X-Ray Fluorescence Spectrometry

X-ray fluorescence spectrometry is used for elemental analysis based on the detection of emitted X-ray radiation from excited atoms. X-rays are short wavelength electromagnetic radiation, a conventional x-ray spectrometer generally utilizes the region of about 0.1 --> 11 nm. This technique is a two-step process that begins with the removal of an inner shell electron of an atom. The resulting vacancy is filled by an outer shell electron. The second step is the transition from the outer shell electron orbital to an inner shell electron orbital. This transition is accompanied by emission of an X-ray photon. The energy of the fluorescent photon is characteristic of the element and is equal to the energy difference between the two electron energy levels. Thus the energy of the fluorescent photon provides qualitative information concerning the elements' identity. The number or intensity of fluorescent photons is characteristic of the amount or concentration of the elements present.

The emission process is similar to other fluorescent measurement techniques. The photon energies are designated (anachronistically) as K, L, or M X-rays depending on the energy level being filled. A K shell (lowest energy, closest to the nucleus) vacancy filled by an L level electron (2^{nd} lowest in energy, one level higher than K shell) results in the emission of a K_{α} X-ray. There are as many possible X-ray lines, or peaks, as there are inner shell electrons, so things can get complicated very quickly. However K lines are the most analytically useful as they are the most intense. K lines are used for elemental analysis of Na --> Ce. Above Ce in atomic number the K lines are so energetic that the current generation of X-ray detectors cannot detect them. The less intense L and sometimes M lines are used to detect elements throughout the rest of the periodic table.

X-ray fluorescence instruments are either energy dispersive x-ray fluorescence (EDXRF) or wavelength dispersive (WDXRF) spectrometers. In either case a source of X-rays is required. In a WDXRF instrument an X-ray monochromator is used prior to the X-rays impinging on the sample. An EDXRF instrument does not possess a monochromator. These multichannel instruments measure all of the emitted X-rays simultaneously, thus EDXRF has the Felgett

(signal-averaging) advantage. One should not get the impression that EDXRF instruments are superior. The best performing (and most expensive, ~150K) instruments are WD systems. Enery-dispersive systems are considerably less expensive (~70K), but the basic tradeoff is less sensitivity. Our instrument is an EDXRF.

The analytical information an XRF spectrometer provides can be both qualitative and quantitative in nature. One of the most important uses of XRF is its capability to provide rapid, real-time qualitative elemental analysis on many types of samples. EDXRF is an excellent qualitative tool. All elements are detected simultaneously and a complete spectrum can be obtained in a matter of minutes. Many analytical problems can be solved solely on the basis of qualitative information. Quantitative information can also be obtained using X-ray fluorescence. These determinations are usually based on a linear relationship between the emitted X-ray intensity and concentration of known standards. A complication, which can be overcome with some effort, are matrix effects which can either suppress or enhance the intensity of emitted X-rays. Standards should be prepared in a matrix which is identical to the unknown. How would you make standards of known Cr concentration in HDPE or Pb in soil? With properly prepared matrix matched standards, accuracy error of less than 1% can be routinely achieved. Devise a plan which intelligently uses EDXRF to aid in the analysis of your sample.

To conclude, here is a summary of XRF and its place in the world of elemental analysis. Once you have determined how you will apply the XRF in your analytical scheme, read the instructions on how to use the XRF.

General

- Qualitative and quantitative analysis of elemental composition of solids and liquids with a minimum of sample preparation.

Common Specific Applications

- Quality control and customer support for catalyst manufacture and plant use.
- Forensic applications in evaluating evidence.
- Determination of surface contamination in semiconductor production.
- Support of mineralogical and geological exploration and waste site

evaluation.

Limitations

- Elemental range is limited to sodium and up.
- Matrix interferences can prevent or limit detection of some elements.
- Standards for quantitative analysis do not always match unknown matrix.
- Detection limits are generally at the parts-per-million level, but is matrix dependent.

Complementary or Related Techniques

- Inductively Couple Plasma (ICP) atomic emission spectrometry provides parts-per-billion sensitivity but requires dissolved samples (extensive sample preparation).
- Atomic Absorption* (AA) is a single element method with parts-per-million or less sensitivity for most elements. AA also requires dissolved samples so sample preparation is intensive.
- Flame Emission Spectrophotometry* is only usable for a handful of elements which can be excited in a relatively low energy flame. Flame emission requires a dissolved sample.
- Neutron Activation Analysis has high sensitivity but requires a nuclear reactor for activation. It is the ultimate in elemental analysis in many respects, but is generally useful for only specialized applications.

* - Available to students in instrumental analysis at EIU.

References used to devise this web page:

1. "Handbook of Instrumental Techniques for Analytical Chemistry" Frank Settle, Editor: "X-Ray Fluorescence Spectrometry", G.J. Havrilla. Prentice Hall 1997.

2. "Principles of Instrumental Analysis", 5th Edition by Skoog/Holler/Nieman, Saunders College Publishing 1998.

Additional References

1. "Handbook of X-ray Spectrometry" van Grieken & Markowicz,

Eds.; Marcel Dekker 1993
2. "X-ray Fluorescence Spectrometry" Jenkins, Wiley, 1988.
3. J.E. Anzelma, J.R. Lindsay, J. Chem. Ed. 1987, 64, A181.
4. Anal. Chem. 1997, 493A.

A few decent web sites on XRF

1. http://www.kevexspectrace.com/
2. http://www.amptek.com/xrf.html
3. A good overall web site for a variety of information on spectrochemical analysis: Spectroscopy home page