as well as mapping of a selected area of a sample. These new possibilities open up the WDXRF technique to heterogeneous samples where segregations, defects or inclusions can now be determined. Coupling these capabilities with standardless analysis permits quantification of up to 79 elements of the periodic table on selected points of the sample.

In this presentation, several applications will be presented in which the power and flexibility of new WDXRF instruments are fully exploited.
The aluminium industry uses pitch as a binder in large scale production of anodes and cathodes. From 2007 Hydro has observed a deterioration in quality for the main raw materials used to aluminium production, coke, pitch, alumina. Though the trace elements from pitch are not the main source of metal impurities, the increasing content in pitch of e.g. Pb, Bi, S, Si, Ca, Fe may have over time larger impact on the final metal quality. Since there are large variations in the trace element content in the pitch materials independent of region or supplier, a reliable, fast and easy to use method for determining pitch impurities has been established in cooperation with one of Hydro’s suppliers. In the course of this cooperation Hydro has taken into consideration most of the aspects necessary to develop a XRF pitch application that is harmonized with the supplier – the standard set, excitation conditions, the amount of measured elements, the total measuring time, the sample preparation method, calibration method and interferences within the material matrix. The work has revealed trend discrepancy on measured results by Hydro, when compared against supplier shipment certificate values. The reason for this deviation has been further explained in inconsistency in used standards, quality of sample preparation and sample surface issues.

EMPIRICAL CALIBRATION OF MINERALS

Sven Erik Bäckman, Andreas Norberg

Degerfors Laboratorium AB, Sverige

Calibration of minerals can be very difficult due to very high levels for major elements to ppm levels. Interferences from X-ray tube and various other elements as line correction to matrix interferences. This paper shows how to develope such a method step by step and how to find all interferences and how to correct them to get as general method as possible.
Whether it is dealing with high-grade hematite, low-grade hematite or magnetite, assays performed on exploration sample, concentrate, internal standard and/or reference material, will always be of paramount financial importance when it comes to the survival of a mining company. In this regard, the existence of a small bias associated with the total iron analysis process could result in millions of dollars of revenue losses for mining companies given the fact that their products are sold in millions of tons. The method entitled “Iron ores -- Determination of Various Elements by X-ray Fluorescence Spectrometry -- Part 1: Comprehensive Procedure” (ISO 9516-1:2003), is the current International Standard Method; it remains widely known and accepted among peers. The prevailing version of this standard however suffers a number of known and documented limitations; it lacks adaptability when dealing with recent developments in the fields of sample preparation by fusion and wavelength dispersive X-ray (WDXRF) spectrometry. This paper examines a simplified version of the ISO 9615-1 analytical method for iron ores. One fusion method using a Claisse® M4™ fluxer is shown to prepare different iron ore types, regardless of where they originate. It also examines the most recent developments to select and apply the corrections (matrix and overlap) for the calibration. This method allows for the simplification of both laboratory and spectrometry processes and so, in comparison with the original ISO method, becomes less restrictive in practice. Furthermore, comparisons will be made between the data collected from this fusion method implemented in combination with a Bruker S4 Explorer WDXRF Spectrometer, and the analytical requirements of ISO. All modifications from the original ISO method parameters (calibration, standards, flux, fluxer, etc.) will also be presented and widely discussed.
DIRECT MEASUREMENT WITH XRF – SAMPLING BUT NO SAMPLE PREPARATION

Bertil Magnusson

SP Technical Research Institute of Sweden

Email: bertil.magnusson@sp.se

XRF can be regarded as a non-destructive technique but in most cases in order to get more reliable results with a lower measurement uncertainty a sample preparation step is performed for solid samples. The preparation can e.g. be homogenizing and subsequent briquetting or fusion into a bead. Analysis can also be performed directly on many samples with the drawback of higher measurement uncertainty but with additional benefits such as less sample handling, better spatial resolution, lower response time, higher sample throughput. In this lecture an overview of direct XRF measurement will be presented using standard wavelength dispersive and energy dispersive instruments as well as handheld instruments and details of three examples will be given

- Analysis of deposits on nuclear fuel rods – sampling on a filter paper
- Determination of thickness of Cu coating on welding wire – direct measurement
- Analysis of sediment and wood cores – XRF footprint along the core

APPLICATION OF RAPID X-RAY DIFFRACTION (XRD) AND CLUSTER ANALYSIS TO GRADE CONTROL OF ORES”

Nicholas Norberg,

PANalytical, Netherlands

E-mail: nicholas.norberg@panalytical.com

The use of high speed detectors resulted in the fact that X-ray diffraction (XRD) became an important tool for quality and process control in mining, steel, cement or aluminum industries. Apart from the composition of an ore sample it provides useful information in terms of quantification of the crystalline phases and the amorphous content. The investigation and relative fractions of the phases present in an ore body can significantly optimize mining and process operations such as flotation, separation, etc..

Traditionally grade control of ores has relied on elemental analysis of sampled materials such as blast cone drill cuttings. This analysis provides a standard elemental suite that is used in grade control to assign mined material as grade blocks to high grade, low grade or waste destinations. In this case the assessment of the mineralogical composition of these samples is more subjective, relying on the visual inspection of collected samples as well as the interpretation of the elemental data.

This presentation aims at outlining rapid X-ray diffraction (XRD) analysis as an additional technique, which has been trialed to establish the mineralogical composition of a sample to supplement the elemental data. Several case studies where XRD can be used for grade control of minerals and base metals will be demonstrated. In addition, alternative quantification methods will be presented besides well known methods such as Rietveld or calibration based analysis.
FERRO ALLOYS ANALYSIS, DISCUSSION OF SAMPLE PREPARATION AND SPECTROMETER SELECTION

Armand Jonkers
PANalytical B.V
Email: Armand.Jonkers@panalytical.com

The analysis of ferro-alloys based on samples prepared as fused beads is discussed in comparison with the analysis as a pressed powder sample. The use of an Eagon-2 muffle furnace is discussed, which allows a whole range of ferro-alloy materials to be prepared. The sample preparation as a fused bead eliminates metallurgical/mineralogical effects and leads to accurate as well as very reproducible results. In the Eagan-2 one can prepare 2 samples simultaneously, which can also serve for making duplicates in order to check on homogeneity of the material. As a demonstration one of the most difficult ferro-alloys (FeSi) is selected to show results in detail. The measurements carried out on a high-performance wavelength dispersive XRF spectrometer (Axios) and on a state-of-the-art Energy-dispersive XRF spectrometer (Epsilon-3), will demonstrate the differences in performance on these two instruments as well as the sample preparation techniques. Both instruments will prove to be a valuable tool in the routine analysis of the materials discussed.

MAKING A 50 KG MGFE Si SAMPLE INTENDED FOR INSTRUMENT CONTROL: EXPERIENCES AND CHALLENGES

Hege Zahl.
Elkem Technology, Norway
Email: Hege.Zahl@elkem.no

Quality control of analytical instruments is performed to ensure results are free from gross error, prove their reliability and demonstrate their conformance with respective analytical requirements. In addition, the quality control data is of substantial value when investigating instrument drift. Ideally, the quality control routines should cover the entire analytical system. However, in order for the quality control system to perform as desired, the control sample material needs to fulfill certain requirements. It is most important that a material intended for control of an XRF instrument and its associated preparation line is homogeneous. This puts strict demands on the selection of the control sample material, together with the subsequent preparation and qualification of the material before it can be used. This presentation will focus on the challenges and experiences when making a control sample for MgFeSi according to “Theory of Sampling” – principles. Statistical testing of the finished material confirmed it was suitable for quality control of the pressed powder pellet XRF method for MgFeSi in Elkem.