

Review of Principles and Application of AAS, PIXE and XRF and Their Usefulness in Environmental Analysis of Heavy Metals

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Abstract: Heavy metals are non-biodegradable and their presence in the environment often results to health hazard. Inside living organism, some heavy metals undergo bio-magnification as they move from one trophic level to another in food chain of ecosystem. As a result, regular evaluations of heavy metals in biotic and abiotic samples are essential in environment studies. Many analytical approaches are used to measure the concentration of metals in environmental samples such as Atomic Absorption Spectrophotometer (AAS), Proton Induced X-ray Emission (PIXE) and X-ray Fluorescence (XRF). This work reviews the principles and application of AAS, PIXE and XRF and their usefulness in metal analysis.

Keywords: Heavy metals, AAS, XRF, PIXE and Environment

I. Introduction

Atomic absorption spectrometry: is an analytical method used for the qualitative and quantitative determination of chemical elements, especially in trace element analysis. The process is based upon the absorption of radiant energy usually in ultraviolet (UV) and visible region (V) of electromagnetic radiation. The process begins with atomization, which is a process that dissociates elements into atoms by heat of several thousand degrees but less than 3000°C. When gaseous solution is employed, emission and absorption analysis is obtained. At this temperature, only a small fraction of mono-atomic particles is excited to a higher electronic state (excited state) which emits radiation and reverts back to ground state almost immediately because it has a short life span of between 10^{-8} to 10^{-9} seconds [1].

The energy of wavelength released during excited state is a characteristic of each element as they revert back to ground state. As they do, they emit electron, which is the basis of flame emission photometry. The wavelength and intensity of emission line is different for each element [2]. However, a large number of the gaseous metal atoms remain in unexcited state of ground state because of low flame energy. These ground state atoms are capable of absorbing radiant energy of their own specific resonance wavelength, which is the wavelength of that radiation the atom will emit if excited from ground state [3]. AAS technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration relies therefore on Beer-Lambert Law which states that absorbance is proportional to the concentration of an analyte sample in a cell [4].

Generally, AAS must consist of a stable source of continuous radiation (a large source); system of lenses, mirror and a slit to define, collimate, and focus the beam; a monochromator for selecting narrow band of wavelength from the source; a sample compartment to hold the sample under analysis; a detector and a readout device [5].

Advantage and Disadvantage of AAS: Some of the advantages include cheapness and comparatively easy and simple to manipulate the machine; sensitivity such that many elements can be determined at ppm level or even less; high precision and accuracy obtained by the calibration curves; absorption signal considerably free from inter-element interferences and above all, atoms of a metal absorb at a well-defined wavelength and over a narrow bandwidth hence isotopes of the same element will not absorb at each other's radiation. Some of the disadvantages include limited application as only about 70 elements excluding earth metals have been detected by this method. Another disadvantage is that AAS cannot yet detect non-metals [6].

Particle-Induced X-Ray Emission (PIXE): is a powerful, yet non-destructive, technique used in the determination of the elemental constituents of a material or sample. When a material is exposed to an ion beam, atomic interactions occur that give off electromagnetic radiation of wavelengths in the X-ray part of the electromagnetic spectrum specific to that element [7]. PIXE takes advantage of the emission generated from materials by impacting sample with two types of ions which are in the form of alpha (α) particles (He^{++}) and protons (H^+) at high energies. These particles knock out elements in the innermost electrons shell called the K-shell. To fill this vacancy, electrons from outer shells replace the inner shell electrons with a covering emission in energy in the form of an X-ray. Each atom has its unique property of atoms allows the analysis of

materials using PIXE [8]. One advantage of a PIXE is that it can be performed both in vacuum as well as outside of a vacuum, in this way; whole samples such as rocks and minerals can be analyzed in a non-destructive manner [9]. Different ranges of samples such as solids (plastics, papers or metals); powdered materials (fly ash, activated carbon, catalysts, and corrosion products) liquids (oils, process waters, and solutions) and aerosol filters (thin film membrane samples) are assayed by PIXE. The Advantages of PIXE include high sensitivity, multi-element capability that analyzes any element from sodium to uranium in a single spectrum [10], non-destructive proton beam that preserves sample after analysis.

X-ray Fluorescence (XRF) Spectrometry: X-ray fluorescence is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology [11].

Principles of XRF: The underlying principles of XRF are similar to PIXE [12]. When materials are exposed to short-wavelength X-rays or to gamma rays, it leads to ionisation of their component atoms which involves ejection of one or more electrons from the atom when the atom is exposed to radiation with energy greater than its ionisation potential. X-rays and gamma rays can be energetic enough to expel tightly held electrons from the inner orbitals of the atom [13]. The ejection of an electron in this way destabilizes the electronic structure of the atom and electrons in higher orbitals "fall" into the lower orbital to fill the hole left behind. When this happens, energy is released in the form of a photon and this energy is equal to the energy difference of the two orbitals involved. As a result, the material emits radiation, which has energy characteristic of the atoms present [14]. The term *fluorescence* refers to the phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy (generally lower).

Advantages and Disadvantages of XRF: Some of the advantages of XRF include non-destructive analytical technique; relatively simple spectra line void of many interference; speed and convenience of the procedure which permits multi-element analyses to be completed in few minutes and high accuracy with precision [15]. Some of the disadvantages of XRF include analysis of relatively large spot of sample (typically >1g); difficulty in quantifying elements lighter than sodium; difficulty in distinguishing variations among isotopes of an element or ions of the same elements in different valence state; difficulty in achieving high sensitivity of weak peak when strong one is present and lastly, high cost of instrument [16].

Comparison of XRF and PIXE: The major difference between the two techniques is the mechanism by which the inner shell electron is emitted [17]. In the PIXE technique, protons or sometimes helium ions are accelerated towards the sample and this ejects inner shell electrons. In the XRF technique, high energy x-ray photons are directed at the sample and this ejects the inner shell electrons. Another major difference is the cost of equipment. PIXE requires ion beam equipment which is extremely expensive. This makes PIXE technique far costlier than XRF. The cost of PIXE machine is in the range of millions of dollars while XRF machine is in tens of thousands of dollars [18]. According to [19], it is expected that XRF would be more sensitive than PIXE because of its lower background. This, however, would only be true in the region just above the secondary target K alpha peak. Therefore, XRF is expected to be better than PIXE in analyzing samples for elements within narrow regions of interest [20].

Comparism of Xrf, Pixe and Aas

The two techniques XRF and PIXE utilize the fact that when an electron is ejected from an inner shell of an atom, an electron in a higher shell drops into this lower shell. This results in the emission of an x-ray photon equal in energy to the energy difference between the two shells. On the other hand, AAS technique uses the fact that free electrons are entered by absorption of optical radiation by free atoms in gaseous state. The incitation of the valence electrons causes the emission of energy in the form of visible light as the same electron falls back into the lower, energy orbital (ground state). Both XRF and PIXE can be analysed samples without destroying the sample. Compact XRF can be used to analyze samples in the field without removing the sample from the environmental field. Hence, large samples which do not fit into AAS chamber can be analysed using compact XRF. PIXE analysis has been done on large works of arts without removing even minute samples which would damage them. AAS requires a chamber or vacuum for analysis to take place. The nebulizer sucks up the liquid sample creating a fine aerosol in which the sensitivity of analysis is dependent on the particulate size of droplets [11].

II. Conclusion

These principles of elemental analysis are the backbone of analytical chemistry and therefore enable proper research. While AAS is still a good approach to elemental elucidation, XRF and PIXE are of more recent technology and scientists are encouraged to utilize the technique for multi elemental precision in research analysis.

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