Analytical Techniques for Trace Element Analysis: an Overview

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Abstract: Different novel analytical techniques have been used for the long time by the researchers for the determination of trace, major and minor elements particularly in coal fly ash, sand, water, nail polish, lipsticks, chips and in plant samples. These include X-ray Florescence techniques like EDXRF& WDXRF, Atomic Absorption Spectroscopy, Neutron Activation Analysis, and Proton Induced X-ray Emission techniques. We have made an attempt to review these techniques, their sensitivity, suitability, minimum detection limits for their applicability to analysis of various samples.

Keywords: AAS, EDXRF, WDXRF, NAA, PIXE, Detection Limit, Sensitivity

1. INTRODUCTION

Techniques for the analysis of trace elements have developed rapidly in response to the increasing need for accurate measurements at extremely low amount of contents in diverse matrices [1]. Many elements occur in a variety of matrices at sufficiently low levels that, when instrumental analytical methods were first developed in the nineteenth century, they were undetectable [2]. As analytical technology improved, and it became known that elements were present at these very low levels, the term ''trace'' was coined to describe them. Although modern analytical methods allow accurate, repeatable determination of elements at such low levels, the generic terms ''trace'' and ''trace element'' are still in use. The boundaries of trace analysis are described by the definition of ''trace element'' in the IUPAC Compendium of Chemical Terminology, Second Edition [2]: ''Any element having an average concentration of less than about 100 parts per million atoms or less than 100 µg/g''. As analytical techniques have become more sophisticated, detection capabilities have improved and, in several fields, this upper boundary of the definition of ''trace'' is now too far away from the capabilities of analysis that new terms such as ''ultra trace analysis'' are in common use. There is no agreement about the range of ultra trace analysis and no rigorous definition. Within the literature, the term is used for the definition of elements at mass fractions less than 10 to-6 and 10 to -8 g/g (1 ppm and 10 ppb) [3].

This review considers the benefits and the drawbacks of some of the analytical techniques used to identify and to quantify different elements in a variety of matrices [4]. We consider the extent to which the results of analysis from different methods are comparable, and the extent of analytical bias between methods. The review considers the final analytical steps and also the preparative and the sampling procedures that are generally common to analysis using any of these instruments and methods.

However, it is important to recognize that systematic biases – from loss of target element, contamination during preparation of the sample, or variability in the recovery efficiency of digestion (or extraction) procedures [5] – can be significant contributors to

the final inter-laboratory variability between methods .When these sources are well controlled, any remaining bias is specifically due to the analytical methods in question. We will give specific consideration to the most commonly used techniques, in particular: atomic absorption spectroscopy, X-ray Florescence techniques like EDXRF& WDXRF, Neutron Activation analysis, and Proton induced X-ray emission techniques.

1. MEASUREMENT TECHNIQUES

This section considers the above most commonly used techniques in trace elements analysis. We shall discuss the benefits and the drawbacks of each technique, compare and contrast the methods, assess the comparability of the methods, and propose possible reasons for systematic bias between the methods. Table-1 summarises some of the essential attributes of the considered techniques [5].

Table-1: Some essential attributes of the considered techniques.

Sr. No.	Techniques	Directly measureable analyte			Possible Difficulties	Expense	Whether multielemental
		Free ions/elements	Ions/elements in complexes	Total elemental conc.			
1	XRF	✓	×	✓	Background problem	High	Yes
2	AAS	✓	✓	✓	Matrix Effects, One element at a time	High	No
3	NAA	✓	✓	✓	Requires nuclear reactor	Very High	Yes
4	PIXE	✓	×	✓	Background problem	High	Yes

2.1 X-Ray Flourescence (XRF) Technique

X-ray techniques have been used widely for trace element analysis. These have found useful applications in analysis of geological materials, steels, cements, archeological samples, forensic samples and environmental samples. A widely used technique in this

domain is X-Ray fluorescence (XRF), which is non destructive and can be used to analyse almost any element in the periodic table from Flourine (Z=9) upwards [6]. Newer developments allow the determination of ultra low atomic no. elements including B,C, O and N.

The sensitivity of XRF depends upon the energy of incident radiation, geometry of the instrument used and the efficiency of the detector. The overall precision of the XRF measurement is usually limited by the statistics of the detected photons. The limit of detection depends upon sensitivity of the instrument and background level of sample matrix being analyzed [7]. The lower limit of detection is expressed by the relation [8]

$$Lower\ limit\ of\ detection\ (LLD) = \frac{3}{M} \times \sqrt{Rb/Tb}$$

where, Rb is count rate at the background, tb is time spent counting background and M is sensitivity of the spectrometer.

Samples to be analyzed by XRF can be coal fly ash, vegetation sample like plant samples, sand, water etc. As an illustration, in vegetation sample, XRF technique comply with desired features like the possibility to perform analysis directly on solid sample. It can be applied to Chips/Films of Nail Polishes [9]. It is less time consuming, requiring less amount of test sample ,having multi element capability with wide dynamic range[10]. The main drawback of XRF instrumentation , restricting more frequent use of the technique for environmental purposes is its limited sensitivity for some pollutants like Pb and Cd and poorer accuracy and precision as compared to atomic absorption spectroscopic techniques. However with the advent of some digital signal processing techniques, precision and accuracy especially in environmental samples are improved drastically[11].

Two configurations of XRF spectrometers are widely used viz. energy dispersive X-ray fluorescence (EDXRF) and wavelength dispersive X-ray fluorescence(WDXRF). EDXRF as analytical tool was used for monitoring of urban air pollution in Chandigarh. Aerosol samples were collected on 47mm diameter, 0.8μm pore size cellulose nitrate filter papers. The elemental concentrations were determined using fundamental parameter approach [12]. Pb in aerosol samples from Mexico valley was determined using EDXRF. This technique being quick , reliable and non destructive was used and compared with atomic absorption spectrometric technique and a good correlation was obtained[13]. Heavy metal contents in fruits and vegetables from Lublin, Poland were analysed using EDXRF. The XRF spectrometer by Canberra was equipped with Si(Li) detector and A/D conversion Canberra 1510 detector. X ray radiation was induced by 109Cd, 55Fe and 241Am. Quantitative analysis was done with AXIL software [14].

Sensitivity of XRF instrument is defined as being the net intensity obtained per unit of concentration. For calculating it, the peak intensities of the analyte have to be measured on certified reference materials (erroneously known in popular language as standards) of composition similar to that of the unknown samples to be analyzed. To calculate the sensitivity, the measured intensities must not be corrected for matrix effects and one must assume a linear relation between intensity and concentration. The sensitivity for each analyte i is calculated from the slope m_i of the calibration line as follows. The general form of the equation for a straight line is $Y = mX + b$…(1). If the calibration line is a plot of the peak intensity I_p of an analyte i as a function of the concentration C_i, the equation (1) becomes $I_p = m_iC_i + I_b$ where the true background intensity I_b is given by the intercept of the calibration line on the Y axis. The slope m_i is then given by

$$m_i = \frac{I_p - I_b}{C_i}$$

where C_i is the concentration of the analyte i in % or ppm. It is the slope of the calibration line that enables to convert measured net intensities into concentrations. [15]

The elemental concentration of Uranium in the samples collected from ground and canal water in Bathinda district of Punjab state, India have been investigated using EDXRF technique. The residue obtained after drying water sample were analyzed using EDXRF spectrometer consisting of Mo anode X- ray tube equipped with selective absorber as an excitation source and Si(Li) detector[16].

2.2 Atomic Absorption Spectrometry

FAAS i.e. Flame atomic absorption spectrometry works by introducing the sample into a flame where it is dissociated into its constituent atoms. Electromagnetic radiation in the UV/Visible part of the spectrum is directed through the flame and is partially absorbed in a manner characteristic of the atoms present. FAAS is relatively inexpensive and simple to operate. It encounters little interference. However, some refractory elements cannot be determined with good sensitivity because flame temperatures are often not hot enough to induce complete atomisation. At its worst, this problem means that trace levels of B,W, Ta, Zr, As and Sn may not be determined by FAAS. FAAS can be used for the analysis of liquid samples only and relatively large sample volumes are required. FAAS is also a relatively slow technique and is best used when only single elements or a few elements are to be determined within a sample. When a large number of elements require measurement, other techniques may be substantially quicker.

The presence of interferences, such as overlapping peaks from interfering species or incomplete atomisation of non-analyte species, can confer positive bias on measurement results. Incomplete atomisation of the target element itself may result in a negative bias when using these techniques. This is exacerbated when there are present matrix effects that often suppress the signal from a known quantity of element within the sample, as compared to the same amount of element in a calibration standard [17].

Characteristic concentration in atomic absorption (sensitivity) is defined as the concentration of an element (expressed in mg/l) required to produce a signal of 1% absorption (0.0044 absorbance units). As long as measurements are made in the linear working range, characteristic concentration can be determined by reading the absorbance produced by a known concentration of the element, and solving the following equation: =

$$Characteristic\ Concentration = \frac{(Conc. of\ Std. \times 0.0044)}{Measured\ Abs.}$$

The characteristic concentration values for each element at different primary wavelengths are listed in the Standard Conditions section. Knowing the expected characteristic concentration allows the operator to predict the absorbance range which will be observed for a known concentration range of the element of interest. The characteristic concentration check value is the concentration of element (in mg/l) that will produce a signal of approximately 0.2 absorbance units under optimum conditions at the wavelength listed. Using the characteristic concentration check, the operator can determine whether instrumental parameters are optimized and whether the instrument is performing up to specifications.

The detection limit is defined as the concentration of the element which will produce a signal/noise ratio of 3. Thus, the detection limit considers both the signal amplitude and the baseline noise and is the lowest concentration which can be clearly differentiated from zero. The standard procedure for establishing detection limits by flame atomic absorption is as follows: Two concentrations of the element are prepared, with entirely separate volumetric glassware used for each to reduce the possibility of contamination to a

minimum. The absorbance means of the two are established as explained below. The lower concentration standard is made approximately 5× the expected detection limit, and the second standard is made twice this concentration. After establishing what are considered to be optimum conditions, take a reading for each standard alternately, ten or more times. A blank reading (solvent only) is made between each standard reading. The sequence is: blank, low-concentration standard, blank, high concentration standard; repeat the sequence. Having obtained the data, make the calculation as follows:

1. Average the two blank readings taken immediately before and after each standard and subtract from the standard reading.

2. Calculate the mean and standard deviation for the set of corrected high-standard readings. Do the same for the set of corrected lowstandard readings.

3. If the ratio of the means does not correspond to the ratio of the concentration prepared to within statistical error, reject the data.

4. If the data pass the ratio-of-the-means test, calculate the concentration detection limit as follows:

$$\text{Detection Limit} : \frac{Standard\ Conc. \times 3\ Std.Dev.}{Mean}$$

The calculation is made independently for each standard concentration, and the detection limit is the average of the two results. Routine analytical measurements at the detection limit are difficult because, by definition, noise makes up a significant percentage of the total measurable signal. By definition, the precision obtained at detection limit levels is ±33% when a 3-standard-deviation criterion is used. Therefore, while it is possible to distinguish analyte concentrations at the detection limit from zero, for good precision it is necessary to limit routine analytical work to concentrations higher than the detection limit. It is important to remember that characteristic concentration expresses the size of the absorption signal, the detection limit considers both the signal amplitude and the baseline noise. As shown in Figure 14, it is possible to have the same characteristic concentration, but different detection limits.[18]

2.3 Neutron Activation Analysis

The term activation analysis refers to identification and quantitative determination by use of radio nuclides produced from a target element. NAA is the most common variant in which neutrons are used to irradiate and to activate the sample. When the measurement is carried out without prior chemical separation, the method is called instrumental NAA (INAA). As a result of a nuclear reaction between the neutron and the isotope of the element of interest, radio nuclides with characteristic half-lives may be produced, emitting radiation of varying energies that may be measured by a suitable detector and are characteristic of the element from which they were produced. Applications of the NAA technique have been in the analysis of very pure silicon (where LODs for some elements may be mass fractions of 10 to-15 or below), the trace determination of elements in biological samples, and the multi-element analysis of airborne particulate matter [19].It can be applied to Analyse the cancerous tissues, trace elements in Human hairs and drinking water. [20][21].

Activation analysis is suited to the analysis of solid samples where these may be irradiated with no dissolution step. Liquid samples may be analysed but pre concentration is often required prior to analysis. Mass fractions down to the 10 to -15 level can be detected.

The detection limit represents the ability of a given NAA procedure to determine the minimum amounts of an element reliably. The detection limit depends on the irradiation, the decay and the counting conditions. It also depends on the interference situation including such things as the ambient background, the Compton continuum from higher energy-rays, as well as any-ray spectrum interferences from such factors as the blank from pre-irradiation treatment and from

packing materials. The detection limit is often calculated using Currie's formula:

DL = 2.71 + 4.65B

Where: DL is the detection limit and B is the background under a gamma-ray peak. This relation is valid only when the gamma-ray background (counting statistical error) is the major interference.[22]

Neutron Activation Analysis sensitivities and accuracy are dependent on the concentration of particular element and radionuclide parameters(i.e. parent isotope abundance, neutron cross section, half life, and gamma ray abundance). Element sensitivities vary from 10^{-3} to 10^{-10} grams per gram of sample.**To Calculate Element Concentration using gamma ray counts:** The procedure used to calculate concentration (i.e., ppm of element) in the unknown sample is to irradiate the unknown sample and a comparator standard containing a known amount of the element of interest together in the reactor. If the unknown sample and the comparator standard are both measured on the same detector, then one needs to correct the difference in decay between the two. One usually decay corrects the measured counts (or activity) for both samples back to the end of irradiation using the half-life of the measured isotope. The equation used to calculate the mass of an element in the unknown sample relative to the comparator standard is:

$$\frac{A_{sam}}{A_{std}} = \frac{m_{sam}}{m_{std}} \frac{\left(e^{-\lambda T_d}\right)_{sam}}{\left(e^{-\lambda T_d}\right)_{std}}$$

where A=activity of sample (*sam*) and standard (*std*), m=mass of the element, λ=decay constant for the isotope, and T_d=decay time. When performing short irradiations, the irradiation, decay and counting times are normally fixed the same for all samples and standards such that the time-dependent factors cancel. Thus the above equation simplifies into:

$$C_{sam} = C_{std} \frac{W_{std}}{W_{sam}} \frac{A_{sam}}{A_{std}}$$

where C=concentration of the element and W=weight of the sample and standard.[23]

Sensitivities and LODs can vary widely with some elements being difficult to detect at all. In principle, NAA offers a robust analysis technique providing very accurate results down to ultra-low concentrations. Most sources of systematic and random error (e.g., interfering nuclear reactions, overlap of spectral lines and dead-time losses) are identifiable, since the physical principles of NAA are well understood and described [24].

Non Destructive Neutron Activation Analysis has proved to be an effective method of analysing trace elements in Soils. More importantly is the fact that the basic major elements which is universally present in soil samples are clearly identified in percentage concentrations and ppm; as well as the key elements needed to enhance the elemental properties of soils such as Al, Fe, Zn and Mn are also found in moderate quantities [25].

Additionally, since NAA is based on principles fundamentally different from the other analytical techniques, it is prone to completely different systematic biases and is therefore extremely useful in the analysis of reference materials or in assessing the comparability of measurement results. However, the throughput of NAA techniques is low, and the technique is expensive.

2.4 Proton induced X-Ray Emission Technique (PIXE)

X-ray emission may also be induced by heavy charged particles (particle-induced X-ray emission, PIXE). Calibration is often by means of thin-film standards, or by using fundamental physical parameters in conjunction with an experimentally determined efficiency curve. Using this technique, LODs of a few ng/cm2 have been claimed for particulate material on ambient air filters for a range of elements, with repeatabilities of 1% and an accuracy of 5% [26].

For a given trace element A with atomic number Z in a given matrix B, the detection limit is determined by statistical fluctuation of background and therefore it is defined by:

$$N_A \geq 3 \times \sqrt{N_B}$$

where N_A is the total number of counts of a characteristic X-ray peak for a given line i of A,

and N_B is the number of background counts included in the full width of half maximum (FWHM) of the characteristic X-ray peak or the detection limit of A in the matrix B is given in units of parts per million by the following Formula:

$$\frac{n_A}{n_B} = \frac{3 \times \sqrt{N_B} \times 10^6}{n_B \times N_P \times \dfrac{\Omega}{4 \times \Pi} \times \varepsilon_f(Z) \times ab(Z) \times \sigma^i_Z}$$

Where n_B is the atomic concentration of the matrix element, n_A is that of the trace element A,

N_p is the number of projectiles, Ω is the solid angle subtended by a detector, and

σ^i_Z, $ab(Z)$, $\varepsilon_f(Z)$ are, respectively, the production cross section of K X-rays for the trace element,

absorption of X-rays by windows and others (air, target) and the detection efficiency.[27]

The trace elements in medicinal plants in Manipur had been detected by PIXE technique as it is one of the most powerful technique for its quick multi elemental trace analysis capability and high sensitivity. Some of the common trace elements determined by this technique are K, Ca, Fe, Zn, Sr. etc. [28].

3. CONCLUSIONS

The analytical methods discussed above have been shown to be effective in detecting and measuring a number of elements in a variety of matrices down to extremely low concentration levels. This brief resume has concentrated on the techniques that most commonly occur when method comparability for trace analysis is assessed in the literature. The requirements on analytical science are becoming increasingly demanding as the boundaries of trace analysis are constantly being pushed downwards. The current challenges in

analytical chemistry surround the ability to quantify, accurately and repeatably, elements with mass fractions of around 10 to -11 (0.01 ppb) or below. This is particularly true for the analysis of pollutants in ambient air, where legislative limits are already approaching these levels [29].

It is essential that, as the amount concentration being measured is lowered, the validity of these measurements remains assured. The dominant source of error in very low level analytical measurements is often the systematic bias of the analytical methodology itself. A wide variety of robust analytical techniques is now available for trace analysis. An important part of the use of these methodologies is to understand and to recognise their capabilities and limitations and to gauge their suitability for the analytical task in question.

4. ACKNOWLEDGEMENT

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