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Technical Note 2015-02A

General Considerations for the Calibration of ED-XRF Spectrometers Using Micromatter Reference Materials

Version March 15, 2017

Micromatter has manufactured XRF calibration standards and reference samples for several decades. Our products contain highest quality materials, such as ultra-pure metals or stable inorganic compounds, which are deposited onto polyester or track-etched polycarbonate by evaporation methods.

Micromatter standards are NIST Traceable Reference Materials[TM]. For details, please refer to Micromatter Technical Note 2015-01.

Introduction: Elemental Analysis

XRF Spectrometry is the method of choice of many analysts for multi-elemental analysis. XRF spectrometry easily and quickly identifies and quantifies elements over a wide dynamic concentration range, from ppm levels up to virtually 100% by weight. XRF spectrometry does not destroy the sample and requires little, if any, sample preparation. It has a very fast overall analysis turnaround time. These factors lead to a significant reduction in the per sample analytical cost when compared to other elemental analysis techniques[1,2].

Chemical elemental analysis techniques typically require destructive and time-consuming specimen preparation, often using concentrated acids or other hazardous materials. Not only is the sample destroyed, waste streams are generated during the analysis process that need to be disposed of, many of which are hazardous. These aqueous elemental analysis techniques often take twenty minutes to several hours for sample preparation and analysis time. All of these factors lead to a relatively high cost per sample. However, if ppb and lower elemental concentrations are the primary measurement need, aqueous instrument elemental analysis techniques are generally superior to XRF.

All elemental analysis techniques experience interferences, both chemical and physical in nature, and must be corrected or compensated for in order to achieve adequate analytical results. Most aqueous instrument techniques for elemental analysis suffer from interferences that are corrected for by extensive and complex sample preparation techniques, instrumentation modifications or enhancements, and by mathematical corrections in the system's software. In XRF spectrometry, the primary interference is from other specific elements in a substance (matrix effects) that can influence the analysis of the element(s) of interest. However, these interferences are well known and documented; and, instrumentation advancements and mathematical corrections in the system's software easily and quickly correct for them. In certain cases, the geometry of the sample can affect XRF analysis, but this can be compensated for various technical and mathematical methods.

Most manufacturers utilize the EDXRF spectrometer technique for its mechanical simplicity and excellent adaptation to portable field use. An EDXRF system typically has three major components: an excitation source, a spectrometer/detector, and a data collection/processing unit. The ease of use, rapid analysis time, lower initial purchase price and substantially lower long-term maintenance costs of EDXRF Spectrometers have led to having more systems in use today worldwide than WDXRF Spectrometer systems. Handheld, field portable EDXRF units can be taken directly to the sample as opposed to bringing the sample to the analyzer and configuring it to fit in an analysis chamber.

Qualitative and Quantitative Analysis

XRF data can be generated in 3 basic forms. The form that will provide the most information or help the user attain a certain goal depends on the application, the sample type, and how the information is meant to be used. Novice users of XRF can often find it complicated to make a decision regarding which type of data is appropriate for their particular uses. Without the proper training, users sometimes rely on quantitative data from an XRF instrument in a situation where that data will lack accuracy or repeatability. Conversely, users who know they cannot rely on quantitative data provided by an instrument in a certain situation may get discouraged, because they have not been trained to compare samples using semi-quantitative data processing.

1. **Qualitative XRF Data: The Raw Spectrum**

XRF raw data is the number of counts of element-specific fluorescent X-ray energies received in an XRF instrument detector. This raw data is visualized in a spectrum graph, where the x-axis represents element-specific fluorescent energies, and the y-axis represents counts or pulses. The spectrum shows peaks where element-specific fluorescent energies were detected. The higher the peak, the more counts of that particular energy were detected. For example, if two similar samples are analyzed and one has a higher peak at 6.4KeV than the other, the one with the higher peak contains more iron (Fe). 6.4KeV is a fluorescent energy that is specific to iron.
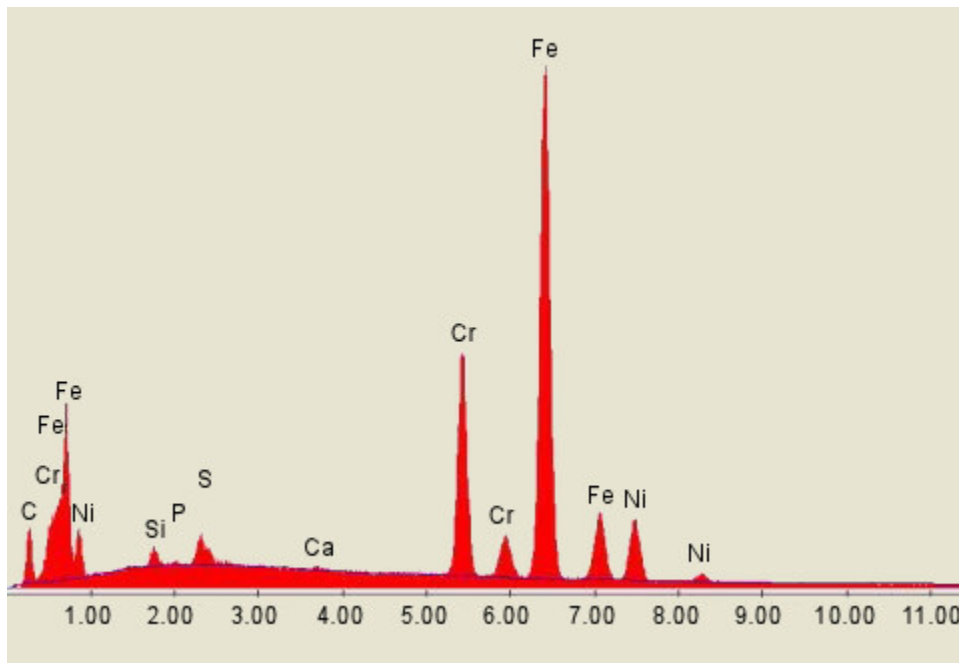
Fig. 1: Energy dispersive XRF spectrum

The raw spectrum consists of qualitative data because it informs the user as to which elements are present in a sample, but does not contain information regarding how much of each element is present unless the data is processed further. Raw XRF data is excellent for analysis of samples that are non-uniform / nonhomogeneous, or for samples where the question of interest is *what is in the sample*, but *'how much'* does not matter. It can also be used to check any questionable quantitative data, because while mathematical data processing can potentially contain mistakes, the raw spectrum never lies. If a peak is present at a certain fluorescent energy, the element to which that energy corresponds is certainly present in the sample.

2. Quantitative XRF Data: Calibrations and Quantification

Quantitative XRF data informs the user as to the absolute quantity of an element present in a sample. This sort of data contains a number and a unit—usually ppm (parts per million) or % weight. Calibrations are created in order to make raw qualitative data into quantitative data. There are several types of calibrations. Two typical methods are FP (fundamental parameters) and empirical calibrations. The fundamental parameters technique uses calibration algorithms loaded into the instrument software. While this may be adequate for some in-situ monitoring work, it may not provide acceptable results for certain samples compared to laboratory based methods[3].

Empirical calibrations are performed by using samples of known concentrations of elements of interest to create a calibration curve that relates the specific known concentrations to peak integrals. This curve can then be used to quantify samples of unknown concentrations by relating the peak integral to the curve built from the known samples. There are some significant differences in how exactly these calibrations are created and how they work depending on the calibration type. Some rely more heavily on math, while others are purely

made by analyzing known samples that are similar to the unknown samples the user wants to quantify[4-7].

Quantitative data can be calculated and reported completely by the instrument, with no additional input required from the user. However, it is important that users understand when quantitative data is reliable. For accurate quantitative data, the following four conditions must be met:

•   The sample must be homogeneous.

•   The calibration used for quantification must be appropriate for the sample material.

•   Standards of known concentration or thickness must be available in order to verify and/or create the calibration.

3. Semi-quantitative XRF Data

In some instances the conditions for reliable quantitative data are not met, but qualitative data is not enough to answer the questions at hand. In these situations, there is a third option. Semi-quantitative data processing allows the user to compare spectral data from samples in order to obtain information regarding the relative concentrations of elements from sample to sample. While this method does not provide absolute concentration values, it can be used to ascertain relative element concentrations between samples; for example, this method would provide information such as "sample A contains approximately 20% more Ag (silver) than sample B." This sort of data is extracted by calculating the area under each peak of interest, which is equivalent to the number of counts. This type of data is appropriate in situations where a calibration and/or samples of known concentrations do not exist, but comparing the samples in terms of element concentration is necessary.

Micromatter XRF Calibration Standards and Reference Samples

Micromatter standards are pure elements or compounds, deposited onto polymer films by ultra-high vacuum techniques, such as electron beam evaporation. The contents of the metal or compound is given in units of area weight ($\mu g/cm^2$), as commonly used in the thin film industry. Users can calculate the thickness of the deposited layer using the theoretical density of the respective bulk material.

Micromatter standards do not contain matrix materials and are therefore not supplied in various 'concentrations'. However, various area weights are available, which can be used for quantitative calibration of XRF spectrometers.

Micromatter standards are ideally suited as direct reference materials for particulate analysis on air filters (PM_c, PM_{10} and $PM_{2.5}$)[8-10] as these samples typically have properties very similar to Micromatter standards, i.e. only very small corrections have to be applied to compensate for matrix effects. However, Micromatter standards have also been used successfully in manufacturing industries and for a variety of analytical specimens[11]. The suitability of Micromatter standards as reference materials for particle induced X-ray emission has been confirmed by Mingay[12].

1. **Energy Calibration**

Micromatter offers XRF standards that cover the periodic system from sodium to bismuth, thus allowing accurate calibration of XRF spectrometers in a wide elemental range. For rapid checks of an instrument's energy calibration, custom multi-element reference samples are available. Unlike Micromatter's XRF calibration standards, multi-element samples are not certified to the same accuracy as quantitative calibration materials because their layered structure causes notable matrix effects, in particular absorption of X-rays emitted in lower deposits by those covering them. Layering several metals or compounds does not affect the energy of the emitted photons.

In order to achieve accurate energy calibration, it is generally not necessary to purchase standards for all elements. Careful selection of a limited number of standards, starting slightly below the lowest atomic number that needs to be measured and including an element above the highest expected atomic number, reduces both cost and the time required for the calibration procedure.

2. **Quantitative Measurements**

Reliable quantitative results can be obtained by calibrating a spectrometer with reference materials of different area weight. Following the general rule that 'Interpolation is better than Extrapolation', standards that cover the expected analytical range should be employed.

For most applications, we recommend recording a calibration curve using standards of 50 $\mu g/cm^2$ and 15 $\mu g/cm^2$, as well as a blank membrane (0 $\mu g/cm^2$). This very basic method has been proven to provide accurate results down to <1 $\mu g/cm^2$. An light weight standard in the 5-8 $\mu g/cm^2$ range may be added to obtain another data point, however, experience has shown that the quality of the calibration is not necessarily improved.

Micromatter generally advises against calibrating with ultra-light reference materials as they cannot be characterized by weighing with the required accuracy. Upon special request, Micromatter can provide ultra-low weight deposits in the 1 $\mu g/cm^2$ range, which are characterized exclusively by EDXRF. These films should preferably be used as 'challenge samples' to verify the accuracy of calibration obtained with regular standards.

100 $\mu g/cm^2$ (and heavier) standards are available to extend the calibration range, however, it should be noted that such standards may show appreciable matrix effects.

Furthermore, calibrations may be verified and checked for consistency against a NIST Standard Reference Material®, such as SRM 2783 (Air Particulate on Filter Media)[13].

Other applications may require refined complex analytical techniques to correlate Micromatter standards to the elemental contents of a particular kind of sample.

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