

ADVANCED TECHNIQUES FOR TRACE ELEMENTS CHARACTERISATION OF MATERIALS

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INTRODUCTION

Modern technology uses high purity materials which have to be characterised by measuring impurities at trace levels. For example, properties of semiconductors are influenced by dopants present at parts per trillion (ppt). Nuclear Materials must be free from neutron absorbing elements below parts per million (ppm) or parts per billion (ppb). The distance over which signals can be communicated in an optical fibre depends on its purity. Characterisation of all such materials requires analytical techniques of adequate sensitivity.

An ideal analytical technique should have the following characteristics :

1. **High sensitivity** : Both in absolute and in relative terms. Absolute sensitivity refers to the smallest number of atoms or molecules that can be measured. Relative sensitivity is given in ppm, ppb or even ppt.
2. **High selectivity** : This is necessary to minimize interference from other elements in the matrix
3. **Broad dynamic range** : This will ensure that elements present in different concentrations can be measured in a single run.

4. **Multielement capability** : This is important when several elements are being determined in a given sample.
5. **The speed of analysis or throughput** is important when a large number of samples have to be analysed
6. **A minimum of sample treatment** is preferred as sample treatment is often time-consuming and can introduce errors.
7. **Low cost.**
8. **A minimum of drudgery for the analyst**

The traditional methods used for trace elements determination are Atomic Absorption Spectrophotometry (AAS) and Neutron Activation Analysis (NAA). In flame AAS, the sample is aspirated into a high temperature flame where the elements get atomised. The spectral lines of the analyte element, produced by hollow cathod lamps, are absorbed by the sample in the flame. The measured optical density is then correlated with the concentration of the sample in solution. In graphite furnace AAS, a small sample volume is vaporised and atomised in a graphite cuvette which is heated electrically by a programmed pulse of high current. In view of the small volume of the sample and of the graphite cuvette, the sensitivity of this method is very high and quite adequate for the analysis of biological samples. However, it is a single element technique and hence time-consuming when several elements have to be analysed in a single sample.

NAA is based on the absorption of neutrons by the analyte element to form radioactive isotopes which can be detected by the emitted gamma rays characteristic of a particular isotope. This method has very high sensitivity for some elements and enjoys the

unique advantage that sample processing after neutron irradiation does not cause errors due to contamination. The sensitivity of the method depends on the neutron flux, cross section for neutron absorption and the half-life of the radioisotope. As a consequence, sensitivity of NAA varies widely from element to element. Further, a neutron source like a nuclear reactor, is required.

In this paper, we will discuss some of the newer techniques being used or under development in the author's laboratory. Of these ICP-MS and Nuclear Microprobe will be discussed in detail. These are modern multielement techniques which have many advantages over conventional methods.

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

ICP-MS makes use of the ability of the high temperature argon plasma to ionise almost all elements and that of the mass spectrometer to detect them with high sensitivity and selectivity. The working principle of the ICP-MS can be understood with reference to fig-1 which shows a schematic diagram of the Sciex ICP-MS system, which is in use in our laboratory. Samples introduced as solutions at (1) are sprayed into the ICP with a nebulizer (2). The ICP heats the sample to 7000 K at (3) where the dissolved solids are vaporised atomised and ionised. A fraction of the ions is sampled through a differentially pumped interface (4) and enters the ion optics (5) where ions get collimated. The ion optics incorporates a central stop to reduce photon noise. The ions are then mass analysed by the quadrupole mass spectrometer (6) and detected by the channeltron multiplier (7) used in the pulse counting mode. The detector (7) is kept off axis to further reduce the photon noise.

As the elemental ions formed are mostly singly charged, unit mass resolution attainable throughout the mass range (3 - 300 amu) with a quadrupole mass analyser has been found to be quite adequate. Mass analysis is carried out either by rapid scanning of the

entire or selected mass range (300 ms typical) or peak hopping to the elemental peaks of interest. The scanning and data processing are done by a computer. The spectral output of the ICP-MS consists of a series of isotope peaks corresponding to the natural isotopes of the analyte ions in solution. Quantitation is straight forward through the use of calibration standards or through stable isotope dilution.

Some of the salient features of this techniques are briefly discussed below :

(a) **Low Special Interference :**

Since a given element has only a limited number of isotopes, the mass spectra obtained in ICP-MS are inherently simple. This is in contrast with the ICP-OES spectrum which is very complex on account of the fact that every element can contribute many spectral lines. The background mass spectrum obtained with deionized water consists of the major ion Ar^+ at mass 40 with a number of minor peaks arising from water and entrained air. Above mass 41, the spectrum is relatively clean (except for Ar at mass 80). These background peaks interfere only with a few elements.

(b) **Low Detection limits :**

Undoubtedly the main attraction of the ICP-MS technique lies in the higher elemental sensitivity obtainable with MS detection that is possible with the emission methods. Since the instrumental background noise is uniformly low across the entire mass range (typically 20 counts/sec) and most elements are efficiently ionised in the ICP (1ng/ml of an element gives 10 - 10 counts/sec), impressive detection limits in the range 0.01 to 1 ng/ml are obtained with the ICP-MS. These limits are superior to ICP-OES and somewhat

comparable to the limits attained in electrothermal atomic absorption spectrophotometry (ETAAS). But ICP-MS offers significantly greater convenience and speed and in addition, the capability for multielement determination which are not possible in ETAAS.

(c) ***Large dynamic range :***

In ICP-MS with ion counting measurements the linear dynamic range for most elements is four decades of concentration. The upper limit is determined by pulse pile up in the electron multiplier and associated electronics at count rates of 10 counts/sec.

(d) ***Isotope measurement :***

A major advantage of ICP-MS is the unique capacity for fast isotope ratio determination in solution samples. Precision of isotope ratio measurements is generally in the range of 0.1 - 1% RSD. Multielement isotope dilution technique with stable isotopes is possible with ICP-MS ensuring very good accuracy in the quantitative analysis.

(e) ***Sample introduction methods :***

Generally in ICP-MS, the conventional pneumatic nebulisers are used for the introduction of solution samples. The pneumatic nebulisation approach is simple and convenient but their efficiency is very low (1%). Hence, some other approaches also have been employed for solution samples such as flow injection of microlitre volumes of sample, electrothermal vapourisation from a graphite furnace and chemical conversion of the analyte to a volatile form that can be introduced into the plasma as a vapour for instance the volatile hydrides of metals such as As, Sb, Bi, Sn etc. To analyse solids directly, laser-ablation method has been recently developed.

Application of ICP-MS

ICP-MS has become one of the most advanced multi element techniques for trace element determination. It has been used in characterising nuclear materials, semiconductors and geological as well as biological samples. It has made it possible for us to characterise rare earth samples of 6N purity. In our laboratory we have developed an on-line solvent extraction techniques for the analysis of uranium. We have set up a laser ablation system for analysing solid samples. A laser vapourisation ICP-MS technique recently developed in our laboratory can be used to analyse small volumes of solutions. As part of a national project for prospecting for platinumoid elements, a NiS fire assay method was developed with a sensitivity of ppb levels for geological samples.

ISOTOPE DILUTION ANALYSIS (IDA)

In trace analysis, as in all physical measurements one is concerned about systematic errors which affects the accuracy of measurement. Isotope dilution analysis is considered an absolute method as it is unaffected by sample treatments. Here a known amount of an enriched isotope (spike) of the analyte element is added to the sample, and the change in isotopic abundance is measured. From isotope ratios and the quantity of spike, one calculates the concentration of the analyte in the sample. Thermal ionisation mass spectrometry has been traditionally used for IDA but it is time consuming and costly. ICP-MS provides a simpler and faster alternative because of its capability to measure isotope abundances with good precision.

An example of isotope dilution analysis is the determination of uranium, plutonium and neodymium in irradiated reactor fuels. Here

good accuracy is obtained in difficult measurements because the isotopic composition does not change under chemical processing necessary to remove most of the radioactivity. IDA has become easier and more widely applicable with the advent of ICP-MS.

Laser Ablation ICP-MS

In most atomic spectroscopic applications, sample preparation time may exceed analysis time by up to 20 times. For example, the digestion of biological materials generally takes several hours. Materials used in the electronics industry such as silicon are not only difficult to dissolve but also get contaminated in the process of dissolution. There has been considerable interest in recent years in reducing sample preparation time by the use of solid sampling techniques. These approaches have additional advantages when the sample is difficult, hazardous or tedious to digest, when errors via contamination, losses or increased dissolved solids (via fusion) may arise during solubilisation. One of the most promising approaches to solid sampling is by the use of laser-ablation. A laser beam focussed on to the sample helps to vaporise the sample, and the vapour is transported to the ICP-MS by a carrier gas. With the availability of NBS reference materials this technique could be standardised and conveniently applied for accurate routine determinations realising high sample throughput. An LA-ICP MS facility has been set up in our laboratory.

Nuclear Microprobe

The Nuclear Microprobe is a recent technique which was originally developed for the study of nuclear materials but currently finding much application in bio-medical and geological sciences. It uses a focused beam of a charged particle (usually proton or deuteron) as a probe and measures the radiations produced as a result of nuclear

reactions. Both elemental concentrations and their distribution within, say, a cell can be obtained. The combination of nuclear reaction analysis (NRA) particle induced X-ray emission analysis (PIXE) and Rutherford back-scattering analysis (RBS) in a single equipment provides the user with flexibility to choose the technique required for a specific application. The recent development of scanning transmission ion microscopy with nanometer resolution has made the nuclear microprobe the surface analytical technique of the decade.

The microprobe essentially needs the accelerator to give an ion beam of MeV energy. The beam is focussed using a focussing lens system after being defined by an object slit. The ion beam of micron dimension is scanned over the sample by mechanically moving the sample with a micro-positioner or raster scanning by deflecting the beam. The residence time of the beam on the sample is normalised with respect to incident ion charge. Charged particle induced emissions like X-rays (PIXE), particles from nuclear reactions (NRA) and backscattered particles (RRS) are detected with appropriate detectors. By deconvoluting the spectra, information on analyte concentration at each point can be arrived at and thus the spatial profile. A nuclear microprobe is under development in our laboratory. Incorporation of raster scanning to the system would make it suitable for bio-medical studies also. PIXE and RBS which can quantitatively analyse medium and high atomic number elements non-destructively with good spatial resolution can be adapted for a wide range of applications.

Surface Analysis by Laser Ionisation (SALI) is another technique under development in our laboratory. This is complementary to other surface analysis techniques like electron probe micro analysis (EPMA) and secondary ion mass spectrometry (SIMS).

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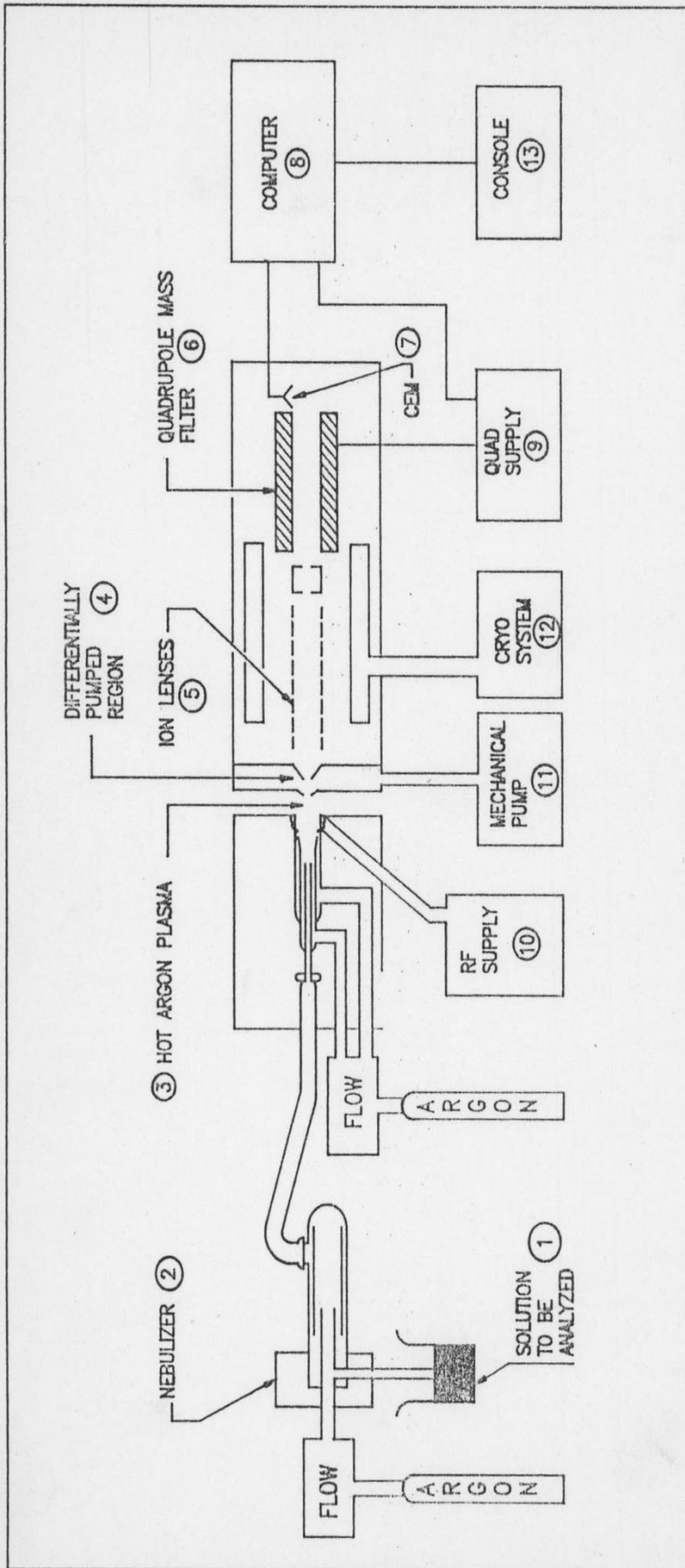


FIG.1. Schematic diagram of ICP-MS