INDUCTIVELY COUPLED PLASMA SPECTROMETER : APPLICATIONS IN ENVIRONMENTAL ANALYSIS

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INTRODUCTION

Much of what we know about the fundamental nature of matter can be related, either directly or indirectly, to some form of spectroscopic observation. The discovery of quantum theory for example, is a direct consequence of spectroscopic observation. In the area of chemical analysis, spectroscopic measurements have been used for qualitative and quantitative analysis at both trace and ultratrace levels. As a result of the wide application of spectroscopic data, the techniques and principles of experimental spectroscopy are of interest to a wide variety of research workers.

To an analyst various kinds of spectroscopic tools are available for qualitative and quantitative analysis. The best possible technique as Slavin^[1] suggests is the method which can solve practical analytical problems. Selection of the appropriate spectroscopic approach for a given study is by no means a trivial problem and depends ultimately on a thorough understanding of the principles of spectroscopy and a knowledge of advantages and limitations of various spectroscopic methods.

The four primary goals of research in experimental spectroscopy are as follows :

- 1. Improved resolution
- 2. Improved sensitivity
 - a) Increased spectrometer efficiency
 - b) Employment of more sensitive detectors
- 3. Increased rate of information transmission
- 4. Development of improved spectral sources * Scientist, National Metallurgical Laboratory, Jamshedpur-831007

The first modern attempt at producing a stable spectroscopic source was the revival of the conventional Lundergardh burners of 1930 by Sir Allan Walsh in 1955 and independently by C.T.J. Alkemade and J.M.W. Milatz to propose a method based on the flame as an atom reservoir rather than an excitation source as in the flame photometry. The method was based on the atomic absorption properties of atoms that had been observed by Fraunhofer over 100 years earlier. Today it is known as Atomic Absorption Spectrophotometry (AAS).

In spite of the stupendous success of the flame atomic absorption, it was soon discovered that ordinary air-acelyene flame used as an atom reservoir did not, in many cases, supply enough energy to completely atomize all samples. Various investigations were looking for alternative hotter flames such s nitrous oxide-acetylene flame. At the same time some investigators were studying the use of various electrical discharges in place of flame. Wendt & Fassel^[2] ultimately developed inductively coupled plasma (ICP) as an emission source. Because of the high temperature of the ICP, the interferences caused by incomplete sample vaporization were virtually eliminated. In their place, however, was the increased likelihood of spectral interferences. This again led to renewed search for detection systems with high resolution. Another advantage of ICP was the ability to excite large number of elements simultaneously that would make multi-element analysis possible.

PRINCIPLE OF ICP GENERATION

Basic Set-up

Figure-1 shows a schematic diagram of three concentric tubes, called outer tube, intermediate tube and inner tube, most frequently



made of silica is used for operating an ICP. The assembly of tubes, called torch is set up in a water cooled coil of an rf generator. Plasma is formed when a gas made electrically conductive by Tesla spark, flows through an rf coil with sufficiently high magnetic field strength. The inductively coupled plasma thus informed, is maintained by heating of the flowing gas in a way similar to the inductive heating of a metallic cylinder placed in the induction coil. The rf currents flowing in the coil generate magnetic field with lines of force axially oriented inside the coil. This induced magnetic field generates high frequency, annular electric currents in the conductor, which is then heated as a result of its ohmic resistance. When the conductor is a flowing gas, a confining tube is needed to prevent it from extending to the coil resulting in a short circuiting. Also a gas should be made to flow so that a thin sheath of cold gas separates the plasma in order to prevent it from melting of the confining tube. The thermal isolation of plasma can be achieved by Reed's^[3] vortex stabilization technique using a tangentially introduced gas flow as

shows in fig.1. For this reason the over gas flow was originally termed as coolant gas flow. But presently it is termed as 'outer gas'. Through the intermediate tube flow intermediate gas and the gas flowing through the innertube is called 'carrier gas' because this gas is used to carry sample to the plasma. Tangential gas flow as proposed by Reed also helped to produce a low-pressure area at the centre of the flame and a stream of gas with relatively small cross-section could 'bore' a hole without disturbing the stability of the plasma. Thus the problem of introducing sample was elegantly overcome.

The plasma flame can be divided into three distinct zones.

- 1. The core fills the region inside the coil and extends few millimetre below and above the coil. The non-transparent core emits an intense continuum and the spectrum of hydrogen and neutral argon.
- 2. Above the coil the core become conical, 'flame-like'. It is bright but slightly transparent. In argon ICP the transition region between the core and this second zone is the best region for analytical observation. Since it yields the highest signal to background ratio (SBR). The region, located 10-20 mm above the coil yields best detection limit.
- 3. The third region of an ICP is the tail flame, which is hardly visible when pure water is nebulized but assumes typical colours as observed in flames when aerosols are injected into the plasma.

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Line selection & Spectral Interference

More than a century ago Harttey ^[4] was the first to investigate systematically the relationship between the concentration of an element and the behavior of its spectral lines using solutions that were excited. Many investigators^[5-6] have worked and prepared comprehensive lists of analysis line for the ICP with appropriate intensity informations. Fassels group ^[7-8] has published a list of 973 prominent lines with estimated detection limits. Recently Boumans^[9] published a list of 350 'most prominent lines' of 64 elements (at least 4 lines per element) as observed with a high resolution spectrometer.

But in actual analysis the limitations upon the use of a particular line Stem from either constraints imposed by the apparatus or by way of spectral interferences originating from the concomitants of the sample.

Apparatus constraints are the spectral range of the instrumentgeometrical and mechanical constraints that limit the minimum distance between spectral lines and the maximum number of lines within a given spectral interval.

The spectral range of a spectrometer depends on the overall optical design, the blaze of the grating, the spectral response characteristic of the detector and the atmosphere in the optical path.

Using a high resolution echelle monochromator Botto^[10] studied the interference of 33 elements upon 22 analysis line and obtained a reduction of 74-99% reduction in critical interferences.

Although the detection limits for ICP reported in most of the literature make it quite altractive for the analysis of pollutants which are normally present from trace to ultra-trace levels. But the picture is idealized in that it refers to pure aqueous, single element solutions. For real samples two points must be considered. First the compromise operating conditions for multielement analysis may require adaptations to minimize specific multiplicative interferences, and this may change detection limits. The second point, however is most important because the picture may be substantially distorted by spectral interferences from major elements. This will worsen the detection limits further. Thus the background signal in the spectral windows of an analysis will appreciably depend upon the sample composition and instrumental operating condition. And as the spectra of the sample is superimposed in the ICP background signal it is important to subtract the correct background from the net signal.

It might appear from the literature that there exists a variety of approaches to background correction but the correction procedures are still governed by the rules of common sense and operator's experience. Basically all the correction techniques reported in the literature are based on the visual inspection of wavelength scans of the samples, standards and blanks to make a judicious choice of the wavelength at which the background is measured.

In our laboratory, we generally take recourse to one of the three methods to get to a true value.

 Addition of levelling reagents : All interferences are removed by adding releasing agents so that net signal is free from any interferences.

- 2) Background equivalent determination : In this method the background equivalents of the different concomitants are determined at the analyte wavelength and the total background equivalent is subtracted from the net signal to arrive at the true signal intensity.
- 3) Computational elimination of interferences : The total effect of the interferents on the analyste signal may be approximated as the sum of 'translational and rotational effect. The translational effect (the background) is independent of analyte concentration and depends only on the interferent concentration. The rotational effect (chemical interference) is a function of both analyte and concomitant concentration. Mathematically it can be represented as

Ya = Yt (1+AX) + BX

Where Ya & Yt are apparent and true analyte concentrations respectively X is the interferent concentration and A & B are the characteristic co-efficients representing the binary analyte-concomitant pair under consideration. Once the A and B are determined either by graphical method or by multivariate linear regression analysis it is very easy to compute the Yt value, free from interference.

Analysis of environmental materials by ICPS

The category of environmental materials includes air, plant material, animal tissue, domestic dust, road dust, industrial and domestic refuse, sewage sludge, water, sediment and soil. All the materials are at present analysed by AAS for their heavy metal contents. The analysts are taking the advantage of multi-element capacity of ICPS to increase the scope of the scan and thus avoid the possibility of overlooking an unsuspected irregularity. In the AAS method two sensitivity enhancing techniques (i) Hydride generation and (ii) Electro thermal vaporization have been adopted for the determination of low level trace analysis. Of the two techniques Hydride generation technique has been shown to be compatible for ICPS as well. However, this method is limited to a small number of elements. On the other hand Electrothermal vaporization which is very effectively used with AAS is not compatible with ICPS. Thus a lot of research is going on to develop heavy metal preconcentration methods compatible with the ICPS.

Air analysis

Air analysis is a very broad topic. ICPS has not so far been widely used in air quality studies. But with the advancements of the technique even air analysis is being done by ICPS. Air samples can be classified into two categories (i) volatile components and (ii) particulate component

Volatile component

Volatile components dispersed in the gas phase can be chemisorbed in a reagent. The reagent is dissolved and aspirated into the ICPS for determination. Elements prone to form volatile compounds includes boron, silicon, germanium, tin, lead, nitrogen, phosphorus, and iodire. All these elements can be readily determined by ICP. No evidence to speciation, however, is possible. But from the screening power of ICPS it is very much possible to put a maximum possible ceiling level of the element.

Particulate component

The analysis of particulate material by ICPS is considerably more promising than that of volatile component. Particulate matters from the air can be collected from air by filters, impingers, gravity settling and electrostatic precipitators, but of these methods filtration is probably the simplest and surprisingly, the most effective. The filter membranes are normally dissolved in oxidizing acids and aspirated to ICPS.

The potential effectiveness of a simple approach just described can be seen from the Table-1. The table is constructed by imagining a practical situation where particles from 1m³ of air sample is collected and leached into 10 ml solution. As an index of usefulness, the detection limit is compared with the threshold limit values (TLV) for a normal 8 hours day per week as adopted by American conference of Governmental Industrial Hygienists, 1977. It can be seen without exception that TLV's exceed detection limits at least by two orders of magnitude.

Table - 1

Analyte	TLV (µg m-3)	D.L. (µg/10ml)	TLV - D.L.
Ag	10	0.1	100
As	500	0.5	1000
Ba(Soluble)	500	0.01	50000
Be	2	0.005	400
Cd	50	0.02	2500
Cr(VI)	50	0.01	500
Cu	1000	0.05	20000
Fe	5000	0.05	100000
Hg	50	0.05	1000
Mn	5000	0.02	250000
Мо	5000	0.1	50000
Ni(soluble)	100	0.3	330
Pb	150	0.5	300
Se	200	1.0	200
Sn	2000	0.5	4000
Те	100	1.0	100
U	200	2.0	100
v	50	0.08	600
Zr	5000	0.08	60000

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Sewage sludge

Sewage sludge often contains relatively high concentrations of heavy metals mostly as a result of industrial input into the sewage system. The metal content is important because of the environmental impact produced by the disposal of the sludge. The concentrations of copper, lead, zinc and cadmium are mostly required in sludge analysis as uncontrolled dumping over a long period can raise the contents of these elements in soil to bring about toxic disorders in crops and livestock.

Generally the sludge samples are digested by aqua regia or nitric acid alone. In some methods, digestion is by preceded by dry ashing. Levels of metals which can be expected in a typical dried sewage sludges are as follows (μ g.g⁻¹): Cu, 400-1000; Pb, 300-1000; Zn 400-2000; Cd. 2-30; Cr; 20-400; Ni, 10-100.

Domestic & industrial refuse

Domestic and trade refuse is familiar enough to need any detailed description to emphasize its heterogeneity. The element of primary interest are the common toxic metals such as copper, lead, zinc, cadmium, mercury, nickel, chromium, silver, beryllium and arsenic. ICPS can be very effectively used for the analysis of such samples especially for beryllium and chromium.

Samples are generally solubilized by strong mineral acids or their mixtures. Typical concentration ranges which may be expected are as follows :

(μg.g⁻¹) Be, O-5; Ba, 20-400; V, 20-100; Mo, 0.5-20; Cr, 30-200; Cu, 50-500; Ag, 0-20; Zn, 50-750; Cd, 0-20; Pb, 50-100; and Fe, 1-10% (m/m)

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