Lecture No. 5

INDUCTIVELY COUPLED PLASMA SPECTROMETRY

by

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INTRODUCTION TO ATOMIC EMISSION SPECTROMETRY

Optical Emission Spectra are observed by dispersing the radiation according to wavelength so that photons of different frequency (ν) appear in the focal plane of a spectroscopic apparatus as an array of monochromatic images of the entrance slit. These images are characterised by their wavelengths (λ) and called spectral lines.

The excitation sources primarily used in the OES are the following:

1. DC or AC arcs
2. High, medium or low voltage sparks
3. Glow discharges with flat or hollow cathodes
4. Lasers
5. Flames
6. Inductively Coupled Plasmas (ICP)
7. Direct Current Plasmas (DCP)
8. Capacitively Coupled Microwave Plasmas (CMP)
9. Microwave Induced Plasmas (MIP)
10. Furnaces
11. Exploding wire or foils

In OES the source not only furnishes the energy for the atomization of the sample but also for the excitation of the free atoms and ions of the elements to be determined.

Solid, liquid and gaseous samples must be brought into a form so that they can be readily evaporated and atomized by interacting with the hot gases in the source. Proper control of the step 'sample introduction' is vital so that the composition of the gas in the source will unambignously represent the sample composition. Only then will the spectrum provide a picture from which quantitative analytical information can be derived.

Sources (1) to (3) and (6) to (9) are electrical gas discharges, at atmospheric or reduced pressure, in which gas is energized by an electric current.

Sample introduction is the most troublesome part of emission spectroscopic analysis. The difficulty is demonstrated not only by the wide diversity of sample introduction technique but also by the large variety of excitation sources.

An element (M) of a sample will be present in an excitation source in the form of diatomic oxide molecule (MO), neutral atom (MI), singly changed ions (MII), doubly charged ions (MIII) and so on. One or two types of species will predominate depending upon the spectrochemical condition of the source. For example in a DC arc it will be mainly neutral atom alongwith some singly charged ions whereas, in a spark at atmospheric pressure or in ICP it is just about reverse.

Quantitative analysis uses an empirical relationship between intensity of a spectral line and its concentration in the sample: a calibration curve. This approach is necessary as the relationship between intensity and concentration cannot be calculated with sufficient accuracy and OES is, therefore, not an absolute method. The intensity of a

spectral line I_{qp} corresponding to a transition between q and p levels is given by

$$I_{qp} = \frac{1}{4\pi} A_{qp} \, n_{xq} \, h \quad qp$$

where A_{qp} is the transition probability

n_{xq} is the population of the upper level of the transition (concentrator in the source)

For a source in local thermal equilibrium (LTE) n_{xq} is related to the concentration of species by the Boltzmann equation

$$n_{xq} = \frac{n_x \, g_q \, \exp \, (-E_q/kT)}{Z_x \, (T)}$$

E_q is the excitation energy (eV) or potential (V) of level q, g_q is the statistical weight level q, T is absolute temp (K), Z_x the partition function of species and k the Boltzmann constant.

Since the relative concentration of the species originating from an element may vary drastically from a source to another, the sets of most sensitive lines will also vary accordingly. Thus in an arc source where neutral atoms prevail atomic lines will be the most sensitive whereas in sources like spark and ICP the ionic lines of many elements will be most sensitive. The other parameters on which the sensitivity depends are the temperature and gaseous atmosphere and types of process that govern dissociation, ionization, recombination etc.

Generally speaking, the most sensitive lines of neutral atoms and singly charged ions of the majority of chemical elements have wavelengths in the region between 160 nm and 600 nm, the in exception being,

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$\lambda < 120$ nm   Ar,F,H,He,Ne
120 nm $< \lambda <$ 190 nm   Br,C,Cl,I,N,O,P,S,Xe
600 nm $< \lambda$ Ca,K,Li,Rb,Rn

The wavelength range accessible with a particular spectrometer depends on the type of blazing of the grating, the geometry of the instrument, the type(s) of detector (usually one or more PMTs) and the gaseous atmosphere in the path of the light.

Multielement capability is inherent in OES technique using an excitation source of sufficiently high temp > 5000 K so that atomic and ionic species dominate. Suitable analysis lines can then be found for elements having widely different ionization potentials and being present at widely different concentrations. For alkali metals, however, a temperature of 5000 K is too high; they are ionized to a large degree so that atomic lines are weak, whereas ionic line emission is absent or negligible as alkali ions behave as noble gases.

A penalty of the multielement capability of OES is the problem of line coincidence, which may cause severe troubles in trace analysis of sample whose major constituents have line rich spectra (e.g Fe,Ni,Co,Cr,Mn,Nb,Ta,Mo,V,W,Sc,Y,Zr, La, rare-earths, platinum metals, Th and U). Spectroscopic equipment with high resolution (band width $\approx$ 0.01 nm) is then often required.

QUANTITATIVE ANALYSIS: CALIBRATION AND INTERFERENCE

Quantitative analysis is based on an empirical relationship between the signal intensity (x) and the concentration of the analyte in the sample. The most frequently used form of the calibration function is the Scheibe-Lomakin equation

$$A = SC^n \qquad \qquad .. \quad (1)$$

where ideally n = 1, departures in both direction i.e n < 1 or n > 1 occur, the former being the more easily explained due to self-absorption or self reversal. Other factors like data reduction using incorrect emulsion calibration constant (photographic), the use of too large or too small background original in the determination of the net signal contribute to make n depart from unity. However, for a small concentration range,

$$\varkappa_A = S.C \qquad \qquad .. \quad (2)$$

S represents the sensitivity which is generally defined as the derivative

$$S = \frac{d\varkappa_A}{dC}$$

If the calibration covers more than one order of magnitude in concentration then a least square fit based on the logarithmic form of equation (1) is statistically more correct approach

$$\log \varkappa_A = n \log C + \log S \qquad \qquad .. \quad (3)$$

The large dynamic range of ICP-OES generally permit the use of both calibration function as in equation (2) and (3). Whereas in sparc excitation source a complex calibration function, such as polynomials, may be indispensable.

Multi Component System

In a system of n components we can expect that in principle the sensitivity of an analysis signal of any one component also depends on the concentration of the n-1 other

components, while n-1 other components may also contribute additively by spectral interference. Thus the signal measured at wavelength 1 (= analysis of component 1) can be written as,

$$\mathfrak{X}_1 = S_{11} (C_2, C_3, \ldots C_n)C_1 + S_{12}C_2 + S_{13}C_3 \ldots S_{1n}C_n$$

where first index of S refers to the wavelength at which measurement is made and the second index to the component that contribute. For example S_{12} is the sensitivity of the signal measured at wavelength 1 for the component 2.

Similarly for wavelengths 2 and n we have,

$$\mathfrak{X}_2 = S_{21}C_1 + S_{22}(C_1, C_3 \ldots C_n)C_2 + S_{23}C_3 \ldots S_{2n}C_n$$

$$X_n = Sn_1 C_1 + Sn_2 C_2 \ldots + S_{nn}(C_1, C_2 \ldots C_{n-1})C_n$$

If one analysis line is used for each component, there exist n equations with n^2 coefficients, which can be determined, for example, by multiple additions if certain conditions are fulfilled, such as the absence of multiplicative interferences (all S_{ii} constant). Then it is possible to determine the corrected concentration of all n components as a sum from the reversed set of equation having the form,

$$C_i = \sum_{j=1}^{j=n} \alpha_{ij} \mathfrak{X}_j$$

where C_i is concentration of i th analyte and the summation over index j extends over all components (= analytes) including analyte i.

For polychromators, a variety of procedures for handling calibrations and interferences corrections for multi

component analyses have been devised. Such procedures are implemented in the manufacturer's software available with the instrument.

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. A plasma is formed when a gas made electrically conductive by Tesla spark, flows through an rf coil with suffi-ciently high magnetic field strength. The inductively coupled plasma thus formed, is maintained by heating of the flowing gas in a way similar to
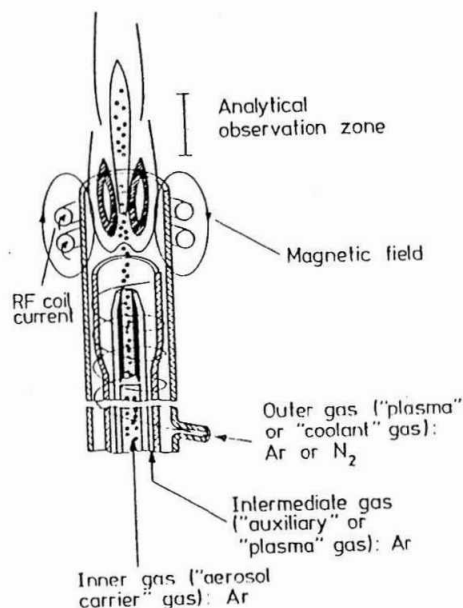
Figure 1

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[1] vortex stabilization
technique using a tangentially introduced gas flow as shown
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 intertube 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).
     This 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 of metals are injected into the plasma.

Parameters to be Optimized

For the defined ICP system six parameters have to be optimized:

1. Power input P (kW)
2. Carrier gas flow Fc (L/min)
3. Observation height h (nm)
4. Outer gas flow Fo (L/min)
5. Intermediate gas flow Fi (L/min)
6. Sample solution feed rate Fs (ml/min)

For a given ICP configuration (generator, coil, torch) the outer gas flow has a lower limit. Too low a flow may result in overheating of the outer tube and consequent destruction of the torch, or in extinction of the plasma. For economic reasons one will work not too far above the lower limit more so since effect of outer gas flow on analytical performance is small. Only in the case of organic solvents it plays an important point (higher Fo is recommended) but it is actually related to the higher power.

The intermediate gas may be omitted with aqueous solutions containing inorganic matter only, but is indispensable to prevent carbon deposits in the torch when organic materials are analysed.

The carrier gas flow is not only a very critical parameter of the ICP but also a nebulizer parameter that governs the amount of aerosol carried to the plasma. The changes in spectral line intensities with the carrier gas flow will reflect the changes in both the aerosol flow and plasma characteristics upto the point where the nebulizer

reaches its saturation level. Frequently this point is at least closely approached when the carrier gas flow is optimum for the ICP i.e the optimum F_c is dominated by the plasma rather than the nebulizer.

Observation height is usually defined as the distance from the centre of the observation zone to the top of the coil. The observation zone is commonly 4-6 mm high and generally starts from 10 mm above the coil.

The sample feed rate depends on the nebulizer, the physical properties (viscosity, surface tension, density) and chemical nature (organic, inorganic) of the sample. For ultrasonic nebulizer salt concentration of upto 1 mg/ml produce negligbly small interference. In case of pneumatic nebulizer five or ten times salt concentration yield negligible interference.

Both net signal as well background increase with power. However signal has been observed to rise more rapidly with power than net signal. Therefore, the highest SBR is found at the lower end of the power range. There is, however, a lower practical limit dictated by plasma stability. A safe minimum power is about 1.1 kW.

RULES FOR THE SELECTION OF COMPROMISE CONDITIONS IN ARGON I.C.P

1. Power, carrier gas flow and observation heights have to be optimised to achieve a high detection power and low interference level. Departing from the optimum working point rapidly worsens either the detection limits (higher power) or interference level (higher carrier gas flow or 'observation' height), or both (lower observation height). Too low a carrier gas flow limits the aerosol flow.

2. Optimum parameters differ somewhat from system to system and if a component in the existing system is modified, this will require reoptimisation of the parameter setting.

3. An optimum working point can be rapidly found by observing (a) SBR variations for single hard line (MnII 257.6 nm) optimize the detection power and (b) the magnitude of the interference effect of KCl for a few soft and hard lines (e.g LiI 670.7, BaI 553.5 ZnI 213.9 and MnII 257.6 nm) to minimize the interference[2].

    ° Power: The lowest possible power is chosen to get a stable plasma. Generally around 1 kW.

    ° Carrier gas flow: Having fixed the power, an observation zone of approx 5 mm in height which is located at 15 mm above the coil is chosen. The carrier gas flow is varied while observing the SBR at MnII 257.6 mm.

    ° Observation height: The matrix effect of 10 mg/ml of KCl on net signal is observed for a few soft and hard lines within a range of ± 2-3 mm from 15 mm height.

    ° Final adjustment: Carrier gas flow may be re-adjusted to minimize the matrix affect of KCl.

Optimum operating conditions used in a typical argon ICP for three group of samples

Parameter	Aq.solutions with inorga- nic matter	Aq. solutions with inorganic & organic matter	Organic solvents (MIBK)
Power (kW)	1.1	1.1	1.7
Outergas flow (L/min)	14	14	18
Intermediate gas flow (L/min)	0.2-1.0	0.7-1.0	0.9-1.0
Carrier gas flow (L/min)	1.0	0.9	0.8
Observation height (mm)	15	15	15
Sample feed rate (ml/min)	1.4	1.4	1.4

Torches for Inductively Coupled Plasmas

The torch is the most critical component of the ICP assembly as it dictates the flow pattern of the gas stream in the ICP. The torch has to be designed to provide an optimum answer to the following performance parameters:

1. Easy ignition of the plasma.
2. Continuous, stable plasma with minimum influence of the injected samples.
3. A sufficiently high sample flow through the plasma tunnel to the observation zone.
4. An optimum sample heating efficiency by a long residence time of the sample in the plasma.
5. A low gas consumption rate.
6. Minimal power requirements to reduce size and cost of the rf power supply.

Allemond and Barnes[3] studied torch design and torch shapes experimentally and by computer simulations involving power input, gas velocity and temperature distribution. Thirty different torches resulting from the combination of two different outer tubes, five different intermediate tubes and three different inner tubes were evaluated. The studies indicated that (i) ignition was facilitated by a reverse flow produced by a venturi effect resulting from a suction hole in the intermediate tube (ii) argon composition could be drastically reduced by careful torch design (iii) the torch with the lowest flow rate showed the best sample confinement.

For routine, multielement work one generally prefers a torch with prealigned tubes as developed by Fassel[4]. In contrast, demountable torches are convenient in research. A demountable torch consists of a torch base into which separate tubes can be fitted and aligned. Separate tubes can

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be easily replaced in case of failure. Other special purpose torches include extended torches, torches with purged side arms to enable plasma radiation in the VUV region to be viewed and torches for operation at reduced pressure.

Influence of the rf on the Spectral Characteristics of Conventional ICPs

Capelle et.al[5] studied the effect of rf frequency on spectral characteristics of argon ICPs. Generators from various manufacturers were used which covered frequencies of 5,27,40,50 and 56 MH_z. The studies revealed:

(1) Both the excitation temperature and the electron number density were found to decrease with increasing frequency.

(2) As a result of (1) both net line intensities and the argon continuum decreased with increasing frequency. However, the lowering of argon continuum intensity exceeded that of the line intensities so that there remained a net gain in SBR when frequency was increased.

(3) Detection limits obtained with a 40 MH_z ICP were much better than those found with 5 MH_z ICP.

(4) The change in frequency from 27 to 56 MH_z did not affect the level of ionization and atomization interferences, which remained low.

Sample Introduction Techniques in ICP-OES

A wide variety of sample introduction devices is used in ICP-OES in order to generate an argon-aerosol mixture from samples of varying nature, form and size.

Pneumatic nabulization is of prime importance for the analysis of liquids. Pneumatic nebulizers used in flame AAS had to be tailored to the requirements of an ICP-OES. Electrothermal atomization devices (carbon rod, tantalum filament, and graphite furnace systems) are useful for analysis of micro samples and are similar to those used in AAS work. Evolution techniques such as hydride generation technique allow to increase the aerosol generation efficiency is also widely used. Despite the fact that the prime merits of ICP-OES lies in the multielements trace analysis of solutions, the direct analysis of solids with ICP-OES is possible. For special problems such as samples which are difficult to dissolve, direct solid nebulization with aid of laser, ark or spark may be useful.

Pneumatic Nebulizers

Several types of nebulizers are used in ICP-OES:

    1.   The concentric nebulizer
    2.   The cross flow nebulizer
    3.   The Babington nebulizer
    4.   The fritted dige nebulizer

Their operation principle is illustrated in Fig.2. In all devices, the sample solution is fed to the nebulizer by forced feed (e.g, with a pump) or aspiration resulting from
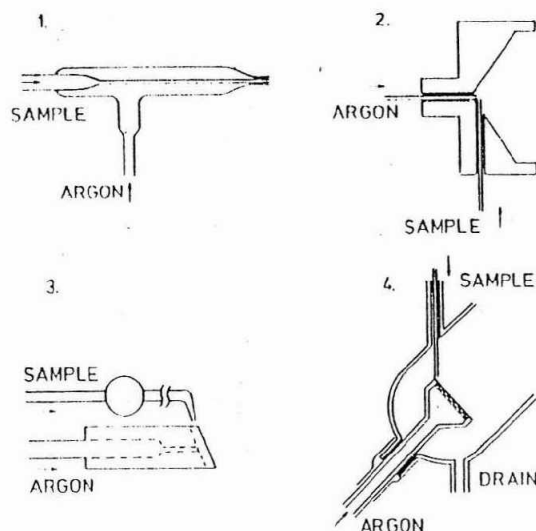
SAMPLE INTRODUCTION TECHNIQUES IN ICP-AES

Figure .2. Types of pneumatic nebulizers: 1, concentric glass nebulizer; 2, cross flow nebulizer; 3, Babington nebulizer; and 4, fritted disc nebulizer.

the venturi effect i.e the effect causing a reduced pressure at the nozzle. The solution is split into droplets under the influence of a high speed gas flow which also acts as a transport gas. Only a small portion of the introduced liquid is nebulized and the larger droplets are sorted out in the spray chamber and flows off to a waste.

Pumps (Peristaltic pumps) are indispensable for cross flow, Babington and fritted disc nebulizers. It may be proved to be advantageous even with a concentric nebulizer because it ensures stable sample uptake and reduces the nebulization effect arising from samples of various viscosity.

The concentric nebulizer or a cross flow nebulizer is adequate for most analytical application. The Babington nebulizer certainly has advantages for the analysis of suspensions and solutions with high solid contents.

To conclude, ICP technique offers following advantages:

° Flexibility in selection of elements without requiring numerous hollow cathode lamps. A decision to determine any element may be made even during the analytical cycle.

° Only one sample preparation for the determination of major and trace elements. The linear dynamic range of the ICP is in order of 10^5 to 10^6, therefore, dilutions can be avoided.

° Enhanced detection limits for many elements, in particular refractory and rare-earths.

° With multielement capability an appreciable reduction in analysis costs.

REFERENCES

1. T.B.Reed: J.Appl.Phys., 32, 821 (1961)

2. P.W.J.M.Boumans and M.Ch.Lux-Steiner: Spectrochim Acta, 36B, 97 (1982).

3. C.D.Allemond and R.M.Barres: Appl.Spectroscopy, 31, 434 (1977).

4. A.Montaser and V.A.Fassel: Anal.Chem., 48, 1492 (1976).

5. B.Capelle, J.M.Mermet and J.Robin: Appl.Spectrosc., 36, 102 (1982).