

REVIEW ARTICLE

## COMPOSITION ANALYSIS OF MATERIALS BY X-RAY FLUORESCENCE SPECTROMETRY

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Over the last 30 years, X-ray fluorescence (XRF) spectrometry has been recognised as one of the most powerful and valuable physical methods for multielement qualitative and quantitative compositional analysis. It offers a fairly good performance over wide range of periodic table elements, requiring minimal sample preparation. It is essentially non-destructive and hardly affected by chemical specification of the analyte. Convenience of operation, reliability and flexibility are among the main features that have made XRF the method of choice for over 20,000 laboratories worldwide.

Today there is a wide variety of XRF instruments available based either on energy or wavelength dispersive method. Principles underlying the latter and the development of the subject over the past three decades is reviewed briefly. The field divides itself into four areas: Excitation Sources, Dispersion Devices, Detectors and Data Reduction. A brief description of each of the above including other aspects of the technique such as sensitivity, resolution and detection limits etc., is given. XRF methods are reasonably sensitive and detection limits for most of the elements is in low ppm range. Attention is drawn to particle size and heterogeneity effects in the sample over which relatively little attention has been paid so far. The application of the technique for small quantity of the specimen, in form of thin film smears, is also described and some of the results obtained at NPL are discussed in this light. In compositional analysis of single crystals of this technique our experience has shown that the data must be interpreted with great caution because of the spurious peaks arising in the spectrogram.

In the end, factors affecting X-ray microfluorescence and light element analysis are discussed along with its possible solution by the emerging field of Synchrotron Radiation X-ray fluorescence analysis (SRXRF).

**Key Words:** Composition Analysis; X-ray Fluorescence Spectrometry; Quantitative Analysis; Data Processing

### Introduction

Over the last 30 years X-ray fluorescence (XRF) spectrometry has been recognised as one of the most powerful and valuable physical non-destructive methods for multielemental qualitative and quantitative compositional analysis. It offers a fairly good performance over a wide range of periodic table elements, requiring minimal sample preparation. Convenience of operation, reliability and flexibility are among the main features that have made XRF the method of choice for over 20,000 laboratories worldwide. In industrial laboratories, a great diversity of samples is usually presented for analysis where quick results are required and XRF is a suitable method normally applied in such situations.

Today various XRF instruments are available based either on energy or wavelength dispersive method to analyse elements from U(92) down to Boron(5). The

principles underlying the latter and the development of the subject over the past three decades is reviewed briefly here.

As regards the principle of the method, the sample is irradiated by polychromatic X-radiation from an X-ray tube. In this process, the elements in the sample are excited to emit their characteristic radiation. This secondary X-ray radiation consists of several emission lines (*K* and *L* series) which are separated into individual wavelengths through diffraction by an analysing crystal of suitable *d*-spacing. This makes simple the task to unambiguously identify elements on the basis of their emission lines and thus to make a qualitative chemical analysis of the sample.

For quantitative analysis, not only wavelength but also the intensity of emitted radiation needs to be measured precisely using scintillation or proportional counter. Broadly speaking the larger the relative intensity of the emission line, the higher is the content of respective element in the sample. However, the fluorescent intensity is not strictly proportional to its concentration because of the differential absorption and interelemental excitation effects in the sample. Thus for any accurate quantitative analysis, comparative samples of known composition (so called calibration standards) with the same matrix are needed. This comparative method is best suited for specific analyses. However, for the determination of an element in an unknown and varying matrix, the matrix effect is usually taken into account indirectly. This is done in a number of ways that can be divided into three main groups:-

- i) *Compensation methods* which include external standard, internal standard and addition or spiking methods etc.
- ii) *Attenuation methods* which include dilution and thin films.
- iii) *Absorption Correction methods* which include scattered intensity method, emission transmission method etc.

With great technological improvements coming up in computer science in modern times, the so called mathematical methods, where interelemental effects are essentially calculated for converting measured intensities into concentration, are becoming more popular. Two types of mathematical procedures have been recognised in this area:-

- a) The *fundamental parameter method* where the algorithms are complex basic equations for the fluorescent intensities of each element.
- b) The *influence coefficient methods* where simple algorithms involving matrix and influence coefficients described by Tertian and Claisse<sup>1</sup> are used.

X-ray fluorescence spectrometry can be divided into four areas: Excitation sources, Dispersion Devices, Detectors and Data Reduction. A brief description of each is given, as follows:-

### Excitation Sources

X-ray tubes are still the most important sources of primary radiation in XRF spectrometry. The spectral distribution of the primary radiation from an X-ray tube is of great importance in XRF analysis. Arai *et al.*<sup>2</sup> have found that in the long wavelength region the intensity from an end window X-ray tube is 2 or 3 times higher than that from side window X-ray tube. These days dual-anode X-ray tubes<sup>3</sup> like Cr-Au, Sc-Mo and Sc-W are also being used. This new innovation was obtained by

coating one anode with a thin film of second target element<sup>4</sup> and this way one can optimise the excitation of both high as well as low atomic number elements by using a single X-ray tube. Successful attempts have been performed by Monty Nichols and Dick Ryon in the year 1985 for micro-fluorescence analysis by using rotating anode as an excitation source.

Recent advances include microfocus and portable tube excitation sources for high resolution and field work respectively. Radioisotopes are also used sometimes because of their stability and small size when continuous and monochromatic sources are required. But the low intensity associated with these sources preclude crystal dispersion and hence are used exclusively in energy dispersion techniques. Electron excitation is well known and utilised in electron probe microanalyzer. A major inconvenience persists in the application of electron excitation in non-metallic materials. The efficiency of electron excitation is theoretically far superior to that of photon excitation, but it loses its charm because of limitation in applied voltage for minimising the background and the limitation in current on account of fear of damage to the material itself. However, the exception is very light elements, B, C, O, F, Na, Mg, Al etc., because here the high excitation efficiency is coupled with low background.

X-ray emission induced by impact of charged particles other electrons, for example, alpha particles and protons, have also been used for analytical purpose. It was found that high energy (1.5 to 2.0 MeV) protons are associated with large cross sections for ionization and very low background, two ideal conditions for very low detection limits<sup>5</sup> in analysis of low *Z* materials.

The latest excitation source for XRF is synchrotron radiation and the high brightness of synchrotron radiation produced by storage rings has considerably enhanced the research capability. In trace element analysis the minimum detection limits have been pushed down from few ppm level to < 1 ppm or pg. In recent years, there has been increasing interest in light element determination (eg. oxygen and carbon) by synchrotron radiation X-ray fluorescence (SRXRF)<sup>6</sup>. Today there are only about 50 electron storage rings worldwide including also those constructed and planned for synchrotron radiation research. It is very complicated as well as an expensive equipment and its availability will thus continue to be limited.

### Dispersion

In wavelength dispersion, the 'analysing crystal' is a very important part of the instrument. Bragg's Law dictates that the inter-lattice spacing in the analyzing crystals must be about the same dimension as the wavelength of emission radiation. To cover the elements of entire periodic table, crystals with *d*-spacing from 1 Å to about 100 Å are needed. LiF is most widely used crystal. 200 cut of LiF can analyze K lines of K(19) to Mo(42) and L lines of In(49) to U(92). Other crystals in common use include PET and TAP. Highly oriented pyrolytic graphite (HOPG) is particularly effective in 3 to 6 Å range and the Langmuir-Blodgett films (Lead Stearate for example) are useful for wavelengths longer than 25 Å. But these Langmuir Blodgett films are rapidly destroyed under high X-ray beams<sup>7</sup>. The biggest impact in the area of dispersion devices for long wavelengths was made by artificial multilayers (alternating layers of high and low atomic number materials with effec-

tive d-spacing in the range 30-200Å). These Layered Synthetic Microstructures (LSMs) were first reported as commercially available for routine X-ray spectrochemical analysis in 1984 and this enhanced the low atomic number capability which has led to novel applications for XRF method including analysis of carbon in coal, steel and cement; boron in glass; and beryllium in metal.

The increasing demand in semiconductor industry for larger dynamic and static Random Access Memory integrated circuits (RAM's) requires oxide layer thickness down to 100Å or even less and therefore, traditional methods for measurement of such layer thickness are difficult to apply<sup>8</sup>. X-ray spectrometer equipped with LSM can determine oxygen levels that are equivalent to 5Å of SiO<sub>2</sub><sup>8</sup>.

The use of LSM's also makes it possible to analyse *L* lines of transition elements instead of their *K* lines with higher accuracy, and this has been applied in the study of implantation depths for arsenic in Si wafers from 0 to 2 μm.

The excitation in ultrasoft region (in elements like O, C and B) is very low because of lower intensity of primary X-rays and low fluorescent yield of light elements. Instead of wavelength dispersive method of Bragg reflections, having high resolution and low reflectivity, monochromatization combining total reflection by a selected mirror and an appropriate filter offered an alternate approach (useful for trace analysis) in order to increase measured intensity with reasonable optical resolution<sup>9,10</sup>. Total reflection is now routinely used in XRF analysis. The advantages of technique have been described by Aiginger and Wobrauschek<sup>11</sup>. Tomoya Arai<sup>10</sup>, has recently observed, by comparing the mirror with synthetic multilayers for the measured intensity of *C-K<sub>α</sub>* and *B-K<sub>α</sub>*, that the intensity from the mirror 3 to 5 times higher than that of synthetic multilayers, which can be attributed to X-ray optics.

### Detectors

The proportional (sealed or flow type) and the scintillation counters still remain the detectors of choice for wavelength dispersion systems. Minor improvements such as using charge sensitive preamplifier so as to have a low noise proportional counter (thus gaining P/B ratio) has been reported in literature. Some effort is being pursued to develop the gas-proportional scintillation counter which is expected to provide better energy resolution.

The whole field of energy dispersion is centered around Si(Li) detector operated at cryogenic temperatures. The need for elimination of liquid nitrogen burden, especially for spectrometers used in remote industrial location, has been partly solved by replacing liquid nitrogen by thermoelectric cooling. However, the promise of room temperature ED detector still remains a dream of tomorrow. Superconducting tunnelling junction has also appeared on the scene recently, but its specific applications in this area are still a subject of discussion.

### Data Reduction

For many years the influence coefficient technique has been the strong force in data reduction. For those many cases, where an approximate number of standards are

available to establish value of coefficients, the approach is still the method of choice, frequently the situation is quality control.

The fundamental parameter approach is receiving more and more attention recently. Computing sample absorption and matrix corrections from fundamental parameters requires measurement or prior knowledge of all bulk element concentrations. Therefore, the applicability of the approach is limited to XRF analysis of metal alloys, oxides or specially prepared matrices of known composition. Recently Rausseau<sup>12-14</sup> proposed a method for calculating influence coefficients from fundamental parameters using one 'reference standard'. According to Gilfrich<sup>15</sup> the fundamental parameter approach with use of only one "type standard" to minimise the effect of uncertain parameters, will ultimately surpass all other data reduction schemes.

### **Sensitivity, Resolution and Detection Limits**

XRF methods are reasonably sensitive with detection limits for most of the elements in low ppm range. The lower limit of detection is normally the concentration equivalent to two standard deviations of the background count rate. Detection limits depend not only on the quality of the equipment used and the matrix involved but also very much on the time available for counting peak and background. Three major factors effecting detection limits are:

- 1) sensitivity of spectrometer for that element;
- 2) background or blank count rate; and
- 3) time available for counting peak and the background.

Many methods offer greater sensitivity for trace element analysis than XRF. It is because of other advantages (in particular, sample preparation) that X-ray spectrometers are employed for this type of work. It may also be mentioned that poor sensitivity of XRF is compensated for by the stability of modern spectrometers. Reliability tests performed at U S Geological Survey (Denver) Lab. have indicated that measurement of same fusion disc 50 times gave relative standard deviation (RSD) equal to counting statistics. On the other hand 49 discs of the same standard, counted one time each, gave RSD equal to three times the counting statistics.

Resolution is defined as ability of the spectrometer to resolve spectral lines. In flat crystal Wavelength Dispersive System (WDS) the resolution is dependent upon the angular dispersion of the analyzing crystal and the divergence allowed by the collimator. It varies normally from 5 to 50eV as compared to about 150eV for secondary target energy dispersive system (STEDS).

### **Specimen Preparation**

Various preparation techniques based on bulk metallic specimens, powder, glass transformed solid solution, liquid and thin film specimens etc. have been described in the literature. Relatively little attention has been paid recently to particle size and heterogeneity effects. According to Claisse and Samson<sup>16</sup> the fluorescent intensity is not significantly affected if the average penetration of X-rays through pure fluorescent compound is at least five times the average size of the particles. The penetration depth is often of 1  $\mu\text{m}$  or less when medium and long wavelength

fluorescence lines are involved which indicates that specimen ground to 10 to  $30\mu\text{m}$  (conventional fine particle size range) may represent a risky situation for an accurate quantitative work. If particle size is relatively constant, the risk of variations in fluorescent intensities is certainly smaller, but this is not generally the case. Our experimental observations too have indicated that the higher accuracy claimed in number of papers in the literature is not supported. We have found discrepancies to be even larger in thin film smear techniques, particularly when the powder sample is a mixture of different hardness materials.

To overcome the particle size effects, fusion and solution techniques have been used popularly for an accurate work. The reliability of results will also depend upon the surface finish of the sample. Use of oxidised surfaces or those with varying degree of roughness will obviously affect the analyte line intensity, particularly for low atomic number elements.

### Analysis of Single Crystals

A new field of application for WDS has been opened by analysis of thin layers especially in semiconductor devices. An example, is study of implantation depths for arsenic in silicon wafers<sup>17</sup>. Our experience on compositional analysis of single crystals have shown that the data must be interpreted with great care because of the spurious peaks arising in the spectrogram. Fig. 1 is a trace of the XRF spectrogram in the limited Bragg  $2\theta$  region of  $30\text{-}40^\circ$  of the same sample of silicon in single crystal and polycrystalline form. It has also been observed that some of the

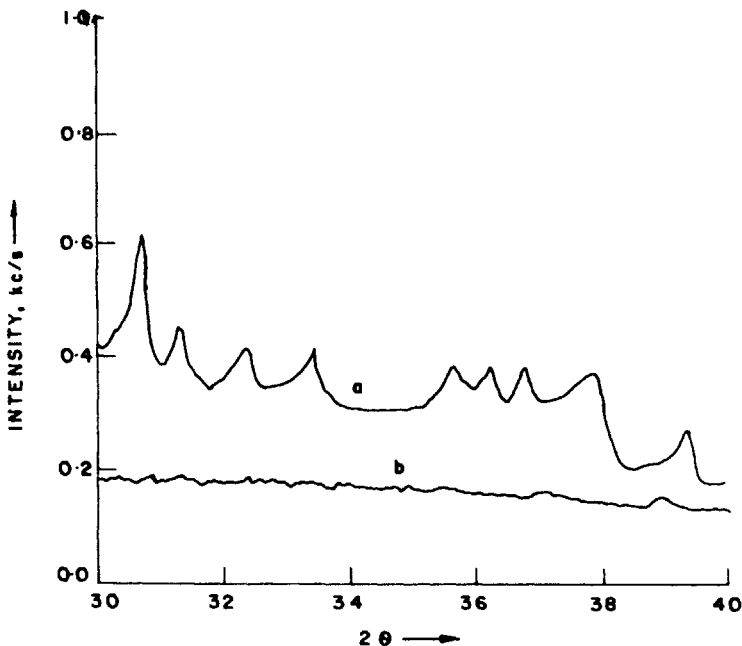


Fig. 1 XRF spectra of high purity silicon sample in:  
a) single crystal form; and b) polycrystalline form

extra reflections are wide and do not have a symmetrical profile. A systematic study is needed to understand their origin precisely.

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X-ray fluorescence (XRF) is a non-destructive analytical technique used for the identification of elements and determination of their concentrations in solid, powdered, and liquid samples [7, 8]. Elements present in samples are detectable by XRF up to 100% and at trace levels, usually below 1 part per million (ppm) [8]. The elements detectable by XRF range from Sodium to Uranium. The wavelength composition of the radiation from the X-ray tube depends upon the choice of anode material. For most applications, the optimal choice is a rhodium anode, although other options such as molybdenum, chromium, or gold may be preferable in certain circumstances [8]. The spectrometric analysis of the various secondary emissions leads to the various IBA techniques [5, 11, 12]. An X-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles that are similar to an electron microprobe (EPMA). However, an XRF cannot generally make analyses at the small spot sizes typical of EPMA work (2-5 microns), so it is typically used for bulk analyses of larger fractions of geological materials. The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible by the behavior of atoms when they interact with radiation. When materials are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized. Analysis using x-ray fluorescence is called "X-ray Fluorescence Spectroscopy." In most cases the innermost K and L shells are involved in XRF detection. A typical x-ray spectrum from an irradiated sample will display multiple peaks of different intensities. X-Ray Fluorescence analysis of the soil samples will be carried out by the X-ray fluorescent spectrometer at FLNR, JINR. Sources of the characteristic X-ray The characteristic X-ray of the elements will be excited by ring-shaped Cd-109 ( $E_{\gamma} = 22.16$  keV,  $T_{1/2} = 453$  days) or Am-241 ( $E_{\gamma} = 59.6$  keV,  $T_{1/2} = 432.2$  years) sources.