

Lecture No. 4

ATOMIC ABSORPTION SPECTROPHOTOMETRY
- PRESENT AND FUTURE

by

Dr. Chandra Sekhar, K, Scientist, N.M.L.

ATOMIC ABSORPTION SPECTROMETRY - PRESENT AND FUTURE

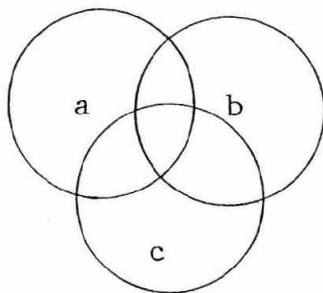
Dr. Chandra Sekhar K
Scientist
Analytical Chemistry Division
National Metallurgical Laboratory
Jamshedpur 831007

INTRODUCTION

The development of analytical chemistry methods is mainly prompted by three aims:

- (a) an improvement of the power of detection,
- (b) increase in analytical reliability in terms of freedom from systematic errors and optimal analytical precision,
- (c) and cost reduction.

These three aims are linked in a dynamic way:



To become competitive any analytical method must meet the following requirements:

- * High sensitivity
- * Best selectivity
- * Good accuracy
- * Rapidity of obtaining the analytical information

HISTORICAL

Spectroscopy is generally considered to have started in 1666, with **Newton's** discovery of the solar spectrum. **Wollaston** repeated Newton's experiment and in 1802 reported that the sun's spectrum was intersected by a number of dark lines. **Fraunhofer** investigated these lines - Fraunhofer lines - further, and in 1823 was able to measure their wavelengths.

Early workers had noted the colours imparted to diffusion flames of alcohol by metallic salts, but detailed study of these colours awaited the development of the premixed air-coal gas flame by **Bunsen**. In 1859, **Kirchoff** showed that these colours arose from line spectra due to elements and not compounds. He also showed that their wavelengths corresponds to those of the Fraunhofer lines. **Kirchoff** and **Fraunhofer** had been observing atomic emission and atomic absorption, respectively.

Atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES) and later atomic fluorescence spectroscopy (AFS) then became more associated with an exciting period in astronomy and fundamental atomic physics. Atomic emission spectroscopy (AES) was the first to re-enter the field of analytical chemistry, initially in arc and spark spectrography and then through the work of **Lunegardh**, who in 1928 demonstrated AES in an air-acetylene flame using a pneumatic nebulizer. He applied this system to agricultural analysis.

Atomic absorption spectroscopy is the term when the radiation absorbed by atoms is measured. The application of AAS to analytical problems was considerably delayed because of the apparent need for very high resolution to make quantitative measurements. Apart from two specialized applications

the identification of some elements in stellar atmospheres and the detection of mercury vapour in laboratory atmospheres, the real potential of atomic absorption was not realized. In 1953, **Walsh** brilliantly overcame this obstacle by use of a line source, an idea pursued independently by **Alkemade**, his work being published in 1955. After a few more years of general unconcern, progress became meteoric. Improved instrumentation, more reliable sources of resonance radiation, hotter flames and non-flame atomizers have enabled the technique to be extended to nearly every metallic element in the periodic table. What was thought of as an intriguing method for determining some trace elements is now used in wider concentration ranges with accuracies that compare well with most other accepted techniques.

THEORY

Atomic absorption follows an exponential relationship between the intensity I of transmitted light and the absorption path length l , which is similar to **Lambert's** law in molecular spectroscopy:

$$I = I_0 \exp(-k_{\nu} l) \quad \dots (1)$$

where I_0 is the intensity of the incident light beam and k_{ν} is the absorption coefficient at the frequency ν . In quantitative spectroscopy, absorbance A is defined by:

$$A = \log(I_0/I) \quad \dots (2)$$

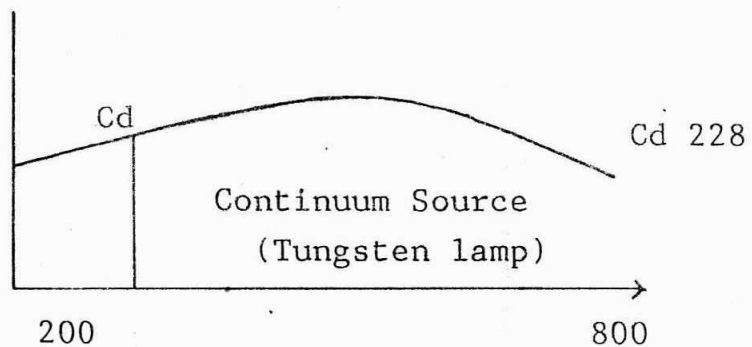
Thus, from equation (1) we obtain the linear relationship

$$\begin{aligned} A &= k_{\nu} l \log e \\ &= 0.4343 k_{\nu} l \end{aligned}$$

From classical dispersion theory k_{ν} is in practical terms proportional to the number of atoms per cubic centimetre in the flame, i.e, A is proportional to analyte concentration.

Atomic absorption corresponds to transitions from low to higher energy states. Therefore, the degree of absorption depends on the population of the lower level. When thermodynamic equilibrium prevails, the population of a given level is determined by Boltzmann's law. As the population of the excited levels is generally very small compared with that of the ground state (that is, the lowest energy state peculiar to the atom), absorption is greatest in lines resulting from transitions from the ground state; these lines are called resonance lines.

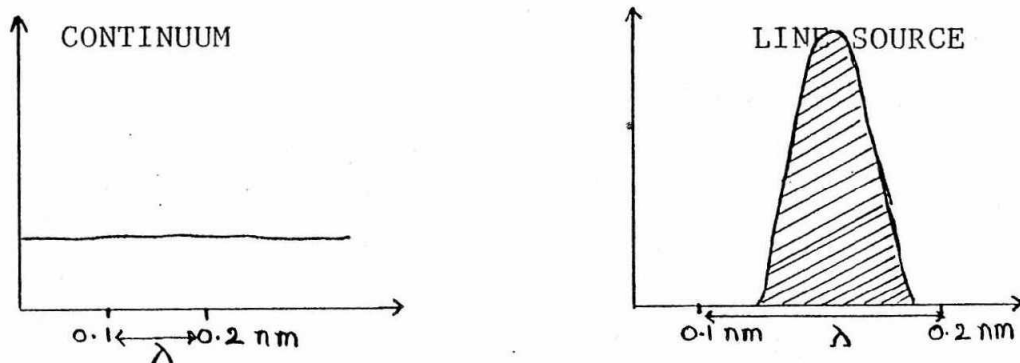
Since we have two levels of well defined energy in AAS we need a source that will provide photons of the same discrete energy or wavelength. We could use a continuous source to provide the specific radiation for the transition $E_{\text{lower}} - E_{\text{upper}}$ but only the very small fraction of the source's output would be at the correct wavelength



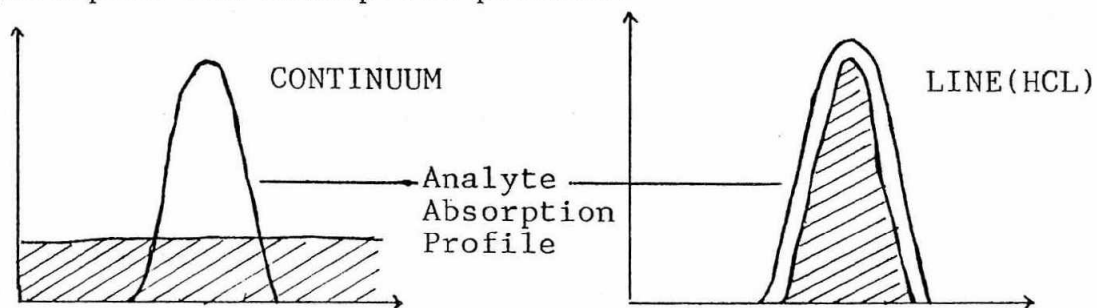
with a continuum source the bulk of the radiation passes through the atom cell is useless, even if we use a spectrometer to select only a small bandpass out of the whole lamp spectrum, the fraction of radiation at the required wavelength is very low. To ensure that, sensitive atomic absorption occurs it is necessary to use a source that emits radiation of a line nature that corresponds to the absorption

line of the analyte atoms in e.g a combustion flame. The advantage of a line source e.g a hollow cathode lamp over a continuum lamp are as follows.

Consider the situation when a continuum and a line source give the same intensity at the detector.



When the radiation is passed through analyte atoms we can superimpose the absorption profile.



It can be seen that only a small part of the continuum radiation can be absorbed whereas all of the HCL radiation can be absorbed. It is possible to use a line source of equivalent width, but then absorption occurs at the 'wings' of the absorption profile which are not as sensitive.

In order to have a population of free atoms, flame is the most commonly used atomization system in AAS. The procedure normally involves the use of pre-mixed laminar flames and two combinations of oxidant and fuel are available with commercial instruments.

- (a) Air-acetylene
- (b) Nitrous oxide-acetylene

In most AAS measurements the optimization of fuel to oxidant ratio is essential to obtain best sensitivity and reduce interferences.

Modifications to Flame Spectroscopy

The limitations of conventional flame cells:

1. The conventional indirect nebulizer and flame systems require relatively large volumes of solution to operate. Only about 10% of solution uptake is delivered to the flame. Attempts to improve the efficiency of premix nebulizers by using **ultrasonic nebulization**, **heated spray chambers** or **hot gases** have been reported, but generally the apparatus used tended to lack simplicity.
2. Atom concentrations in flames are limited by the **dilution effects** of the relatively high flow-rate of unburnt gas used to support the flame, and the **flame gas expansion** which occur on combustion.
3. Solutions with high sample matrix or analyte concentrations may undergo incomplete solute vaporization and gaseous dissociation because of the **short transit time** in the flame cell. Some elements are prone to **compound formation** and some elements are strongly ionized.
4. Although in many ways solutions are ideal analytical matrices, in certain situations the analysis of solid samples may be preferred. It is difficult to nebulize viscous oils, and certain other common organic solvents may extinguish the flame when sprayed.

To overcome the above limitations, a number of modifications to the flame cell have been proposed.

- ° Pulse nebulization
- ° Branched uptake capillaries
- ° Kahn sampling boat
- ° Delves sampling cup

Development of the Continuum-source Method

The requirement of a separate atomic spectral lamp for each element has often been identified as a drawback of line-source atomic absorption measurement. The costly investment in individual primary radiation sources and the unproductive 'down time' due to lamp changes between analyses are economically unattractive particularly in laboratories where many samples are routinely analyzed for a large number of elements. Moreover, further development of AA instrumentation for simultaneous multielement analyses is severely restricted by optical alignment problems incurred with individual lamps. A single primary radiation source which emits an intense continuous spectrum would potentially overcome these limitations.

In the earlier days of atomic absorption analysis when new elements were being continuously investigated, a primary continuum source was used in conjunction with high resolution spectrograph and photographic detection as an expedient means of experimentally determining the relative sensitivities of various absorption lines particularly for those elements for which HCL were not available. In 1962, **Gibson, Grossman and Cooke** suggested the use of a primary continuum source as an alternative to individual atomic spectral lamps for analytical atomic absorption measurements. The inherently lower sensitivity and non-linear calibration curves with a continuum source and a medium dispersion monochromator were observed experimentally. Part of the loss in sensitivity could be regained by using multipass optics and an extended path length by using multiple burners in tandem and a long

absorption flame tube. Simultaneous multielement continuum-source atomic absorption with a wave-length modulated echelle polychromator are currently of considerable analytical interest. This system dubbed **SIMAAC** is capable of measuring simultaneously upto 16 pre-selected analytical wavelengths.

WHAT CAN THE METHOD DO ?

- (a) Thirty-two elements have been measured by the method, mostly metals.
- (b) Detection limits are typically a factor of two poorer than those observed with line-source instrumentations using the same atomizer, except for the elements whose analytical lines fall at very short wavelengths (e.g Zn and Cd), which are about 10-fold poorer than line-source measurement.
- (c) Background correction for non-specific absorption is automatic and is performed with only a single lamp.
- (d) The dynamic range of the continuum-source method is far greater (typically 5 order of magnitude) than is ordinarily considered to be characteristic of absorption measurement.
- (e) Atomic emission measurements can be made on the same instrumentation and, unlike with line-source instrumentation, remain background corrected.

Non-flame Atomization

Combustion flames, though cheap to produce, stable in operation and, depending on the gas mixture used, able to give a wide range of temperatures, nevertheless have certain serious disadvantages. Chief of these is that the atomic vapour always contains other higher reactive species. It is therefore not possible to predict with any certainty exactly how a given mixture of elements may respond in absorption or

indeed how a non-absorbing species may affect or interfere with the elements to be measured. Many attempts have been made to produce the atomic vapour in a completely neutral or unreactive medium, and various electrical methods have been proposed to introduce the necessary amount of heat energy into the system.

Electrothermal Atomizers

The development of electrothermal atomizers can be traced back to the work of A.S.King in 1905 and 1908. The use of a graphite furnace for generating atoms as the absorbing medium in analytical atomic absorption spectroscopy was first described by L'vov.

The literature on electrothermal atomization atomic absorption (ETA-AAS) contains numerous examples of how chemical interferences can affect the degree and rate of atom formation. The most frequently reported interference effect found to arise in electrothermal atomization occurs when the sample matrix contains halide salts.

Commercial atomizers are generally based on the design first described by Massmann and as it is operated under non-isothermal conditions, this design is associated with numerous chemical interference effects. In 1978, L'vov focused attention on the need to design the graphite furnace such that a constant temperature environment was obtained. It was proposed that under such conditions, and particularly when used with integrated absorbance, matrix interferences can be reduced. L'vov also proved quantitatively that if the vapour temperature is increased, greater dissociation of the analyte, chloride takes place and vapour-phase interferences are reduced. To achieve a more constant temperature within the atomiser, L'vov proposed three modifications:

- rapid furnace heating,
- platform atomization, and
- probe atomization.

Rapid furnace heating, by means of a capacitive discharge, has attracted only limited interest due to the rather bulky power supply required. Presently, the most widely accepted modification to the graphite furnace is the application of the graphite platform, which requires minimal alteration to the atomiser tube. A disadvantage of the platform, however, is that the thermal lag between the platform and the tube is limited and sample vaporization is not entirely delayed until an equilibrium tube temperature has been attained. By designing platforms of greater mass the delay in heating can be increased, but this reduces the rate and possibly the efficiency of atomization resulting in a loss of sensitivity.

The alternative approach suggested by L'vov to achieve high vapour temperatures within the graphite furnace is probe atomization. Two principal advantages of the probe, as compared with the platform are: (i) improved control of the actual temperature that the atoms experience and (ii) rapid heating of the atomization surface by the tube radiation, as the probe-head has a relatively low mass.

Hydride Generation AAS

For some elements the disadvantages of flame AAS can be overcome by production of gaseous hydrides of the element, limited to only a few elements from:

Ga, Sb, Sn, As, Bi, Te, Se

Each elements has difficulties in conventional AAS because of

the absorption of primary radiation of HCL lamps by flame at low wavelengths (200-283 nm) - especially true for wavelengths close to 200 nm. Also atomization efficiency in the flame for some of the elements is poor. The above elements from gaseous hydrides with low boiling points and so hydride vapour can be separated from the rest of the matrix.

The main advantages of hydride generation are:

1. Removal of the analyte from the rest of the matrix.
2. Improved atomization efficiency due to low dissociation temperature.

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