



iCE 3000 Series AA Spectrometers

Methods Manual

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Methods Manual

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Using This Manual

This chapter provides information about this manual.

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About this Manual

This Thermo Scientific™ *iCE 3000 Series AA Spectrometers Methods Manual* introduces and describes the Atomic Absorption Spectrometry (AAS) techniques and methods used for analyses. For information about the operating procedures for the iCE 3000 Series AAS system, we recommend that you read the *iCE 3000 Series AA Spectrometers Operating Manual*.

Who Uses this Guide

This *iCE 3000 Series AA Spectrometers Methods Manual* is intended for all personnel the need to perform measurements with the iCE 3000 Series mass spectrometer.

Scope of this Guide

The *iCE 3000 Series AA Spectrometers Methods Manual* includes four main parts with the following chapters:

Part I - Principles of AA Spectrometry

Four chapters give a general introduction into the AA Spectrometry. They also describe the absorption and emission processes, the line sources, atomizers, furnace, monochromators, and detectors used for AA Spectrometry. Finally, techniques used for sample introduction are described.

Part II - Atomic Absorption Instrumentation

A couple of chapters describe single and double beam instruments, causes of background interference, background correction methods, the flame atomizer, the burner, the history of the furnace and the furnace components, the furnace autosampler, the electronic system, and the signal and data processing.

Part III - Methodology

Multiple chapters describe the Flame AAS, calibration techniques, different kinds of interferences, the furnace and matrix interferences. They give an introduction into quality assurance planning and quality control. This part also provides information about sample handling, the fusion technique, use of acids, microwave digestion techniques, digestion of metallurgical and geological samples, the water analysis, and methods for soils and sludges.

Part IV - Cookbook

This part provides a cookbook for typical elements.

Related Documentation

In addition to this *iCE 3000 Series AA Spectrometers Methods Manual*, Thermo Fisher Scientific provides the following documents for the iCE 3000 Series AAS instruments:

- *iCE 3000 Series AA Spectrometers Pre-Installation Requirements Guide*
- *iCE 3000 Series AA Spectrometers Operating Manual* – describes the installation, alignment and use of the Spectrometer and accessories.
- *SOLAAR Software Manual* – describes the use of the SOLAAR Software user interface to control the iCE 3000 Series AAS and examine the absorption data.
- *SOLAARsecurity Software Manual* – gives a description of the SOLAARsecurity Software, together with instructions on how to carry out all the main operations.

The *iCE 3000 Series AA Spectrometers Operating Manual* represents the Original Operating Instructions. Thermo Fisher Scientific provides this *iCE 3000 Series AA Spectrometers Methods Manual* as an additional reference document for the iCE 3000 Series AAS instruments.

The SOLAAR Software also provides Help.

A printed version of the *iCE 3000 Series AA Spectrometers Operating Manual* is shipped with the instrument.

Typographical Conventions

This section describes typographical conventions that have been established for Thermo Fisher Scientific manuals.

Signal Words

Make sure you follow the precautionary statements presented in this manual. The special notices appear different from the main flow of text:

Tip Points out possible material damage and other important information in connection with the instrument.

Data Input

Throughout this manual, the following conventions indicate data input and output via the computer:

- Messages displayed on the screen are represented by capitalizing the initial letter of each word and by italicizing each word.
- Input that you enter by keyboard is identified by quotation marks: single quotes for single characters, double quotes for strings.
- For brevity, expressions such as “choose **File > Directories**” are used rather than “pull down the File menu and choose Directories.”
- Any command enclosed in angle brackets < > represents a single keystroke. For example, “press <**F1**>” means press the key labeled *F1*.
- Any command that requires pressing two or more keys simultaneously is shown with a plus sign connecting the keys. For example, “press <**Shift**> + <**F1**>” means press and hold the <Shift> key and then press the <F1> key.
- Any button that you click on the screen is represented in bold face letters. For example, “click **Close**”.

Topic Headings

The following headings are used to show the organization of topics within a chapter:

Chapter 1 Chapter Name

Second Level Topics

Third Level Topics

Fourth Level Topics

Contacting Us

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| Brochures and Ordering Information | www.thermofisher.com/AAS |  |
| Service Contact | www.unitylabservices.com |  |
| Technical Documentation SharePoint | <p>❖ To get user manuals for your product</p> <ol style="list-style-type: none"> 1. With the serial number (S/N) of your instrument, request access on our customer SharePoint as a customer at www.thermoscientific.com/Technicaldocumentation 2. For the first login, you have to create an account. Follow the instructions given on screen. Accept the invitation within six days and log in with your created Microsoft™ password. 3. Download current revisions of user manuals and other customer-oriented documents for your product. Translations into other languages may be available there as well. |  |
| Customer Feedback | <p>❖ To suggest changes to this manual</p> <p>You are encouraged to report errors or omissions in the text or index. Send an email message to the Technical Editor at documentation.bremen@thermofisher.com.</p> |  |

Introduction

In any textbook or manual on Atomic Absorption Spectrometry (AAS) it is customary to give an overview of the subject, an introduction containing the history, theory and background to AAS, the instrumentation required and a methodology section. The following text is no exception and is arranged in this order. To be of more practical help, a larger methodology section is provided and arranged by matrix type to enable the analyst to prepare the sample type ready for analysis.

Historical Background

The technique of AAS can be thought of as having its origin in 1666 with Isaac Newton who used a prism to separate the colors of the solar spectrum. Wollaston in 1802 recorded his observation that the spectrum of sunlight which was at the time thought to be continuous, was in fact interrupted by dark lines. Later in 1814 Fraunhofer found a series of lines in the visible region of the solar spectrum and labeled the principal lines alphabetically without identifying their chemical origin.

In 1832, Brewster, who is associated with the invention of the kaleidoscope investigated the absorption of light by various vapors and suggested that Fraunhofer lines were due to certain vapors in the sun's atmosphere. Kirchhoff in 1860 deduced from Fraunhofer's results the presence of certain elements in the solar atmosphere and with Bunsen in 1861 laid the foundations of a new method of chemical analysis using flames. Fraunhofer and Kirchhoff had been observing atomic absorption and atomic emission respectively. Foucault demonstrated the reversal of spectral lines, for example when the spectral source is surrounded by atomic vapors from the substance emitting the spectrum and the atomic vapors absorb the radiation that they themselves are emitting.

In 1902 Wood illustrated the emission-absorption relationship by heating sodium in a partially evacuated glass bulb and irradiated the bulb with light from a sodium flame. He demonstrated an increase in absorption effect by heating the bulb more strongly. Wood named the lines emitted and absorbed by sodium atoms as resonance lines and carried out experiments to show the possibility of using the resonance effect to detect traces of mercury. This may have been the first analysis carried out by atomic absorption spectrometry. Wood does not seem to have been able to impress either chemists or spectroscopists who were more interested in emission spectroscopy and few followed in the field of atomic absorption and its applications. The advances made by

Introduction

What is Atomic Absorption Spectrometry (AAS)?

Kirchhoff, Bunsen, Foucault and Wood did interest astronomers who used atomic absorption to study the composition of the solar and stellar atmospheres.

In 1924 Angerer and Joos studied the atomic absorption spectra of metals in the iron group and Frayne and Smith in 1926 of indium, gallium, aluminium and thallium. Hughes and Thomas in 1927 studied the absorption and resonance effects of mercury. Lunegardh in 1928 demonstrated atomic emission spectroscopy (AES) in an air-acetylene flame using a pneumatic nebulizer. In 1930 Mueller and Pringsheim published an atomic absorption method of measuring mercury content of air thereby carrying on Woods original project of 1913 and 1919.

The first real applications of atomic absorption to chemical analysis were made by Walsh in 1955, and Alkemade in the same year. Walsh made significant contributions to the development of AAS as an analytical tool. He used the hollow cathode lamps as a line source, greatly reducing the resolution required for successful analysis. As photomultipliers had become available, the problems associated with measuring absorption with a photographic plate were eliminated. His introduction of modulation into the system, permitted the detector to distinguish between absorption and emission by atoms at the same wavelength. He also utilized the flame for atomization.

What is Atomic Absorption Spectrometry (AAS)?

Atomic absorption is a process involving the absorption by free atoms of an element of light at a wavelength specific to that element, or put more simply, it is a means by which the concentration of metals can be measured.

In Atomic Spectrometry, emission, absorption and fluorescence, energy is put into the atom population by thermal, electromagnetic, chemical and electrical forms of energy and are converted to light energy by various atomic and electronic processes before measurement. Atomic Absorption Spectrometry is useful not only for the identification but also the quantitative determination of many elements present in samples. The technique is specific, in that individual elements in each sample can be reliably identified and it is sensitive, enabling small amounts of an element to be detected down to around $1 \mu\text{g g}^{-1}$ (1 ppm),

i.e., one part in one million using straightforward flame procedures. Lower levels can be determined down to .001 ppm using more sophisticated procedures which will be covered later in the text.

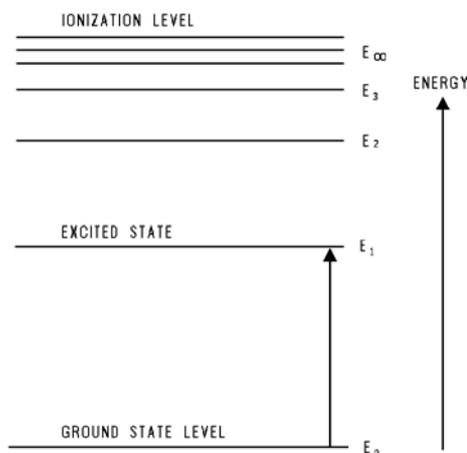


Figure 2-1. Energy level diagram

When a sample or sample solution is burned in a flame or heated in a tube, the individual atoms of the sample are released to form a cloud inside the flame or tube. Each atom consists of a positively charged nucleus surrounded by a number of electrons in rapid motion around the nucleus. For each electron in each atom there is a discrete set of energy levels that the electron can occupy. The spacing of the energy levels is different for each electron in the atom, but for similar atoms corresponding electrons have identical spacing. The energy levels are usually labeled E_0 , the ground state, through E_1 , E_2 etc. to E_∞ .

For an unexcited atom, each electron is in the ground state. To excite the atom, one or more electrons can be raised to the first or higher energy levels by the absorption of energy by the atom. This energy can be supplied by photons or by collisions due to heat. Those electrons furthest from the nucleus require least energy to go from the ground state E_0 to the first energy level E_1 . The energy E corresponds to the energy gap between the ground state and the first energy level.

$$E = E_1 - E_0$$

The energy required for this transition can be supplied by a photon of light with an energy given by:

$$E = h \cdot \nu$$

where h = Planck's constant and ν the frequency.

Introduction

What is Atomic Absorption Spectrometry (AAS)?

This corresponds to a wavelength (λ) of:

$$\lambda = \frac{h \cdot c}{E}$$

where c = speed of light in vacuum.

However, for all non-conducting elements (insulators) and for most of the electrons in the atoms of conducting elements, the energy gap E_1-E_0 , is very large and thus a very energetic photon, perhaps in the vacuum UV or X-Ray region, would be required to excite the atom. Metallic and metalloid elements, contain so-called valence electrons, which are relatively loosely bound to the nucleus and which can be excited by photons of wavelengths in the optical range 190-900 nm. For each atom of a metal or metalloid the energy gap E_1-E_0 for a particular valence electron is nearly identical. Furthermore, the energy gap is not found in any other element. If light of sufficiently narrow wavelength range, centered on

$$\frac{h \cdot c}{E_1 - E_0}$$

is sent through a cloud of various atoms, only atoms of one particular element will absorb photons. Hence the selectivity of the atomic absorption technique.

Atoms in the cloud move at high speed and collide with each other, and absorb over a very narrow range of wavelengths. The width of a typical absorption line is about 0.001 nm. For atomic absorption instrument purposes, an emission source with an emission line of the same frequency and a width of about 0.001 nm is normally used. This requirement is satisfied by an emission spectrum of the element of interest, generated by a hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL). Another requirement to obtain a high absorption signal is that most atoms should be in the ground state and a large number of electrons should be able to be excited to the first state when a photon of correct frequency is absorbed. The number of atoms in the ground state and first excited state is given by the general statement of the Maxwell-Boltzmann law which will be discussed later.

Theory of Atomic Absorption Spectrometry

In the following text we shall be considering that section of the electromagnetic spectrum which covers the wavelengths from 190-900 nm, i.e., the ultra violet and visible regions.

Absorption

The absorption of energy by atoms follows well known physical laws which provide us with a basis for quantitative analytical chemistry. The radiant energy or photons, absorbed by atoms are generally in the form of very narrow lines of characteristic wavelength originating from the visible or ultraviolet spectrum. During the absorption process the outer valence electrons of the atoms are promoted to a higher orbital and the atom is electronically excited. There is a relationship and equilibrium between the populations of excited and unexcited atoms involving photons, and between atomic absorption and atomic emission spectroscopy.

A photon behaves in a similar manner to an alternating electric field and interacts with the negatively charged electrons in an atom. Under certain conditions a photon can be absorbed by an atom. The energy levels in an atom are quantized, that is they have certain well defined energies. As a consequence of this, the photon energy, $h\nu$, must be exactly equal to the energy gap between a filled energy level E_0 the ground state, and an unoccupied energy level E_1 the first excited state, as represented below:

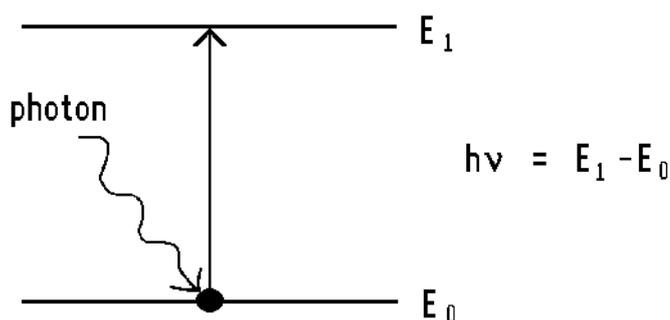


Figure 3-1. Absorption process

The wavy arrow represents a photon colliding with and being absorbed by a ground state atom E_0 . The vertical arrow represents the simultaneous excitation of the atom from ground state E_0 to the excited state E_1 . This process involves an electron being promoted from a filled

atomic orbital to a more energetic orbital, normally unoccupied. The absorption process can be described by an over simplified Bohr Orbit diagram as shown for a typical atom of lithium.

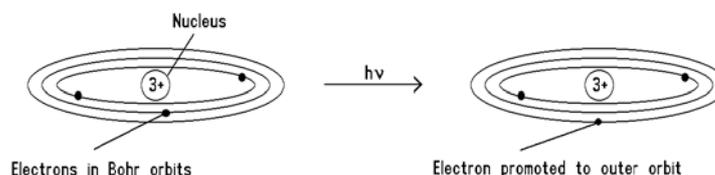


Figure 3-2. Bohr orbit representation of light absorption by a lithium atom

This is a simple representation of absorption, as transitions between orbitals within the same electronic shell can be induced, as well as transitions between different electronic shells. An example of the former, is the promotion of an electron in a 4s orbital in a potassium atom to the 4p orbital by light of wavelength 766.5 nm.

Emission

The process of emission is the reversal of absorption. The atom in an excited energy level can revert to the ground state by emitting energy as a photon as represented below:

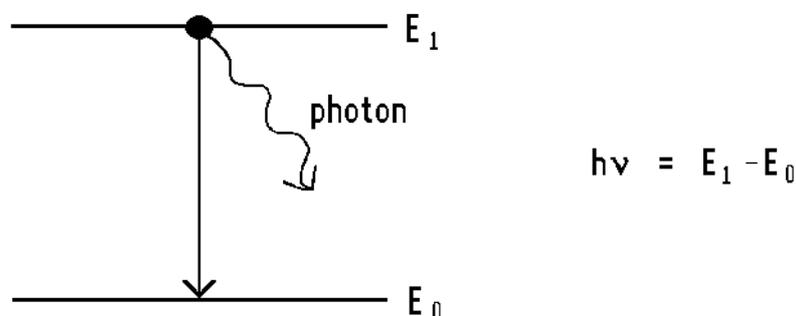


Figure 3-3. Emission process

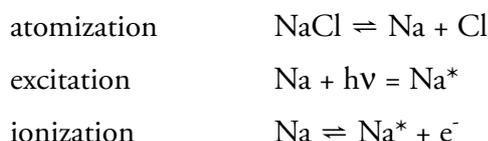
The photon of energy $h\nu$ is equal to the energy gap ($E_1 - E_0$). The emission of a photon when the electron moves to the unexcited state from the excited state, forms the basis of emission spectroscopy. In this technique the light generated in the emission process is measured at a specific wavelength. In any atom there are numerous permitted energy levels and numerous transitions permitted between different excited energy levels and the ground state. The existence of numerous upper excited states means that the equilibrium between ground state atoms and excited atoms is not quite as simple as the diagram above makes out. For the sake of clarity and for the purpose of illustrating the principle of emission, the higher energy states are disregarded and the ground state and the first excited state of the atom is discussed.

Formation of Free Atoms

To generate free atoms the atomizer must supply energy to break the chemical bonds between atoms of a molecule. An atomizer such as a flame, carbon atomizer or plasma must provide sufficient energy to break these bonds to free the atoms. A plasma is defined as “any luminous volume of gas having a fraction of its atoms or molecules ionized.” The energy required to break these bonds influences the numbers of free atoms produced from a sample. How efficiently the bonds are broken and the free atoms generated, depends on the type of bonds that need to be broken when atomized. For example, the energy requirement for iron may be different if iron is ionized, as in a solution of iron chloride or complexed as a solution of iron EDTA. Even though the iron concentration was the same, a different analytical signal would be obtained for each. This phenomenon provides the basis for understanding chemical interference which is a problem in atomic absorption and atomic emission spectroscopy. This observation explains why cool atomizers are not as efficient as hot atomizers for many elements and will be covered more fully later in the section on interference.

Production of Free Atoms in a Flame

The ability to produce uncombined and un-ionized atoms in an atomic vapor determines the success of an atomic absorption or fluorescence analytical procedure. In a flame at a temperature of 2000-3000 K the fine droplets of a solution contain molecules in solution previously aspirated. The solvent evaporates leaving behind small solid particles. These particles melt and vaporize and the vapor consists of mixtures of compounds that decompose into free atoms which though transitory under these conditions, enable atomic spectra to be observed. The individual metal atoms which have been atomized absorb energy by collision and become either excited or ionized as shown in the simplified example for sodium chloride below:



As can be seen, the flame atomizes the sample as shown by the first reaction. The atom is excited by the energy from the light source in the second reaction, which removes the atoms and if excessive heat is applied, ionization occurs which removes atoms as well.

It has been pointed out by de Galan and Samaey (1) that the degree of atomization varies from one element to another in a given plasma and it was this factor more than any other which influences analytical sensitivity. As dissociation and ionization are similar processes it is

possible using the Saha (2) equation to calculate degrees of ionization of atoms into ions and electrons for various elements at different temperatures and partial pressures.

The Saha Equation:

$$\log K = -\frac{U}{4.573T} + \frac{5}{2} \cdot \log T - 6.49 + \log \frac{g_{k^+} \times g_e}{g_k}$$

where:

K = the equilibrium for the ionization process above

g terms are statistical weights of the species shown as suffixes

U is the ionization potential in cal mol⁻¹

T is the temperature Kelvin.

Production of Free Atoms in an Electrothermal Atomizer

An electrothermal atomizer is normally a small cylindrical furnace, tube, cuvette or cell made from graphite which can be heated to a high temperature by resistive heating after passing a high current through it. To atomize samples the cell must be capable of reaching 2000°C for most elements, and up to 3000°C for the more refractory elements. The ability to retain a substantial proportion of the analyte material in the observation zone for a short period of time, greatly increases sensitivity. L'vov (3) first suggested the basic requirement to achieve such sensitivity was that the rate of formation of the free atoms must be equal to, or greater than, the rate of removal from the optical path. To satisfy this criteria, it would appear that the cylindrical or tube type furnace of atomizer fulfills this condition better than open filament atomizers. The mechanism by which free atoms are produced in the cell depends on a number of factors such as:

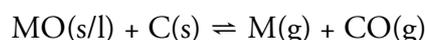
- compounds present in the cell at the atomization temperature of the element being measured
- material from which the cell is constructed
- atmosphere in the cell
- rate of heating
- final temperature attained in the cell
- supply of atoms

Atoms are removed from the observation zone by the following processes:

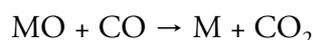
- diffusion
- gas expansion
- convection
- recombination of atoms

The supply and removal functions combined give an overall response curve. There are several different theories which have been used to describe the mechanism of atom release from the walls of a graphite tube furnace. Fuller (4) contributed greatly and in 1977 reviewed the whole subject of electrothermal atomization. It would seem that at the point of atomization in the tube the process would be simpler than in a flame. Various possible reactions have been examined thermodynamically.

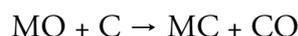
Evaporation of metal oxides, for example Sb_2O_3 , may occur before the atomization temperature is obtained if their oxides have high vapor pressures. The problem is more acute if metal chlorides are present, as they are more volatile and are lost at a temperature below that required for atomization. If thermal dissociation of metal oxide occurs, the degree of dissociation can be calculated for various temperatures using thermodynamic data. The degree of dissociation is controlled by the amount of oxygen liberated and carbon present. The reduction of the furnace metal oxides by the furnace carbon takes place according to the following equation:



which is the mechanism believed to be relevant for most elements. The following reaction can also take place.



It is possible for carbide formation to occur between some elements and the graphite furnace. For elements such as aluminium, calcium and chromium the formation of the carbide occurs at a lower temperature than that required to produce gaseous atoms.



Thermodynamic calculations predict that elements such as lead and cadmium which are easily atomized on carbon, are even more readily atomized on tantalum. Those elements that are difficult to atomize on carbon, are even more difficult to atomize on tantalum tubes.

To demonstrate that atomization is a kinetic process, two types of theoretical treatment are described. L'vov studied atomization using increasing temperature conditions and his theory is more suitable with an open atomizer and when the pyrolysis stage has a ramp program.

Fuller looked at atomization using isothermal atomization conditions, his theory reduces to a simple exponential function and is applicable to the modern atomizer which is designed to heat up in a short time. This theory can also be used to explain the isothermal pre-atomization temperature pyrolysis step where interfering compounds are removed.

Kinetic theories of atomization appear to give more useful information than thermodynamics. The ratio of $N(\text{max})$ to $N(\text{integrated})$ where N is the number of atoms being measured at a point in time, can be compared to find the conditions where either peak height or integrated peak area measurements give the best results. Integration has been shown to give better results for low temperature and low atomization rates. Using the kinetic theory it should be possible to predict whether or not a certain element can be determined in a particular matrix and select optimum operating temperatures. Fuller used this approach after certain simplifications and assumptions were made using first order kinetics and similar kinetics for both high and low concentrations. The kinetic approach has been used for the pyrolysis stage to determine interference effects which are different to those encountered in a flame.

The Boltzmann Distribution

The electron in an excited atom involved in transitions to a higher energy level is that electron with the least energy. In chemical terms this is the valence electron. An electron can be promoted from the ground state to an upper excited state by heating a population of atoms. If a whole population of atoms is heated, the actual number of electrons in any particular orbital can be calculated by the Maxwell-Boltzmann equation. This states that if there are N_1 atoms in an excited state and N_0 atoms in the ground state, then

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-(\Delta E)/(KT)}$$

where:

E = energy difference between the ground state and excited state

T = the temperature of the atom population in K

K = Boltzmann constant

$\frac{g_1}{g_0}$ = statistical weights in the energy states 0 and 1

This law assumes that the population of atoms has attained a constant uniform temperature. It not only applies to excitation of electrons but also to vibrational energy, rotational energy etc. It is extremely important in that it enables us to calculate how many atoms in the system will be excited by the flame, graphite furnace, an electrical discharge or plasma.

The Boltzmann distribution theory assumes that they are single energy levels. When these atoms are placed in a strong magnetic field, these energy levels may split into a number of sublevels $(2J_i + 1)N_i$, where N_i is the population of these single energy levels. This is known as the Zeeman effect, which is covered more fully in the section on background correction.

The Beer-Lambert Law

The absorption that takes place in an atomic absorption system follows Beer's law, which is

$$I_1 = I_0 e^{-a,b,c}$$

$$A = a b c$$

or where:

$$T = \frac{I_1}{I_0} \quad ((T = \text{Transmission}))$$

Therefore

$$A = \text{absorbance} = -\ln T$$

where:

I_1 = intensity of light leaving solution after absorption

I_0 = intensity of light falling on a solution before absorption

a = absorption coefficient

b = path length through sample

c = concentration of the solution

The Beer-Lambert Law is the fundamental law, which relates absorption in a solution to concentration of individual components in a solution. Although the basic principles of the Beer-Lambert Law apply to AAS it is not possible to use this relationship in the same way. This is because solutions (molecular concentrations) are homogeneous throughout the sample absorption path and the free atoms in the flame are not constant throughout the light path. Hence the Beer-Lambert Law cannot be used directly to determine the concentration of an atom generated from a solution. It is necessary instead to use this equation:

$$\text{Total absorption} = \text{constant} \times Nf$$

where the total absorption is equal to a constant times the number of free atoms in the light path, which is independent of temperature and energy of transition and relates the amount of absorption with the number of atoms in the light path.

The free atoms in the light path are in dynamic equilibrium with the sample solution and the products of combustion in the flame. The number of free atoms is proportional to the concentration of the element in the solution. A calibration graph can be constructed which relates concentration with absorption. The number of excited atoms varies with change in temperature although the number of excited atoms is small compared with the number of free atoms in that population. It can be shown that the bulk of the atoms remain in the ground state at temperatures normally encountered in flame atomizers. The unexcited atoms do not contribute to the emission signal, but are capable of absorbing energy and contribute to the absorption signal. The ground state is the most populated for a given population of atoms and is within experimental error independent of temperature. The following equation shows that there is no term relating the absorption wavelength to the total absorption. This indicates that the total absorption is independent of the absorption wavelengths which cannot be said of emission:

$$\int_0^{\infty} K_{\nu} d\nu = \frac{\pi e^2}{mc} N_0 f$$

where:

K = absorption coefficient at frequency ν

e = charge on an electron

m = mass of an electron

N_0 = number of absorbing atoms at energy level 0 (ground state)

c = speed of light

f = oscillator strength of the absorption line

The Basic Atomic Absorption System

To make measurements in atomic absorption spectrometry it is necessary to produce a population of ground state atoms as efficiently as possible and pass resonance radiation of the element to be measured through the population of atoms. In an ideal system the light-measuring end of the system should only measure at the wavelength being absorbed, as any other radiation sensed decreases the sensitivity of the measurement.

The layout of a basic flame atomic absorption spectrometer is shown below.

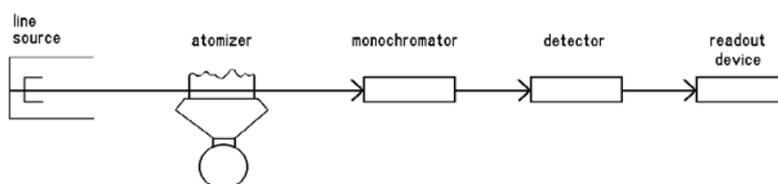


Figure 4-1. Basic flame spectrometer

Light from a line source of characteristic wavelength for the element being determined passes through the flame into which has been sprayed a fine mist of the sample solution. The region of the spectrum to be measured is selected by a monochromator. The isolated spectral line falls on the photomultiplier, the detector and the output is amplified and sent to a readout device meter, digital or analogue, to a chart recorder or through a computer data processing system, printer or digital display unit. The intensity of the resonance line is measured twice, once with the sample in the flame and once without. The ratio of the two readings is a measure of the amount of absorption, hence the amount of element in the sample. In a system not using a flame the atomizer is replaced with an electrothermal graphite furnace or other cell to produce the atoms. To avoid measuring the emission from the excited atoms at the same wavelength, the lamp is modulated usually at 50 Hz or higher, and the amplifier tuned to the same frequency. This means that the continuous radiation signal from the atomizer is not measured.

The same or similar components are used to measure flame emission or atomic fluorescence. To carry out emission measurements the source lamp is removed and the radiation from the atomizer modulated at the amplifier frequency. In fluorescence the energy from the source is usually passed through the flame at right angles to the optical axis of the monochromator and the source once again modulated to avoid measuring thermally excited emission from the flame.

Instrumentation for fluorescence, emission and absorption spectroscopy has essentially two parts with different functions and consists of an atomizer to produce ground state atoms and an optical system consisting of a resonance source, the spectrometer and detector.

Line Sources

The hollow cathode lamp is the only type of light source widely used in atomic absorption spectrometry, its main feature is the narrow absorbing spectral line. In molecular electronic spectroscopy quartz-halogen filament lamps, deuterium or xenon arc lamps are normally used. Called continuum sources, they emit light over a wide spectral range, and used with a monochromator the wavelength of interest can be isolated. A primary radiation source suitable for atomic absorption measurements must emit a sharp resonance spectrum at a half-width of 0.001 nm. With emission lines of 0.01 nm half-width appreciable absorption is obtained.

Vapor discharge tubes were readily available for the more common volatile metallic elements such as mercury, however the sealed hollow cathode lamp, which has undergone considerable development and improvement in reliability and intensity, has been found to be the best source. Another line source which is no longer popular or in wide spread use is the microwave and radio frequency excited electrodeless discharge lamp.

Vapor discharge lamps have a much higher intensity with better signal to noise ratios and better detection limits, and should have an advantage over hollow cathode lamps, however at the low currents required, these lamps tend to be more unstable and are less advantageous. Modern hollow cathode lamps are better for stability and line width than the earlier vapor discharge lamps.

Hollow Cathode Lamps

The hollow cathode lamp is stable, reliable, has a long operating life and is the standard source in Atomic Absorption Spectrometry. Lamps may be expected to run in excess of 5000 mA hours without failure and many have been known to run twice as long. The hollow cathode discharge lamp is known as a fine line source capable of producing spectra where fine structure could be studied. Early versions of the lamp were demountable, allowing the lamp to be taken apart and the cathode changed.

Sealed-Off Hollow Cathode Lamps

The earliest sealed-off lamps consisted of a glass tube with the electrode sealed inside with an optical window at one end made of glass or silica depending on the wavelength and attached with a thermosetting resin or vacuum wax. The construction of a typical lamp is shown in Figure 4-2.

The two electrodes are sealed in the glass envelope and the window located at the opposite end to the cathode. Electrical connections are made through a standard octal plug at the base of the lamp. The cathode is shaped in the form of a hollow cup inside which the discharge takes place. This cup is constructed of or contains the element of interest whose spectra is required. A mica shield holds the structure rigid and helps to contain the discharge inside the cathode cup. The cup usually has an internal diameter of about 2 mm, to concentrate the discharge into a small area and produce a high intensity line. The available energy appears to dissipate in the metal resonance line rather than in the filler gas in this type of construction. The lamp is usually filled with an inert gas such as helium, argon or neon. Highly purified inert gases are used and the glass is out-gassed at high temperature to remove impurities adsorbed onto the surface of the glass. The emission line of the inert filler gas must not coincide with the resonance line of the metal of interest. Neon has a higher ionization potential than argon and thus is preferred for those elements with higher ionization potential because it improves the intensity of the discharge.

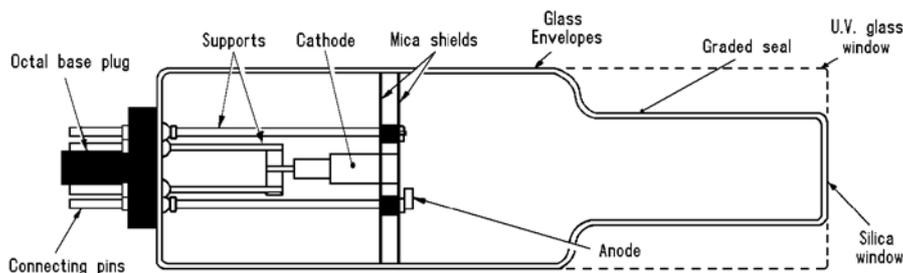
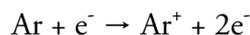


Figure 4-2. Hollow cathode lamp

When a voltage of 300 - 400 V is applied between the anode and cathode the discharge is set up and argon is ionized by the anode and becomes a positive argon ion by the mechanism of:



The positive Ar^+ ion is attracted and accelerated toward the metal cathode where it dislodges or “sputters” excited metal atoms into the space inside the hollow cathode. Argon more effectively collides with the metal cathode knocking metallic atoms into the discharge, which improves the sensitivity of the discharge. The excited atoms emit energy of their own characteristic wavelength before returning to the ground state and the emitted light is used as the light source for the AAS system.

After the atoms return to the ground state they form a cloud of free atoms, which return either to the walls of the glass lamp or to the metal cathode. If the atoms in the cathode are hot, they produce spectral line broadening caused by the Doppler effect. This is detrimental to the operation of the AAS as “wings” are produced on these broadened emission lines, which cannot be absorbed by the free atoms of the sample.

The end window of the lamp may be constructed of UV glass or silica. Silica is usually used for wavelengths in the ultraviolet range less than 300 nm and glass is usually used for the visible end of the spectrum. If silica is used, it is attached with a graded seal. Lamps are usually operated from 2 to 15 mA depending upon the element and design of the lamp. Manufacturers' maximum lamp current settings should be followed and never exceeded. In many cases it is beneficial to run the lamps at lower current than recommended to prolong the life of the lamp and to increase the sensitivity of the determination by running at about 75% maximum rating.

A typical line spectrum for nickel is shown in [Figure 4-3](#), which gives the resonance lines of high intensity and narrow bandwidth and are those lines absorbed by the free atoms of the elements to be determined. The resonance line for nickel at 232.0 nm is clearly seen as the most intense line.

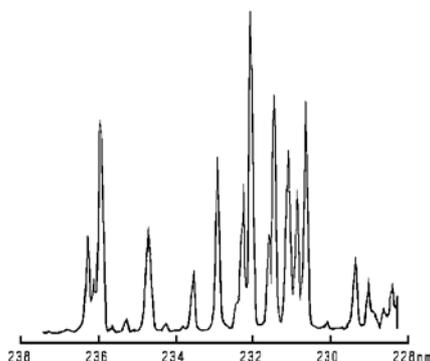


Figure 4-3. Part of line spectrum from a nickel hollow cathode lamp

Boosted Output Lamps

In this lamp, the cloud of atoms which is usually formed in front of the cathode is excited by a secondary discharge. The atoms enhance the sensitivity of the resonance radiation by contributing rather than diminishing the absorption. The secondary discharge is of higher current, usually 300-400 mA, with a low voltage. Such lamps gave improved signal to noise ratio, however their higher degree of complexity seemed to make them less reliable and short lived. Sullivan

and Walsh (5) used this type of hollow cathode lamp, but as they appeared to have no real advantage over the lamps described above, they are no longer commercially available.

Slotted Cathodes

To increase the amount of light from the hollow cathode lamp entering the monochromator, the optics can be designed to match the “tangential astigmatic” image of the cathode (6). This is formed after off-axis reflection from a concave mirror, to the shape of the entrance slit of the monochromator. This image is not formed in instruments with lens-only optics and to achieve this effect, slotted cathode lamps were developed.

Multi-Element Lamps

A multi-element lamp has a cathode, which is composed of more than one element. Although the number and type of elements that can be brought together in a cathode is limited, this type of lamp is useful if the same 2 or 3 elements are routinely analyzed. For example a Ca/Mg lamp can be useful in water analysis. Warm up and change over times can be reduced. The alloy for the cathode should contain those elements proportional to their sputtering rates and able to operate at the required current for optimum use. As the elements sputter at different rates they lose their intensity and are lost in turn. It is convenient to use a multi-element lamp if there is only one position for the hollow cathode lamp (i.e. no lamp “turret”). Like the hollow cathode lamp, the multi-element lamp needs only a short warm up period of 5 to 20 minutes. A disadvantage of this lamp is that the resonance line intensities of the individual elements is reduced when brought together in one cathode and the overall performance is poorer. Also, if the lamp fails, then all the elements are lost.

Electrodeless Discharge Lamps

Electrodeless discharge lamps (EDLs) provide a more intense spectral source for some elements than the hollow cathode lamp, in particular the volatile elements As and Se. The electrodeless lamp consists of a small sealed cavity with a small quantity of the element, or salt of the element, surrounded by an inert gas at low pressure. The cavity is surrounded by a coil which is supplied with RF power from a generator, which resonates at a chosen frequency and vaporizes the element to excite the atoms to produce the desired spectrum. While EDLs were useful for instruments with inefficient optical systems, the benefits obtained were marginal, although some improvement in detection may occur in some cases. The major problem with the EDL is instability. Electrodeless lamps were first developed for use in Atomic Fluorescence

Spectroscopy (AFS) and were microwave excited. These lamps were far more intense than the hollow cathode lamps, but more difficult to stabilize. Radio frequency excited discharge lamps compared with the microwave excited discharge lamps are less intense but more reproducible. Commercially available radio frequency lamps had a built in starter and ran at 27 MHz from a simple power supply but are now no longer available.

Lasers

Tunable dye lasers are now available and can provide high intensity spectral lines of narrow bandwidth. They are described as tunable, but in reality they only cover a wavelength range of 30-50 nm for a particular dye. The dye then needs to be changed for the wavelength ranges. The high cost of lasers currently outweighs the advantages.

Atomizers - Flame

A combustion flame provides the most convenient, stable and economic source of atomic vapors. For the production of free atoms and chemical effects of radicals and other substances present in the flame, the flame temperature is important. A range of temperatures from 2000 to 3000 K can be produced from fuel and oxidant mixtures which are safe to handle. Combustion gas mixtures vary and at the same or different temperatures may not have the same analytical properties.

Propane, hydrogen and acetylene can be used as fuel gases and air or nitrous oxide used as the oxidant. Pure oxygen is rarely used as an oxidant as its burning velocity is too high and is difficult to control, although it is sometimes mixed with argon or helium. Any of the above gases can be combined using an oxidant/fuel ratio to give either a lean, stoichiometric or a rich mixture flame. A lean flame has less fuel than a stoichiometric flame which has less than a fuel rich flame. The air/acetylene flame is extensively used as it enables about 30 common metals to be determined.

The sensitivity of some elements in an air/hydrogen flame is not much less than in an air/acetylene flame, except the interference may be worse because of the formation of stable substances in the flame from the sample solution. Elements which form stable monoxides give lower sensitivity in hydrogen based flames.

Air/propane mixtures were formerly used for those elements which were easily atomized. These included the alkali metals, and cadmium, copper, lead, silver and zinc. The air/propane flame gives better sensitivity for these elements, although the detection limit may be no better than the air/acetylene flame.

Air/acetylene flames are used for elements which do not form highly refractory oxides such as calcium, chromium, cobalt, iron, magnesium, molybdenum, nickel, strontium and the noble metals. Better sensitivity may be obtained in the cooler fuel rich flame for the refractory oxide metals than in a stoichiometric flame. Those elements which show a lower sensitivity in air/acetylene flames have a dissociation energy for the metal-oxide (M-O) bond greater than 5 eV. For example: Al-O, 5.98 eV; Ti-O, 6.9 eV; Zr-O, 7.8 eV; Ta-O, 8.4 eV.

Nitrous oxide/acetylene flames produce a higher temperature than the equivalent mixture of oxygen and nitrogen due to exothermic decomposition reactions. Temperatures of about 3000 K are produced, which is not much less than that produced by an oxy-acetylene flame, but as the burning rate is slower, is much safer to handle. Nitrous oxide has been used as an oxidant for both hydrogen and propane, however the nitrous oxide/hydrogen flame gives poor sensitivity and is highly oxidizing compared with the nitrous oxide/acetylene flame.

The nitrous oxide/hydrogen flame is useful in overcoming carbide formation and gives better sensitivity for those elements which form refractory oxides. It is useful for improving the sensitivity of emission band spectra produced by metal oxide species and is recommended for those elements readily atomized when dissolved in organic solvents. Benzene, xylene and petroleum can be aspirated directly into the flame without causing excessive luminescence because the critical C/O ratio at which luminescence appears is not exceeded.

Nitrous oxide/propane or butane have some of the interference reducing properties of nitrous oxide/acetylene flame while handling like air/acetylene, but again the sensitivity is poor. The two most important flame types continue to be air/acetylene and nitrous oxide/acetylene.

Studies of flames based on air or nitrous oxide with hydrogen or acetylene, indicate that the best sensitivity nearly always occurs above the inner core of the laminar flame, usually 0.3 - 0.5 cm above the burner slot. At this point the air/acetylene and nitrous oxide/acetylene flames are in thermal equilibrium while the air/hydrogen flame reaches thermal equilibrium at about 1.5 cm. In hydrogen flames, the position of best sensitivity may be unstable.

The gas flow rate and thermal expansion of flame gases after combustion contribute to the dilution effect of atoms and residence time of atoms in the radiation beam. The best sensitivity at a given temperature is given by the smallest combustion gas to sample volume ratio. Air/propane gives better sensitivities than air/acetylene for elements completely atomized at 2200 K. If hydrogen is used, more hydrogen is required, which partly explains why the nitrous oxide/hydrogen mixture gives poorer performance than nitrous oxide/acetylene.

The formation of free carbon effects the reducing properties of the flame. As the fuel/oxidant ratio is increased in a hydrocarbon flame, the concentration of free carbon or small carbon containing radicals increases, until the carbon agglomerates and effectively removes the carbon activity. This is the critical carbon/oxygen (C/O) ratio transition point and for certain elements their sensitivity increases to a maximum at the critical C/O ratio. Organic solvents increase the critical C/O ratio and metals aspirated in organic solvents have higher sensitivities than when in aqueous solutions. The critical C/O ratio is higher for acetylene than propane and for hydrogen the carbon activity is missing. Measured flame temperatures depend on a number of factors, these include flame gas ratios, the method used, and the experimental assembly. The success of the hotter nitrous oxide/acetylene flame is due to the high critical C/O ratio.

Furnace

Combustion flames are inexpensive to produce, stable in operation and give a wide range of temperatures depending on the gas mixtures used. They do however have serious disadvantages as the atomic vapors always contain other reactive species. It is not possible to predict how different mixtures of elements may respond in absorption and how non-absorbing species may interfere with elements to be measured. Attempts have been made to produce the atomic vapor in neutral or nonreactive medium and various electrical ways have been proposed to obtain the heat necessary.

Monochromators

Resolution

The function of the monochromator is to isolate light emitted from the primary radiation source and to isolate the most intense resonance line from non-absorbing lines close to it. These lines may come from the cathode metal or the filler gas in the hollow cathode lamp. Depending on the type of lamps used a good monochromator should be able to separate lines from the most complicated source spectrum.

A monochromator should be capable of separating two lines 0.1 nm apart or less when operating at minimum slit width. The better the monochromator, the smaller the slit width will be before further narrowing of the slits has no more effect on resolution. The minimum spectral band paths is 0.01 nm for very good instruments.

Another function of the monochromator is to isolate the resonance line from the molecular emission and other background continua originating from the flame. To prevent all the radiation emanating from

the flame from saturating the detector, the monochromator is placed after the sample cell and not before as in conventional ultraviolet instruments. The maximum slit height is the diameter of the source image at the primary slits. If the slits were longer than the pre slit optics, unwanted radiation would enter the monochromator during absorption measurements.

Prism or Grating

Prisms or Gratings are the two different devices used for dispersion of the wavelengths. The difference in performance between a prism and a grating is:

1. Prisms that are not made of glass give high dispersion in the ultraviolet end of the spectrum which decreases with increasing wavelength.
2. The dispersion of the gratings is almost constant throughout the spectrum and is dependent on the number of grooves per unit width, the spectral order and the focal length of the collimator.

Prisms are useful in that many elements have resonance lines which occur in the U.V. All the light transmitted from a spectrum is single "order" so that the energy concentrated in a particular line is higher and has less stray light and other spurious reflections. Prisms have poor resolution in the range beyond 240 nm increasing to 450 nm.

As holographically etched gratings are now more economical and reproducible they are becoming widely used. The light energy passed falls off rapidly in the higher order and gratings are blazed to give a maximum diffraction at a particular wavelength, so that either the first or second order are used. In some instruments two gratings may be used to cover the range from 180 - 400 nm and 400 - 860 nm.

Detectors

The Photomultiplier

The function of a detector is to measure the intensity of the light radiation falling on it and the most common type of detector is the photomultiplier. The detector must be able to cover the spectral range from 190 - 860 nm which poses some problems for sensitivity, particularly at the longer wavelengths. Photomultiplier sensitivity is determined by how photo-sensitive the coating material is on the cathode.

Materials commonly used to construct these detectors are:

Alloys of antimony, bismuth and/or silver. Most of these provide sufficient output at wavelengths down to 190 nm.

Cesium-antimony cathodes operate well up to 500 nm however output falls at 760 nm.

Trialkali cathodes of antimony-sodium-potassium-cesium respond well up to 850 nm.

Gallium arsenide cathodes have a good response up to the high wavelengths.

Important characteristics of a photomultiplier are its dark current and noise which increases as the voltage is applied. An amplification factor of greater than 100 is achieved by increasing the voltage over the dynode system. The gain (g) of a photomultiplier increases exponentially with the interdynode voltage V. The relationship is:

$$g = KV^{0.7n}$$

where:

n = number of dynodes.

The high voltage supply should be stabilized to 0.05% or better.

The photomultiplier is a series of electrodes (or dynodes) each with an emissive surface and a positive potential relative to the previous electrode. When a photon hits the emissive surface an electron is ejected is accelerated and strikes the next dynode ejecting more electrons, until a shower of electrons reach the anode. In this way a single photon striking the emissive surface generates a whole shower of electrons and produces a significant electrical signal. The sensitivity of the system is dependent on the voltage between the dynodes. The higher the voltage the higher the amplification. Too much causes a noisy signal and is adjusted to give an acceptable signal to noise ratio (S/N). It is important to choose the photomultiplier to cover the wavelength range one is interested in as the output signal varies with the wavelength used.

Shot noise is the actual statistical variations in output caused by electron showers generated between dynodes as the dynode voltage increases. It is proportional to the square root of the intensity of radiation falling on the photocathode.

Complementary Sample Introduction Techniques

Although flame AA is perfectly adequate for determining low levels of elements in the mg L^{-1} range, it is often necessary to measure much lower levels. To accommodate these demands other sample introduction techniques have been developed as follows:

The Sampling Boat

Kahn et al (7) developed a system using a tantalum boat which could be pushed into a flame after the sample had been carefully evaporated. This was achieved by bringing the sample boat close to the flame, then finally inserting it to record a high narrow absorption peak. The boat was 5cm in length and 1 - 2 mm wide and deep and tantalum was chosen because of good conductivity and resistance to heat. The device was useful for the volatile elements such as As, Cd, In, Pb, Hg, Se, Ag, and Tl. A large volume of 1 mL could be evaporated and heated to give sensitivity of $0.0001 \mu\text{g/mL}$ for Cd and Ag.

Delves Cup

A device which uses a platinum loop and a nickel crucible is called the Delves Cup (8). This cup is mounted in a flame beneath a nickel or silica tube which has a hole in its underside. The sample becomes partially atomized and passes up into the tube where it remains in the optical path for a longer time than in a conventional flame. Lean flames or comparatively cool air/propane flames are used with this system to determine volatile elements such as lead, cadmium and thallium. This technique is mainly used as a screening method for lead and can be used to measure down to less than $100 \mu\text{g L}^{-1}$ (100 ppb) lead for whole blood. Various metal crucibles have been used such as tantalum, stainless steel and molybdenum. The nickel tube has been replaced with ceramic and or silicon carbide tubes

Slotted Tube Atom Trap (STAT)

A development from the above technique is the slotted tube atom trap. It consists of a silica or quartz tube 120 mm long \times 8 mm internal diameter with a 50 mm slot in the bottom and a 40 mm slot above it and is usually restricted for use with the 50 mm path length burner using the air/acetylene flame. It is based on an early design by Watling 1977 (9), which had two slots 120° apart and parallel to each other.

The tube is positioned over the burner with the longer slot directly above the flame which effectively “traps” the atoms. This provides a longer residence time for the metal atoms produced in the flame as it condenses them into a more confined space. The tube is normally conditioned for about 10 - 15 minutes by aspirating a solution of 1%*m/v* of lanthanum chloride solution to coat the tube to prevent devitrification and to possibly increase the surface area.

Those elements which show enhanced sensitivity with this device are thermally disassociated in the hot primary reaction zone of a fuel lean air/acetylene flame. These elements are referred to as the volatile elements which are characterized by low dissociation energies M-O or M-Cl. The elements that show this enhanced response are shown below:

Table 5-1. Elements showing an enhanced response^a

| Ib | IIb | IIIb | IVb | Vb | VIb |
|----|-----|------|------|----|-----|
| Cu | Zn | (Ga) | (Ge) | As | Se |
| Ag | Cd | (In) | Sn | Sb | Te |
| Au | Hg | Tl | Pb | Bi | |

^a () indicates no data or limited applications

Elements with relatively high M-O dissociation energies such as the high atomic weight transition metals and the refractory elements which are normally best determined in a nitrous oxide/acetylene flame, do not show any improvement with the STAT. Nitrous oxide/acetylene cannot be used with the quartz tube, as it will melt in the much hotter flame.

This technique is quite useful for rapid screening of a sample to determine whether or not it satisfies a particular criteria, as it is simple and quick to use. Levels down to 50 ppb for lead in blood have been determined. Cadmium at the 5 ppb level has also been reported. The advantage of this technique is a 3 - 5 times increase in sensitivity over conventional flame AAS and quicker sample throughput compared with a graphite furnace system.

Aliquot Microsampling Technique

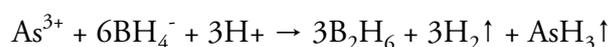
The device to carry out aliquot sampling normally consists of a small PTFE block with a well at the top end and a hole drilled through to the opposite side to enable the capillary tube of the nebulizer to be attached. A plastic micro-pipette tip may be used instead of the PTFE block and can be attached to the instrument within a matter of seconds.

This technique is known under a variety of names such as direct injection, aliquot or pulsed or Hoescht cup nebulization. It is primarily used to inject small discrete amounts of sample into the flame AAS normally between 50 - 100 μ l. The advantage of this accessory is that if only small amounts of sample are available, more than one element can

be determined from this small sample volume and may be analyzed with the same speed of a continuous flame system. The sensitivities obtained with this technique are only marginally lower than when an equilibrium or steady state due to continuous aspiration is achieved in the normal flame AAS mode. This technique also enables the injection of solutions containing higher levels of dissolved solids of between 12 - 15% to be injected, compared with the 5% normally allowed for some burners. The reproducibility of this technique is within 2% when using peak height measurement.

Hydride Generation Technique

Many elements are difficult to determine by flame AAS because their primary resonance lines are below 200 nm where the absorption by the flame gases is strong. Electrothermal atomization with background correction can be used to study these elements, but an alternate approach is to use the property of some metals to form hydrides. The hydride then can be decomposed to an atomic vapor without directly being in a flame. A number of elements which form volatile hydrides are antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin. Formerly hydrides were generated by zinc-hydrochloric acid reduction and collected in a balloon before passing the vapor into an argon-hydrogen flame. A more efficient reducing agent is 1% sodium borohydride solution which is prepared in 0.1% NaOH. The solution containing the acidified sample is reacted with sodium borohydride as follows:



The B_2H_6 is then hydrolyzed to boric acid.

The hydride produced is carried usually in a stream of inert gas to the atomizer which is a silica T piece tube mounted in the flame. The AsH_3 then decomposes to As and is measured in the usual manner. The response for arsenic and antimony varies with their valence state in that the +5 state gives a poorer response than the +3 state. These elements should be reduced with potassium iodide prior to hydride generation. Similarly tellurium, selenium, must be in the +4 state and not the +6 state.

There is some evidence of interference by other species in the tube itself and precautions must be taken to avoid these. One such problem is residual hydrogen chloride vapor.

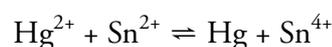
Easily reduced elements such as silver, cobalt, nickel, gold and copper have been reported to suppress the production of hydride producing elements. The metal ions which are reduced by the sodium borohydride precipitate out as a fine dispersion of free metals which catalyzes the hydride. One solution is to add a higher concentration of hydrochloric acid to dissolve these metals. The main advantage of the hydride system,

is that the flame gases are not absorbed at the wavelength used, provided the hydrogen produced does not burn. As there is a longer residence time for the atoms, greatly increased sensitivity is obtained compared with flame AAS.

Mercury Cold Vapor Technique

Mercury is the only element apart from the inert gases with appreciable vapor pressure at room temperature. The procedure used for mercury analysis is similar to that of the hydride system, except that the evolved Hg does not have to be heated as it is already in the atomic form. The silica T piece can also be constructed from glass.

The reduction of the mercury is carried out in a similar manner to the other hydride forming elements and can be reduced with either sodium borohydride or tin II chloride, which proceeds according to the following reaction:



The mercury vapor is flushed out of the system into the T piece and measured. Some enclosed systems with silica windows use a circulating pump and allow the mercury vapor to reach equilibrium with the argon gas.

The longer residence time in the tube also increases the sensitivity 100 times compared with flame AAS. Background correction is not normally required. Some reducible elements such as gold, silver, palladium and platinum can interfere with reduction. Detection limits of $< 1 \text{ ng mL}^{-1}$ are obtainable by this technique.

Mercury Amalgam System

This system consists of a copper, gold, silver or platinum gauze, placed inside a tube surrounded by a resistance wire heating coil. Some systems use gold sand in place of the metal gauze. The principle behind this device makes use of the ability of mercury to form amalgams with the above mentioned metals. The mercury vapor can be produced by hydride generation or continuous flow equipment. Mercury from air samples may also be passed over the gold sand to produce a mercury amalgam.

Although the continuous flow hydride generation system is adequate for Hg at the ppb level, the amalgam device can measure mercury at the 20 ng L^{-1} level. This is achieved by passing mercury vapor across the gold gauze to produce the amalgam. The mercury is collected for a defined period of time usually between 0.5 to 2 minutes and then re-vaporized with the action of heat and passed to the detection system. The timing and the amount of heat is controllable, as is the flow of

argon, which carries the mercury vapor straight into the atom cell of the spectrometer. A much stronger absorbance signal is obtained than when the mercury vapor is transported directly into the spectrometer with no preconcentration. The signal is then measured by either peak height or area.

Flow Injection Analysis

In 1975, unsegmented flow methods were described for the first time and are now referred to as flow injection analysis (FIA). In this technique the flow is not segmented by air bubbles and hence differs from the segmented flow system used in autoanalyzers. The sample is injected into the flowing stream instead of directly aspirated into the flame and before physical or chemical equilibrium has been attained, the signal is recorded.

More recent work has shown that segmenting the carrier stream with air bubbles introduced immediately before the sample injection loop, improves analytical sensitivity when used with a typical spray chamber configuration. This technique is known as segmented flow injection analysis (SFIA).

The device is quite simple. The carrier containing the sample in solution is pumped in a continuous fashion and aspirated in the nebulizer. Flame techniques normally use a sample volume of 0.5 - 2 mL for the determination of an element by continuous aspiration. The advantage of this system is that small sample volumes between 10 and 200 μL can be injected when using SFIA coupled with flame AAS. High dissolved solids can be tolerated and viscosity effects minimized, by dilution of the sample prior to aspiration. The various release agents and ionization suppressants can also be introduced into the SFIA-AAS system. Interference effects may be minimized by adding various reagents or by carrying out a chromatographic separation on stream. It is possible to enhance the sensitivity of the determination using a preconcentration step such as liquid-liquid extraction or ion-exchange. High sample throughput can also be achieved with this technique and automation of the sample preparation can be adapted to the SFIA system.

Atom Trapping Technique

This device is used to increase the residence time of atoms in the flame of conventional AAS. A single or double silica tube is mounted in the flame with cooling water passing through the tube. The solution to be measured is aspirated in the normal manner for a fixed period of time, usually from 1 to 2 minutes and the metals are trapped on the relatively cool surface of the silica at 350 - 400°C. The cooling water is forced out using argon, nitrogen or air and the tube rapidly heats up in the flame

Complementary Sample Introduction Techniques

Atom Trapping Technique

producing a concentrated cloud of atoms. The peak height or area is then used to measure the transient signal. A detection limit in the ppb range is obtained which is much lower than in conventional flame AAS.

Optical Systems

Single Beam Instruments

The typical single beam instrument which uses a pre-slit optical system is shown in [Figure 6-1](#), viewed from above:

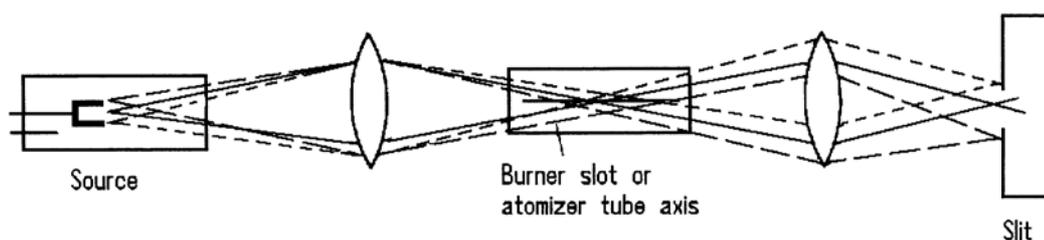


Figure 6-1. Single beam instrument

In this single beam spectrometer, as in any other single beam spectrometer, the light falling on the detector is proportional to the light transmitted through the sample. To obtain the absorbance, it is necessary to take a reading through the blank and then again through the sample, using a source with stable intensity. The system should be stable over the entire period during which the measurements are being made, so that reagents and standards do not have to be run at regular intervals. Modern hollow cathode lamps and electrodeless lamps emit the same intensity over long periods, although no source is completely without drift. The effects of source variation can, to a large extent, be overcome by using double beam optics.

There are a number of different optical layouts for a single beam instrument such as the Littrow, Ebert, and Czerny-Turner. A grating may be mounted in a monochromator in a number of ways, see [Figure 6-2](#) in the Littrow.

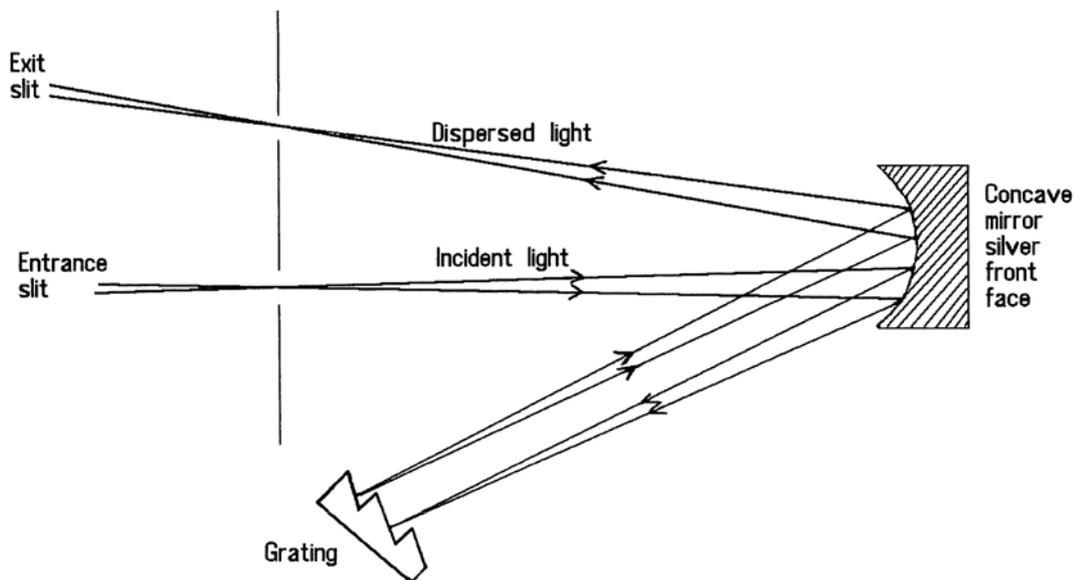


Figure 6-2. Littrow monochromator

Another arrangement is the Ebert mounting, which uses a large spherical mirror to collimate and focus the beam, see [Figure 6-3](#):

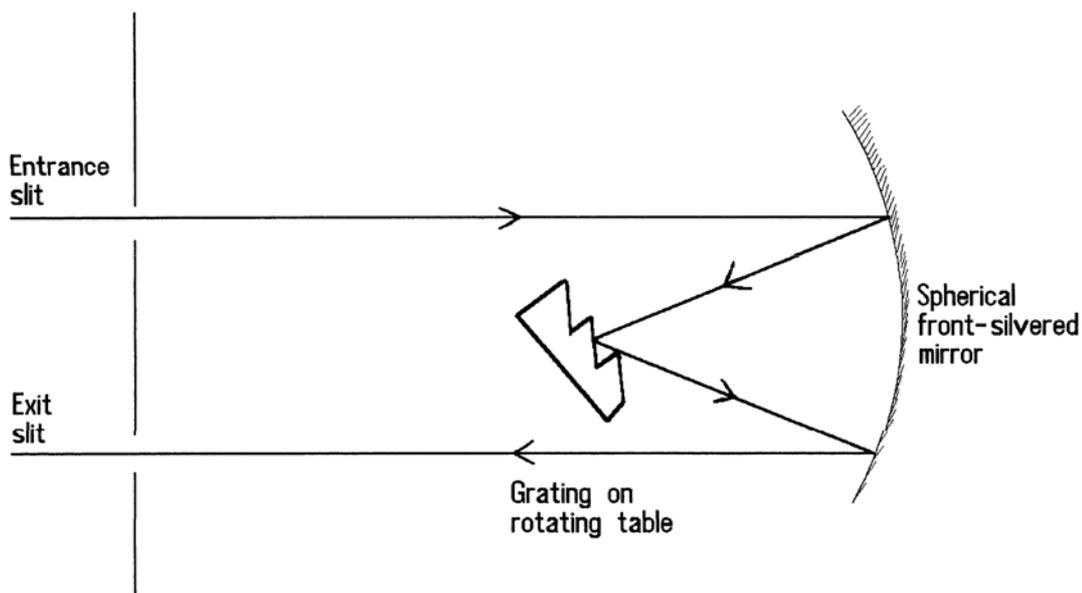


Figure 6-3. Ebert monochromator

A more highly energy efficient single beam system can be designed, using the Ebert configuration with a low number of optical components. This allows lower photomultiplier gain to be used, with lower lamp currents improving the base line noise levels. Accurate wide dynamic range background correction can be provided, while the problems of drift can best be tackled at source by designing stable lamps and power supplies. This approach was used with great success in the layout, see [Figure 6-4](#).

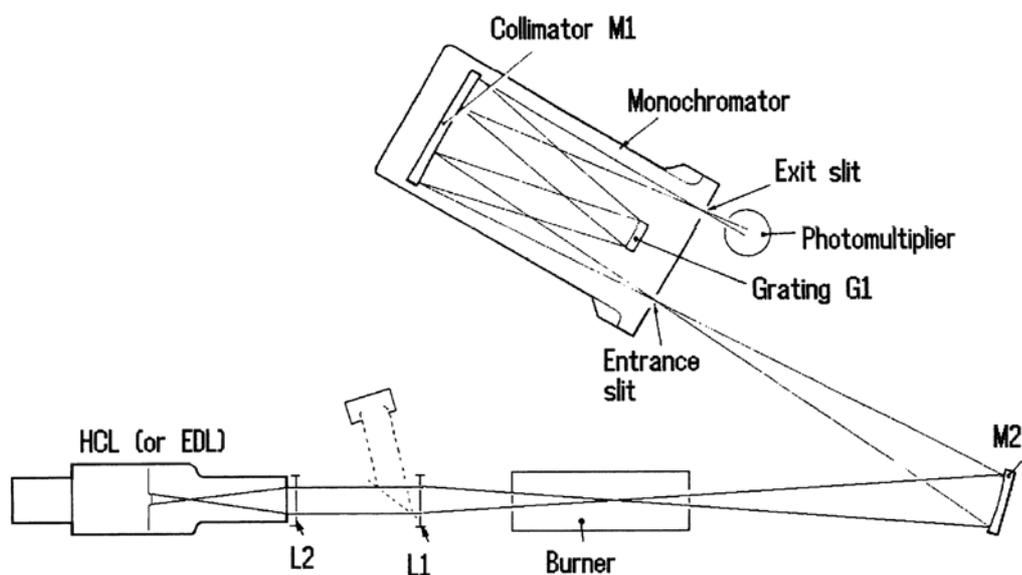


Figure 6-4. Ebert configuration

Czerny and Turner replaced the large Ebert mirror with two small spherical mirrors mounted symmetrically, see [Figure 6-5](#).

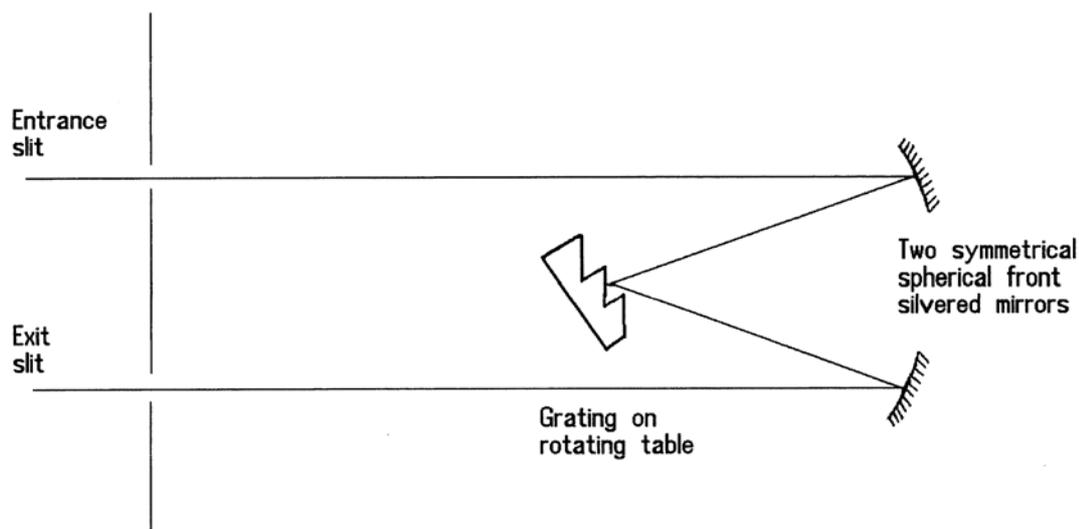


Figure 6-5. Czerny-Turner monochromator

The Czerny-Turner mounting is popular for atomic absorption spectrometers, as it combines economy, with relative freedom from aberrations.

Double Beam Instruments

The light from the source is split into two beams by means of a rotating half-silvered mirror, or by a beam splitter which is a 50% transmitting mirror. This directs the beam alternatively through the flame and along a path which by-passes the flame at a frequency usually at 50Hz or higher. Once past the flame, the beams are recombined with a half-silvered mirror, see [Figure 6-6](#):

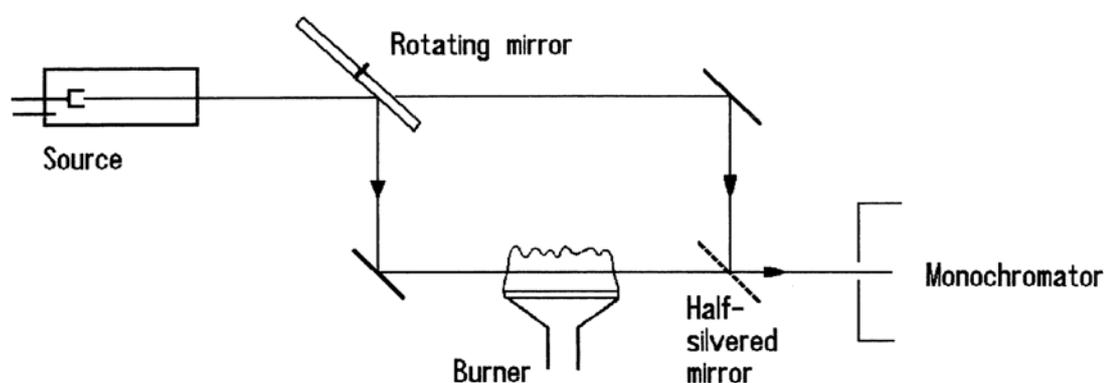


Figure 6-6. Basic double beam optical system

At the detector end, the output signals which correspond to each beam are divided, amplified separately and compared in a bridge circuit. The out-of-balance signal is then compensated electronically and converted to absorbance.

A double beam atomic absorption spectrometer does not have the advantages of a double beam ultraviolet or visible spectrometer. True absorbance can be measured in an ultra violet or visible system as the reference beam of energy passes through the cell, which can contain everything, except the sample being measured. In the atomic absorption system, the reference beam does not pass through the flame. If the reference beam passed through a second flame, the noise characteristics could not be guaranteed to be similar, as the flame is a dynamic system.

The normal double beam system only corrects for variations in primary source intensity and detector response. It does not correct for any spurious absorption or scatter in the flame and it will not correct for changes taking place in the primary source lamp, particularly during warm up. A further disadvantage is that 50% of the incident energy is wasted.

Background correction can be achieved by using a double beam instrument, which incorporates the deuterium or continuum source and positioning it as shown in Figure 6-7.

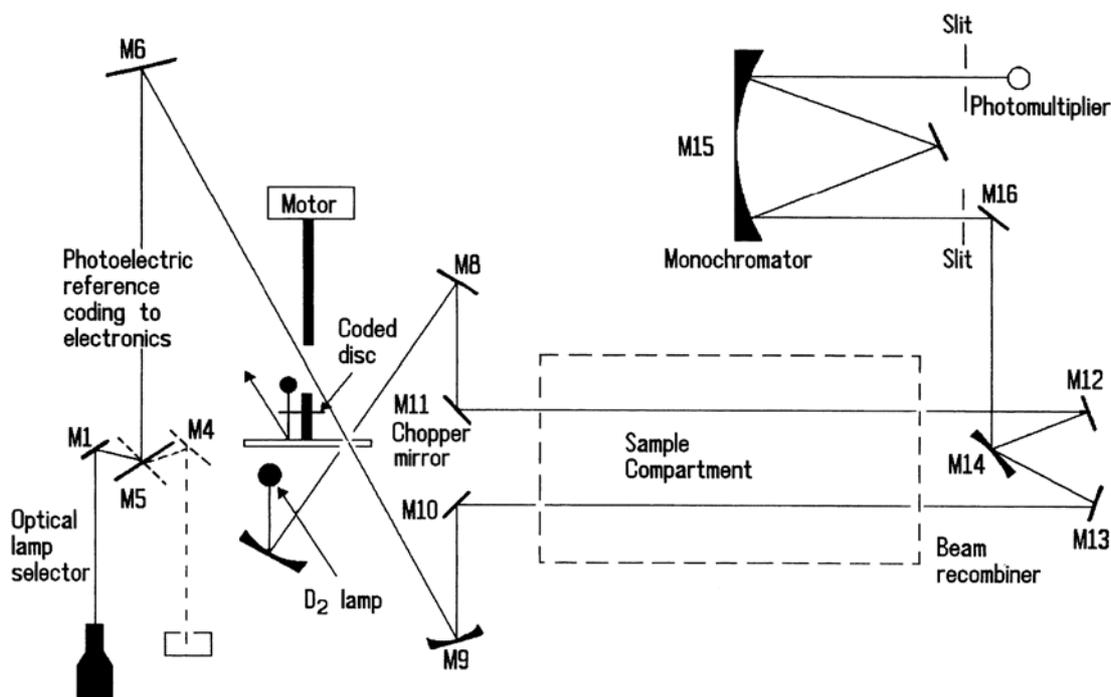


Figure 6-7. Double beam instrument with background correction

The deuterium lamp and the hollow cathode lamp are positioned, so that the chopping mirror reflects the light from both lamps, along the sample beam in alternate pulses. The instrument then measures the total absorbance in the sample channel and the background in the reference channel, using their respective electronics. The background channel is subtracted by the output circuitry from the sample channel, to give the corrected absorbance. In this mode the double beam instrument is essentially operating as a single beam instrument, as the reference beam is inoperative.

A single beam instrument gives background correction by incorporating the continuum source and chopper together, with a “double beam” read-out system. This is sometimes referred to as “quasi double beam” or dual channel system. This type of instrument with background correction, can correct only detector response drift.

In some instruments true double beam operation with background correction is possible. Such a system incorporates four electronic channels and one detector and corrects for drifts in both source lamps, as well as electronic drifts. There is usually at least one static beam splitter in each optical channel, and relative noise levels are adversely affected. Static beam splitters lose 50% of their incident light energy, however a rotary chopper in conjunction with pulsed lamps overcomes

this problem. The lamp pulse must be shorter than the chopping frequency, otherwise the chopper partially crosses the beam affecting the beam shape, and the efficiency of background correction in electrothermal atomization. Any phasing problems with pulsed lamps are overcome by the use of a coding disc on the chopper as shown above. The usual practice is to incorporate a static device at a point in the optical path, to overcome the difficulty of beam splitting and recombining.

Stockdale Optics

This system was designed to offer the high energy throughput of a single beam design, with the drift-free performance of a double beam arrangement. The configuration which combines these properties has been named the Stockdale configuration. The optical diagram is shown in Figure 6-8:

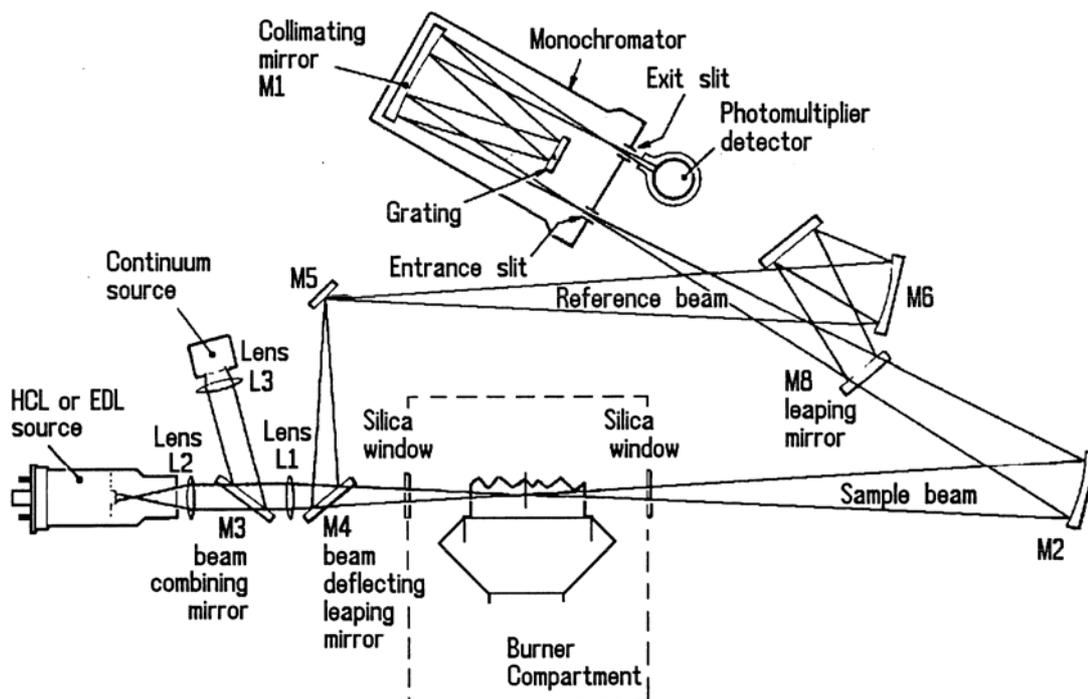


Figure 6-8. Stockdale configuration

To understand the operation of this system, compare this with in Figure 6-4. Note that it is the same, except components M4-M8 have now been added.

When the instrument's auto zero function is activated, the mirrors M4 and M8 drop into the radiation path by-passing the flame and the radiation is then deflected by mirrors M5, M6 and M7. The absorbance signal is integrated for a short period of time and the value stored by the microprocessor. Mirrors M4 and M8 flip out of the radiation path,

returning the system to single beam mode, and allowing the beam to pass through the flame. The absorbance is then measured again. The difference between the first-reading, the reference measurement and the second reading the “sample” measurement, without any sample being aspirated, is the measurement of the absorbance of the flame itself. This measurement is stored as the zero absorbance offset. When a run is made with this type of system, with either a standard or a sample, the mirrors M4 and M8 again drop into place, deflecting the beam into the reference channel. The reference absorbance is then stored. The mirrors lift out of the beam and the absorbance of the standard or sample and flame are measured and the reference result subtracted. The result is the absorbance of the flame and the sample. Subtraction of the zero offset then gives the true sample absorbance. Any drift in the instrument, for example the lamps output, affects both reference and sample absorbance equally, and so is canceled out when the two readings are subtracted, so that completely drift free results are obtained.

Background Correction

Some background absorption is continually present in a flame spectrometer from the C_2 , CH and OH species, and is allowed for when the blank solution is analyzed. However, it is necessary to eliminate changes in absorption, which occur when a sample is introduced to the atom cell, which are not caused by the atoms of the analyte, but by all other species or matrix present in the sample. Compare the two spectra of a sample and a blank below. Figure 7-2 is in the presence of background interference, Figure 7-1 is not.

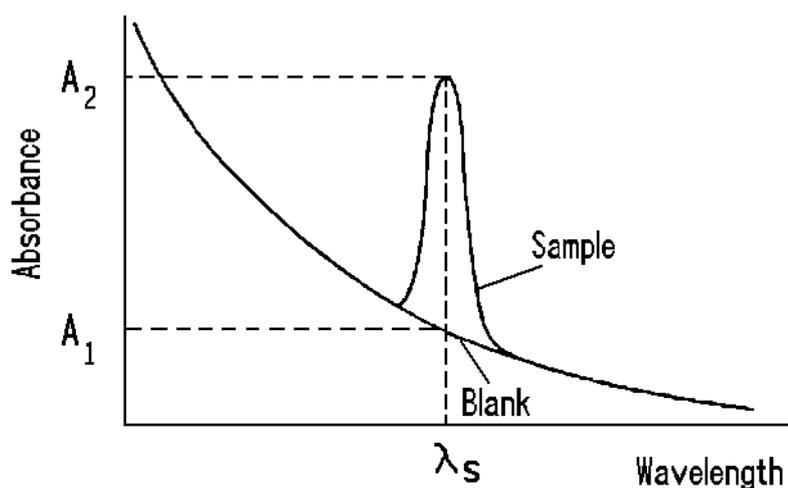


Figure 7-1. Absorption spectrum of sample and blank

In Figure 7-1, the background absorption for both the blank and the sample is the same, due to molecular absorption and light scattering. The actual absorbance of the sample at wavelength λ can be determined by subtracting the absorbance without the sample from the absorbance with the sample ($A_2 - A_1$). In practice this is done by adjusting the value of A_1 to zero, to give the true reading directly.

In Figure 7-2, because the background absorption for the sample is higher than that for the blank, using $A_2 - A_1$ (or setting A_1 to zero) will not give a correct value for the sample's absorbance and it will be overestimated. Estimating the value of A_3 and using $A_2 - A_3$ to determine the true absorbance value will be more accurate.

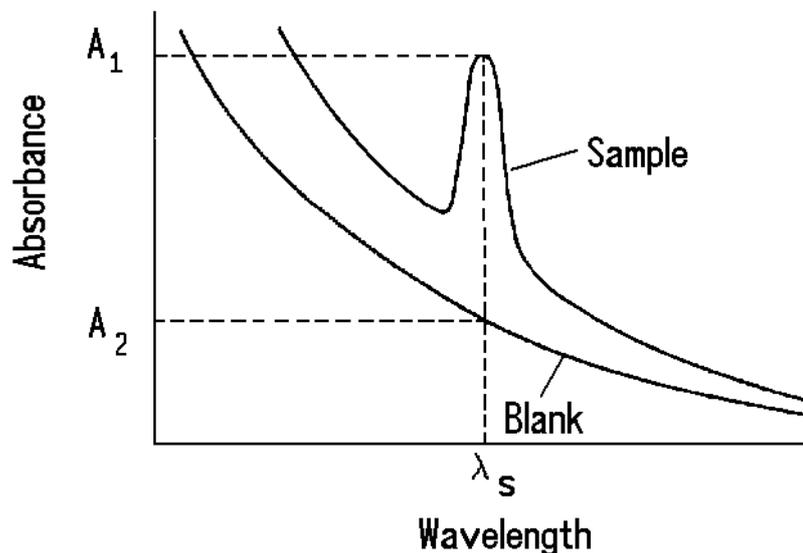


Figure 7-2. Absorption spectrum of sample and blank in the presence of background interference

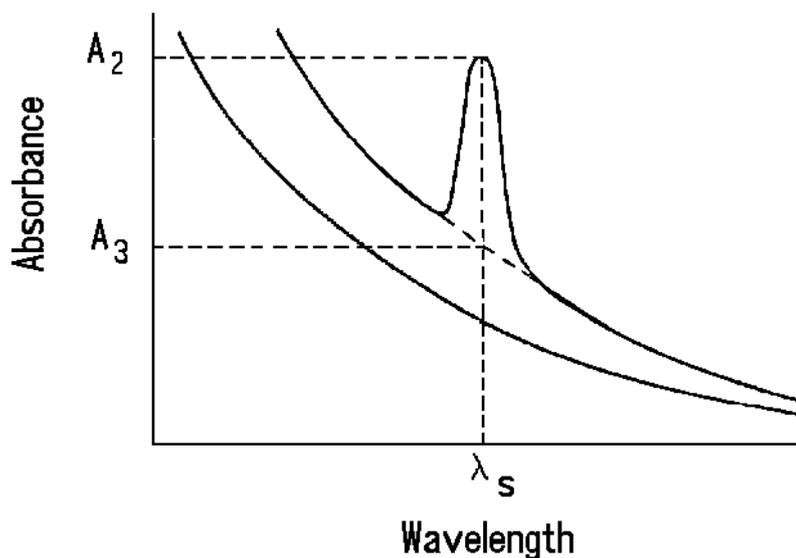


Figure 7-3. Comparison of sample absorbance and measured absorbance in the presence of background interference

Causes of Background Interference

Molecular Absorption

Molecular absorption is caused by other species of absorbing molecules introduced into the atom cell, along with the sample. As molecules absorb over a much wider range of wavelength than atoms, and may be present in much higher concentrations than the atoms of the sample, some absorption may occur at the same wavelength as the element analyzed. Interference due to molecular absorption is particularly a problem when large concentrations of alkali metal and alkaline earth metal halides are present e.g. sodium fluoride, potassium chloride.

Atomic Absorption

Interference may be caused by other species of absorbing atoms present in the sample, which have similar spectral lines. For example, antimony in a nickel sample can interfere with the determination of nickel. This is generally more rare and depends on the concentration of the interfering atom.

Light Scattering

Introducing particles into the atom cell can cause the light to scatter allowing less light to reach the detector and therefore an apparent increase in absorption. The effect is similar to fog or smog, which results in the scattering of sunlight decreasing the amount of light reaching the earth.

Background interference is not always a problem for all systems, although certain types of atom cells such as electrothermal and graphite furnace, are more prone than others. Few of the molecules likely to be present in an atom cell can absorb visible light or infra-red radiation and usually only the ultra-violet light is absorbed. Light scattering, is also an effect high enough to be a problem in the ultra-violet region of the spectrum. Therefore, background interference is usually only problematical at wavelengths below 350 nm.

Background Correction

Causes of Background Interference

Methods of Background Correction

There are at least five ways to correct for background absorption effects:

- Blank method
- Dual line method
- The continuum lamp method
- Zeeman method
- Smith-Hieftje method

Blank Method

The first method used, is to run a blank in the flame at the resonance line of the metal being determined, then run the sample on its own in the flame. The two readings are then subtracted, and the difference between the two is the absorbance of metal in the sample. If the blank consists of only deionized water, then this does not take into account the above mentioned interferences.

Dual Line Method

The dual or two line method, requires that two readings are made with the same hollow cathode lamp, at different wavelengths, a few nanometers apart. This method relies on the assumption, that scattering of light by non-atomic species is independent of wavelength, when measured within a few nanometers of the absorption wavelength. The first measurement, is at the primary absorption wavelength of the atom of interest. This measures a combination of absorbance by the atom of the element of interest and the non-atomic species. A second measurement is taken at a nearby non-absorbing wavelength, which measures the absorbance of the non-atomic species only. Subtraction of the two readings, gives the atomic absorbance of the element of interest. This method was originally developed for the single beam instrument, however it does have two important disadvantages:

1. The two absorbance measurements take place sequentially and good background correction will only be obtained, if the population of non-atomic species is the same for both readings. This is unlikely to be true of a graphite furnace system, as the concentration and distribution of smoke particles after successive atomization phases, will not necessarily be the same.

2. The non absorbing line for the element used for the measurement of non-atomic absorbance, may not be sufficiently close in wavelength to the main atomic absorption resonance line. The two wavelengths must be close, to ensure identical absorption coefficients for the non-atomic species.

The Continuum Lamp Method

This system consists of using two lamps, a hollow cathode lamp of the element of interest and a deuterium continuum lamp. The hollow cathode lamp emits a very narrow line width of around 0.002 nm and the deuterium arc lamp emits approximately over the wavelength range 200-340 nm. The deuterium arc lamp is a simple electrical discharge between two electrodes, in an atmosphere of deuterium gas. Most of the emitted radiation is generated from electronically excited molecules of deuterium and therefore will have a wide spectral range.

When the sample is introduced to the instrument and atomized, the signal reaching the detector is in the form of a square wave and the alternating voltage generated is proportional to the difference in the absorption of the two beams. The light from the hollow cathode lamp is absorbed by both the sample and the background, while the light from the deuterium lamp is absorbed almost entirely by the background. The difference in absorption between the two beams is due to the sample absorption only.

A broad band light source from the deuterium lamp will give only a negligible reading for a very sharp absorption line. [Figure 8-1](#) shows light reaching the detector through a monochromator with a spectral band pass of 0.2 nm. Even though the peak absorbance for a sharp atomic line of width 0.004 nm is high at 0.6 ABS, the detector is receiving light at all wavelengths within the monochromator bandpass. The measured absorbance is 0.012, which can be calculated by multiplying the absorbance 0.6 x the line width 0.004nm and dividing by the slit width of 0.2 nm. This is 2% of the peak absorbance value and

the detector hardly notices this small amount of absorbance by the atom cell. A wider band pass than 0.2 nm would reduce this percentage even further.

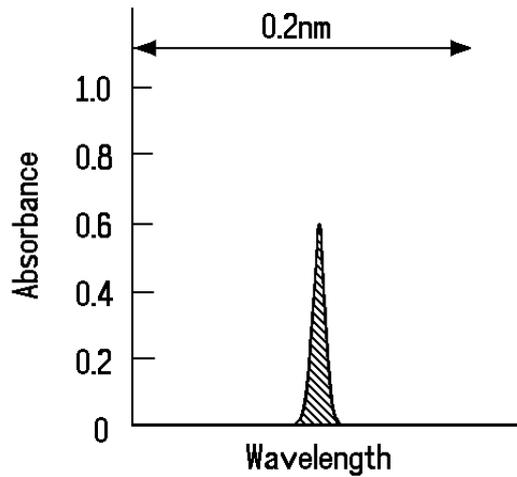


Figure 8-1. Measurement of absorbance using a broad band source (no background signal present)

Figure 8-2 illustrates what would happen if a background signal were actually present when the sample element was being absorbed. A narrow absorption band is superimposed on the flat background signal. Over the monochromator bandpass or slit width of 0.1 to 1.0 nm, the spectrum due to the background absorption, can usually be assumed to be flat.

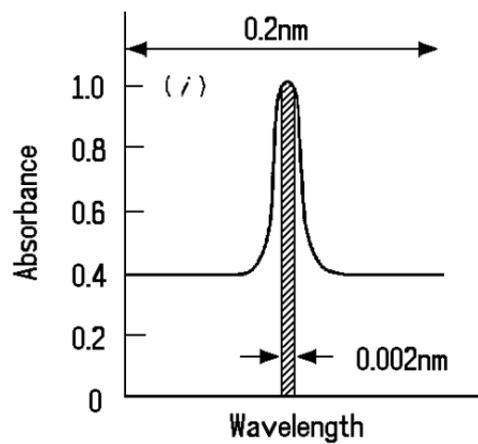


Figure 8-2. Light absorption from hollow cathode lamp

In Figure 8-2, the shaded narrow line shows the light absorbed from the hollow cathode lamp. The emission from this lamp, has a much narrower line width than the sample absorption line and only the center of the absorption line is sampled.

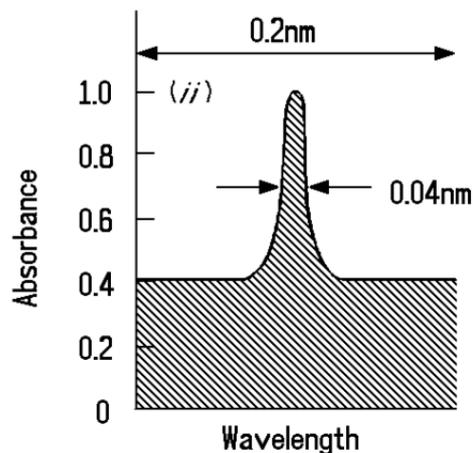


Figure 8-3. Light absorption from deuterium lamp

In Figure 8-3, the shaded portion shows the light absorbed by the deuterium lamp. As the emission from the lamp is very much broader than the sample absorption, an average value of the absorbance is taken over the whole bandpass of the monochromator. The absorption peak will be much narrower than shown, and the average absorbance slightly above 0.4. The sample absorbance after subtracting the background should be 0.6 (1.0 - 0.4). This is the absorbance signal that would be measured if the spectrum was scanned at very high resolution, or if there was no background signal.

The deuterium arc system is a widely used system, able to cope with most background correction problems. One failing is an inability to differentiate between sharply varying background signals. Another difficulty is that it is not always easy to align the two beams exactly along the light path, through the atom cell, in a graphite furnace AAS.

The Zeeman Effect Method

An intense magnetic field is used in this system (10), to broaden either the emission from the lamp, or the absorption spectrum of the sample. This enables the absorption signal to be measured very close to the atomic absorption line. The magnet can be placed around the lamp, or the atom cell, although the most commonly used orientation is around the atom cell. If the magnet is placed around the hollow cathode lamp, the lamp design must be modified, as the magnetic field affects the operation of the lamp.

The Zeeman effect is the dividing of a single spectral line into three or more components when the radiation source is placed in a magnetic field. It results from the different energy changes caused by interactions between the magnetic field and the spin and orbital magnetic moments of an atom. The “normal” Zeeman effect arises when an atomic system having a spin quantum number of one, is viewed in a direction perpendicular to the magnetic field. The single spectral line becomes split into three components, generally symmetrical about the original non-field spectral line. An example is shown below for magnesium at 285.2 nm.

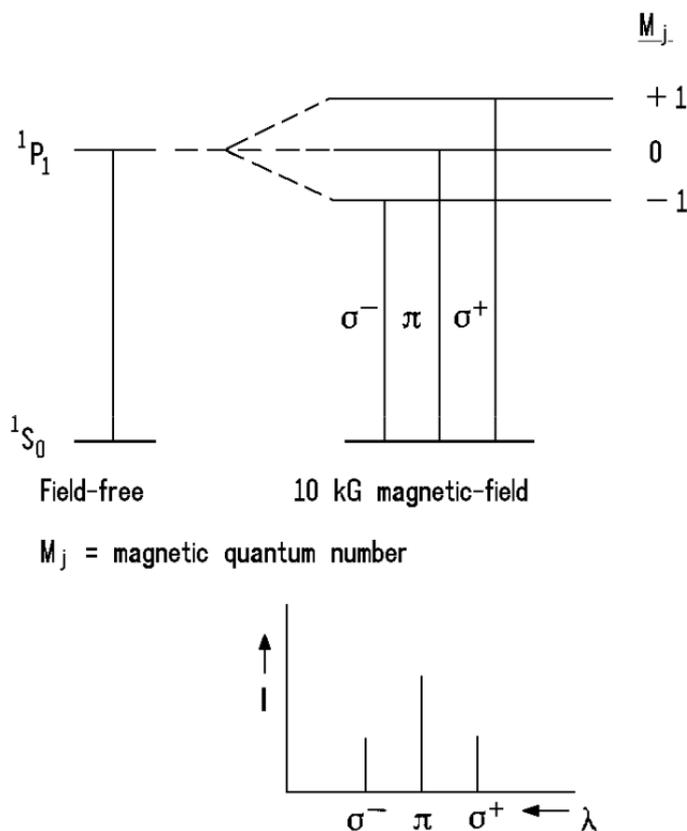


Figure 8-4. Zeeman splitting in the “Normal” case

The three components consist of a π and two δ lines (labeled - and +) with an intensity ratio of 1:2:1. When a 10 kG field is applied, the components are shifted from the p component by 0.0038 nm. Examples of elements showing the normal effect are Be, Mg, Ca, Sr, Ba, Zn, Cd, Pb, Ag and Hg. The bulk of the elements however show the “Anomalous” Zeeman effect, where more than three components are produced. The sodium D-lines have been used as an example, here the D1 line is split into four lines (two π and two δ lines) and the D2 lines into six lines (two π and four δ lines). In general, the Anomalous

Zeeman components are symmetrical about the field-free line, with the π lines shifted less than the δ lines. The figures below show the various combinations for sodium and other elements:

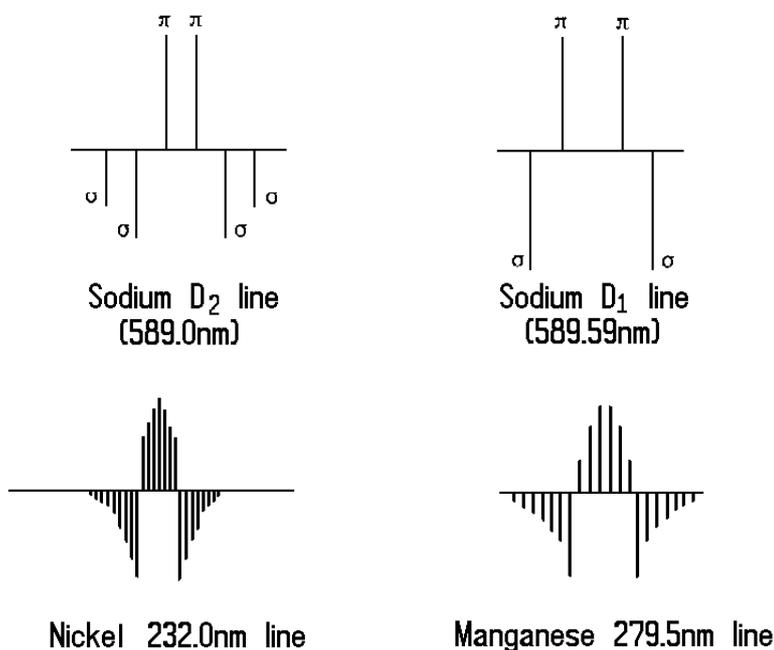


Figure 8-5. Zeeman splitting in the "Anomalous" case

To understand how the effect can be utilized for background correction, consider first the normal Zeeman effect case. When the magnetic field is applied to the sample vapor, the π line is polarized in the horizontal plane and the δ lines are polarized vertically with respect to the magnetic field. If the incident light is alternatively polarized parallel and perpendicular, then several effects occur.

The broad band background or scattering effects are not polarized and both polarized light beams are attenuated equally. When the incident light is polarized parallel to the field, the beam is attenuated by atomic absorption plus any background. Incident light polarized perpendicular to the field is attenuated by the background only, as the components are shifted and do not attenuate the beam. Therefore, alternate measurements can be made, the background only reading, subtracted from the atomic absorption plus background signal and hence read-out of atomic absorption obtained.

Some of the advantages of this technique are:

Only one light source is used, eliminating alignment problems.

The background is sampled at the wavelength of sample absorption, overcoming the problem of highly structured backgrounds.

Only very close atomic lines separated by approximately 0.01 nm are a problem.

The technique is not limited to lamps operating in the ultraviolet region.

Some of the disadvantages of this technique would include:

There is some loss of sensitivity, up to 50%, depending on the element, because the perpendicular component is partly absorbed by the sample.

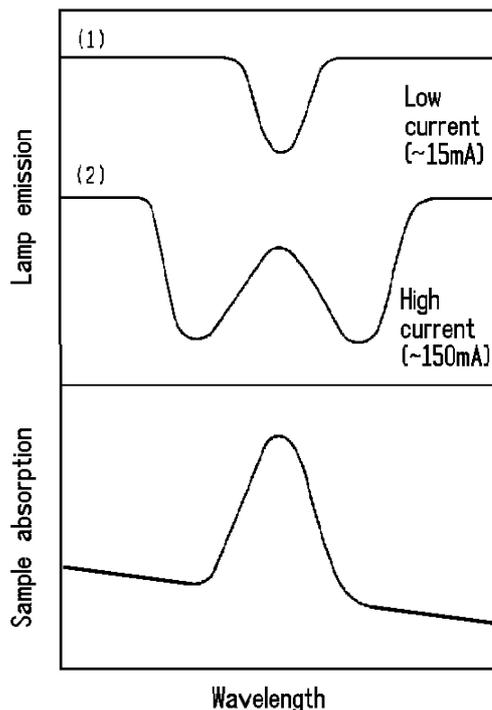
At high concentrations the working curve can turn downwards, an effect known as “rollover”. To avoid this problem it is necessary to limit the working range for some elements.

The technique is rather expensive.

Special hollow cathode lamps are required if the magnet is placed around the lamp. The difficulty associated with placing magnets around the lamp, is that the magnetic field used to generate Zeeman splitting, also interacts with the ions in the hollow cathode. This causes the emission from the hollow cathode lamp to be noisy, which in turn introduces imprecision.

Smith-Hieftje Method

A single light source is used for this method and the spectral output profile of the lamp is modified to measure the background (11). This is achieved by operating the lamp alternatively at low and high current. At low lamp current, the narrow hollow cathode lamp emission line is used to measure the absorbance at the peak of the atomic absorption line of the sample. At high lamp current, self absorption causes a broadening of the lamp output, with a dip appearing in the center of the emission profile. The total specific and non-specific absorbance is measured at low lamp current, while at high lamp current, the measured absorbance is essentially due to the background or non-specific absorption.



Labeled Components: (1) Low Current - measures the absorbance of both sample and background.
(2) High Current - measures mainly the background absorbance.

Figure 8-6. Smith-Hieftje background correction

The sample absorbance is the difference between the two absorbance readings. At high lamp current, there will be some absorption by the sample and this leads to a loss of sensitivity of a factor of two or three, depending on the element.

The advantages of the Smith-Hieftje system are the use of a single light source of any wavelength, and the ability to correct at the sample absorption line. Highly structured backgrounds can be corrected. The calibration curves are linear to an absorbance of 0.7.

The disadvantage of the technique is that the electronics cannot be economically incorporated into an existing spectrometer as extensive changes would be required in the electronics. Another drawback is that when analyzing for the more volatile elements the life of the hollow cathode lamp is shortened by the high current pulses.

Improvements in the analytical method, such as sample pre-treatment, can sometimes reduce the background signal. There is however a practical limit to how much background absorption can be corrected for. The use of background correction methods, will also reduce the precision of the determination.

Flame Atomizer

Nebulization

Sample introduction is a most important part of any AAS system. Usually the sample enters the flame base as a liquid droplet, and numerous steps are involved before the metal of interest leaves it in the form of an oxide and the sample is eventually atomized. Many of the larger drops do not evaporate completely and pass through the flame unaffected, taking with them the element of interest. The residue left behind after evaporation does not contribute to the absorption signal and passes through the flame without further decomposition to free atoms.

The function of the nebulizer is to produce an aerosol. The basic operation involves drawing up the sample at high velocity through a capillary tube to a fine jet, which forms a liquid aerosol or mist, before injection into the flame. A schematic diagram is shown in [Figure 9-1](#):

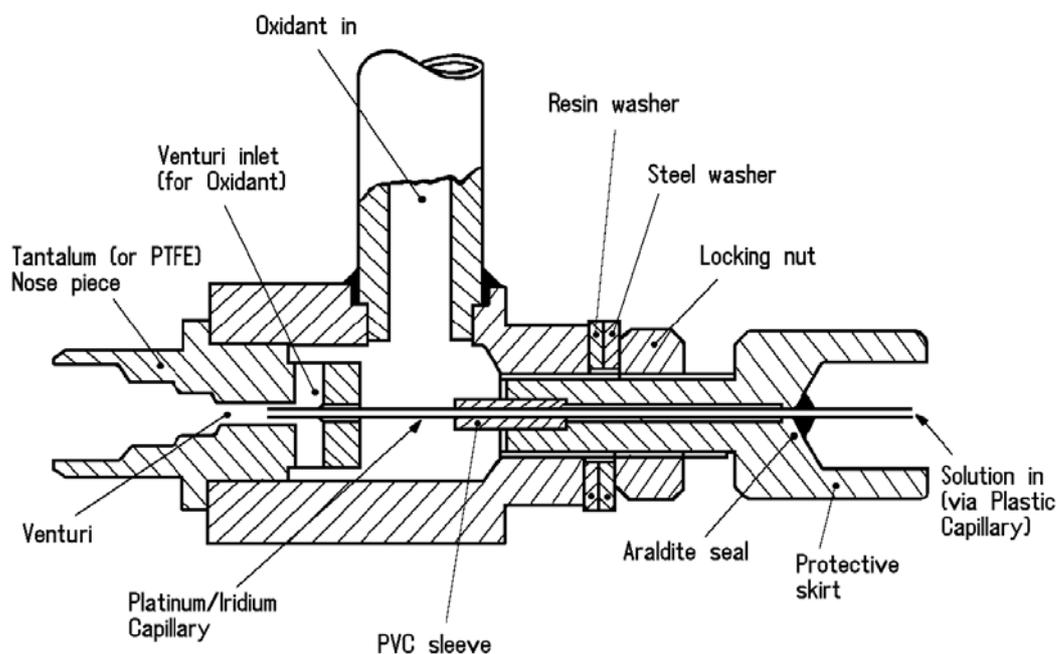


Figure 9-1. Nebulizer

The high flow of oxidant gases such as air, nitrous oxide or oxygen, draw the sample up through the polyethylene or P.T.F.E. capillary tube by the Venturi effect. The high gas flow rate across the end of a capillary, creates a pressure drop, and as the pressure in the capillary tube is below

that of atmospheric pressure, the solution is forced up the capillary. The high speed of the gas flow creates a turbulence, which breaks up the solution as it passes out of the capillary, to produce an aerosol.

The drop size can be further reduced by placing an impact bead made of borosilicate glass, an alloy, or plastic, in front of the orifice. As well as providing the aerosol, the nebulizer enables mixing of the sample, oxidant and fuel. Some instruments allow adjustment of the nebulizer capillary, to enable optimization of sample uptake and drop size. The impact bead may also be adjusted.

An alumina disc can be incorporated on the nebulizer end of the spray chamber, to remove memory effects. Spray from a nebulized solution which may arrive at this disc by rebounding from the impact bead, will run off and be drained away. Without the disc, droplets form at the plastic surface to be re-nebulized later, when other solutions are being aspirated, producing significant errors.

The fuel inlet is also attached to the spray chamber, which mixes with the sample aerosol. In some systems, there may be baffles or spoilers to filter out the larger drops. In addition a drain is required which must be filled with liquid, to prevent the possibility of flashback and explosion. The nebulizer is only about 10% efficient, with 90% of the solution passing to waste.

The spray chamber and nebulizer are usually constructed of an inert material such as fluoroplastic. A nebulizer can be constructed from a platinum-iridium alloy, with a tantalum nose piece which is resistant to acid attack. Efficiency of the nebulizer depends on a number of factors, such as flow rates, surface tension, density, viscosity, saturation vapor pressure, jet size and the geometry of the jet.

Nebulization efficiency depends on the solvent type. Solvents have physical properties that vary, such as surface tension. The lower the surface tension, the easier it is to break the liquid into drops. Organic solvents give finer aerosols than water and the nebulization is more efficient.

Ideally the solution to be aspirated should be homogeneous, as blockage of the capillary can occur if any solid material enters the end of the capillary. Filtration is not always suitable, as fibers from the filter paper may also block the tubing.

Ultrasonic Nebulization

Ultrasonic nebulizers have been used for flame work, but they are prone to “memory” effects, as traces of the aspirated sample may remain in the nebulizer chamber to contaminate the next sample. However, there may be an increase in sensitivity over conventional nebulizers.

Thermospray Nebulization

Nearly complete vaporization of the liquid is achieved at the rate with which it is supplied to the vaporizer. The superheated mist which is produced, is carried in a supersonic jet of vapor to the flame. Nonvolatile molecules are preferentially retained in the droplets of mist. They are charged positively, or negatively, according to statistical expectations for random sampling of a neutral fluid containing discrete positive and negative charges.

Burners

Several types of burners are used for different combinations of gases. The 5cm single slot burner is normally used for the nitrous oxide/acetylene flame, although air/acetylene can also be used. A longer 10cm slot burner is used for air/acetylene flame, but must not be used for nitrous oxide/acetylene. The longer path length burner gives an increase in sensitivity over the shorter 5cm burners by about 30-50%, depending on the width of the slot.

Another type of burner is the Boling burner with a triple slot, which enables up to 12% dissolved solids to pass through without the build up of deposits on the jaws. For some elements the sensitivity is better, while for other elements, sensitivity is worse than that produced with a single slot.

Long path length burners have the ability to handle more concentrated sample solutions, similar to multi slot burners. Blockage occurs in burners of simple square cross section jaws, as a result of turbulence induced at the lower edge of the jaws. The greater the flow rate, the greater the turbulence, and eventually the deposition of salts and blockage of the burner. Nucleation of salt deposits is caused by imperfections in the machining of the jaw surfaces, so these should be

polished to a mirror like finish. With streamlining or “flaring” of the jaws, there is less likelihood of blockage. Such a burner is shown in Figure 10-1:

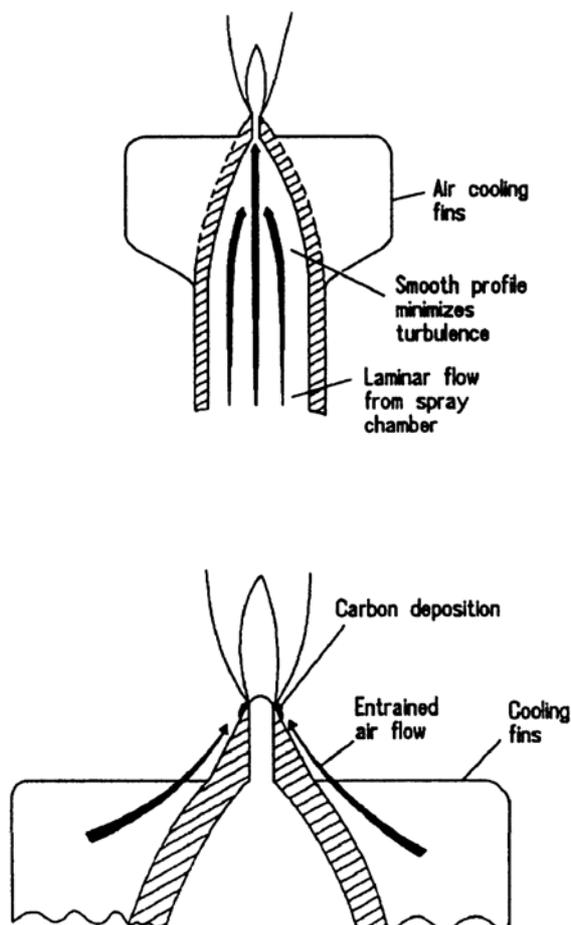


Figure 10-1. Burner

The first type of burner was based on the Bunsen, then a plate with holes was placed on top which was known as the Meker burner. The thicker the plate, the better the flame stability. Such burners are best suited to flames of low burning velocity and are occasionally used for atomic emission spectrometry. Circular burners are still preferred for atomic fluorescence spectrometry.

Burners are normally constructed of stainless steel, aluminium or titanium and are finned to dissipate the heat. The slot width of the burner is also important, as it effects the cooling and stability of the flame.

Flame height is normally between 5 -10 cm. To operate the flame safely, the linear velocity of the gas flow through the slot should be about three times faster than the speed at which the flame can travel. This is known as the burning velocity, which ensures that the flame cannot travel

backwards and cause an explosion, or flashback, in the spray chamber. The gas volume flow rates are about the same for each flame and are largely determined by the flow of the oxidant gas. Depending on the type of gases used, burners must be altered to give different linear flow rates. The linear flow rate of the gas, is determined by two factors: the volume flow rate v , and the area of the slot a , according to the relationship:

$$\text{flow rate} = v/a$$

Electrothermal Atomization

History of the Furnace

In 1908, A. S. King of the Mount Wilson Observatory, introduced the first electrothermal atomizer furnace. He studied the neutral spectra of cesium, calcium, copper, iron, mercury, rhenium, sodium and tungsten, produced after heating a graphite tube to about 3000°C in an atmosphere of hydrogen. In 1940, R. B. King used a wound resistance furnace of alundum at 1400°C for Cu, Cd and Fe.

L'vov (12) in 1961, described the use of the graphite furnace, where the sample was placed on an electrode located beneath a hole in the tube. The heated furnace was 5-10 cm in length and 3 mm in diameter. The atomization temperature was achieved by striking an arc between the sample electrode and the graphite tube. In a modified version of this system, L'vov atomized the sample by passing a current through the narrow portion of the electrode to the graphite tube. This tube was also heated, to prevent recondensation of the atomic vapor, as shown in the L'vov Furnace diagram below:

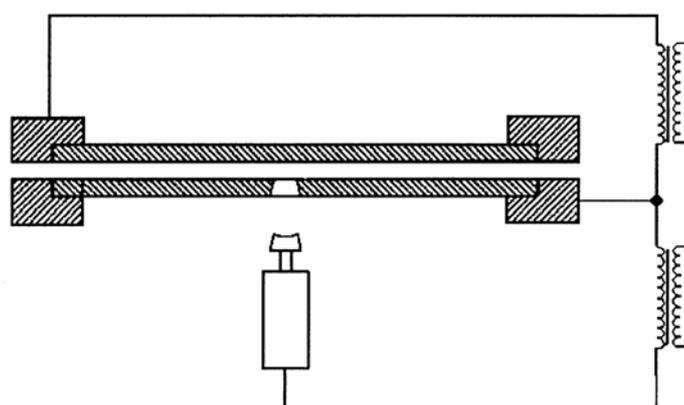


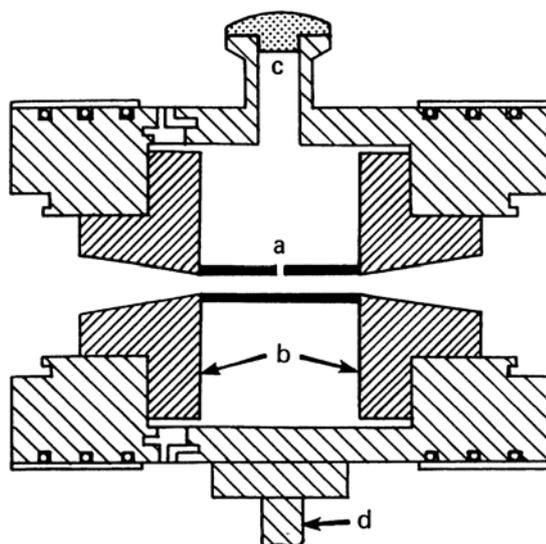
Figure 11-1. L'vov furnace

This device was placed in a purge chamber and the electrodes placed on a turntable. L'vov also used the deuterium lamp continuum for background correction, which is now known as a dual channel spectrometer. He placed metal liners such as tungsten or tantalum in some tubes and later used pyrolytic graphite tubes. His tube was used as an atom cell, rather than as a vaporizer.

In 1968, Woodriff (13) and Massman (14) considered this type of atomizer as an analytical atomic absorption tool and used enclosed furnaces, utilizing the graphite's own resistance to heat the sample. Since that time, a number of electrothermal atomizers have been described in the literature. These fall into three groups.

- Tubular graphite atomizers of the Massman or “mini-Massman”.
- Open filament atomizers of graphite or metal.
- Vertical crucible or “well” furnaces.

In the Massman furnace and the commercially available form described by Manning and Fernandez (15), the tube dimensions are approximately 5 cm in length and 6.5 mm in diameter. See diagram below:



Labeled Components: a = graphite tube, b = graphite cones, c = sample inlet port, d = water-cooled steel jacket

Figure 11-2. The Massman cuvette

A 2 mm hole is placed halfway along the graphite tube to deliver samples from 2 -200 μl volume. The tube is supported between water-cooled steel end cones, which make the electrical connections to a low voltage supply and are insulated from the mounting. The device is held within a metal casing containing an inert atmosphere such as argon, to prevent oxidation of the tube. The operating cycle of this system consists of three phases:

- The drying phase, at 100°C to remove the solvent.
- The ashing, or pyrolysis phase, at a higher temperature to remove organic or matrix material.

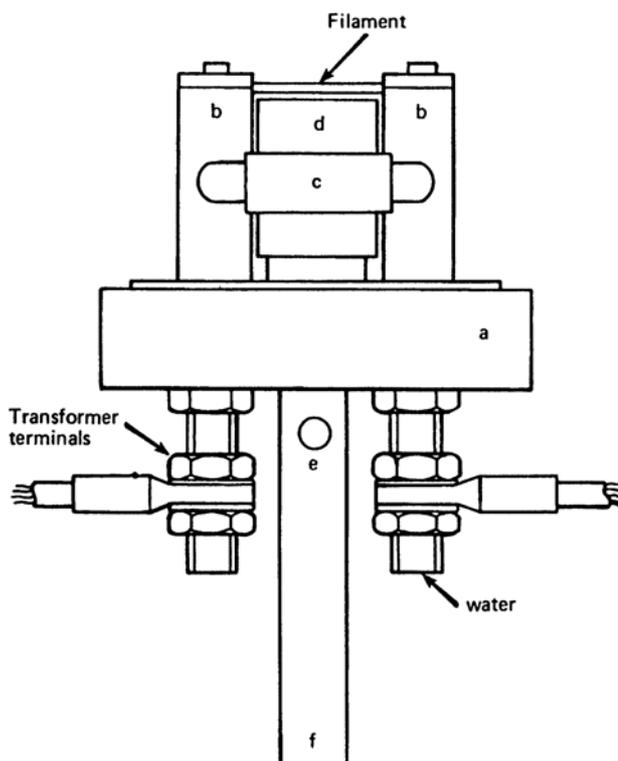
- The third phase, to convert the residue into an atomic vapor.

Woodriff's (13) furnace was of a more massive construction and operated at a constant temperature, unlike the latter program sequence. Liquid samples were introduced in a nebulized form in a stream of inert gas. Solid samples were placed in a small graphite boat and pushed into the atomizer.

All commercially available atomizers are based on the Massman principle of resistance heating. The main difference between furnaces is the dimension of the graphite tubes. If a furnace is large, it takes too long to attain its operating temperature and relative background absorption is greater, although larger sample volumes can be accommodated with better precision and relative sensitivity. With a small furnace, improved absorption efficiencies are obtained. The small volume tube has shorter atomizer times and better absolute sensitivity. However, the limitations on size of sample volume injected, result in poor sensitivity and accuracy. Most present day atomizers are a compromise between the two extremes.

In 1969, West and William's (16) carbon filament atomizer appeared to offer possibilities for atomic absorption and fluorescence. The design was simple: a carbon rod 40 mm long and between 1 and 2 mm in diameter, supported between two stainless steel electrodes connected to a low voltage supply. The atomizer was enclosed in a Pyrex glass chamber purged with argon. Silica windows allowed the light from the radiation source to pass just above the surface of the rod for AA and at

90° for fluorescence. At 0.5 W, less power was required. The system was further simplified by replacing the glass chamber with a vertical flow of argon. A typical carbon filament atomizer is shown in [Figure 11-3](#):



Labeled Components: a = base, b = water-cooled electrodes, c = water link between electrodes, d = laminar flow box, e = inlet for shield gas, f = support item for reservoir

Figure 11-3. Rod atomizer as used by West

The sample volume that can be loaded on to the carbon rod is only 5 μl . Replacement of the carbon rod with the platinum or tungsten loop, a tantalum boat or a ribbon, enables larger 20 μl volumes to be injected. Experimentation has also been carried out using a graphite braid, which gives greater surface area for larger sample volumes.

Carbon rod and tubular atomizers require similar programs of drying, ashing and atomization. The sensitivity of the carbon rod system is expected to be lower than the tube type, as the atomic vapor is not forced to remain in the observation zone. However, as the atom supply function is extremely fast due to low thermal mass and high initial density of free atoms, the analytical sensitivity is good. The relative detection limits are not appreciably improved due to the small sample size.

Furnace Components

In most modern graphite furnaces, the materials used in its construction are fairly inert, to avoid the possibility of contamination when heating occurs. Blankfirings of the graphite cuvette should give low blanks. Typical impurity levels in graphite used for cuvette manufacture are given in [Table 11-1](#):

Table 11-1. Typical impurity levels in graphite

| Element | Impurity ($\mu\text{g g}^{-1}$) |
|---------|-----------------------------------|
| B | 0.01 |
| Ca | 0.20 |
| Cu | 0.10 |
| Fe | 0.20 |
| Mg | 0.05 |
| Si | 0.20 |
| V | 0.01 |
| ash | 2.0 |

The graphite tube itself and some support contacts are made from graphite. Properties of Ringsdorff RWO type graphite are as follows:

Table 11-2. Properties of Ringsdorff RWO type graphite

| Item | Property |
|--|---|
| Specific electrical resistance | $8.5 \Omega \text{ mm}^2 \text{ m}^{-1}$ |
| Thermal conductivity | $0.35 \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| Density | 1.75 g cm^{-3} |
| Machineability | excellent |
| Maximum grain size | $75 \mu\text{m}$ |
| Porosity (pores $>1\mu\text{m}$ as % total volume) | 13% |
| Flexible strength | 400 kp cm^{-2} |
| Shore hardness | 30 |
| Typical coefficient of linear expansion | $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ |
| Melting point | $3,500^\circ\text{C}$ |

A typical graphite furnace is shown in [Figure 11-4](#):

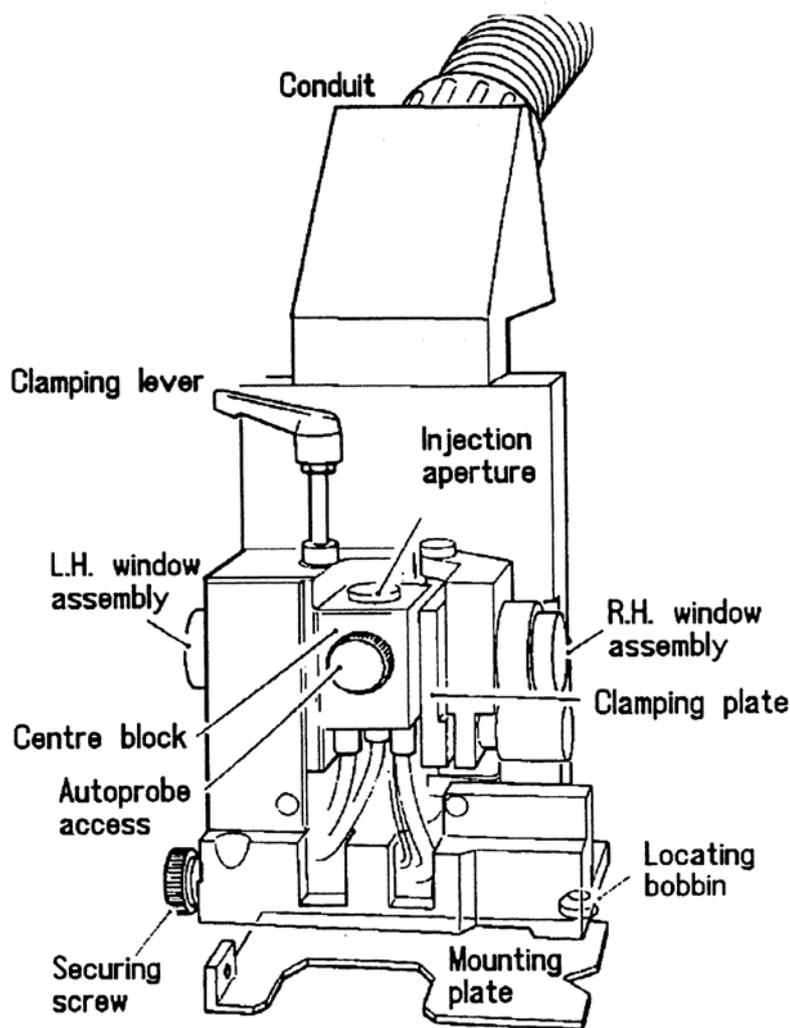


Figure 11-4. Furnace head

The design of a modern graphite furnace atomizer is a compromise between theoretically desirable properties and the restrictions placed on the designer by available electrical and mechanical components. For example, to obtain high sensitivities and reduced interferences, it would be beneficial to produce the highest heating rates possible over the entire length of the graphite cuvette. However, to avoid overheating the mechanical and electrical contacts of the electrothermal atomizer, it is necessary to water cool the end contacts. This in turn leads to a temperature gradient along the length of the graphite cuvette, which increases the possibility of condensation problems and chemical interferences.

Totally Enclosed Graphite Environment

A typical graphite head is shown in [Figure 11-4](#):

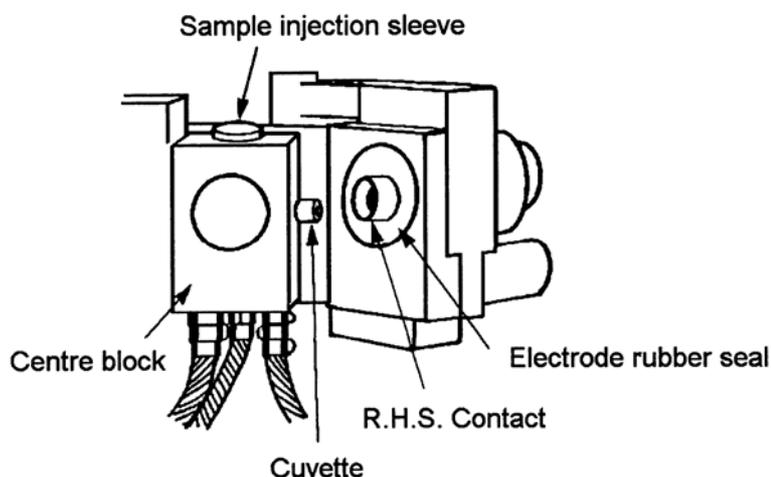


Figure 11-5. Graphite furnace head

The right contact can be clearly seen. When the furnace is sealed by turning the clamping lever an all graphite environment exists around the graphite cuvette. The main advantage of this type of design, is that a non-corrosive environment is maintained.

The Closed Furnace - end design

The main advantage of a closed furnace design configuration is that gas can be introduced at controlled flow rates, from the ends of the cuvette, down to the center of the cuvette and out through the injection port. The various flow rates of gas can be controlled via the software in the computer system of the instrument. The available gas flow options with this particular system is as follows:

- (1) 0 mL min⁻¹
- (2) 100 mL min⁻¹
- (3) 200 mL min⁻¹
- (4) 300 mL min⁻¹

The advantages associated with this are:

An inert gas flow of 300 mL min⁻¹, during the drying phase of the furnace cycle, enables the same droplet to be dried quickly and smoothly.

An inert gas flow of 300 mL min⁻¹, during the charring or ashing phase, enables efficient removal of smoke or matrix.

During the atomize phase, the gas flow is normally stopped, however, it may be useful to reduce sensitivity during the atomize phase for some applications and flow rates of between 100-300 mL min⁻¹ may be used.

Alternative gases can be used in any phase of the furnace cycle. The gas type is user selectable. A typical example may be to use oxygen during the charring phase. In the determination of samples containing high concentrations of organic material such as blood, or serum, a carbonaceous residue may build up inside the cuvette. This can be reduced with the use of oxygen ashing during the furnace cycle. When oxygen or air is used in this cycle, it is more correctly referred to as the “ashing” phase. After this phase, it is recommended to add an extra phase with inert gas only, to eliminate oxygen from the cuvette prior to the atomize phase.

Temperature Control

The main aim of any well designed electrothermal atomizer is to produce the best sensitivity, i.e., the highest peak measurement for a given analyte concentration present in the graphite tube. The maximum absorbance of the atomization peak, and hence the ultimate sensitivity, is determined by two opposing processes, the rate of atom production in the graphite tube and the rate of atom loss from it. Rate of atom loss is governed by the tube parameters, such as geometry and porosity, and furnace head design considerations, such as cooling and inert gas flow.

Atom production rates are now known to be directly proportional to the rate of temperature increase of the graphite tube. If the rate of temperature increase can be improved, all other parameters having been

optimized, analytical sensitivity will also improve. This was shown by L'vov, who predicted that a sample would have to be atomized within less than 0.1 second, for maximum sensitivity to be achieved.

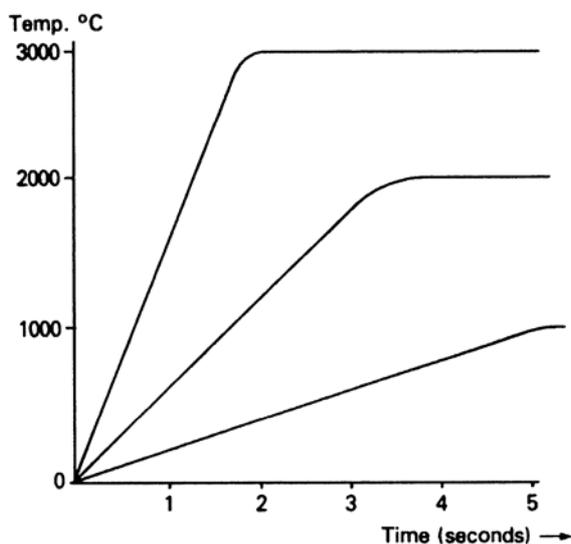


Figure 11-6. The effect of final temperature on temperature rise-time of a cuvette using voltage feedback control

In early Massman furnace designs, the conventional method of controlling tube temperature was to calculate the voltage necessary to sustain a given temperature and apply this voltage to the ends of the graphite tube. The tube temperature would increase ballistically towards the set temperature as shown in [Figure 11-6](#).

However, the method results in a rise-time which is too slow for the maximum sensitivity to be attained. Volatile elements such as Pb, Cd, Zn, Hg, Te, etc., are an exception, where a high atomization temperature can be set to give a fast temperature rise-time.

In temperature controlled electrothermal atomizers, the tube temperature is measured by a sensor and this is fed back to the power supply and used to control the voltage applied across the tube. This is a “proportional control system”, as the power applied is a function of the difference between the actual temperature and the set temperature. Control systems in use in present day instruments originate from the work of Lundgren et al (17) who, in 1974, proposed a method of direct cuvette temperature measurement and feedback control, in which the maximum output of the power supply is applied across the graphite tube, until the desired temperature is reached. The power is then reduced to a level just sufficient, to maintain the desired temperature for the rest of the atomization phase. Temperature controlled heating results in a very rapid initial rate of temperature increase, thus leading to

improved sensitivity. The rate of temperature increase is almost constant, irrespective of the final set temperature and is illustrated in Figure 11-7.

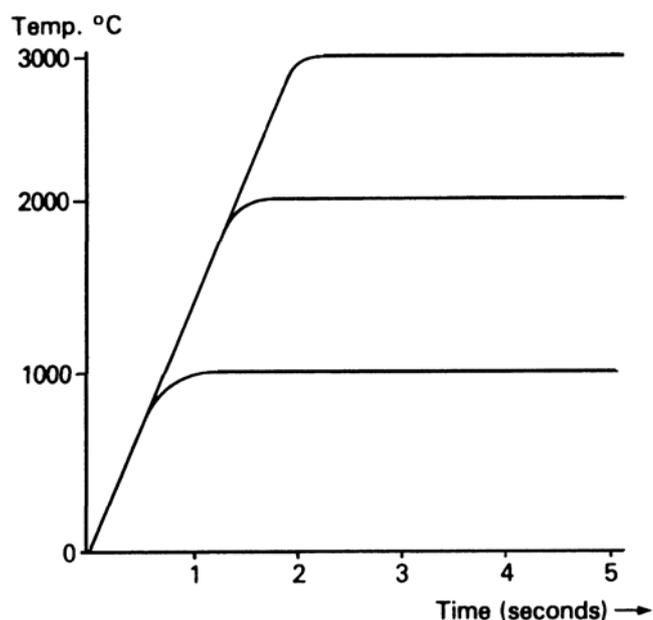


Figure 11-7. The effect of final temperature on temperature rise-time of a cuvette using temperature feedback control

When underpowered, the graphite furnace's initial rate of temperature rise is in excess of $2500^{\circ}\text{C sec}^{-1}$, which is the consequence of using a small graphite tube and very accurate temperature control. As a result of much faster and more efficient atom production, appreciably lower final

temperatures can be set to obtain the same sensitivity than would be possible when operating in a conventional voltage control mode as shown in Figure 11-8.

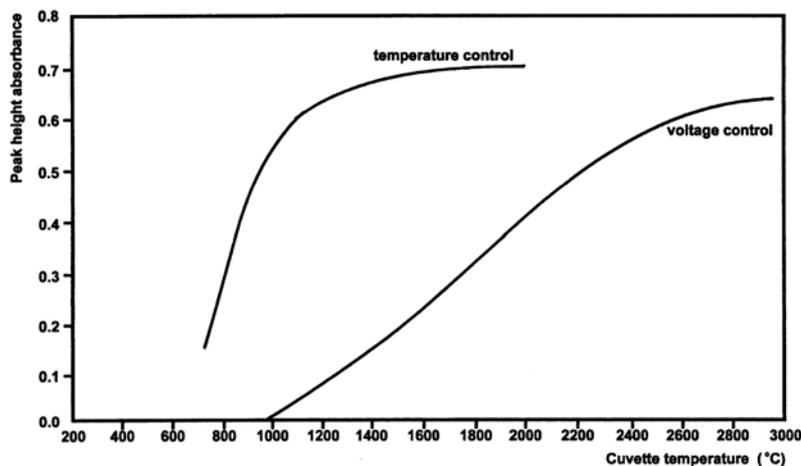


Figure 11-8. Sensitivity for Pb under voltage and temperature control conditions

To reach a peak height absorbance of 0.6 A, voltage control requires a set temperature of 2600°C, whereas temperature controlled heating to only 1100°C produces the same result. When sufficient atomization temperature is applied, the analytical signal remains constant over a wide temperature range. Assuming an atomization temperature is used which lies on the plateau region, small fluctuations in temperature will not affect the analytical result.

The following summarizes the benefits of temperature control:

- Higher analytical sensitivity is obtainable compared with voltage control.
- Lower atomization temperatures can be used.
- The use of lower temperatures increases tube lifetime.
- There is less variation in the final temperature attained from one cuvette to another and during the lifetime of each cuvette.
- Faster temperature rise-time and atom formation, make it possible to use shorter atomization times.

As heating rates of greater than 2000°C sec⁻¹ are normal, to obtain full benefit of temperature control, it is necessary to be able to measure the actual temperature of the cuvette in real time. Temperature control systems based on thermocouples, or computer predictions that estimate temperatures, are therefore suspect. The only method with both

response characteristics and required accuracy to measure temperature, is one based on an optical technique such as a pyrometer. A silicon photo-diode represents such a device which has an extremely fast response time and is capable of detecting and controlling temperatures in the range 600 - 3000°C. An end on view is shown in [Figure 11-9](#).

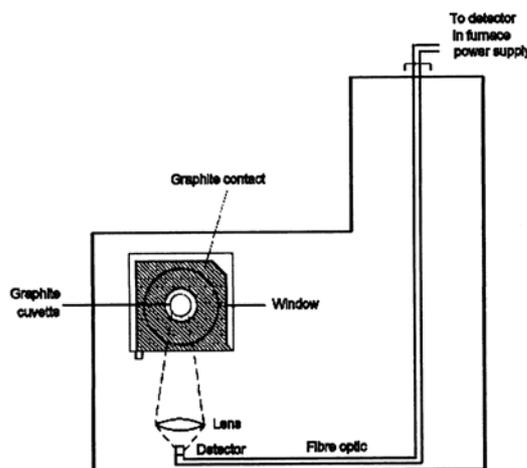


Figure 11-9. End-view of the graphite furnace

Radiation from the graphite cuvette is focused by means of a lens onto one end of a fiber optic, which is placed underneath the graphite cuvette. The lens is kept free from dust, by passing the gas used to maintain an inert atmosphere around the graphite tube, over the lens. The fiber optic is linked directly to the silicon photo-diode, which is housed in the power supply. This serves two purposes:

The photo-diode is temperature sensitive. Removing it from the neighborhood of the hot tube and its cyclic heating effect, means no continual adjustments have to be made to overcome variations in response.

When placed close to the power leads on the head unit it can be affected by pick-up noise. Placing it away from power cables overcomes this problem.

Choice of Cuvette Materials

The most important parameters for a suitable cuvette material are summarized below:

- Good thermal and electrical conductivity.
- Chemical inertness.
- Very low levels of metallic impurities. Low porosity.
- Good machineability.

- Low thermal expansion and high rigidity.
- High melting point.

Of the various materials available, graphite most closely approximates to this specification. Graphite is manufactured from materials such as carbon black and petroleum coke, ground and mixed with binders such as pitches, coal tars and phenolic resins. Extrusions of the material are made and then heated slowly to about 1300°C in an inert atmosphere. The binding material is thus “coked” forming a solid carbon material “amorphous” carbon, which is hard and brittle. To obtain graphite, a final electrographitizing process is required whereby the amorphous carbon is resistively heated to approximately 3000°C, forming the true graphite material with the above properties. Cuvettes made from normal graphite are given the name “electrographite cuvette”.

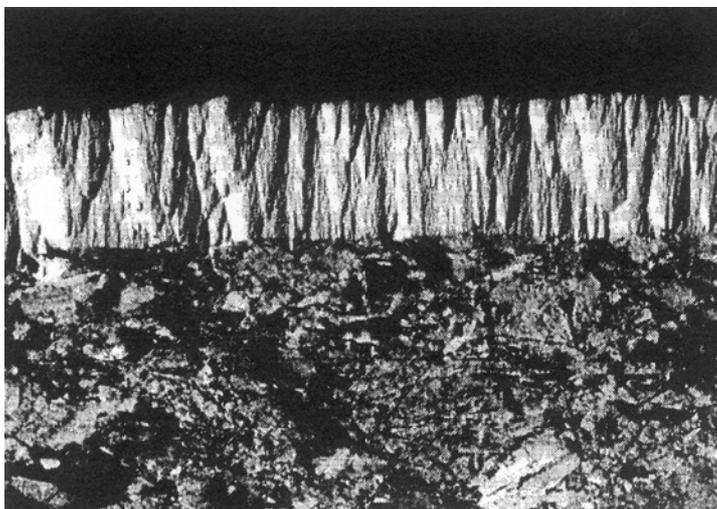


Figure 11-10. Pyrolytic structure on a graphite substrate

Although electrographite is suitable as the tube material, there are some limitations to its use. The most important of these are porosity and the reactivity of normal graphite, characterized by the formation of carbide with certain elements. It has been found that a coating of pyrolytic graphite overcomes many aspects of these problems. Lersmacher et al. (18), at the Philips Forschungslaboratorium in Aachen developed a method of making such coatings in 1979. This method has since been used on a commercial scale by the leading manufacturer of graphite materials. The pyrolytic graphite layer is formed on the electrographite cuvette substrate by the “hot wall” method of coating. The item to be coated is placed in a heated enclosure containing an atmosphere of hydrocarbons such as methane, at temperatures up to 2500°C. Such conditions lead to the formation of a layer of pyrolytic graphite, which due to various constraints, cannot exceed a few millimeters in thickness. Normal coating thickness is usually in the range 30-50 µm.

Figure 11-10 shows a photomicrograph of the surface structure of a pyrolytic graphite coating on a electrographite substrate.

The contrast between the highly ordered structure of the coating and the random, porous nature of the substrate, is readily demonstrated. Tubes coated by this technique produce a significant improvement in performance compared with the electrographite tubes.

Pyrolytic graphite as a material has many desirable properties, notably low gas permeability and good resistance to chemical attack. L'vov has shown that vapor losses are about 33% less with a pyrolytically coated tube, thus improving the atom residence time in the tube and increasing the analytical sensitivity. It also resists oxidation better than electrographite by a factor of about ten times. Due to its resistance to chemical attack, carbide formation is reduced and therefore elements such as V, Mo, Ti, W, Si, etc. may be determined with greater improvement in analytical sensitivity and much less memory effect.

Tubes coated by this technique have not fully overcome all the problems however, because the pyrolytic layer gradually thins as material sublimates, until eventually the electrographite substrate is exposed. At this point, the analytical sensitivity decreases rapidly, until performance similar to that of an uncoated electrographite tube is reached. Coated tubes may last significantly longer, but analytical performance begins to deteriorate long before the tube actually breaks.

In 1984, Philips Analytical introduced a new type of furnace tube which was made entirely of pyrolytic graphite. These tubes were made using a modification to the original coating technology developed by Lersmacher et al (18). A photomicrograph of a cross section of such a tube is shown in [Figure 11-11](#):

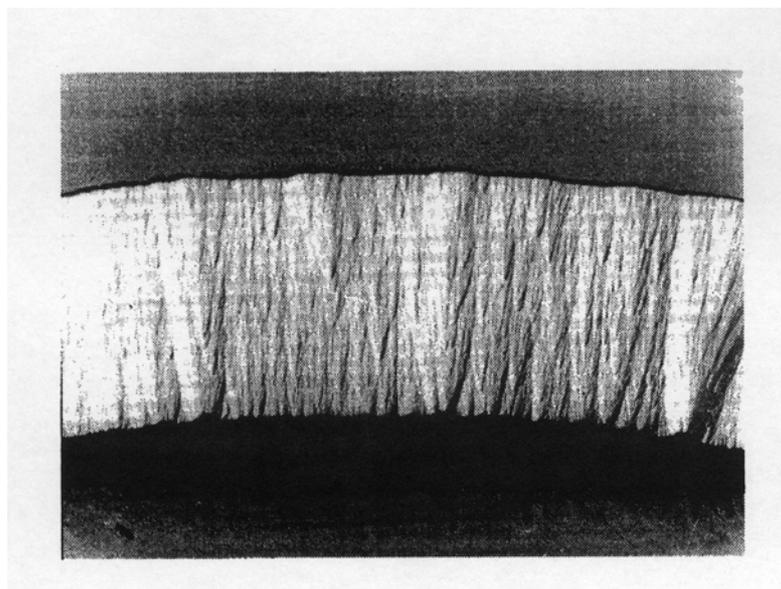


Figure 11-11. Cross-section of a Totally Pyrographite Cuvette (TPC)

The structure of the tube wall consists of many conical crystallites, which radiate normally from the inner wall surface. These tubes, or Totally Pyrographite Cuvettes (TPC), have superior performance compared with pyrolytically coated tubes. They make use of the other benefits of pyrolytic graphite which cannot be fully utilized, by a thin coating on an electrographite substrate.

Compared with a number of materials, pyrolytic graphite has the highest strength-to-weight ratio over the temperature range up to 3000°C and is about 5 - 10 times better than electrographite. One advantage of the high strength-to-weight ratio, is that tubes can be made with a reduced wall thickness.

The reduced wall thickness gives rise to a lower thermal mass, which in turn means that TPCs have increased heating rates compared with pyrolytically coated, or electrographite tubes. The highest heating rate obtained occurs at the lower temperatures. For example, a heating rate of 4000°C sec⁻¹ was measured for a TPC between 400 - 600°C. Pyrolytic graphite is a highly anisotropic material, i.e., the physical properties in one crystal direction are quite different to those at right angles to this direction. In the direction parallel to the tube surface, pyrolytic graphite is one of the best heat conductors. In the direction vertical to the surface, heat conductivity is lower by a factor of 300. These properties mean that heating along the tube is rapid and isothermal for a greater length. Heat conduction outwards is poor, so that outer layers act as insulators. This reduces heat loss and electrical power dissipated, in reaching any given temperature. The end result, is a furnace tube which gives more consistent performance over a longer lifetime.

Methods to Eliminate Interferences

There are at least three ways to eliminate interferences. These are matrix modification, platform atomization and probe atomization.

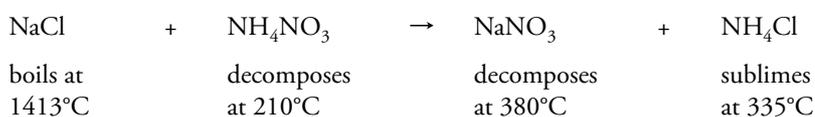
Matrix Modification

A matrix modifier allows the use of higher ashing temperatures to remove some of the background matrix. It achieves this by combining with the element of interest to produce a more stable compound, which can be ashed at a higher temperature.

To prevent loss of sample during the ash phase of a graphite furnace atomization run, a salt is added to the sample. Its function is to convert the element of interest into a more stable salt, to prevent loss. Normally the nitrate salts are less volatile than the chloride salts and it is an advantage to use nitric acid to digest the sample, rather than hydrochloric acid.

Some chloride salts of arsenic, cadmium and mercury are volatile and lost during the ashing stage. It is not desirable to have a lower ashing temperature, as the background signal may increase. To prevent loss of volatile compounds, add nitric acid and boil off the HCl. Arsenic, selenium and tellurium can also be stabilized by adding nickel ions. For example, nickel ions added to arsenic forms a nonvolatile nickel arsenide. Cadmium may be stabilized by the addition of 2% ammonium phosphate. Mercury may also be stabilized by adding sulphide ions to form mercury sulphide. The relative volatility of chloride is a disadvantage in furnace AAS, although in flame AAS it is an advantage, as dissociation to atoms in the flame is speed up.

Some matrix modifiers combine with salts, which are nonvolatile to produce more volatile products, thereby removing the interfering matrix. If a high concentration of sodium chloride is present which causes background, a 50% solution of ammonium nitrate can be added to the sample. This has the following effect:



Platform Atomization

The single most important aspect of interference control, is to achieve isothermal atomization of the sample. This is the original concept of electrothermal atomization described by L'vov in 1961.

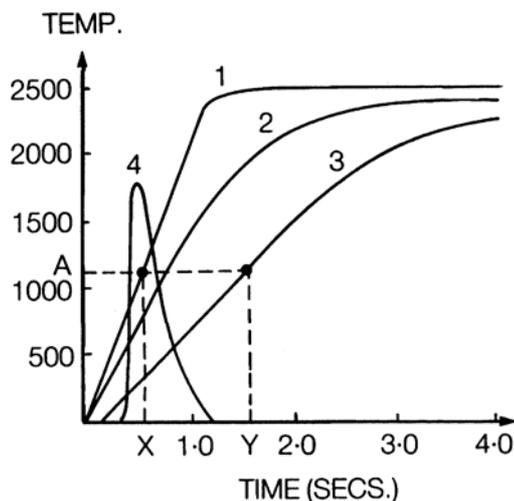
The concept of platform atomization was first described by L'vov in 1978. Platform atomization can approach isothermal atomization by delaying the atomization of samples from a graphite platform, depending on the type of matrix and element. An advantage of platform atomization, is a reduction in background signal due to the greater thermal decomposition of molecules in the vapor phase, compared to tube wall atomization.

A platform is a thin rectangular shaped piece of graphite, normally prepared from solid pyrolytic graphite, which is positioned in the center of the conventional graphite cuvette.

The original platform touched the walls only at each edge and hence platforms could only be heated by cuvette wall radiation as conductive heating was minimal.

More recent platforms fit into a slot at the ends of the graphite cuvette and do not come into direct physical contact with the hot center portion of the cuvette. Conductive heating from the cuvette has been totally eliminated. The platform is heated by tube wall radiation and the platform temperature, initially lags behind the tube wall temperature, by several hundred degrees. The platform takes several seconds longer to reach a constant temperature, which may be less than the wall

temperature. The relationship between the tube wall, gas phase and platform temperatures is shown below, together with a peak profile typical of the more volatile elements.



Labeled Components: Curve 1 is for the graphite tube wall
 Curve 2 is for the gas phase
 Curve 3 is for the platform
 Curve 4 is the peak profile for a volatile element
 A represents the atomization temperature for that element
 X and Y are the peak times from the tube wall and platform respectively

Figure 11-12. Temperature-time profiles for platform atomization

In [Figure 11-12](#), the actual temperature at which atomization occurs is shown as “A” and for tube wall atomization this occurs at time “X”. The non-isothermal nature of the tube wall temperature and the lower gas phase temperature at time “X” are evident from the plots. When a platform is employed, atomization of the volatile element still occurs at the same temperature “A”, but the appearance time is much later at time “Y”. At time “Y”, it can be seen that the tube wall temperature has been stable for a period of time, and more importantly, the gas phase is hotter than the platform. Under these conditions, the atomized analyte and matrix do not condense and therefore vapor phase interferences are minimized.

Probe Atomization

Isothermal atomization can be achieved by use of probe atomization in ETA-AAS. The Autoprobe consists of a mounting holder, a motor and the graphite probe on which samples are injected. The temperatures required are generally higher than conventional graphite furnace AAS. For example, a drying temperature of 250 - 300°C has been used to dry

a 10 µl aqueous sample in 10 - 20 seconds. Ashing or pyrolyzing temperatures can be determined by performing an “ash plot” on a particular sample matrix.

The following six steps are required for graphite probe atomization.

1. The sample is automatically injected on to the probe which is inside the graphite cuvette.
2. The sample is dried and ashed or pyrolyzed.
3. The spectrometer then auto-zeros.
4. After the auto-zero, the probe is withdrawn from the graphite cuvette and the furnace heats up to the pre-set atomization temperatures.
5. When the cuvette temperature has stabilized, the probe is automatically inserted into the constant temperature environment for isothermal atomization and analytical measurement.
6. Finally, a cuvette and probe clean stage is initiated.

The complete procedure is automated. The process is shown in [Figure 11-13](#).

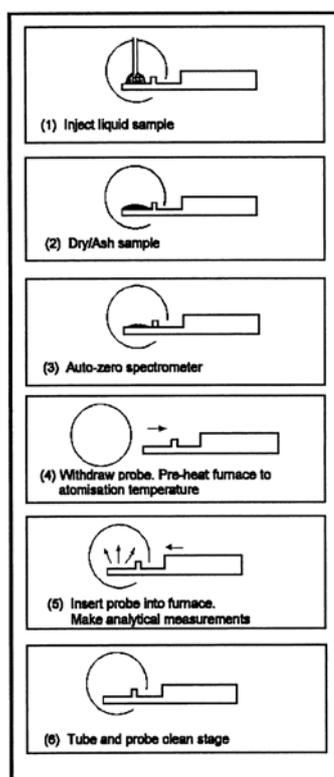


Figure 11-13. Procedure for probe atomization

Furnace Autosampler

To achieve optimum performance and sensitivity from a graphite furnace system, it is necessary to use an autosampler. The advantages of a microprocessor controlled furnace autosampler, incorporating a precision syringe, with sophisticated wash routine, over a manually operated micropipette are twofold.

1. The user can set up furnace cycles for analysis and leave the furnace running unattended for prolonged periods.
2. Improved precision and reduced cross contamination are apparent.

To provide flexibility of use, a furnace autosampler usually offers the following features:

- Carousel layout for wash, matrix modifier, blank/diluent, master solution and positions for up to 50 samples.
- Samples may be diluted or concentrated.
- Programmable recalibration for each elemental analysis.
- Programmable injection volumes from 1 μl to 70 μl .
- Automatic washing of pipette tip.
- Up to 100 resamples per sample.
- Enables probe atomization to proceed automatically.

Some systems prepare standards from a master solution which are then diluted with a blank/diluent, and will also accept standards prepared manually on an individual basis. Matrix modification may also be carried out automatically. An advantage of an autosampler, is the reproducible injection of the sample once the correct position of the pipette tip has been determined. This is very important to achieve precision.

Cross contamination is always a potential problem with furnace autosamplers, because the same capillary is used for injecting solutions of different concentrations and composition.

Electronic System

In a typical AA spectrometer, the hollow cathode lamp (HCL) is driven by a stabilized power supply which is modulated, so that lamp light output is pulsed at 200 Hz. Lamp current can be adjusted to give a required output. The decoding circuitry detects modulated light, which is in the form of an AC signal and separates it from any stray light manifested as a DC signal. In background correction mode, the deuterium lamp is switched on during the “dark” period of the HCL. The flame is controlled and ignited by the gas control logic, which operates various solenoid valves to select required gases and flow rates.

Radiation is detected by the photomultiplier and converted to an electrical signal and gain is controlled by adjusting voltage output of the extra high tension (EHT) power supply. The energy meter indicates light energy throughput of the system, which is useful when optimizing lamp position or monochromator setting for maximum intensity.

To convert intensity to absorbance, it is necessary to use a logarithmic amplifier. This is under control of the auto-zero function, which enables an absorbance reading of zero to be selected for any particular light level.

Signal And Data Processing

Before any data processing is performed, a signal must first be detected and processed to make it suitable for acceptance by the microcomputer. The signal must be generated in such a way, that it contains enough information about the absorbance signal or signals, to enable results of the desired accuracy to be obtained. For example, there would be little point in designing a high accuracy curve correction program for electrothermal atomization, if the resolution of the peak reader were relatively poor. As with all processing systems, the quality of result produced by an atomic absorption instrument, will be only as good as the weakest part of the signal/data processor chain. Thus, the starting point should be the design of the spectrometer itself.

A major aim is to reduce the noise level on the signal, to improve the quality of the raw data. The major types of noise are listed below.

- Shot noise, which is signal to noise ratio and is proportional to intensity.
- Flame noise, which is detected as absorption or emission.
- Concentration noise.
- Noise from other components, for example, lamp, electronics.

The optical system should transmit as much energy as possible to give minimum shot noise, etc. This suggests a relatively simple optical system with as few components, particularly reflecting surfaces, as possible. The system should also ensure, that the smallest possible amount of light from the incandescent walls of a graphite furnace reaches the detector. The decoding electronics can then more readily separate this contribution by the “wanted” modulated emission, from the hollow cathode or electrodeless discharge lamp.

Flame AAS

Optimization of Operating Parameters

Parameters which will affect both precision and sensitivity are bandpass, lamp current, burner height, burner alignment, fuel flow, flame type and impact bead adjustment. The use of background correction and choice of integration time will affect the precision. Analytical sensitivity can be modified by the use of alternative lines and switching out of the impact bead. Some interferences which result in reduced sensitivity can be overcome by the use of an appropriate buffer.

Sensitivity

The analytical performance of an atomic absorption spectrometer is usually expressed in the form of a list of elements with their associated sensitivities and detection limits. In atomic absorption, the term “sensitivity” has a special meaning and is defined as that concentration of the element in ppm (or $\mu\text{g mL}^{-1}$ or mg L^{-1}) in aqueous solution, which gives an absorbance of 0.0044, equal to a 1% absorption of the transmitted radiation. Knowledge of the sensitivity value for a particular element is useful, because from it the optimum concentration range for that element may be computed. Normally, this optimum concentration range lies between 20 and 200 times the sensitivity value. For example magnesium, whose quoted sensitivity is 0.003 mg L^{-1} , the optimum range is $0.06\text{--}0.6 \text{ mg L}^{-1}$. It is also useful for determining whether or not the instrument parameters have been adjusted to fully optimize the instrument, and as a check to determine how well the various standards have been prepared.

To optimize the accuracy of the analysis, an absorbance range between 0.1–0.8 A is required. At low absorbance readings, the reading accuracy is limited, while at high absorbance values, such factors as stray light may cause considerable deviations from Beer's Law, with consequent loss in accuracy. Sensitivities are checked by aspirating a freshly prepared aqueous solution of the element, to give an absorbance reading of about 0.1. Instrumental parameters are then adjusted for optimum sensitivity, or greatest deflection. The concentration of the element in mg L^{-1} giving 0.0044 absorbance may then be easily calculated.

Detection Limits

Detection limit is a statistical function which takes into account blank levels, sensitivity and signal to noise ratios. The detection limit is defined as that concentration of an element in mg L^{-1} , which gives a reading equal to three times the standard deviation of a signal measured close to the blank level. The standard deviation is calculated using at least 10 sequential readings.

By making use of the scale expansion facilities built into instruments, a small signal can be magnified to more readable proportions. However in expanding the scale, small random fluctuations or noise are also magnified. The noise level is present on the zero absorbance base line and on the absorption signal, and there will be a smallest concentration of a particular element that can be distinguished from the baseline noise signal. The detection limit is a statistical measure of this concentration. These effects are apparent whether an instrument has a meter, or a digital readout.

On instruments which incorporate signal integration, the relative effect of the noise can be reduced and signal/noise ratios improved by the use of long integration times, for example from 0.1 to 100 seconds. The noise evident in scale expansion originates from small instabilities in lamp output, nebulizing system, amplifier, flame, photomultiplier detector and readout system. Detection limits depend on the noise, or more specifically, the signal to noise ratio and are therefore a function of the performance of the various instrumental components. The sensitivity as defined above is not noise dependent and is a direct function only of the atomization, nebulization and flame processes.

Precision and Accuracy

Factors effecting Output Signal

A number of effects contribute to the uncertainty in the final signal displayed on any readout system. The sources of error are:

- Fluctuations in hollow cathode lamp emission signal
- Photomultiplier “shot noise”
- Electronic (Johnson) “noise”
- Flame fluctuations
- Nebulization and atomization “noise”
- Inaccuracies in the readout system

- Random and systematic errors incurred in sample preparation
Inter-element interferences

Some of the factors are under the control of the operator. Clearly sources of error in sample preparation should be recognized and interferences should be controlled. Other factors are taken into account in the design of the equipment.

It is generally found that flame fluctuations give rise to the greatest degree of uncertainty in the signal. These derive from variations in oxidant and fuel flow rates, draughts and noise from inconsistent sample nebulization and atomization.

If the hollow cathode lamp emission is sufficiently high in intensity, it will exhibit low noise characteristics. At present hollow cathode lamps are satisfactory for most elements, although work is always continuing to improve the brightness and stability of lamps for particular elements. For elements such as arsenic and selenium, the use of electrodeless discharge lamps may improve the signal to noise ratio. Copper is an example of an element, which is so efficiently atomized in the flame that photomultiplier “shot noise”, usually small compared with flame noise, is the limiting factor. However this condition is rare. Johnson or electronic “noise” is also negligible in modern amplifiers and photomultiplier detectors.

In addition to the small high frequency fluctuations or “noise” on the lamp signal, the mean signal may well drift. Such a drift, provided it is less than about 5% per hour, will not noticeably affect the precision or accuracy of the analysis. The extent of the drift can be taken into account when calculating results, or by correcting the drift by adjusting the amplification as necessary. A double beam system automatically and continuously makes this correction.

Inaccuracies in the readout system may under some circumstances be a limiting factor. Meter readout systems have relatively poor linearity and narrow dead-band characteristics. Quality recorders and digital readout systems show good linearity, as well as narrow dead-band. Flame fluctuations are usually the main source of uncertainty in the signal, but when these become very low, the source of greatest noise might be the readout system. It is thus worthwhile spending time optimizing the flame conditions to obtain the lowest noise level, particularly if scale expansion or concentration readout is used.

Analytical accuracy does not depend on purely instrumental precision, it depends also on reducing random and systematic errors in sample preparation. In addition, accuracy will be made worse if high concentrations of matrix elements are present in the sample solution.

Types of Errors

We can categorize errors into two types, random and systematic.

Random errors occur when a different result is obtained each time a measurement is repeated. They can be reduced by taking an average of the low and high readings.

Systematic errors can arise through incorrect calibration or errors of method. For example the presence of interferences in AAS will give a reading which is consistently low or high. This type of error cannot be remedied by averaging the results. If an interfering process is causing a low reading, then no amount of repetition will make the reading any higher. Systematic errors are responsible for any significant differences between the measured value and the correct value.

Precision

Precision is a measure of how repeatable a given set of results are, or how close they are to each other. The validity of a set of replicate results can be obtained by measuring the precision, or relative standard deviation of the group. Poor precision is indicated by a wide spread of individual results and confidence in their accuracy as calibration, or sampling points, is reduced. The calculation of precision is carried out in the following way:

Find the average value \bar{x} of a set of replicate results consisting of n measurements of individual value \bar{x} .

$$\bar{x} = \frac{\sum x}{n}$$

The standard deviation s is then given by

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}$$

The relative standard deviation is then:

$$RSD = \frac{(s \times 100)\%}{(\bar{x})}$$

Manual calculations of precision values are tedious and time consuming. Precision values become higher or worse as the analytical signal becomes progressively lower. Precision values for blanks can easily be 50-100%, and 1-2% can be expected for absorbance values in the range 0.2-0.5 A, for an optimized system.

The significance of standard deviation is that if a large enough number of measurements is made then 68% of the results will differ from the mean value by no more than s . This means that one result in every three will lie outside the stated precision. In practice it is desirable to be more confident about results.

It is more usual to use twice the standard deviation as a measure of precision, as 95% of the results will lie between $\bar{x} - 2s$ and $\bar{x} + 2s$. This means that only one result in twenty is likely to lie outside the stated precision. This definition of precision is sometimes referred to as the 95% confidence level.

Flame AAS

Precision and Accuracy

Calibration

The correct preparation of standards and calibration graphs is as important as sample preparation. Normally, the same stock solutions used for flame AAS can be employed in electrothermal atomization techniques. To prevent contamination, glassware for flame analysis should be kept separate from glassware for ETA work, due to the high concentrations used in flame AAS. The standard solutions should be prepared using high purity metals, or compounds, dissolved in high purity reagents. Alternatively, commercially available standard solutions may be used, provided they have sufficiently low levels of contaminating species present.

When preparing stock and calibration solutions, it is important to select the correct acid to dissolve the calibration material. The correct acid will keep the metal ions in solution, improve solution lifetimes and prevent subsequent problems arising during ETA. For example, hydrochloric acid if used to prepare lead solutions, will result in difficulties during ashing procedures due to the volatility of lead chloride. Another example is the selection of sulphuric acid, which is difficult to dry smoothly and also can have severe depressive effects during atomization with certain elements.

Solutions prepared using organic solvents must be carefully handled and appropriate containers selected, because of the use of organo-metallic materials in the manufacture of plastic ware. Mold release agents and anti-oxidants are readily leached from container walls by many organic solvents, resulting in high levels of contamination. Even simple aqueous solutions can remove soluble materials such as zinc stearate from plastic surfaces.

Calibration Solutions

Working calibration solutions are prepared from stock solutions, which are normally 1,000 ppm in concentration. The stock solution is then diluted in steps with clean pipettes or burettes into volumetric glassware. Glassware is suitable for the dilution steps but not for storing diluted solutions for any period of time.

It should be remembered that $\text{ppm} = \mu\text{g mL}^{-1} = \text{mg/liter}$. The suggested maximum dilution factor used in any one step is twenty times or a minimum of 5 mL diluted to 100 mL, due to increased inaccuracies involved in pipetting smaller volumes.

To prepare a 0.01 ppm or 10 ppb concentration standard by dilution from a 1,000 ppm stock solution, the following scheme is suggested:

Take 10 mL of 1000 ppm solution and dilute to 100 mL. This gives a concentration of 100 ppm.

Take 10 mL of 100 ppm solution and dilute to 100 mL. This gives a concentration of 10 ppm.

Continue the same dilution steps in sequence, producing intermediate concentrations of 1 ppm, then 0.1 ppm and finally 0.01 ppm.

The same dilution is possible in one step using a plastic tipped micropipette, but is not generally recommended for the highest accuracy. For example, 10 microliters of a 1000 ppm solution when made up to 1 liter will give a 0.01 ppm solution.

The final working standards should be acidified with an appropriate mineral acid for aqueous solutions, or the same acid or acids used during sample preparation. Stabilization of working solutions is very important, as most solutions in the low ppm concentration range are subject to hydrolysis and absorption effects. These effects are well known and documented in most analytical handbooks. Examples of elements which are prone to hydrolysis are Sn, Ti, As and Sb. Tin is normally stabilized with a relatively high concentration of hydrochloric acid, never nitric acid which leads to large losses of tin from solution.

The lifetime of prepared standard solutions is variable. As a general rule 1,000 ppm stock solutions should be stable for at least six months. However, the more dilute the solution, the shorter the lifetime. An acidified solution of 5-10 ppm, in an appropriate container, may only be stable for one week. In principle, solutions with concentrations below the 1 ppm level should be prepared immediately before analysis, although the individual solutions themselves might be stable for periods of more than one day.

Calibration Procedure - Direct Method

There are two basic procedures available for calibration purposes, a direct interpolation method and the standards additions technique. Direct concentration readout by either method is now possible with modern computer controlled instruments. The choice of which method to use depends on several considerations.

In a graphite furnace system, the ashing phase of a furnace cycle destroys the sample matrix before the atomization stage and the analyte is atomized from a simple compound, such as the oxide form. If the sample is a simple compound, it is possible to prepare a set of calibration standards containing only that compound. For example, the sample may be predominantly lead nitrate, therefore standards need only be

prepared from lead nitrate stock solution. If, however, the analyte is a trace metal in a known concentration of simple matrix, then matched standards should be employed. For example, if determining bismuth in a 1% steel matrix, then the bismuth standards should contain an appropriate amount of steel to bring each standard up to 1% in steel.

The calibration graph is normally linear at low absorbance values only, and the sample has to be diluted to be within this range, if manual techniques are employed. A set of standards, at least three times to obtain good precision, three times being normally the minimum requirement.

A blank solution should be included to allow for any signal due to analyte present in reagents used in sample preparation. For each standard, the measured absorbance values for flame, or peak heights or areas for graphite furnace, are plotted against the known concentrations, enabling a calibration graph to be constructed. Subsequently, sample concentrations can be read off directly from the graph.

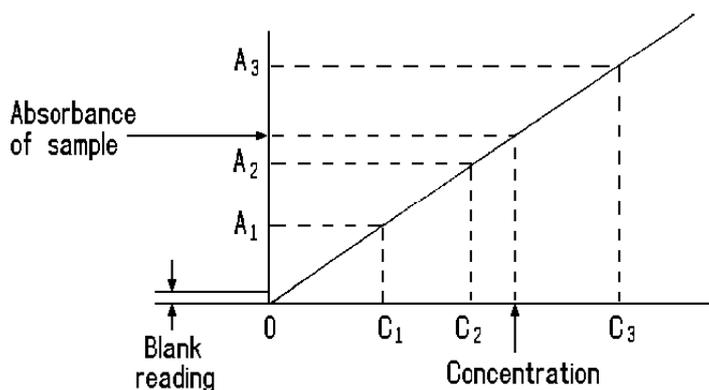


Figure 16-1. Calibration graph (direct calibration)

A typical direct calibration curve for a blank and three standards is shown above. The values A_1 to A_3 are absorbance values obtained from standards containing concentrations of C_1 to C_3 of analyte. The absorbance and concentration increase along the y and x axis respectively. These curves may be plotted manually after subtraction of the blank and the concentration of the sample read directly from the graph.

It is now much easier to use the computational power of microprocessor technology. The most suitable equation or algorithm, which most accurately defines the calibration curve must be found and the simplest approach is to use a "least squares fit" procedure. Although this is apparently the pairs of data points and the line must by definition pass through each point. This will not happen when a general least squares fitting routine is used, as the coefficients are chosen to minimize the sum of the squares of the distances of each point from the line. Only

if the form of the equation chosen happens to exactly fit the data will this distance be reduced to zero. Normally there will always be an error in the calculated concentration.

In some instruments, a technique using segmented parabolic functions is used instead of a least squares algorithm. This is shown in [Figure 16-2](#).

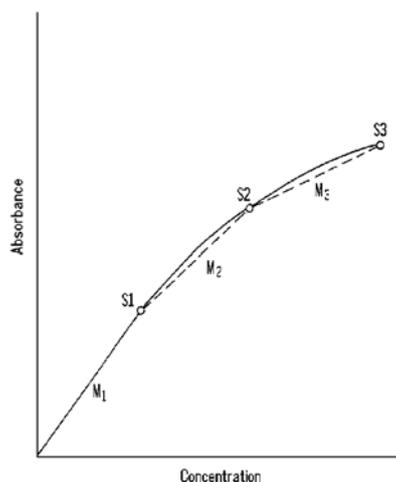


Figure 16-2. Segmented curve fitting

The system works as follows. The blank is measured first, followed by each standard starting from the lowest concentration. The straight line gradient between the blank and the first standard, is compared with that between the first and second standard. If the two gradients are within 40% of each other in the direction of the concentration axis, or within 10% toward the absorbance axis, the calculation will proceed. If the segment gradients are within these limits, the mean value of the two gradients is calculated and is used to define explicitly a segment of a parabola between calibration points 1 and 2 and 3. The mean of the gradients of the previous segments is used to check for excess curvature. The complete calibration function is therefore built up segment by segment, with checks for excess curvature being made at each calibration point.

Normal calibration procedures can now be accomplished simply and quickly, without recourse to manual plotting of results, by using automatic sampling devices linked to microcomputer data processing. Some systems with autosamplers will prepare standards from a master solution, which increases the accuracy by removing variability associated with different analysts' dilution techniques.

Matrix Matched Standards

Aqueous standards and simple calculation procedures are used when matrix components in the sample do not interfere with the analytical signal. However, in many cases interference does exist. To overcome interference, matrix matched standards are used to calibrate the analysis. For example, in ETA for the determination of Pb in whole blood, the matrix causes a 30% suppression of signal using tube wall atomization. A solution to this problem is to use whole blood standards containing additions of 0, 0.5, 1.0, 2.0 and 3.0 $\mu\text{mol l}^{-1}$ Pb. These whole blood standards are treated in exactly the same way as the samples, using a 1 : 4 dilution with 1% HNO_3 . Calibration is achieved by subtracting the endogenous Pb content from the standard additions. This method can only be used if the major sample matrix components are known, or do not vary much from sample to sample.

Standard Additions Technique

Direct calibration techniques work well for simple solutions, where matrix effects are negligible, or constant for all samples in a batch. For more complex solutions and samples where matrix effects are variable, and cannot be removed, the method of standard additions must be used. This method should always be employed initially to check for interference effects, before choosing the best calibration method.

The technique is as follows:

Take several aliquots of the sample solution and add known concentrations of the analyte to all but one aliquot. In the following example where the anticipated analyte concentration in the sample is approximately 0.04 ppm, each solution will have a final volume of 10 mL. Shown in the table below are aliquot volume, and standard analyte solution added to each aliquot. Deionized water is then added to make up the final volume.

Table 16-1. Aliquot volume and standard analyte solution

| Solution number ^a | Sample volume (mL) | 0.2 ppm standard volume (mL) | Water (mL) | Total volume (mL) | Added concentration (ppm) |
|------------------------------|--------------------|------------------------------|------------|-------------------|---------------------------|
| 1 | 0 | 0 | 10.0 | 10.0 | 0.00 |
| 2 | 5.0 | 0 | 5.0 | 10.0 | 0.00 |
| 3 | 5.0 | 0.1 | 4.0 | 10.0 | 0.02 |
| 4 | 5.0 | 2.0 | 3.0 | 10.0 | 0.04 |

^a Solution Numbers are as follows:

1 is a blank solution.

2 is a sample solution which is diluted by a factor of 2, without addition of analyte.

3 is a sample with the first addition of a known concentration of analyte.

4 is a sample with the addition of a known concentration of analyte, containing twice the concentration level of that in solution number 3.

Each solution is then measured in triplicate and the absorbance values obtained. Typical results could be as shown in the table below for a series of peak height measurements.

Table 16-2. Peak height absorbances

| | Peak height absorbance | Peak height abs. corrected for blank |
|---------------|------------------------|--------------------------------------|
| Blank | 0.050 | |
| Zero Addition | 0.200 | 0.150 |
| Addition 1 | 0.490 | 0.440 |
| Addition 2 | 0.800 | 0.750 |

The corrected peak height absorbances can be manually plotted against the concentration of added analyte or by using the computer to directly calculate the answer. In the graphical method, the plotted line is extrapolated backwards to cut the concentration axis. The intercept value corresponds to the analyte concentration for solution without added analyte. This is illustrated diagrammatically in [Figure 16-3](#).

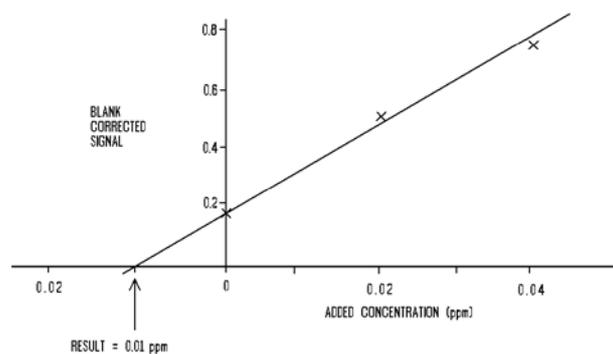


Figure 16-3. Calibration graph - standard additions

A normal calibration graph using aqueous standards of the same concentration as the added analyte in Additions 1 and 2, can be constructed. To determine whether or not chemical interferences occur, the slopes of the standard additions graph and the normal calibration graph can be compared. If the two graphs are parallel, it can be assumed that any interferences are minimal and may be safely ignored. Under these conditions calibrations against simple aqueous standards is possible. If the graphs have different slopes, then interferences must be assumed to be present and calibration has to be accomplished by the standards additions method.

The standard additions method assumes that added analyte will react in exactly the same manner during analysis as the analyte already in the sample. In other words, inorganic lead nitrate added to a sample containing an organometallic compound of lead, is assumed to react as organic lead. This is not necessarily found to be true in practice. Any background absorbance will not be compensated for using the standard

additions method. In the absence of simultaneous background correction facilities, the background must be corrected before the calibration graph is constructed. For maximum accuracy, the final absorbances measured for all the standard additions solutions must fall on the linear portion of the calibration graph. Should there be doubt concerning the accuracy of the determination, a certified standard reference material such as the range of BCS or NIST standard materials must be run through the complete method.

If no convenient standard material exists, the sample should be pretreated to effectively remove the matrix. This may be achieved by acid digestion or extraction, wet or dry ashing etc., and the remaining, essentially aqueous, solution analyzed.

The method described above involves making a considerable number of solutions. For ETA an alternative technique can be employed. Standard additions can be carried out in the graphite tube, thus avoiding the handling operations necessary to make extra solutions. A manual technique is to inject the sample solution into the tube, dry and ash it as normal, but stop the furnace cycle at this point. After allowing the tube to cool slightly, the aqueous addition standard is then injected into the graphite tube on top of the ashed sample. The whole furnace cycle is then restarted with a dry phase and the final recorded absorbance is that due to the analyte in the sample plus the added analyte. In this way the required number of determinations can be obtained using only the sample solution and a range of simple aqueous standard solutions. Computers and autosamplers allow this method to be performed automatically and interpret the data, calculate the intercept point and display the result.

Linearity

It is essential for the standard additions method, and convenient for the normal calibration procedure, to work in the linear portion of the calibration graph. This can only be established by making a wide range of standards and measuring their signals. The limit of linearity for the graph can then be assessed and the maximum working concentration range for linearity calculated.

Linearity is affected by concentration effects, as an excess concentration of free atoms in a small analytical volume, gives less than expected absorbance values. The instrument should be operated over the range 0-0.4 absorbance units whenever possible, as above this level curvature almost always occurs. Some spectrometers are able to detect curvature in the standard addition plot and ignore the high values. Only the linear portion of the plot is used to define the sample concentration.

Non-Linearity

Non-linearity can be introduced by the various damping effects in the instrumentation, such as the result of long time-constants in the detector system and slow response chart recorders. With increasing concentration the degree of dissociation is less, resulting in a lower proportion of free atoms being available at higher concentrations, causing curvature.

Calibration graphs for many elements are linear up to almost 0.5 A and most of the remainder give only slight curvature to 1 A. An exception is nickel which shows curvature. Its main resonance line at 232.0 nm occurs in a densely populated spectrum region and the curvature therefore depends on the bandpass and available monochromator resolution. Excessive curvature can also result when changing from one gas combination to another without readjustment of observation height or gas flow rates.

There are occasions when a calibration graph shows curvature away from the concentration axis. Examples are barium and europium in a nitrous oxide/acetylene flame, or gold, potassium and sodium in the air/acetylene flame.

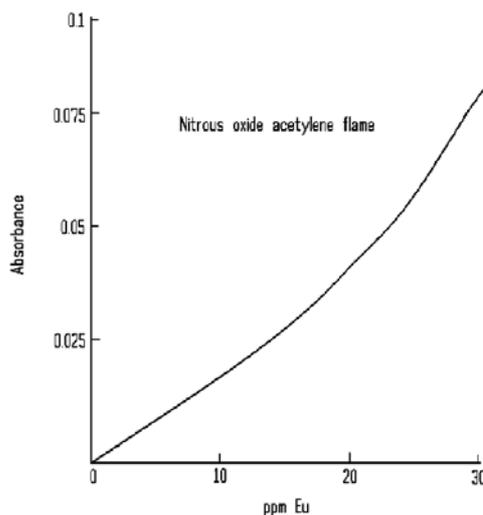


Figure 16-4. Upward-curving calibration for europium

This effect is caused by ionization, as a higher proportion of the element is ionized at very low concentrations. Ionization is also noticeable at temperatures above the optimum for a given element. To correct for ionization, an ionization buffer is added.

Interferences

Interference effects in AAS have traditionally been classified into chemical, physical and spectral interferences. Although background effects and their correction are sometimes classified as physical interference. Interferences in flame AAS are few and well defined and can be divided into five types: Spectral, Physical, Chemical, Ionization and Non-specific absorption.

Spectral Interference

Spectral interference due to line overlap is very rare in atomic absorption spectrometry. This type of interference can be overcome by either separation of elements prior to analysis, or by use of an alternative wavelength. AAS is highly specific for a given element. The wavelengths at which individual elements absorb are well defined and the possibility of two elements absorbing at exactly the same wavelength is so remote, that the technique is generally recognized to be free of spectral interference. The few well documented cases where this interference effect has proved significant, are shown in the table below:

Table 17-1. Spectral interferences

| Analyte | Analyte wavelength (nm) | Interferent | Interferent wavelength (nm) | Separation (nm) |
|-----------|-------------------------|-------------|-----------------------------|-----------------|
| Vanadium | 308.211 | Aluminium | 308.215 | 0.004 |
| Lead | 216.999 | Antimony | 217.023 | 0.024 |
| Copper | 217.894 | Antimony | 217.919 | 0.025 |
| Nickel | 213.095 | Antimony | 213.147 | 0.052 |
| Lithium | 323.261 | Antimony | 323.252 | 0.009 |
| Cadmium | 228.802 | Arsenic | 228.812 | 0.010 |
| Europium | 324.753 | Copper | 324.754 | 0.001 |
| Manganese | 403.307 | Gallium | 403.298 | 0.009 |
| Calcium | 422.673 | Germanium | 422.657 | 0.016 |
| Platinum | 271.904 | Iron | 271.903 | 0.001 |
| Manganese | 279.482 | Iron | 297.470 | 0.012 cont... |
| Magnesium | 285.213 | Iron | 285.213 | < 0.001 |
| Gallium | 287.424 | Iron | 287.417 | 0.007 |

Table 17-1. Spectral interferences, continued

| Analyte | Analyte wavelength (nm) | Interferent | Interferent wavelength (nm) | Separation (nm) |
|-----------|-------------------------|-------------|-----------------------------|-----------------|
| Copper | 324.754 | Iron | 324.728 | 0.026 |
| Copper | 327.396 | Iron | 327.445 | 0.049 |
| Silver | 338.289 | Iron | 338.241 | 0.048 |
| Nickel | 352.454 | Iron | 352.424 | 0.030 |
| Aluminium | 396.153 | Iron | 396.114 | 0.039 |
| Strontium | 460.733 | Iron | 460.765 | 0.032 |
| Cobalt | 253.649 | Lead | 241.173 | 0.003 |
| Palladium | 247.643 | Lead | 247.638 | 0.005 |
| Gallium | 403.298 | Manganese | 403.307 | 0.009 |
| Cobalt | 253.649 | Mercury | 253.652 | 0.003 |
| Chromium | 359.349 | Mercury | 359.348 | 0.001 |
| Vanadium | 250.690 | Silicon | 250.690 | < 0.001 |
| Iron | 213.859 | Zinc | 213.956 | 0.003 |

As the absorption line for copper is 324.754 nm and that of europium of 324.753 nm, there can be a problem for the determination of a low level of copper, in the presence of a high level of europium. The overlap of molecular bands and lines for calcium hydroxide on barium at 553.55 nm, would also be a problem.

Sodium chloride appears to give a strong molecular absorption at the 217.0 nm lead line, which affects lead determination. Background correction may be used to overcome this type of interference.

Physical Interference

Physical interference due to viscosity effects can be overcome by carefully matching solvent and matrix of standards and samples. For example, aqueous standards should not be used when measuring a sample in an organic solvent.

Chemical Interference

The response of an element at its resonance wavelength may sometimes be dependent on another component or components in the sample solution. This effect is usually known as chemical interference.

A population of free atoms of the element in the flame must be generated before absorption at the resonance wavelength can occur. The number of free atoms and therefore the amount of atomic absorption in the flame is dictated by equilibrium constants. Any constraints on the system causing shifts in the equilibrium will constitute a chemical interference.

Stable Compound Formation

Common anionic species such as phosphate, sulphate, aluminate, and other oxygenated anions depress the absorption of the alkaline earth metals in the air/acetylene flame. The chemical compounds formed are relatively stable at the air/acetylene flame temperature and the formation, slags, aluminium alloys, feeding stuffs, etc. and must be overcome.

Various methods of overcoming this type of interference are available:

1. Removal of the interfering anion(s) by chemical or by ion exchange techniques

These methods are not often used as they detract from the essential simplicity of atomic absorption analysis.

2. Additions of an excess of the interfering anion(s) to both sample and standard solutions

The method is simple, but may reduce the analytical sensitivity of the element to be determined to below a useful limit.

3. Use of a hotter nitrous oxide/acetylene flame for the alkaline earth elements

While the flame temperature is sufficiently high to completely overcome anionic interferences, another effect known as ionization is introduced. This is discussed in the section on Ionization.

4. Addition of a “releasing agent”

This is probably the most commonly used technique. A releasing agent is the salt of a metal, which will form a stable compound with the interfering anion. Lanthanum and some other rare earth chlorides are very effective, and strontium chloride may act as a releasing agent for calcium and magnesium in the presence of the interfering anions. Some chelating agents, particularly the disodium salt of ethylene diamine tetra-acetic acid (EDTA), are effective in overcoming anionic interference by active chelation of the metal to be determined, rather than by reaction with the anionic species. The releasing agent method is unsuccessful only when the extent of the anionic interference is very large.

Ionization

This interference is usually observed in high temperature flames such as nitrous oxide/acetylene and is characterized by enhanced response of the element being determined when another more easily ionized element is added. An equilibrium exists in the flame between free atoms and ions. For elements having relatively low ionization potentials, the proportion of ions will be high. If a second easily ionized element is introduced into the flame, the equilibrium for the element of interest is shifted towards the atomic state, producing an enhancement in analytical sensitivity. Failure to recognize this effect leads to erroneously high results.

Elements which are ionized in the air/acetylene flame include the alkali metals and gold, although many other metals are ionized to a small extent. Elements which are ionized to a significant extent in the nitrous oxide/acetylene flame include the rare earths, alkaline earth metals and Al, B, Ga, In, Sc, Ti, Tl.

Whenever any element is determined in the nitrous oxide/acetylene flame, the presence in the sample solution of a large excess of another element will almost certainly increase the absorbance. The interference is effectively overcome by adding an excess of easily ionizable metal salt such as cesium or potassium chloride to both standard and sample solutions. Sufficient metal, normally around 1000-2000 ppm, should be added, so that the absorbance reaches a "plateau", to overcome the interference. This will often give a very significant improvement in sensitivity. As each metal in Group 1 of the periodic table is more easily ionized in the order Li, Na, K, Rb, Cs, then each element below the other in the periodic table may be used to suppress ionization of the element above it. For example if in the analysis of sodium, the sodium were ionized, then a salt of potassium would be added to suppress ionization. This occurs according to the law of mass action and is demonstrated by the equations below:



There is now an excess of e^- from the ionization of K, as it is more easily ionized the equilibrium for Na is pushed to the left, ($\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$) to produce more Na atoms.

Non-Specific Absorption

This type of interference is caused by molecular absorption or by light scattering due to salt particles. It is more serious in furnace AAS than in flame AAS and is easily overcome by the use of background correction.

Furnace Interferences

Sample Spreading

The process of sample drying can cause interferences. When a sample is injected into the graphite cuvette, the position, size and shape of the crystals formed during the drying stage may affect the efficiency of the atomization process. Use of an automatic pipette and autosampler can help eliminate this problem.

Solid Sample Interferences

The problem of calibration in solid sampling GFAAS is due mainly to the presence of interferences occurring during atomization of samples. These chemical interferences may arise from sample constituents such as chloride, or from a difference in atomization rate of the analyte, caused by occlusion of the analyte in the solid matrix. In both cases, platform atomization and matrix modification procedures help to eliminate, or reduce these interferences.

To analyze solid samples, select a solid sample with a similar matrix to sample, but with a known analyte content for calibration standards. This should be either a standard reference material SRM, or prepared standard which has been previously analyzed.

After a short period of time using solid samples, a carbonaceous residue will build up inside the platform and should be removed. In certain circumstances, solid samples can be calibrated against aqueous standards. The type of calibration procedure chosen, depends upon the requirement of individual laboratories.

Matrix Interferences

Stable Compound Formation

Many of the refractory elements including Ba, B, Mo, Ti, V, and W react with graphite to form stable refractory carbides. As a result, they are extremely difficult to determine using an electrographite tube. Pyrolytically coated electrographite tubes greatly enhance the signal, and are preferred for the determination of refractory elements.

Certain elements, such as Al, Ba, Be, Ca, Cr, Ga, Ge, Hf, Li, Mg, Nb, Pu, Si, Sr, Ta, Th, Ti, U, V, Y, and Zr, form stable nitrides at temperatures higher than 600°C. In these cases argon, rather than nitrogen, must be used as the inert gas.

Volatile Compound Formation

The formation of volatile compounds can be used beneficially to eliminate interfering chlorides. It is also possible to volatilize analyte chlorides during the ashing phase, which can lead to depressed results if the standards do not contain the same amount of chloride.

Vapor Phase Interferences

Temperature equilibrium has to be established during atomization, to prevent vapor phase interferences. Analytical results are highly dependent upon the type and condition of the sample. Without temperature equilibrium, different compounds or states of a given element may require different atomization temperatures.

The example most documented in the literature for vapor phase interferences, is the interference of metal halides on volatile elements such as lead or cadmium. In many analyses, the main difficulty is the presence of a high concentration of sodium chloride, for example, in the analysis of biological or sea-water samples.

The interference of magnesium chloride on lead takes place during the vaporization and atomization of analyte and matrix during the atomization phase in the furnace cycle. The situation can be understood more easily by the inspection of the following equilibrium:



At lower temperatures, the equilibrium lies to the right side of the equation and thus favors the formation of lead chloride molecules. This reduces the lead atom population and causes reduction of the lead atomic absorption signal. At higher temperatures the equilibrium lies to the left side of the equation, resulting in an increase in the lead atom population.

In the early L'vov furnace, samples were atomized into a steady state high vapor temperature. This system reduced analyte halide formation and consequently reduced interferences.

However, in the Massman design, analyte and matrix are atomized into a rapidly changing temperature environment. Volatile elements are atomized at low temperatures and analyte halide formation is increased. This results in a reduction in the free analyte atom formation and increased interference. Various methods have been used to reduce these

interferences, such as matrix modification, platform atomization and probe atomization. All three methods delay the volatilization and atomization of analyte until the vapor phase temperature has reached a constant temperature.

Furnace Interferences

Matrix Interferences

Quality Assurance (QA) And Quality Control (QC)

It is important to follow a set of operating principles during sample collection and analysis, which will produce reliable data of defensible quality. This is known as quality assurance and enables the analyst to have a high level of confidence in the accuracy of analytical results. Quality control and quality assessment are important aspects of quality assurance.

Quality Assurance Planning

To carry out a quality-assurance program, a QA plan is essential. The plan should include the following:

- Staff organization and responsibilities
- Sample control and documentation procedures
- Standard operating procedure for each analytical method (SOP)
- Analyst training requirements
- Preventative maintenance procedure for equipment
- Calibration procedures
- Corrective actions
- Internal quality control activities
- Performance audits
- Data assessment procedures for bias and precision
- Data reduction, validation, and reporting.

A cover sheet should outline objectives and include an organization and responsibilities section which assigns specific functions to each participant in the program.

Sample control and documentation procedures allow a sample and its derivatives to be traced through all stages, from collection to analysis and results. Documentation is always important, but is particularly so when more than one person is involved in the program.

A standard operating procedure for the analytical method should describe the method in such detail that an experienced analyst unfamiliar with the method can follow it and obtain acceptable results.

Training for analysts must be specified. The analyst must have sufficient training, as the quality of the results will vary with the type of analysis, the number of analyses required, sample characteristics and experience of the analyst.

Equipment maintenance procedures are required. A strict preventative maintenance program will reduce instrument malfunctions, maintain calibration and reduce working time lost.

The reduction, validation, and reporting of data are the concluding features of a QA program. The parameters of an analytical instrument must be optimized to obtain meaningful measurements. The QA plan should also specify the correction factors necessary to calculate the results. Standard units of mass, volume, or concentration should always be used in the report and a specified method used for reporting results below the method detection limit. Each result or set of results should be accompanied by a statement of uncertainty.

Quality Control

Quality control may be either internal or external. All competent analysts use some form of QC to produce credible results. However, a good quality control program consists of the following:

- Certification of operator competence
- Recovery of sample after pretreatment
- Recovery of known additions
- Analysis of externally supplied standards
- Analysis of reagent blanks
- Calibration with standards
- Analysis of duplicates
- Maintenance of control charts.

The analyst has to demonstrate competence before being allowed to carry out work which is to be reported. For most inorganic and organic chemical analyses, demonstration of acceptable single-operator precision and bias is sufficient. A minimum of four replicate analysis of an independently prepared check sample should be analyzed. The concentration of this sample should be between 5 and 50 times the method detection limit (MDL).

The recovery of known additions must be part of a regular analytical protocol. Known additions are used to verify the presence or absence of matrix effects. Always verify the amount of interference when a new matrix type is to be analyzed. When the analyte of interest is absent and duplicates are not necessary, carry out a recovery of known additions for 10% of the samples. When analyzing duplicates, the sum of the duplicates and known additions must equal at least 10% of the number of samples. The known additions should be between 5 and 50 times the MDL, or between 1 and 10 times the normal level, whichever is greater. Known additions should not be used above the demonstrated linear range of the method and concentrated standards should be used so that volume change in the sample is negligible.

When the analysis of known additions does not result in acceptable recovery, analyze externally supplied standards at least once each day. Use laboratory control standards with a concentration between 5 and 50 times the MDL or near sample normal levels, whichever is greater. Use certified reference materials where possible as laboratory control standards. National Institute of Standards and Technology (NIST) Standard Reference Materials are ideal if available. Prepare internal reference materials independently from the standards used for calibration.

Whenever new reagents are used, analyze reagent blanks. A reagent blank must also be analyzed after any sample, which has a concentration greater than that of the highest standard, or when there is a risk of carry over from one sample to the next.

When calibrating with standards, measure three different dilutions of the standard daily by analyzing one or more standards within the linear range. Report analytical results which are within the range of the standard dilutions used. Only report values above the highest standard when greater linear range has been demonstrated, no instrument parameters have changed and the value obtained is less than 1.5 times the highest standard. The lowest reportable value is the MDL, provided that the lowest calibration standard is less than 10 times the MDL. When subtracting a blank, report the result even if it is negative.

Analysis of duplicate samples is effective for assessing precision when most of the samples have measurable levels of the constituent being determined. 5% or more of the samples should be analyzed in duplicate. The analysis of duplicates and known additions in matrices should be representative of the samples analyzed in the laboratory.

Three types of control charts are commonly used in laboratories and are essential for quality control.

Means chart for standards - Laboratory control standards (LCS) or calibration checks standards (CCS)

Means chart for background or reagent blank results

Range chart for replicate analyses.

Quality Assurance (QA) And Quality Control (QC)

Quality Control

The Sample

To achieve good results, it is extremely important that all of the following requirements are observed:

Knowledge of the history and environmental conditions relating to the origin of the sample.

Method of collection of the sample.

Correct preparation, handling and storage.

Failure to take into account all of these requirements, will produce results which are meaningless.

Sample Collection

Serious contamination may occur if the empty sample container has not been cleaned properly and rinsed with acid and deionized water prior to sample collection. Contamination from a previous sample may also result from not cleaning containers correctly.

Sample Storage

Having obtained the sample, two important questions need to be considered:

How can the sample be stored, if analysis cannot be carried out immediately?

How long can the sample be kept?

In an ideal situation, the sample should be analyzed for the element of interest immediately. If this cannot be done, then the preservation of the sample has to be carried out. The biggest risks in storage, and particularly long term storage, are the loss of metal from the sample over a period of time, and the possibility of contamination. As it is possible to determine metals in practically everything, a certain protocol or QA program should be followed, depending on the type of sample and the element to be determined in it.

It is much easier to clean out the container if a sample is dealt with immediately. If the sample has been stored for a long time, the suspended particles may settle to the bottom of the bottle, resulting in loss of some sample particles as well as making cleaning more difficult.

Sample Preparation

A sample received in a laboratory is rarely in the form which allows for direct introduction into the AAS, therefore some form of sample preparation is necessary. There are at least five methods of sample preparation used by the analyst which are:

- Wet Ashing or Acid Digestion
- Fusion
- Pressure Dissolution >
- Dry Ashing
- Microwave Oven Digestion

Wet Ashing or Acid Digestion

For flame AAS, the sample is always introduced as a liquid to the instrument and to achieve this state, an acid digestion is often used. Subject to the type of sample, various acids can be used.

The solid sample is dissolved in an acid or mixture of acids. Typical acids used are hydrochloric, nitric, aqua regia, (which is a 3:1 mixture of HCl and HNO₃), perchloric, hydrofluoric, and sulphuric. The acid or mixture of acids used for any particular application is highly sample dependent. For example, most metals will dissolve in hydrochloric or nitric acid, or a mixture of both, aqua regia.

Biological materials with simple matrices will dissolve in nitric acid, however more complex matrices may also require perchloric acid. Perchloric acid is also useful for breaking up strong fluoride complexes. Hydrofluoric acid is used to break up silicates in both geological and biological samples. Sulphuric acid is used in a similar manner to perchloric. All acids for dissolution procedures must be of high purity. 'AnalaR' grade is usually sufficient for most analyses. To be required when the final measurement is by furnace AAS.

Wet ashing or acid digestions are usually carried out in pyrex glassware, although when using acids such as hydrofluoric or when metals such as sodium are being analyzed, teflon or platinum ware is preferred.

Fusion Technique

Another method of sample dissolution is the fusion technique. Here the sample is weighed into a metal crucible, mixed with a suitable flux and fused over a hot flame. The resulting melt is leached in either water or acid. This technique is easily automated, which increases the speed of analysis greatly.

Several different fluxes have been used. Sodium carbonate is suitable for simple matrix fusion or for samples which are high in sulphur. Sodium tetraborate and lithium metaborate have been used for samples fluoride is a specialized flux, used for the determination of rare earth metals. Sodium peroxide is a universal flux and has a wide range of analytical applications to numerous sample types.

Fusion is sometimes used in conjunction with acid digestion, when the acid mixtures used have not totally dissolved the sample. The residue is filtered and then fused, usually with sodium peroxide. The two portions are combined and then measured by AAS for total metal.

As in acid digestions, the reagents used must be of high purity to avoid contamination. Fusions are usually carried out in metal crucibles, of nickel, platinum or zirconium.

The major disadvantage of this technique is the introduction of a large quantity of salt to the sample matrix. This can cause background and interference effects in the flame. Care must be taken to avoid burner blockage. In the furnace, the presence of high salts will greatly affect the measurement and therefore this technique has limited application for furnace analysis.

Pressure Dissolution

This technique is used when volatile elements may be lost using other sample preparation techniques. The sample is sealed inside a 'Parr' bomb, or a quartz or silica Carius tube, with a mixture of acids. The bomb is then placed in an oven at around 150°C, usually overnight. The combination of temperature and pressure aids dissolution of the sample. This method has been used to determine mercury and silicon.

Dry Ashing

This technique is used for samples, which have a high carbon content. The sample is heated in air in an oven until all the organic material has been burned away. Volatile elements for example arsenic, can be lost at high ashing temperatures and various ashing agents such as magnesium nitrate, have been used to prevent this loss. After ashing the residue is dissolved in hydrochloric or nitric acids. Dry ashing has been used for samples such as coals, resins and plant material.

Microwave Oven Digestion

This technique consists of placing the sample and acids in a sealed polycarbonate or teflon bottle or bomb and heating in a microwave oven. Again, it is the combination of temperature and pressure which

effects dissolution of the sample. This technique is also useful for the measurement of volatile metals. The major advantage of the technique is in analysis time, which is in minutes, rather than hours.

Preconcentration and Separation Techniques

These techniques are a means by which the sample can be concentrated prior to introduction to the AA. Even though a sample is in solution it may not be possible to measure the element directly by flame or furnace AAS and to bring the element of interest into the working range of the instrument, it will be necessary to concentrate the sample. Alternatively, separation of the analyte from the matrix prior to measurement to reduce interference effects will be required. The methods of concentration are:

- Evaporation
- Liquid-Liquid Extraction
- Ion Exchange Separation
- Co-precipitation.

Evaporation

The most common type of technique is to evaporate the solution down by boiling off some of the solvent to concentrate the metals, taking care not to lose the more volatile elements. The disadvantage of this technique is that the matrix is also concentrated, which results in interference such as molecular absorption and scattering in the light path. This technique is not suitable for volatile metals.

Liquid-liquid Extraction

Liquid-liquid extraction is another technique, which concentrates and separates the sample and matrix. The complexing of metals with an organic compound is used to concentrate the sample. After pH adjustment, the metals in solution are complexed with a suitable agent such as dithizone or ammonium pyrrolidine dithiocarbamate (APDC) and extracted into an organic solvent. APDC complexes with a wide variety of transition metals over a large pH range. Solvents used for flame AAS are typically methyl isobutyl ketone (MIBK) or diethyl isobutyl ketone (DIBK). Other solvents however, such as chloroform may be used for furnace AAS. Organic solvents generally give an enhancement effect in the flame.

Ion Exchange Separation

A technique which uses an ion exchange resin can be used to concentrate metals from a large solution volume. The pH is adjusted and the exchange material loses Na^+ in exchange for the metals. The metals are then eluted and transferred to the AAS. Both anionic and cationic resins are used. The method consists of passing the solution containing the pH adjusted analyte through the exchange column and then eluting with a lower pH solution to remove the metals of interest. Usually several washes are required to ensure complete removal of the metals. The analyte can be adsorbed on to a resin and then the solid sample measured in the graphite furnace.

Co-Precipitation

This is another specialized separation procedure, in which the analyte is precipitated with an insoluble salt. Insoluble hydroxides such as lanthanum and iron are used. Co-precipitation of the hydride forming elements such as As, Se, Te, Sb, and Bi with lanthanum hydroxide has been used for the measurement of these elements in copper.

The Sample

Preconcentration and Separation Techniques

Fusion Technique

Fusions and the ignition of precipitates is normally carried out in a crucible in a muffle furnace, although gas burners may also be used. Certain conditions apply, if damage to the platinum crucible is to be avoided.

A variety of materials can be used for the crucible, of which pure platinum metal is the most common, and also the most expensive.

Use of Platinum Crucibles

Platinum metal is inert to most common reagents and sample materials, and can withstand temperatures in excess of 1000°C. Nevertheless, certain precautions should be taken to ensure that the crucibles have a long life.

The inner cone of a Bunsen flame must not touch the platinum at any point, otherwise a carbide of platinum is formed and the platinum becomes very brittle. For the same reason a yellow flame should never be used. Meker and Amal burners are preferable to Bunsen burners because they combine a very hot flame with a small inner reducing one.

Platinum becomes permeable to the flame gases at high temperatures and the substance inside the crucible may be reduced. If the heated crucible is covered, a strongly reducing atmosphere is produced. Iron (III) oxide, heated in this manner is partly reduced to the metal, which then alloys with the platinum.

The surface of the platinum will always tarnish when heated, because of the formation of a film of iron (III) oxide, unless the crucible is first cleaned with acids. Iron stains can be removed by heating 1 g of NH_4Cl in the covered crucible, using the full heat of the burner. Fusion with potassium bisulphate is also effective. New platinum crucibles should be boiled with HCl before use, to remove iron which will alloy with platinum when heated.

During the heating process, platinum vessels should not be supported on metal supports, placed on iron wire gauze or on the metal plate in front of the muffle furnace, or on any dirty surface while being cooled. Suitable support and cooling plates can be made of silica, slag, or similar refractory material. Hot crucibles must not be cooled by being plunged in cold water.

Platinum tipped tongs should always be used to handle platinum apparatus. Solid nickel tongs can be used to safely handle platinum at below red heat. Iron or nickel plated tongs should not be used.

Ignition of Precipitates

Moist precipitates, wrapped in filter paper can be dried by placing the crucible on the frontal plate of a hot muffle furnace. Ideally, the filter paper and organic matter are first completely charred, by placing the platinum vessel near the open end of the muffle furnace, until nearly all the carbonaceous matter has been burnt off. It is then placed in the hot region of a well ventilated furnace, for completion of the ignition. Damage to the platinum is avoided if this technique is followed.

Fluxes for Fusions

Acid fluxes attack platinum less than alkaline fluxes and are recommended when iron is determined in silicates. As all fluxes attack platinum slightly, traces of platinum may be measured in the final solution. The following fluxes can be used in platinum apparatus, provided oxidizing conditions are maintained and the substance is free from organic matter.

- Sodium or potassium carbonate - very slight attack.
- Sodium carbonate mixed with nitrate or nitrite - slight attack.
- Borax - harmful at high temperature.
- Sodium or potassium hydrogen sulphate - slight attack above 700°C which may be minimized by the presence of ammonium sulphate.
- Sodium or potassium hydrogen fluoride - extremely slight attack.
- Lithium metaborate - extremely slight attack.

Substances which may be Heated in Platinum

The following compounds may be heated without significant effect on the platinum:

- Barium sulphate, sulphate or oxides of metals that are not readily reduced
- Alkaline earth carbonates and oxalates
- Alkali and alkaline earth chlorides

- If the alkaline earth chlorides are heated above 1000°C, there is some attack, because chlorine is liberated at the air/platinum junction.

Platinum dishes can be used for evaporation of:

- Hydrofluoric acid, sulphuric acid with or without hydrofluoric acid
- Hydrofluoric acid and nitric acid in the absence of the other halides
- Hydrochloric acid in the absence of oxidizing agents
- Alkali hydroxide and carbonate solutions. Atmospheres of CO₂, N₂ and H₂ have no deleterious effect.

Substances which Attack Platinum

Acids

Platinum is immune from attack by most single mineral acids. It is slowly dissolved by prolonged heating with concentrated sulphuric and phosphoric acids, although the action is extremely slow and is negligible. Aqua regia and other mixtures of hydrochloric acid with oxidizing agents readily dissolve platinum on heating and must be avoided.

Reactant Compounds

Compounds of the following anions attack the metal and should not be heated in platinum apparatus.

- Cyanides, hydroxides, oxides, peroxides, nitrates and nitrites of the alkali metals
- Nitrates and nitrites of the alkaline earth metals
- Ferrocyanides and ferricyanides of the alkali and alkaline earth metals
- Lithium carbonate readily forms the oxide when heated, therefore, unlike the other alkali carbonates, cannot be ignited in platinum vessels.

The following non-metals and metalloids should also be avoided.

- Sulphides or mixtures containing sulphur and an alkaline substance
- Phosphorus, arsenic, antimony and their alloys
- Magnesium pyrophosphate attacks platinum at temperatures above 900°C and silicates, silica, alumina, and magnesia attack platinum above 1500°C, below this temperature there is no action.

Fusion Technique

Crucibles made from Other Metals

Metal Reactants

Metals which alloy with platinum when heated such as molten bismuth, copper, gold, lead, silver, tin, zinc and base metals should not be used. Neither should any compounds of these metals such as lead oxide and sulphide, silver chloride, stannic oxide etc., which are easily reduced.

Selenium, sulphur and tellurium should not be heated in platinum as they cause platinum to become brittle.

Prolonged heating in an oxidizing flame, or burning carbon, coal or coke, produces a gray or black film which spreads and may lead to the development of cracks.

Gas Effects

Some atmospheres may affect platinum on heating. If ammonia is present, the surface of the platinum becomes darker and develops a porous crystalline appearance. If sulphur dioxide or sulphur trioxide is formed, the platinum surface gradually becomes coated with platinous sulphide. Chlorine converts the metal to a porous mass, as a result of the formation and decomposition of platinous chloride. Highly unsaturated organic gases and vapors will also disintegrate the metal.

Cleaning Platinum

The platinum crucible can be boiled with nitric or hydrochloric acid in a beaker covered with a watch glass. The two acids should never be used mixed together in the same solution.

A mixture of equal parts of hydrofluoric and hydrochloric acids can also be used.

To remove insoluble fusion residues, heat the vessel filled with potassium hydrogen- fluoride, sodium or potassium hydrogen-sulphate, or borax, at fusion temperatures.

A gray or black film on the platinum can be removed by polishing with silver sand or fine pumice.

Crucibles made from Other Metals

Silver Crucible

Silver crucibles are recommended for fusion with alkali hydroxides as platinum is not suitable. The melting point of silver is 960°C and care must be taken not to overheat the crucible. It is less resistant than gold to attack by molten hydroxides.

Gold Crucible

Gold has a melting point of about 1060°C and is sometimes used for alkali hydroxides, as it is not attacked to any marked extent. Its use has been recommended for opening up silica rock for determination of iron.

Nickel Crucible

Nickel can be used for fusions with alkali hydroxides and with sodium peroxides. It is more resistant to sodium peroxide than the other metals. Nickel crucibles cannot be used for weighing precipitates, as the surface rapidly becomes coated with a film of oxide.

Iron Crucible

Iron is sometimes used instead of nickel crucibles for fusions of sodium peroxide. Iron crucibles have a much shorter life, but are comparatively inexpensive.

Graphite Crucible

Elements which attack platinum in high concentrations such as Cu and Pb may be determined after fusion in this type of crucible. Graphite crucibles may be used for LiBO_2 fusions. Although less expensive, they have a limited life.

Fusion Technique

Crucibles made from Other Metals

Acids

To choose a suitable acid or acid mixture for the sample to completely dissolve, it is important to know the properties of the sample matrix and the main elements and compounds within it. The choice of acid or mixture of acids, is governed by the oxidizing and reducing agents efficiency in dissolving the matrix. To be efficient, the acid must form a soluble salt with the metal ion being determined.

Hydrochloric, perchloric and nitric acids are commonly used to digest samples for analysis. Combinations of acids are also used. For example, to digest botanical material, a mixture of hydrofluoric and nitric acid may be used to achieve dissolution.

The interaction between the acid or mixture of acids and the digestion container should also be considered. For example, hydrofluoric acid should not be used in quartz or glass containers.

In the microwave field, stability of an acid, vapor pressure, and interaction of combined acids must be considered before coupling microwave energy with acid in closed microwave-transparent plastics. Sulphuric acid has a relatively high boiling point (339°C) and can melt most plastics.

Single Acids

Hydrochloric Acid

Concentrated hydrochloric acid (HCl) is excellent for some metal oxides and metals that are oxidized more easily than hydrogen. Hydrochloric acid at high pressure and temperature attacks many silicates and numerous refractory oxides, sulphates and fluorides, to produce generally soluble chloride salts.

As concentrated hydrochloric is not an oxidizing acid, it is not used to digest organic materials, although it is an effective acid for basic compounds such as amines and alkaloids in aqueous solutions and some organometallic compounds. Hydrochloric acid is used to hydrolyse natural products for the analysis of amino acids and carbohydrates. Under high pressure or in the presence of strong oxidants, hydrochloric acid may decompose to produce chlorine gas. Teflon PFA vessels may be used at high temperatures with this acid.

Hydrofluoric Acid

Hydrofluoric acid (HF) is used for dissolving silica based materials. The silicates are converted to SiF_4 , which can be evaporated leaving other elements of interest. Hydrofluoric acid can be combined with other acids to prevent silica from tying up trace elements in biological and botanical matrices. As hydrofluoric has a low boiling point of 106°C for 49% w/w solution and a high vapor pressure, it is easily evaporated. In closed containers a partial pressure of nearly 8 atmospheres at 180°C is obtained. If the fluoride ion concentration is high, stable metal fluoride complexes are formed and can be kept in solution. Rare earth fluorides are sparingly soluble and may be lost from solution under these conditions.

Those handling hydrofluoric acid should be aware of its hazardous nature. It is poisonous and can be absorbed into the body if left in contact with skin, causing severe burns. Adequate protective clothing should be used. If HF does come into contact with the skin it should be washed away immediately. The fume cupboard extraction system should be required.

Nitric Acid

Nitric acid (HNO_3) is a strong oxidizing agent, which can be obtained in high purity suitable for trace level analyses. It can be used for liberating trace elements from botanical and biological matrices to form highly soluble nitrate salts. As nitric acid has a relatively low boiling point of 120°C , decompositions are time consuming when carried out in open vessels. To break down a complex organic matrix, it is usually necessary to have a temperature above 120°C , or the addition of another oxidizing agent such as perchloric acid or hydrogen peroxide.

Under the excitation of microwave energy, nitric acid can reach a temperature of 176°C which is more than 50°C above its boiling point. The pressure obtained in the closed vessel at this temperature is under 5 atmospheres. Substantial increases in oxidation potential are achieved at this temperature and pressure, resulting in faster reactions.

Perchloric Acid

Hot concentrated perchloric acid (HClO_4) is a strong oxidizing agent, which completely decomposes organic materials and attacks metals unresponsive to other acids. The hot acid is used to take elements to their highest oxidation state.

Extreme safety precautions are required when using this concentrated acid, particularly at elevated temperatures. Hot concentrated perchloric acid is potentially explosive when in contact with organic materials and

easily oxidized inorganics. Cold concentrated and hot dilute perchloric are less hazardous. As this hazard exists, fume hoods, scrubbers and duct work must meet required specifications and standards.

As hot perchloric acid reacts explosively with organic matter, perchloric acid should not be used in the microwave. The use of this acid under microwave heating conditions will have to be specifically studied as the temperature and pressure profile is different to that of other acids. After heating, the Teflon PFA container requires cooling with liquid nitrogen and disposal of chlorine gas. Accidents using conventional methods have occurred with mild heating conditions, therefore rapidly increasing the temperature of this acid is clearly a potential hazard.

Safety Precautions

Do not add to hot organic samples. HNO_3 is added first to oxidize easily oxidized organics. Once the solution has cooled, then perchloric acid may be added. If HNO_3 is kept in excess of HClO_4 in solution, the solution is safer. Heating HClO_4 and organics may cause a violent explosion. Avoid repeated digestions in ordinary wooden fume cupboards. Stainless steel fume hoods are adequate, if there is ample washdown water available. Never allow samples containing HClO_4 to boil dry. The danger of perchloric acid arises from the contact with hydroxyl compounds which give rise to unstable perchlorate esters. Another group of compounds which are particularly hazardous with perchloric acid, are fats or wax. At high temperature, the fats hydrolyze to produce an alcohol which instantaneously decomposes.

Phosphoric Acid

Phosphoric acid (H_3PO_4) will digest alkali metals, a wide range of aluminium slags, chrome, and iron ores. This acid has been used to digest iron based alloys for specific trace constituents which would have volatilized using hydrochloric acid. For phosphoric acid temperatures of 240°C can be attained with just 3 atmospheres partial pressure. Its low vapor pressure, enables relatively high temperatures to be obtained without damaging the digestion vessel.

Sulphuric Acid

Concentrated sulphuric acid (H_2SO_4) is used for the decomposition of alloys, hydroxides, inorganic oxides, metals, ores and organic tissues. Concentrated sulphuric acid is one of the few acids that can melt Teflon PFA before it boils, consequently careful monitoring of the temperature is required. The temperature range can Concentrated sulphuric acid

destroys almost all organic compounds. When the temperature is raised a few degrees above its normal boiling point of 339°C for a solution containing 98.3%, w/w of H₂SO₄, digestion times are reduced.

Tetrafluoroboric Acid

Tetrafluoroboric acid (HBF₄) is used for the decomposition of geological samples containing silicates which require high temperature attack. At 227°C, the partial pressure of tetrafluoroboric acid in the closed vessel is only 5.7 atmospheres. An advantage of using tetrafluoroboric over hydrofluoric acid, is that much higher temperatures can be achieved without high pressures and decomposition of the acid.

Mixed Acids

Combinations of acids in both open and closed vessels are chosen for their ability to decompose individual components of a particular matrix and to dissolve the complexed elemental salts formed with a second acid.

The calculation of temperature for an acid mixture requires knowledge of the heat capacity of that mixture. Mixed acid temperatures and pressures have now been evaluated for the microwave environment. Nitric, hydrochloric, and hydrofluoric acids have relatively low boiling points and large accompanying partial pressures. Phosphoric, sulphuric and fluoroboric acids have low partial pressures at comparable temperatures and have relatively high boiling points. If one acid is combined from each group, a mixture can be produced with a partial pressure less than that of the lower boiling acid. The vapor pressures of a solution may be lowered by mixing acids.

The following acid combinations have been used:

- Nitric and phosphoric acids for tissues
- Nitric and hydrofluoric acids for biological and botanical samples
- Tetrafluoroboric acid with a nitric-hydrofluoric mixture for sludge
- Aqua regia for mine tailings and geological samples

When organic materials are decomposed in closed vessels with acid, the pressures obtained are higher than those obtained with highly oxidized materials such as some alloys, ceramics, minerals, and ores. It is important to monitor the increasing temperature and pressure during the digestion process. When the amount of the material that can be safely digested is determined, the material may be routinely decomposed with the confidence.

Microwave Digestion Techniques

Many of the sample digestion techniques currently in use today have been in use for about 100 years. Heating samples in open beakers over flames and hotplates is still widely practiced. The digestion procedure is tedious, time consuming and labor intensive. Some of the acid digestion procedures, such as those involving perchloric acid, are potentially hazardous.

There is however an alternative and that is the microwave digestion technique which is both quicker and safer. The microwave system functions by using a combination of acid, temperature and pressure. A microwave transparent container used for acid dissolution should be made from perfluoro-alkoxy (PFA) teflon [poly(tetrafluoroethylene)]. It has been successfully used for:

- Acid dissolution of bone
- Biological tissue
- Botanical matrices
- Steels
- Geological species such as ores, zircons and rocks
- Soils
- Environmental samples
- Metals from sediments

As the sample is rarely introduced to the instrument in the solid form, the sample matrix needs to be destroyed or decomposed with acid. For flame AAS the sample is always presented to the instrument in solution. Although several methods of solid sampling have been used with the graphite furnace AAS, these in general have limited application and samples are introduced in solution form. The microwave digestion technique has a number of advantages, as follows:

- Digestion times are faster, more controllable and amenable to automation.
- Microwave dissolutions have faster reaction rates with higher temperatures than conventional digestions and are sealed in the container.
- The containers are made from an inert polymer, which will not contaminate the sample or absorb microwave energy.

- The caps are designed to vent safely in case of excess pressure build up.

Contamination is reduced as the container is sealed during digestion and volatile elements are not lost. With open-beaker acid dissolution procedures, significant amounts of arsenic, boron, chromium, mercury, antimony, selenium, and tin are lost at relatively low temperatures.

It is possible to use smaller amounts of reagents reducing contamination, and so obtain a reduction in blank values compared with open-beaker digestions.

Digestion Of Metallurgical Samples

Microwave digestion is a particularly effective means of accelerating dissolution of metallic samples. Samples should ideally be in powder form, however, metals may be fine wires, filings, shavings or turnings. For most analyses concentrated reagent grade acids are usually adequate, however for trace element determinations ultrapure acids are recommended.

Metallurgical samples interact in a number of ways with microwave radiation. Many metals and metallurgical samples dissolve safely by microwave methods and present no difficulties, however, iron based alloys spark when subjected to microwave radiation. If the dissolution is carried out in a closed vessel, sparking can present a serious safety hazard as the hydrogen gas produced can be ignited. When attempting to digest a sample for the first time, the acid and the sample should be allowed to react thoroughly, before placing the open vessel in the microwave oven. If a closed vessel is required, all oxygen must be purged from the container.

For steel samples, a multiple addition technique is required and the sample should be exposed to microwaves for a minimum period of time. The sample can be reacted in an open beaker for 2 min. and for a further 1 min. in the microwave oven, followed by a second addition of acid and return of the sample to the microwave oven for an additional minute. This procedure is repeated to achieve dissolution. As teflon containers cannot be used for hot H_2SO_4 acid mixtures, tall glass beakers are preferred.

Steel

Steels are iron based alloys which contain various amounts of C, Ni, Cr, Mn, and other elements. As there is a wide variety of steel types, no single procedure can be used, however, aqua regia and perchloric acid may be used to digest many steel samples.

Copper Reverberatory Slags

Slags which consist chiefly of SiO_2 , CaO , Al_2O_3 , Fe_2O_3 and a large number of other minor and trace constituents, are by-products of the commercial production of metals from ore. Slags, glasses and other amorphous silicate materials dissolve easily without loss of volatile SiF_4 under microwave conditions. The acid mixture containing HF can be adjusted to match the varying concentrations of Si in the sample. Boric

acid complexes unreacted HF, redissolves precipitated fluorides, acts as a matrix modifier for AAS, and enables conventional glassware to be used for storing the proposed sample solutions.

Super Alloys

Heat and corrosion resistant based alloys of Ni, Cr and Co easily dissolve in a few minutes using microwave techniques, but may require several days by conventional methods. As metals generate large volumes of gas during acid digestion, care should be taken to vent these gases when opening a sealed container. The container should be cooled in an ice bath, then carefully opened in a fume hood.

Pb-Sn Solder

Some materials which dissolve easily contain constituents that have different solubilities. If a Pb-Sn solder is dissolved and heated with HNO_3 and HF, the tin will precipitate as metastannic acid and the lead as PbF_2 . To prevent the precipitation of PbF_2 , HBF_4 is used in the presence of HF and the temperature reduced by adding an ice cube to the reaction mixture. As the ice will not absorb microwaves, the metal will dissolve at the hot metal sample-acid interface, while the bulk of the solution remains cool.

TiO₂ Waste

As TiO₂ waste contains 50% carbon and 50% titanium dioxide with traces of Fe, Nb, Ta, Th, U, and V, HF must be avoided to prevent precipitation of U and Th fluorides. A high level of carbon can also interfere with recovery of the metals. The sample is ashed to remove the carbon and fused in a zirconium crucible with sodium peroxide. The fusion products are easily dissolved in mineral acids.

Fusions should never be used for dissolution if an acid treatment will achieve the objective as the fusion solutions are frequently contaminated with a high level of salts of Ca, K and other elements. Fusion solutions will require matrix matching of the flux content in the standard and sample solutions.

Digestion Of Geological Samples

Geological sample digestion is complicated by the variety of sample types. Many minerals such as chromite, ilmenite, and quartz are extremely acid resistant and difficult to dissolve, even with microwave techniques. A fusion technique using Na_2O_2 or $\text{Li}_2\text{B}_4\text{O}_7$ is normally used for these samples. Caustic molten Na_2O_2 is required for the highly refractory chromite, while quartz and similar minerals can be fused with $\text{Li}_2\text{B}_4\text{O}_7$. After the material has been fused with the flux, an acid is used to dissolve the elements of interest.

Phosphate Rock

As phosphate rock contains high levels of calcium and silicon, HF used to dissolve the silicon may precipitate CaF_2 . However, if the calcium content is $>50\%$, CaF_2 may not redissolve after adding boric acid. If HBF_4 is used instead of HF, precipitation of CaF_2 can be avoided. Nitric acid is also used in the presence of HBF_4 . It is possible to prepare Portland cement and high Ca slags by this technique.

Tin Ore

Many ores contain 80% quartz or more and are resistant to acid attack, including HF. For some ores microwave digestion can leach the metallic fraction from the quartz, although in others, the tin is resistant to leaching by HF alone and to prevent the tin from hydrolyzing, HNO_3 is avoided. A $\text{Li}_2\text{B}_4\text{O}_7$ fusion is required in a Platinum crucible, followed by heating with HF and H_2O .

Sulphide Ore

These ores consist of copper, iron and nickel sulphides, with varying amounts of silicate minerals. For total recovery of selenium and arsenic for analysis, it is necessary to dissolve the sulphides. The sample is digested under pressure with HNO_3 , which prevents the loss of volatile chlorides of these elements. Final digestion of the sample is completed with HCl. This method is useful for determining sulphide minerals from mines, mills and smelters.

Gold Ore

A large sample size >25 g is required to determine gold. In the ore, gold may be present as metal, alloy, or a compound that makes acid digestion unsuitable. To extract the gold from sulphide ores, it may be necessary to use aqua regia digestion for complete recovery. After this preliminary procedure, an HBr-Br₂ extraction, followed by methyl isobutyl ketone (MIBK) extraction, is carried out.

Water Analysis

To analyze for elements in water, it is important that the correct type and amount of acid is added. The wrong acid may result in the loss or poor recovery of the metal from the sample. An important factor to consider is at what concentration level is the metal likely to be. If the element is expected to be in the low parts per billion (ppb) or ng/g level, then the acid concentration is important, as the sample is most likely going to have to be determined using ETA. The acid concentration should then not be more than about 3% total acid in the final sample, so that the life of the graphite tube is not severely shortened and no interference effects are introduced.

When a sample is collected, a decision has to be made on which fraction is retained, to be analyzed for dissolved, suspended, total or acid extractable metal. This will determine whether or not the sample should be filtered prior to the addition of acid and which acid is to be used.

It is important to wash the sample container with acid and rinse with deionized water before sample collection, to eliminate contamination. If the sample is not acidified properly, there may be loss of metals by adsorption on to the walls of the container.

Containers made from PTFE, polypropylene or linear polyethylene with polyethylene caps, may be used for sample collection. The use of borosilicate glass is acceptable, although Bakelite caps with metal liners must be avoided. Soft glass containers must not be used for samples containing metals in the microgram/liter range. Dark brown bottles, or light absorbing glass bottles, should be used for the determination of silver. Glass bottles and filtering equipment must be acid rinsed before use. As aluminium is leached from glassware, PTFE or polypropylene equipment and beakers can be used as an alternative.

Preservation of Water Sample

If only dissolved metals are required the sample must be filtered before adding acid. The sample should then immediately be acidified with concentrated nitric acid (HNO_3) to $\text{pH} < 2$. Normally 1.5 mL of AnalaR grade per liter of sample is sufficient for short term preservation. For samples which are alkaline or have a high buffer capacity, 5 mL of concentrated acid should be added. If both dissolved and suspended metals are required, the filter and suspended solids residue should be dried, then digested as soon as possible.

Samples containing mercury may only be stable up to 5 weeks. To preserve mercury in the sample 2 mL of 20% w/v $K_2Cr_2O_7$ solution in 50% v/v nitric acid should be added to each liter of sample. Avoid storing the sample in refrigerators contaminated with mercury. Water samples should not be stored in plastic bottles in mercury contaminated laboratories, as mercury vapors can pass through plastic bottles and may subsequently cause an increase in the sample.

Sample Separation Treatment

To determine dissolved metals in an unacidified sample, filter the water through a 0.45 μm membrane filter. The water that passes through the filter contains the dissolved metals. Material retained by the 0.45 μm filter membrane contains the suspended metals. Total Metals include all metals, both inorganically and organically bound and dissolved and particulate. They are obtained after digestion of the entire sample. Acid extractable metals are those which are obtained when hot dilute acid is added to the sample prior to filtering.

GPR grade nitric appears to be adequate for rinsing and soaking of glassware. For sample pretreatment, only high purity acids such as AnalaR or Aristar should be used.

After acidifying the sample, store it in a refrigerator at 4°C to prevent loss in volume due to evaporation. Samples are stable for up to six months if the metal levels are several ppm. For samples containing metals in the ppb range, the sample should be analyzed as soon as possible after collection.

Avoid contamination of the deionized water, the collection container, membrane filters and filter funnels. The container used for sample collection must be thoroughly washed with a metal free non-ionic detergent, rinsed at least 6 times and soaked in an acid bath for 24 hours.

The acid bath should contain 50% HNO_3 acid for quartz, PTFE or glass containers. Other acids that can be used are 50% HCl prepared by addition of 1 part conc HCl to 1 part H_2O or aqua regia (3 parts conc. HCl + 1 part conc. HNO_3). It is recommended that the container with glassware in it should be heated and maintained at 70°C for 24 hours.

Chromic acid or chromium free substitutes can be used to remove organic material from glassware, which is rinsed with HNO_3 to remove the Cr and finally rinsed several times with deionized water. Do not use chromic acid on plastic containers, or if chromium is to be determined. For plastic materials use either 50% HNO_3 or 50% HCl. Deionized water should always be used for rinsing, standard preparations, and sample dilution.

There is always the possibility of airborne contamination such as dust particles, soot and aerosols in the laboratory environment. To provide a clean environment, a high quality fume cupboard and extraction system, laminar flow clean air benches or “clean” laboratory facilities are required. This is particularly important, when measuring low $\mu\text{g}/\text{liter}$ (ppb) levels of metals using an electrographite furnace. Blanks which include acid or reagent are carried through the digestion procedure to determine levels of impurities. It would only take one particle of dust containing Cd to land on the graphite tube of a ETA to give a positive response.

Sample Preparation

A sample as apparently uncomplicated as water may be treated with different acids, depending on the metals of interest.

Always prepare blanks for each acid digestion performed. Run the acids and reagents through the same digestion procedure as the sample. If the acids and reagents give a positive absorbance value, this can be subtracted from the sample results.

Nitric acid is one of the most useful acids for digestion. The nitrate ions produced in solution are an acceptable matrix for both flame AAS and ETA. Generally, nitric acid is sufficient to oxidize easily oxidized samples.

Other acids such as perchloric, sulphuric, and hydrochloric may be required for complete digestion of the sample. However, some of these acids can interfere with the analysis of some metals and are not as good as the HNO_3 matrix for electrothermal atomization.

Combinations of $\text{HNO}_3/\text{H}_2\text{SO}_4$ or HNO_3/HCl are suitable for easily oxidized organic matter. $\text{HNO}_3/\text{HClO}_4$ or $\text{HNO}_3/\text{HClO}_4/\text{HF}$ are suitable for organic matter or minerals which are more difficult to oxidize. It may be necessary to dry ash some samples, if a large amount of organic matter is present.

It is important to confirm recovery of metal for each digestion and analytical procedure used.

Dissolved Metals by Air/Acetylene Flame

The following elements may be determined directly by air/acetylene AAS: Sb, Bi, Cd, Ca, Cs, Cr, Co, Cu, Au, Ir, Fe, Pb, Li, Mg, Mn, Ni, Pd, Pt, K, Rh, Ru, Ag, Na, Sr, Tl, Sn, and Zn. For the determination of Ca, or Mg, add lanthanum as a releasing agent.

Liquid-Liquid Extraction Prior to Flame AAS

The following metals can be determined by this technique if present in low levels: Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Ag, and Zn.

The method consists of chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK), followed by aspiration into the flame. This is normally achieved by adjusting the pH of the sample and the water blank, to the same pH as the standards.

To obtain optimum extraction efficiency for elements, the following pH ranges are recommended (19).

Table 26-1. pH range for optimum extraction

| Element | pH range for optimum extraction |
|---------|---------------------------------|
| Ag | 2-5 (complex unstable) |
| Cd | 1-6 |
| Co | 2-10 |
| Cr | 3-9 |
| Cu | 0.1-8 |
| Fe | 2-5 |
| Mn | 2-4 (complex unstable) |
| Ni | 2-4 |
| Pb | 0.1-6 |
| Zn | 2-6 |

The optimum pH value is 2.3 ± 0.2 for Ag and Pb extraction. The Mn complex deteriorates rapidly at room temperature, but can be preserved for a few hours if chilled to 0°C.

Direct Determination with Nitrous Oxide/Acetylene

This procedure can be used for the following metals: Al, Ba, Be, Mo, Os, Rh, Si, Th, Ti, and V.

A suitable ionization buffer such as potassium chloride should be added to both sample and standard solutions for Al, Ba, Mo, Ti, and V determinations.

Extraction Prior to Nitrous Oxide/Acetylene Determination

Concentrations of Al less than 900 µg/L (900 ppb) and Be at concentrations less than 30 µg/L (30 ppb), can be determined by this method. Chelation with 8-hydroxyquinoline is achieved and extracted with methyl isobutyl ketone (MIBK), for direct aspiration in a nitrous oxide/acetylene flame.

Fe at concentrations greater than 10 mg/L interferes by suppressing Al absorption. The addition of hydroxylamine hydrochloride /1,10-phenanthroline, effectively reduces interference due to iron. If turbid solutions are allowed to settle, Mn concentrations up to 80 mg/L do not interfere. At pH 8.0, Mg forms an insoluble chelate with 8-hydroxyquinoline and the Al complex is removed as a co-precipitate. The Mg complex forms slowly over 4 to 6 minutes. If the solution is extracted immediately after adding buffer, the interference by Mg on Al can be avoided.

Mercury Determination in Sea-water, Brines & Effluents High in Chloride

These high salt solutions require as much as 25 mL of 4% m/v KMnO_4 to break up organo-mercury compounds. The chlorides are converted to free chlorine gas during the oxidation step. The free chlorine can be removed by adding excess hydroxylamine sulphate and passing clean nitrogen through the sample, before the mercury is reduced. No stannous chloride should be present at this stage, or a loss of mercury may be observed.

Electrothermal Atomization Method

This method is suitable for low ppb levels of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, and Sn, provided suitable matrix modifiers are added. If HCl has been used for the digestion, Sb and Sn cannot be determined.

Metals by Continuous Flow Hydride Generation

This method is suitable for As, Se, Hg and other volatile metals which produce hydrides. Sodium borohydride in the presence of HCl and metal, will produce a metal hydride.

Arsenious As(III) and selenious acid Se(III) are converted instantaneously to their respective hydrides by sodium borohydride in acid solution. As(V) is reduced relatively slowly by sodium borohydride to As(III) at room temperature at a pH of 1 or less. The absorption response for As(V) is much slower than that of As(III). To determine total As the inorganic As should be in the As(III) state. During the acid

digestion both inorganic and organic forms of As are oxidized to As(V) and then quantitatively reduced to As(III) with sodium or potassium iodide, prior to reaction with NaBH_4 .

The Se(VI) oxidation state of Se is not measurably reduced by sodium borohydride, and it is necessary to reduce Se(VI) formed during the acid digestion procedure to Se(IV) by heating with hydrochloric acid. Care must be taken not to reoxidize the analyte by chlorine. The reduction efficiency depends on temperature, reduction time and HCl concentration. The HCl concentration and heating time must be adjusted to obtain equal response for both Se(VI) after reduction and Se(IV) solutions of equal concentrations.

The concentration in most natural waters of selenium is less than 10 mg/L (10ppb). Seleniferous soils may contain from one hundred to several thousand micrograms of dissolved selenium per liter.

Volatile selenium in the sample maybe determined after stripping with air or nitrogen in alkaline hydrogen peroxide. To estimate selenium in suspended particles, first determine total selenium, filter the sample and then repeat the analysis for total selenium in solution. If the filtered sample has a yellow color and an odor of hydrogen sulphide, selenopolysulphides may be present. If Se is present as selenopolysulphides, the results are compared with total selenium analysis before and after acidification. The solution is then stripped with nitrogen allowed to settle for 10 minutes and refiltered.

Selenium in the filtered water sample can be determined directly. Normally HCl will convert Se(VI) to Se(IV) and the value calculated for Se will be the sum of the two species. A low result may be obtained when samples contain an unknown masking agent. A method of standard additions with known concentrations of both species may be used to test for this effect.

If the recovery is poor when determining organic selenium, the interfering organics can be removed by passing the acidified sample through a resin. It is possible that some dissolved organo-selenium compounds may also be removed by this treatment and it will be necessary to determine total selenium in the untreated sample as well. Interfering iron may also be removed with a strong anion exchange resin.

Soils And Sludges

All soils may be traced back to parent rocks, irrespective of whether sedentary or transported materials processes are involved. As a result of these processes, all rock-forming material can occur in soil, in addition to minerals formed as a result of pedogenic processes. Although there are a large range of minerals that may occur in soil, silicates and oxides mainly predominate, except under peculiar circumstances.

Digestion Method for Soil

The main method of soil digestion is to use aqua regia, which is normally HCl:HNO₃

(3:1) although ratios of 4:1 have been used for sludges and soils. For silicate soils, the bound metals are not released by aqua regia alone. The metals that can be recovered with aqua regia are Zn, Cu, Ni, Cd, Cr, Pb, Co, Mn, Fe. For samples that are highly calcareous and frothy, extra nitric acid should be added before adding aqua regia and heating. Soils which contain high levels of organic matter should be heated slowly at first. Peaty soils cannot be treated in this manner and must be ashed at 450°C before the digestion. It should be noted that copper is lost on ashing.

A sodium carbonate fusion or HF dissolution must be used for uncontaminated soils, as the metals present will be in the soil matrix and not easily soluble in acids alone. Other acid digestion methods are likely to give smaller recoveries for uncontaminated soils.

Sludges

Place 1 gram of sludge which has approximately 15% total solids, in a preweighed digestion vessel. To determine the sample on a wet weight basis reweigh and calculate the weight of sample. To determine on a dry weight basis, the sample should be dried to constant weight using a vacuum oven at 100°C.

If the sample is high in solids, dry ash the sample to remove much of the organic material. As dry ashing can lead to variable precision and bias in results depending on the type, size of the sample and metal being analyzed, only use this technique for samples where the metal is not lost through volatilization.

Dry Ashing Sludges

To remove residual water, the shaken or mixed sample is added to a platinum or silica evaporating dish and evaporated to dryness on a steam bath. The dish is then placed in a muffle furnace and heated until the sample becomes a white ash. Do not heat above 400-450°C, if volatile elements are to be determined. For sodium determinations, heat to 600°C.

The ash or residue remaining, should be dissolved in a minimum amount of conc. HNO_3 and warm H_2O . It can then be filtered and made up to volume in a 100 mL volumetric flask, with a final HNO_3 concentration of 1%.

Cookbook

Introduction

The Atomic Absorption Cookbook contains information for the choice of instrumental conditions and possible interference effects for flame, furnace and vapor determination of all the elements that can normally be measured by atomic absorption spectrometry. It is important that the information contained herein is used as a guide to the correct instrumental conditions, rather than as a list of absolute parameter settings. The data given for each element relates to its determination in aqueous solution. These settings may, in some cases, require small changes because of interference effects caused by other components present in real samples. The quoted parameters will, therefore, provide a starting point from which the optimum parameters for a particular determination may be quickly and easily established.

Further information on the general principles of sample treatment, and on the theory of, and instrumentation for, atomic absorption spectrometry is contained in the introducing chapters of the AAS Methods Manual.

Sensitivities

Sensitivity, or characteristic concentration or mass, is defined as the concentration or mass of the element that will generate a signal of 0.0044 absorbance units when measured under the default instrumental conditions.

Flame sensitivities quoted are for the Universal burner; where appropriate, use of the air/acetylene burner will increase the sensitivity by up to a factor of 2.

Interferences

Details are given of some interference effects, which affect the response of a particular element. It should be remembered that the effects of volatility and viscosity of different solvent and matrix solutions will affect the response of all elements. These effects may be overcome by the use of calibration standards containing the same matrix and reagent concentrations as the sample solutions, or by the technique of standard additions calibration.

| Aluminium | Al |
|-----------------------------|-----------------------|
| Atomic no. | 13 |
| Atomic mass | 26.9815 |
| Primary wavelength (nm) | 309.3 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 100% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.3 mg/L |
| furnace characteristic mass | 3.6 pg |
| Emission wavelength (nm) | 396.2 |
| Secondary wavelength | Sensitivity reduction |
| 394.4 nm | 2× |
| 396.2 nm | 1.2× |
| 308.2 nm | 1.5× |

Flame details

| | |
|------------------------|---------------------------|
| Flame type | Nitrous oxide/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.1 - 4.4 |
| Signal | 30 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. Iron and/or sulphate depress the response.
 - Match standards and samples for these species if they are present.

Furnace details

| | |
|--------------------------|-----------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1500 |
| Atomize temperature (°C) | 2300 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 5 µg/L gives about 0.1 A |

1. Aluminium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Perchlorate ion causes a depressive interference.
 - Avoid the use of perchlorate ion.
 - otherwise-
 - Match all solutions for this species.
3. Air borne contamination is the single most likely cause of poor results.
 - Take great care to avoid contamination.
 - Minimize sample handling.
4. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.

| Antimony | Sb |
|-----------------------------|-----------------------|
| Atomic no. | 51 |
| Atomic mass | 121.75 |
| Primary wavelength (nm) | 217.6 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.23 mg/L |
| furnace characteristic mass | 9.9 µg |
| vapor characteristic conc. | 0.3 µg |
| Emission wavelength (nm) | 217.6 |
| Secondary wavelength | Sensitivity reduction |
| 231.1 nm | 2× |
| 206.8 nm | 1.2× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 1.0 -1.3 |
| Signal | 25 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 50%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.12 mg/L.
3. Copper or lead at concentrations greater than 1 g/L cause a spectral interference at 217.6 nm.
 - Use one of the alternate lines.
4. Acids cause a depression of the response.
 - Match the acid concentrations in all solutions.

Furnace details

| | |
|--------------------------|---------------------------------------|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 800 (no modifier) 1200 (modifier) |
| Atomize temperature (°C) | 2300 |
| Modifier | 30 µg of nickel as nickel nitrate |
| Signal | 20 µL of 12 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Antimony halides are volatile.
 - Avoid the use of halide acids.
 - otherwise-
 - Carefully optimize the ash temperature to avoid losses.
3. Spectral interferences from lead and copper are possible at the 217.6 nm line.
 - Use the secondary wavelength at 206.8 nm should be used if a large excess of either metal is present.
 - or-
 - Use Zeeman background correction if available

Vapor details

| | |
|-------------------------------|---|
| Measurement delay (seconds) | 40-50 |
| Carrier gas flow (mL/min) | 150-250 |
| Pump speed (RPM) | 30-40 |
| EC90 furnace temperature (°C) | 900 |
| Reductant | 0.5 - 1.0% m/V sodium borohydride solution stabilized with 0.5% m/V of sodium hydroxide |
| Acid reagent | 50% v/v (5M) hydrochloric acid |
| Signal | 7.0 µg/L gives about 0.1A |

1. Only Sb(III) can be reduced to the hydride.
 - Reduce Sb(V) to Sb(III)
 - by heating at 80-100°C with 4 M hydrochloric acid.
 - or-
 - by reduction with 2-5% m/V potassium iodide.
2. Gold, copper, nickel, platinum, palladium, and cobalt cause major interferences.
 - Use thiosemicarbazide or 1,10-phenanthroline as masking agents.
 - or-
 - Use 5 - 7 M hydrochloric acid to form stable chlorocomplexes.

| Arsenic | | As |
|-----------------------------|--|-----------------------|
| Atomic no. | | 33 |
| Atomic mass | | 74.9216 |
| Primary wavelength (nm) | | 193.7 |
| Bandpass (nm) | | 0.5 |
| Lamp current | | |
| normal use | | 75% |
| best sensitivity | | 75% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 0.4 mg/L |
| furnace characteristic mass | | 5.2 pg |
| vapor characteristic conc. | | 0.2 µg |
| Emission wavelength (nm) | | 235.0 |
| Secondary wavelength | | Sensitivity reduction |
| 197.2 nm | | 2× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.1 - 4.6 |
| Signal | 40 mg/L gives about 0.4 A |

1. The Slotted Tube Atom Trap with an inert gas/hydrogen flame improves the characteristic concentration to 0.06 mg/L.
2. The nitrous oxide flame reduces or eliminates many interferences.
3. Scatter effects are common at 193.7 nm.
 - Use background correction eliminate their effect.

Furnace details

| | |
|--------------------------|--------------------------------------|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 400 1200 (with Ni modifier) |
| Atomize temperature (°C) | 2100 2600 (with Ni modifier) |
| Modifier | 20 µg of nickel as nickel nitrate |
| Signal | 20 µL of 6 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.

Vapor details

| | |
|-------------------------------|---|
| Measurement delay (seconds) | 40-50 |
| Carrier gas flow (mL/min) | 150-250 |
| Pump speed (RPM) | 30-40 |
| EC90 furnace temperature (°C) | 900 |
| Reductant | 0.5-1.0% m/V sodium borohydride solution stabilized with 0.5% m/V of sodium hydroxide |
| Acid reagent | 50% v/v (5M) hydrochloric acid |
| Signal | 7.0 µg/L gives about 0.1 A |

1. As(III) can be reduced to the hydride more easily than As(V), and so gives better sensitivity.
 - reduce As(V) to As(III) either
 - by heating at 80-100°C with 4M hydrochloric acid
 - or-
 - by reduction with 2-5% m/V potassium iodide.
2. Gold, copper, nickel, platinum, palladium and iron cause major interferences.
 - Use thiosemicarbazide or 1,10-phenanthroline as masking agents
 - or-
 - Use 5 - 7M hydrochloric acid to form stable
 - chlorocomplexes.

| Barium | | Ba | |
|-----------------------------|--|-----------------------|--|
| Atomic no. | | 56 | |
| Atomic mass | | 137.34 | |
| Primary wavelength (nm) | | 553.6 | |
| Bandpass (nm) | | 0.5 | |
| Lamp current | | | |
| normal use | | 100% | |
| best sensitivity | | 75% | |
| best precision | | 100% | |
| Performance | | | |
| flame characteristic conc. | | 0.13 mg/L | |
| furnace characteristic mass | | 6.8 pg | |
| Emission wavelength (nm) | | 524.2 | |
| Secondary wavelength | | Sensitivity reduction | |
| 350.1 nm | | 12x | |
| 455.4 nm | | 5x | |

| Flame details | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.1 - 4.4 |
| Signal | 15 mg/L gives about 0.4 A |

1. The nitrous oxide flame reduces or eliminates many interferences, but causes ionization of the barium.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

| Furnace details | |
|--------------------------|--------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1600 |
| Atomize temperature (°C) | 2750 |
| Modifier | none recommended |
| Signal | 20 µL of 8 µg/L gives about 0.1 A |

1. Barium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Serious emission effects can occur.
 - Carefully align the furnace head.
 - Use the reduced height bandpass setting.
 - Use a lower atomization temperature.

| Beryllium | Be |
|-----------------------------|-----------------------|
| Atomic no. | 4 |
| Atomic mass | 9.01218 |
| Primary wavelength (nm) | 234.9 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.008 mg/L |
| furnace characteristic mass | 0.16 pg |
| Emission wavelength (nm) | 234.9 |
| Secondary wavelength | Sensitivity reduction |
| none | |

| Flame details | |
|------------------------|---|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.2 - 4.6 |
| Signal | 0.8 mg/L gives about 0.4 A |
| 1. | Acetic, fluoboric, nitric, sulphuric, and other acids enhance the response. |
| 2. | Silicon, magnesium, and aluminium depress the response. <ul style="list-style-type: none"> • Add hydrofluoric acid to all solutions to reduce this effect. |

| Furnace details | |
|--------------------------|--|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2600 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 0.2 µg/L gives about 0.1 A |
| 1. | Background absorption and scatter are common. <ul style="list-style-type: none"> • Use background correction. |
| 2. | Perchlorate ion causes a depressive interference. <ul style="list-style-type: none"> • Avoid the use of perchlorate, -otherwise- • Match all solutions for this species. |
| 3. | Neutralize acidic solutions with ammonia to <ul style="list-style-type: none"> • improve sensitivity • increase the maximum ashing temperature to 1600°C. |

| Bismuth | Bi |
|-----------------------------|-----------------------|
| Atomic no. | 83 |
| Atomic mass | 208.9806 |
| Primary wavelength (nm) | 223.1 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.23 mg/L |
| furnace characteristic mass | 6.1 pg |
| vapor characteristic conc. | 0.36 µg |
| Emission wavelength (nm) | 223.1 |
| Secondary wavelength | Sensitivity reduction |
| 306.8 nm | 3.5× |
| 222.8 nm | 2.2× |
| 206.2 nm | 8× |
| 227.7 nm | 14× |
| 202.1 nm | 70× |

Flame details

| | |
|------------------------|---------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 25 mg/L gives about 0.4 A |

1. The 100mm slot burner improves the sensitivity by about 30%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.08mg/L.
3. No serious interferences have been reported for bismuth in the air/acetylene flame.

Furnace details

| | |
|--------------------------|------------------------------------|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 350 1000 (with nickel modifier) |
| Atomize temperature (°C) | 1600 |
| Modifier | 30 µg of nickel as nickel nitrate |
| Signal | 20 µL of 7 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.

Vapor details

| | |
|-------------------------------|--|
| Measurement delay (seconds) | 40-50 |
| Carrier gas flow (mL/min) | 150-250 |
| Pump speed (RPM) | 30-40 |
| EC90 furnace temperature (°C) | 900 |
| Reductant | 0.5 - 1.0% m/V sodium borohydride solution stabilized with 0.5% m/V of sodium hydroxide. |
| Acid reagent | 50%v/v (5M) hydrochloric acid |
| Signal | 8 µg/L gives about 0.1 A |

1. Gold, copper, nickel, platinum, palladium, silver, cobalt, selenium, and tellurium cause major interferences.
 - Use thiosemicarbazide or 1,10-phenanthroline as masking agents
 - or-
 - Use 5 - 7M hydrochloric acid to form stable chlorocomplexes.

| Boron | | B |
|-----------------------------|-----------------------|----------|
| Atomic no. | 5 | |
| Atomic mass | 10.81 | |
| Primary wavelength (nm) | 249.8 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 100% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 8 mg/L | |
| furnace characteristic mass | 830 pg | |
| Emission wavelength (nm) | 518.0 | |
| Secondary wavelength | Sensitivity reduction | |
| none | | |

| Flame details | |
|--|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 800 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> 1. No serious interference effects have been reported for boron. 2. The nitrous oxide/hydrogen flame may improve the sensitivity. | |

| Furnace details | |
|---|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1300 |
| Atomize temperature (°C) | 2700 |
| Modifier | 5 µg of calcium or barium as the hydroxide |
| Signal | 20 µL of 1000 µg/L gives about 0.1 A |
| <ol style="list-style-type: none"> 1. Boron forms a stable nitride. <ul style="list-style-type: none"> • Use argon, not nitrogen, as the inert furnace gas. 2. Boron forms a very stable carbide. <ul style="list-style-type: none"> • Severe memory effects may occur. | |

| Cadmium | | Cd |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 48 | |
| Atomic mass | 112.40 | |
| Primary wavelength (nm) | 228.8 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 50% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.013 mg/L | |
| furnace characteristic mass | 0.6 pg | |
| Emission wavelength (nm) | 326.1 | |
| Secondary wavelength | Sensitivity reduction | |
| 326.1 nm | 500x | |

| Flame details | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 1.0 - 1.3 |
| Signal | 1.5 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 50%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.004 mg/L.
3. A large excess of silicate depresses the response of cadmium.
 - Match samples and standards for this species.
4. High levels of dissolved solids may cause background signals.
 - Use background correction.

| Furnace details | |
|--------------------------|--|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 300 600 (with modifier) |
| Atomize temperature (°C) | 900 1000 (with modifier) |
| Modifier | 10 µg of palladium as palladium nitrate -or- 20 µg of ammonium nitrate -or- 20 µg of magnesium nitrate |
| Signal | 20 µL of 0.8 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Ammonium phosphate (5 µg) is also an effective modifier, but can cause a spectral interference.
 - Use Zeeman background correction with phosphate modifier.

| Cesium | | Cs |
|-----------------------------|--|-----------------------|
| Atomic no. | | 55 |
| Atomic mass | | 132.9055 |
| Primary wavelength (nm) | | 852.1 |
| Bandpass (nm) | | 0.2 |
| Lamp current | | |
| normal use | | 100% |
| best sensitivity | | 100% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 0.07 mg/L |
| furnace characteristic mass | | 3.5 pg |
| Emission wavelength (nm) | | 852.1 |
| Secondary wavelength | | Sensitivity reduction |
| 455.5 nm | | 130× |

| Flame details | |
|--|-----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 7 mg/L gives about 0.4 A |
| 1. Ionization causes an interference. | |
| • Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |
| 2. Large excesses of mineral acids depress the response. | |
| • Match samples and standards for acid type and concentration. | |

| Furnace details | |
|--|--|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2500 |
| Modifier | none recommended |
| Signal | 20 µL of 4.5 µg/L gives about 0.1 A |
| 1. Emission effects can occur. | |
| • Use the reduced height bandpass setting. | |
| • Carefully check the furnace alignment. | |

| Calcium | | Ca |
|-----------------------------|--|-----------------------|
| Atomic no. | | 20 |
| Atomic mass | | 40.08 |
| Primary wavelength (nm) | | 422.7 |
| Bandpass (nm) | | 0.5 |
| Lamp current | | |
| normal use | | 100% |
| best sensitivity | | 75% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 0.009 mg/L |
| furnace characteristic mass | | 0.8 pg |
| Emission wavelength (nm) | | 239.9 |
| Secondary wavelength | | Sensitivity reduction |
| 239.9 nm | | 200x |

| Flame details | |
|------------------------|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.0 - 4.4 |
| Signal | 1.0 mg/L gives about 0.4 A |

- Oxyanions such as phosphate, aluminate and silicate depress the response.
 - Add a releasing agent (0.1% m/V lanthanum) to all solutions,
-or-
 - Use the nitrous oxide/acetylene flame, but then
 - ionization will cause an interference
 - add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
- Samples and standards should be matched for mineral acid type and concentration.

| Furnace details | |
|--------------------------|--------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2600 |
| Modifier | none recommended |
| Signal | 20 µL of 1 µg/L gives about 0.1 A |

- Serious emission effects can occur.
 - Carefully align the furnace head.
 - Use the reduced height bandpass setting.
 - Use a lower atomization temperature.
- Air borne contamination is the single most likely cause of poor results.
 - Take great care to avoid contamination.
 - Minimize sample handling.

| Chromium | | Cr |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 24 | |
| Atomic mass | 51.996 | |
| Primary wavelength (nm) | 357.9 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.05 mg/L | |
| furnace characteristic mass | 0.7 pg | |
| Emission wavelength (nm) | 425.4 | |
| Secondary wavelength | Sensitivity reduction | |
| 429.0 nm | 6× | |
| 359.4 nm | 1.5× | |
| 360.3 nm | 3× | |
| 425.4 nm | 4× | |

| Flame details | |
|--|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.0 - 4.4 |
| Signal | 5.0 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> The nitrous oxide flame reduces or eliminates many interferences, but then <ul style="list-style-type: none"> Ionization causes an interference. Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |

| Furnace details | |
|---|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2500 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 0.8 µg/L gives about 0.1 A |
| <ol style="list-style-type: none"> Emission effects can occur. <ul style="list-style-type: none"> Use the reduced height bandpass setting. Background signals are often small at the chromium wavelength. <ul style="list-style-type: none"> Use background correction only if it is shown to be necessary. | |

| Cobalt | Co |
|-----------------------------|-----------------------|
| Atomic no. | 27 |
| Atomic mass | 59.9332 |
| Primary wavelength (nm) | 240.7 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.06 mg/L |
| furnace characteristic mass | 3 pg |
| Emission wavelength (nm) | 345.4 |
| Secondary wavelength | Sensitivity reduction |
| 304.4 nm | 8× |
| 242.5 nm | 1.2× |
| 241.2 nm | 2× |
| 252.1 nm | 6× |
| 243.6 nm | 6× |
| 352.7 nm | 15× |
| 346.6 nm | 40× |
| 341.3 nm | 40× |

Flame details

| | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.8 - 1.0 |
| Signal | 6.0 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 50%.
2. Large excess of other transition metals may affect the response.
 - Match samples and standards for these species.

Furnace details

| | |
|--------------------------|-----------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2100 |
| Modifier | none |
| Signal | 20 µL of 4 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Oxidizing acids depress the response.
 - Use hydrochloric acid where possible.
 - Match the acid content of all solutions.

| Copper | | Cu |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 29 | |
| Atomic mass | 63.546 | |
| Primary wavelength (nm) | 324.8 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 50% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.033 mg/L | |
| furnace characteristic mass | 1.8 pg | |
| Emission wavelength (nm) | 324.8 | |
| Secondary wavelength | Sensitivity reduction | |
| 327.4 nm | 2× | |
| 217.9 nm | 4× | |
| 216.5 nm | 6× | |
| 222.6 nm | 20× | |
| 249.2 nm | 100× | |
| 244.2 nm | 300× | |

| Flame details | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.8 - 1.1 |
| Signal | 3.5 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 30%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.015 mg/L.
3. Large excess of other transition metals in the presence of mineral acids depress the response.
 - Match all solutions for these species.

| Furnace details | |
|--------------------------|-------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 850 |
| Atomize temperature (°C) | 2100 |
| Modifier | 50 µg of ammonium nitrate |
| Signal | 20 µL of 2.0 µg/L gives about 0.1 A |

1. Copper halides are volatile.
 - Use nitric acid for sampler preparation.
 - Avoid the presence of halides where possible.
 - or-
 - Carefully optimize the ash temperature to avoid losses.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.

| Dysprosium | | Dy |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 66 | |
| Atomic mass | 162.50 | |
| Primary wavelength (nm) | 421.2 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.24 mg/L | |
| furnace characteristic mass | 45 pg | |
| Emission wavelength (nm) | 404.6 | |
| Secondary wavelength | Sensitivity reduction | |
| 416.8 nm | 10× | |
| 404.6 nm | 1.2× | |
| 418.7 nm | 1.4× | |
| 419.5 nm | 1.6× | |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 25 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. Sulphuric and phosphoric acids enhance the response.
 - Match all solutions for these species.

Furnace details

| | |
|--------------------------|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2700 |
| Modifier | none |
| Signal | 20 µL of 50 µg/L gives about 0.1 A |

1. Dysprosium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids cause a decrease in response.
 - Use hydrochloric acid for sample preparation if possible.
4. Other rare earths and base metals interfere.
 - Match all solutions for major components.

| Erbium | | Er |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 68 | |
| Atomic mass | 167.26 | |
| Primary wavelength (nm) | 400.8 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.24 mg/L | |
| furnace characteristic mass | 100 pg | |
| Emission wavelength (nm) | 400.8 | |
| Secondary wavelength | Sensitivity reduction | |
| 408.8 nm | 7× | |
| 386.3 nm | 1.5× | |
| 415.1 nm | 1.7× | |
| 389.3 nm | 4× | |
| 393.7 nm | 8× | |
| 381.0 nm | 9× | |
| 390.5 nm | 18× | |
| 394.4 nm | 18× | |

| Flame details | |
|--|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 25 mg/L gives about 0.4 A |
| 1. Ionization causes an interference. | |
| • Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |

| Furnace details | |
|---|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2700 |
| Modifier | none |
| Signal | 20 µL of 120 µg/L gives about 0.1 A |
| 1. Erbium forms a stable nitride. | |
| • Use argon, not nitrogen, as the inert furnace gas. | |
| 2. Emission effects can occur. | |
| • Use the reduced height bandpass setting. | |
| • Carefully check the furnace alignment. | |
| 3. Oxidizing acids cause a decrease in response. | |
| • Use hydrochloric acid for sample preparation if possible. | |
| 4. Other rare earths and base metals interfere. | |
| • Match all solutions for major components. | |

| Europium | Eu |
|-----------------------------|-----------------------|
| Atomic no. | 63 |
| Atomic mass | 151.96 |
| Primary wavelength (nm) | 459.4 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 100% |
| best sensitivity | 100% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.15 mg/L |
| furnace characteristic mass | 25 pg |
| Emission wavelength (nm) | 459.4 |
| Secondary wavelength | Sensitivity reduction |
| 333.4 nm | 11× |
| 462.7 nm | 1.5× |
| 466.2 nm | 1.5× |
| 321.1 nm | 8× |
| 311.1 nm | 11× |
| 321.3 nm | 15× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.1 - 4.5 |
| Signal | 15 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. Aluminium and silicon depress the response.
 - Match all solutions for these species.

Furnace details

| | |
|--------------------------|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2600 |
| Modifier | none |
| Signal | 20 µL of 30 µg/L gives about 0.1 A |

1. Europium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids cause a decrease in response.
 - Use hydrochloric acid for sample preparation if possible
4. High concentrations of base metals interfere.
 - Match all solutions for major components.

| Gadolinium | | Gd |
|----------------------------|-----------------------|-----------|
| Atomic no. | 64 | |
| Atomic mass | 157.25 | |
| Primary wavelength (nm) | 407.9 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 80% | |
| best sensitivity | 80% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 12 mg/L | |
| Emission wavelength (nm) | 440.2 | |
| Secondary wavelength | Sensitivity reduction | |
| 419.1 nm | 2.5× | |
| 368.4 nm | 1.2× | |
| 478.3 nm | 1.2× | |
| 405.8 nm | 1.2× | |
| 405.5 nm | 1.5× | |
| 367.4 nm | 30× | |
| 404.5 nm | 30× | |

Flame details

| | |
|------------------------|--------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 1200 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

| Gallium | Ga |
|-----------------------------|-----------------------|
| Atomic no. | 31 |
| Atomic mass | 69.72 |
| Primary wavelength (nm) | 287.4 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.44 mg/L |
| furnace characteristic mass | 22 pg |
| Emission wavelength (nm) | 403.3 |
| Secondary wavelength | Sensitivity reduction |
| 403.3 nm | 2× |
| 294.4 nm | 1.1× |
| 417.2 nm | 1.5× |
| 250.0 nm | 9× |
| 245.0 nm | 12× |
| 272.0 nm | 20× |

| Flame details | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.2 - 4.6 |
| Signal | 50 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. The sensitivity drops sharply when the pressure in the acetylene cylinder becomes low because of acetone carryover.
 - Change the cylinder when the internal pressure drops below 7 kg/sq cm (100 lb/sq in).

| Furnace details | |
|--------------------------|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 900 |
| Atomize temperature (°C) | 1800 |
| Modifier | none |
| Signal | 20 µL of 25 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Perchloric acid and alkali and alkaline earth metal halides cause severe interferences.
 - Avoid the presence of these species if possible.

| Germanium | Ge |
|-----------------------------|-----------------------|
| Atomic no. | 32 |
| Atomic mass | 72.59 |
| Primary wavelength (nm) | 265.2 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.9 mg/L |
| furnace characteristic mass | 35 pg |
| Emission wavelength (nm) | 265.2 |
| Secondary wavelength | Sensitivity reduction |
| 269.1 nm | 3× |
| 259.3 nm | 2× |
| 271.0 nm | 2.5× |
| 275.5 nm | 2.5× |
| 204.2 nm | 5× |
| 303.9 nm | 20× |
| 209.4 nm | 25× |

| Flame details | |
|--|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.2 - 4.6 |
| Signal | 100 mg/L gives about 0.4 A |
| 1. No serious interference effects have been reported. | |

| Furnace details | |
|---|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 850 |
| Atomize temperature (°C) | 2700 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 40 µg/L gives about 0.1 A |
| <ol style="list-style-type: none"> Background absorption and scatter are common. <ul style="list-style-type: none"> Use background correction. Germanium halides are volatile. <ul style="list-style-type: none"> Keep the concentration of halide ion in the solutions as low as possible. Carefully optimize the dry phase to avoid losses. Add 1% m/V of sodium hydroxide to all solutions to improve sensitivity and precision. | |

| Gold | Au |
|-----------------------------|-----------------------|
| Atomic no. | 79 |
| Atomic mass | 196.9665 |
| Primary wavelength (nm) | 242.8 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.12 mg/L |
| furnace characteristic mass | 4.2 pg |
| Emission wavelength (nm) | 267.6 |
| Secondary wavelength | Sensitivity reduction |
| 267.6 nm | 2× |
| 312.3 nm | 900× |
| 274.8 nm | 1100× |

Flame details

| | |
|------------------------|---------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.8 - 1.1 |
| Signal | 12 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 30%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.05 mg/L.
3. Cyanide depresses the response.
 - Match all solutions for this species.
4. Other platinum group metals influence the response.
 - Match all solutions for these species
 - or-
 - Add uranium or lanthanum (1% m/V) as a releasing agent.

Furnace details

| | |
|--------------------------|-----------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 800 |
| Atomize temperature (°C) | 1900 |
| Modifier | 50 µg of nickel as nickel nitrate |
| Signal | 20 µL of 5 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Chloride ion interferes.
 - Keep the chloride ion concentration as low as possible.

| Hafnium | | Hf |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 72 | |
| Atomic mass | 178.49 | |
| Primary wavelength (nm) | 307.3 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 80% | |
| best sensitivity | 80% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 9.0 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 368.2 | |
| Secondary wavelength | Sensitivity reduction | |
| 295.1 nm | 8× | |
| 377.8 nm | 10× | |

| Flame details | |
|--|--------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 1000 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> The formation of stable Hf-O bonds depresses the response. <ul style="list-style-type: none"> Add ammonium fluoride (1% m/v) to all solutions. Iron enhances the response. <ul style="list-style-type: none"> Match all solutions for this species. | |

| Furnace details | |
|---|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2700 |
| Modifier | none recommended |
| Signal | not available |
| <ol style="list-style-type: none"> Hafnium forms a stable nitride. <ul style="list-style-type: none"> Use argon, not nitrogen, as the inert furnace gas. Emission effects can occur. <ul style="list-style-type: none"> Use the reduced height bandpass setting. Carefully check the furnace alignment. This element is very insensitive. <ul style="list-style-type: none"> Instrumental and performance data are limited. | |

| Holmium | Ho |
|-----------------------------|-----------------------|
| Atomic no. | 67 |
| Atomic mass | 164.9303 |
| Primary wavelength (nm) | 410.4 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 80% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.37 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | 405.4 |
| Secondary wavelength | Sensitivity reduction |
| 417.3 nm | 5× |
| 405.4 nm | 1.3× |
| 416.1 nm | 2× |
| 404.1 nm | 5× |
| 410.9 nm | 10× |
| 412.7 nm | 13× |
| 422.7 nm | 25× |
| 413.6 nm | 35× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.2 - 4.6 |
| Signal | 40 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 950 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |

1. Holmium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids cause a decrease in response.
 - Use hydrochloric acid for sample preparation.
4. High concentrations of other rare earths and base metals interfere.
 - Match all solutions for major components.

| Indium | | In |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 49 | |
| Atomic mass | 114.82 | |
| Primary wavelength (nm) | 303.9 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 80% | |
| best sensitivity | 80% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.3 mg/L | |
| furnace characteristic mass | 26 pg | |
| Emission wavelength (nm) | 451.1 | |
| Secondary wavelength | Sensitivity reduction | |
| 451.1 nm | 3× | |
| 325.6 nm | 1.1× | |
| 410.5 nm | 2.9× | |
| 256.0 nm | 12× | |
| 271.0 nm | 20× | |
| 275.4 nm | 30× | |

| Flame details | |
|--|------------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 30 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> Large excesses of aluminium, copper, magnesium, zinc, and phosphate depress the response. <ul style="list-style-type: none"> Match all solutions for these species. The sensitivity drops sharply when the pressure in the acetylene cylinder becomes low because of acetone carryover. <ul style="list-style-type: none"> Change the cylinder when the internal pressure drops below 7kg/sq cm (100 lb/sq in). | |

| Furnace details | |
|--|------------------------------------|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 750 |
| Atomize temperature (°C) | 2100 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 30 µg/L gives about 0.1 A |
| <ol style="list-style-type: none"> Indium is a volatile element. <ul style="list-style-type: none"> Carefully optimize the ash phase to avoid losses. Halide ion cause severe interferences. <ul style="list-style-type: none"> Add excess nitric acid to all solutions -or- Use magnesium nitrate modifier. | |

| Iridium | | Ir |
|-----------------------------|--|-----------------------|
| Atomic no. | | 77 |
| Atomic mass | | 192.22 |
| Primary wavelength (nm) | | 208.9 |
| Bandpass (nm) | | 0.2 |
| Lamp current | | |
| normal use | | 75% |
| best sensitivity | | 50% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 0.6 mg/L |
| furnace characteristic mass | | 220 pg |
| Emission wavelength (nm) | | 380.0 |
| Secondary wavelength | | Sensitivity reduction |
| 264.0 nm | | 3× |
| 266.5 nm | | 3.5× |
| 237.3 nm | | 4× |
| 285.0 nm | | 4.5× |
| 250.3 nm | | 5× |
| 254.4 nm | | 7× |
| 292.5 nm | | 7× |
| 351.4 nm | | 30× |

Flame details

| | |
|------------------------|---------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 1.1 - 1.3 |
| Signal | 60 mg/L gives about 0.4 A |

- The response is depressed by the presence of many other metals.
 - Match all solutions for these species.
- Other platinum group metals interfere.
 - Add uranium or lanthanum (1% m/V) as a releasing agent.

Furnace details

| | |
|--------------------------|-------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1400 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | 20 µL of 250 µg/L gives about 0.1 A |

- Background absorption and scatter are common.
 - Use background correction.
- Use the less sensitive 264.0 nm wavelength to improve precision.
- Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.
- Base metals and large excesses of precious metals interfere.
 - Match all solutions for these species.

| Iron | Fe |
|-----------------------------|-----------------------|
| Atomic no. | 26 |
| Atomic mass | 55.847 |
| Primary wavelength (nm) | 248.3 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.05 mg/L |
| furnace characteristic mass | 1.5 pg |
| Emission wavelength (nm) | 372.0 |
| Secondary wavelength | Sensitivity reduction |
| 372.0 nm | 10× |
| 248.8 nm | 2× |
| 252.3 nm | 2× |
| 271.9 nm | 3× |
| 302.1 nm | 4× |
| 296.7 nm | 11× |
| 373.7 nm | 12× |
| 305.9 nm | 20× |

Flame details

| | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.8 - 1.0 |
| Signal | 5.0 mg/L gives about 0.4 A |

- The 100 mm slot burner improves the sensitivity by about 40%.
- Many minor interferences are encountered.
 - These are critically dependent upon the precise flame conditions used.
 - Match all solutions for major components if maximum accuracy is required
 - or-
 - Use a fuel lean nitrous oxide/acetylene flame, but then
 - Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|-----------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2100 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 2 µg/L gives about 0.1 A |

- Background absorption and scatter are common.
 - Use background correction.
- Iron has a high risk of contamination.
 - Take particular care when preparing solutions.

| Lanthanum | La |
|-----------------------------|-----------------------|
| Atomic no. | 57 |
| Atomic mass | 138.905 |
| Primary wavelength (nm) | 550.1 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 80% |
| best sensitivity | 80% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 28.0 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | 579.1 |
| Secondary wavelength | Sensitivity reduction |
| 418.7 nm | 1.5× |
| 365.0 nm | 7× |
| 392.8 nm | 7× |
| 403.7 nm | 7× |
| 407.9 nm | 7× |

Flame details

| | |
|------------------------|--------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 3000 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|-------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2700 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | not available |

1. Lanthanum forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.
3. Lanthanum forms a stable carbide.
 - This can cause memory effects.

| Lead | Pb |
|-----------------------------|-----------------------|
| Atomic no. | 82 |
| Atomic mass | 207.2 |
| Primary wavelength (nm) | 217.0 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.07 mg/L |
| furnace characteristic mass | 1.8 pg |
| Emission wavelength (nm) | 405.8 |
| Secondary wavelength | Sensitivity reduction |
| 283.3 nm | 2.5× |
| 261.4 nm | 40× |
| 368.4 nm | 100× |

Flame details

| | |
|------------------------|--------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 7 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 30%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.03 mg/L.
3. The 283.3 nm line is brighter, gives a better signal-to-noise ratio, and is often preferred for routine use.
4. High concentrations of aluminium, silicon, strontium, magnesium and calcium cause minor interferences.
 - For maximum accuracy, match all solutions for these species.

Furnace details

| | |
|--------------------------|---|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 800 |
| Atomize temperature (°C) | 1200 |
| Modifier | 50 µg of ammonium nitrate -or- 50 µg of lanthanum nitrate -or- 50 µg of magnesium nitrate -or- 50 µg of ascorbic acid |
| Signal | 20 µL of 2.5 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. The secondary line at 283.3 nm is often preferred.
 - It is brighter, so that the signal to noise ratio is better.
 - The response is more linear, especially with Zeeman background correction.
 - Background signals are often significantly reduced.
3. Lead halides are volatile.
 - Keep the concentration of halide ion in the solutions as low as possible.
 - Carefully optimize the dry phase to avoid losses.
4. Ammonium phosphate (5 µg) is also an effective modifier, but can cause a spectral interference at the 217.0 nm line.
 - Use Zeeman background correction with phosphate modifier.

| Lithium | Li |
|-----------------------------|-----------------------|
| Atomic no. | 3 |
| Atomic mass | 6.941 |
| Primary wavelength (nm) | 670.8 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.008 mg/L |
| furnace characteristic mass | 1.1 pg |
| Emission wavelength (nm) | 670.8 |
| Secondary wavelength | Sensitivity reduction |
| 323.3 nm | 250x |
| 610.4 nm | 3400x |

| Flame details | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.8 - 1.1 |
| Signal | 0.8 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 40%.
2. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
3. Strontium causes an apparent enhancement because of molecular absorption by Sr-OH species.
 - Match all solutions for these species.

| Furnace details | |
|--------------------------|-------------------------------------|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 800 |
| Atomize temperature (°C) | 2700 |
| Modifier | none recommended |
| Signal | 20 µL of 1.5 µg/L gives about 0.1 A |

1. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
2. Alkali metal and alkali earth metal halides interfere.
 - Add sulphuric or phosphoric acid to all solutions.

| Lutetium | | Lu |
|-----------------------------|--|-----------------------|
| Atomic no. | | 71 |
| Atomic mass | | 174.97 |
| Primary wavelength (nm) | | 336.0 |
| Bandpass (nm) | | 0.2 |
| Lamp current | | |
| normal use | | 100% |
| best sensitivity | | 100% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 3.0 mg/L |
| furnace characteristic mass | | n/a pg |
| Emission wavelength (nm) | | 451.9 |
| Secondary wavelength | | Sensitivity reduction |
| 337.7 nm | | 2.2x |
| 331.2 nm | | 2x |
| 356.8 nm | | 2x |
| 298.9 nm | | 10x |
| 451.9 nm | | 12x |

Flame details

| | |
|------------------------|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.2 - 4.6 |
| Signal | 300 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |

1. Lutetium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.
4. Excess amounts of other rare earths and base metals interfere.
 - Match all solutions for these species.

| Magnesium | | Mg |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 12 | |
| Atomic mass | 24.305 | |
| Primary wavelength (nm) | 285.2 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.003 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 285.2 | |
| Secondary wavelength | Sensitivity reduction | |
| 202.6 nm | 40× | |
| 279.6 nm | 100× | |

Flame details

| | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 0.3 mg/L gives about 0.4 A |

- The 100 mm slot burner improves the sensitivity by about 40%.
- Phosphate, aluminate, silicate and other oxyanions depress the response.
 - Add a releasing agent (e.g. 0.1% m/v of lanthanum or strontium) to all solutions
 - or-
 - Use a Nitrous oxide/ acetylene flame, but then
 - Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|--------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | 20 µL of 0.15 µg/L gives about 0.1 A |

- Background absorption and scatter are common.
 - Use background correction.
- Magnesium has a high risk of contamination.
 - Take particular care when preparing solutions.
 - Clean the furnace carefully if magnesium nitrate modifiers have been used.

| Manganese | | Mn |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 25 | |
| Atomic mass | 54.9380 | |
| Primary wavelength (nm) | 279.5 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.02 mg/L | |
| furnace characteristic mass | 0.6 pg | |
| Emission wavelength (nm) | 403.0 | |
| Secondary wavelength | Sensitivity reduction | |
| 403.0 nm | 10× | |
| 279.8 nm | 1.3× | |
| 280.1 nm | 2× | |
| 321.7 nm | 2000× | |

| Flame details | |
|------------------------|-------------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 2.0 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 30%.
2. Silicon depresses the response.
 - Match all solutions for this species.
3. Molybdenum and tungsten depress the response, especially when the pressure in the acetylene cylinder becomes low, due to acetone carryover.
 - Change the cylinder when the internal pressure drops below 7 kg/sq cm. (100 lb/sq in).
 - Match all solutions for these species.

| Furnace details | |
|--------------------------|-------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 900 |
| Atomize temperature (°C) | 1800 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 0.7 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Chloride interferes slightly.
 - Add nitric acid (1% v/v) to all solutions.

| Mercury | Hg |
|-----------------------------|-----------------------|
| Atomic no. | 80 |
| Atomic mass | 200.59 |
| Primary wavelength (nm) | 253.7 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 2.7 mg/L |
| furnace characteristic mass | 58 pg |
| vapor characteristic conc. | 0.26 µg/L |
| Emission wavelength (nm) | 253.7 |
| Secondary wavelength | Sensitivity reduction |
| none | |

Flame details

| | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 1.1 - 1.3 |
| Signal | 300 mg/L gives about 0.4 A |

- The 100 mm slot burner improves the sensitivity by about 50%.
- The Slotted Tube Atom Trap improves the characteristic concentration to 0.85 mg/L.
- Reducing agents (e.g. stannous ion) enhance the response by reducing mercuric ion to mercury metal.
 - Match the concentration of reducing agent in all solutions.
- Many other interferences can occur.
 - Cold vapor generation is the preferred method of analysis.

Furnace details

| | |
|--------------------------|---|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 200 500 (with modifier) |
| Atomize temperature (°C) | 750 |
| Modifier | 50 µg of ammonium dichromate -or- 500 µg of gold -or- 500 µg of palladium |
| Signal | 20 µL of 75 µg/L gives about 0.1 A |

- Background absorption and scatter are common.
 - Use background correction.
- Mercury is extremely volatile.
 - Add matrix modifier to reduce the volatility is essential.

Vapor details

| | |
|-------------------------------|--|
| Measurement delay (seconds) | 40 - 70 |
| Carrier gas flow (mL/min) | 50 - 150 |
| Pump speed (RPM) | 30 - 40 |
| EC90 furnace temperature (°C) | n/a |
| Reductant | 0.5 - 1.0% m/V sodium borohydride solution stabilized with 0.5% m/V of sodium hydroxide -or- 0.5 - 5.0% m/V stannous chloride solution |
| Acid reagent | Minimum 5% V/V hydrochloric acid. |
| Signal | 6 µg/L gives about 0.1 A |

- Atomic mercury vapor is formed at room temperature.
 - A heated atom cell is not required.
- Organo-mercury compounds are not easily reduced.
 - Destroy these species by oxidation with an acidic solution of permanganate or dichromate ion.
 - Reduce excess oxidizing agent with hydroxylamine hydrochloride immediately before analysis.
- Major depressive interferences are caused by copper, nickel, bismuth, iron, selenium, gold, silver and the platinum group metals.
- The vapor characteristic concentration was measured using the borohydride reductant.
 - The stannous chloride reductant gives slightly poorer sensitivity, but the detection limit is a little better.

| Molybdenum | | Mo |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 42 | |
| Atomic mass | 95.94 | |
| Primary wavelength (nm) | 313.3 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 50% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.1 mg/L | |
| furnace characteristic mass | 4.8 pg | |
| Emission wavelength (nm) | 390.3 | |
| Secondary wavelength | Sensitivity reduction | |
| 390.1 nm | 3.8× | |
| 317.0 nm | 1.5× | |
| 379.8 nm | 1.8× | |
| 319.4 nm | 2.0× | |
| 386.4 nm | 2.2× | |
| 315.8 nm | 4× | |

| Flame details | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 10 mg/L gives about 0.4 A |

1. Ionization causes an interference in the Nitrous oxide/
acetylene flame.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. Sulphate enhances the response.
 - Add the ionization buffer as the sulphate salt.
3. A rich air/acetylene flame can be used, but many interferences occur.

| Furnace details | |
|--------------------------|--------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1800 |
| Atomize temperature (°C) | 2750 |
| Modifier | none recommended |
| Signal | 20 µL of 6 µg/L gives about 0.1 A |

1. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
2. Molybdenum is very nonvolatile.
 - Use high ash temperatures to remove the matrix.
 - Background correction may not be required if all the matrix has been removed.

| Neodymium | | Nd |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 60 | |
| Atomic mass | 144.24 | |
| Primary wavelength (nm) | 492.5 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 100% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 4.0 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 492.5 | |
| Secondary wavelength | Sensitivity reduction | |
| 490.2 nm | 3.2× | |
| 463.4 nm | 1.3× | |
| 471.9 nm | 2× | |
| 489.7 nm | 2× | |

Flame details

| | |
|------------------------|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 400 mg/L gives about 0.4 A |

1. Ionization causes an interference.
2. Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |

1. Neodymium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.

| Nickel | | Ni |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 28 | |
| Atomic mass | 58.71 | |
| Primary wavelength (nm) | 232.0 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 50% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.05 mg/L | |
| furnace characteristic mass | 3.6 pg | |
| Emission wavelength (nm) | 341.5 | |
| Secondary wavelength | Sensitivity reduction | |
| 305.1 nm | 4x | |
| 231.1 nm | 2x | |
| 341.5 nm | 2x | |
| 234.6 nm | 4x | |
| 346.2 nm | 8x | |
| 351.5 nm | 12x | |
| 303.8 nm | 12x | |
| 233.8 nm | 25x | |

| Flame details | |
|---|-----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.8 - 1.0 |
| Signal | 5 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> The 100 mm slot burner improves the sensitivity by about 30%. A large excess of iron enhances the response. <ul style="list-style-type: none"> Match all solutions for this species. | |

| Furnace details | |
|---|--------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2500 |
| Modifier | none recommended |
| Signal | 20 µL of 5 µg/L gives about 0.1 A |
| <ol style="list-style-type: none"> Background absorption and scatter are common. <ul style="list-style-type: none"> Use background correction. Carefully clean the furnace head if nickel modifiers have been used. | |

Cookbook

| Niobium | Nb |
|-----------------------------|-----------------------|
| Atomic no. | 41 |
| Atomic mass | 92.9064 |
| Primary wavelength (nm) | 334.4 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 100% |
| best sensitivity | 100% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 22 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | 405.9 |
| Secondary wavelength | Sensitivity reduction |
| 358.0 nm | 1.1x |
| 405.9 nm | 1.1x |
| 334.9 nm | 1.2x |
| 408.0 nm | 1.4x |
| 335.8 nm | 1.5x |
| 412.4 nm | 2x |
| 357.6 nm | 2.5x |
| 353.5 nm | 3x |

Flame details

| | |
|------------------------|--------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 2000 mg/L gives about 0.4 A |

1. Iron and fluoride enhance the response.
 - Match all solutions for these species.

Furnace details

| | |
|--------------------------|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |

1. This element is very insensitive.
 - Instrumental and performance data are limited.

| Osmium | Os |
|-----------------------------|-----------------------|
| Atomic no. | 76 |
| Atomic mass | 190.2 |
| Primary wavelength (nm) | 290.9 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 100% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.75 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | not available |
| Secondary wavelength | Sensitivity reduction |
| 301.8 nm | 2.6× |
| 305.9 nm | 2× |
| 426.1 nm | 2.6× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.1 - 4.5 |
| Signal | 75 mg/L gives about 0.4 A |

- Osmium metal can plate out on to glassware.
 - Prepare all solutions in 0.1M sulphuric acid to reduce this effect.
- The Os(VIII) is 5x more sensitive than the Os(IV).
 - All solutions must contain osmium in the same oxidation state.
 - Os(IV) can be oxidized to Os(VIII) by refluxing with 5M nitric acid.
- Osmium is highly toxic, and appropriate precautions must be taken.

| Palladium | | Pd |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 46 | |
| Atomic mass | 106.4 | |
| Primary wavelength (nm) | 247.6 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.13 mg/L | |
| furnace characteristic mass | 9 pg | |
| Emission wavelength (nm) | 380.0 | |
| Secondary wavelength | Sensitivity reduction | |
| 340.5 nm | 3× | |
| 276.3 nm | 3.5× | |

Flame details

| | |
|------------------------|---------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 12 mg/L gives about 0.4 A |

1. Large excesses of mineral acids and other transition metals affect the response.
 - Match all solutions for these species if they are present.
2. Other platinum group metals interfere.
 - Add uranium or lanthanum (1% m/V) as a releasing agent.

Furnace details

| | |
|--------------------------|------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2200 |
| Modifier | none recommended |
| Signal | 20 µL of 12 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.
3. Other platinum group metals do not cause severe interference at up to 100× excess.

| Phosphorus | | P |
|-----------------------------|-----------------------|----------|
| Atomic no. | 15 | |
| Atomic mass | 30.9738 | |
| Primary wavelength (nm) | 213.6 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 200 mg/L | |
| furnace characteristic mass | 3000 pg | |
| Emission wavelength (nm) | 526.0 | |
| Secondary wavelength | Sensitivity reduction | |
| none | | |

| Flame details | |
|---|----------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 20,000 mg/L gives about 0.4 A |
| 1. No serious interferences have been reported for the determination of phosphorus. | |

| Furnace details | |
|--|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2600 |
| Modifier | 50 µg of lanthanum as lanthanum nitrate |
| Signal | 20 µL of 3500 µg/L gives about 0.1 A |
| 1. Background absorption and scatter are common. | |
| <ul style="list-style-type: none"> • Use background correction. | |

| Platinum | | Pt |
|-----------------------------|--|-----------------------|
| Atomic no. | | 78 |
| Atomic mass | | 195.09 |
| Primary wavelength (nm) | | 266.0 |
| Bandpass (nm) | | 0.5 |
| Lamp current | | |
| normal use | | 75% |
| best sensitivity | | 50% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 1.5 mg/L |
| furnace characteristic mass | | 56 pg |
| Emission wavelength (nm) | | 266.0 |
| Secondary wavelength | | Sensitivity reduction |
| 293.0 nm | | 3.5x |
| 306.5 nm | | 2x |
| 262.8 nm | | 2.5x |
| 283.0 nm | | 3.5x |
| 273.4 nm | | 4x |
| 270.2 nm | | 4.5x |
| 248.7 nm | | 5x |
| 299.8 nm | | 6x |

| Flame details | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 1.0 - 1.2 |
| Signal | 150 mg/L gives about 0.4 A |

1. The Slotted Tube Atom Trap improves the characteristic concentration to 0.9 mg/L.
2. Many other metals affect the response.
 - Match all solutions for all major species present.
3. Other platinum group metals interfere.
 - Add uranium or lanthanum (1% m/V) as a releasing agent.

| Furnace details | |
|--------------------------|------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2500 |
| Modifier | none recommended |
| Signal | 20 µL of 70 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Oxidizing acids depress the response and reduce the precision.
 - Use hydrochloric acid for sample preparation.

| Potassium | | K |
|-----------------------------|-----------------------|----------|
| Atomic no. | 19 | |
| Atomic mass | 39.102 | |
| Primary wavelength (nm) | 766.5 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.008 mg/L | |
| furnace characteristic mass | 0.53 pg | |
| Emission wavelength (nm) | 766.5 | |
| Secondary wavelength | Sensitivity reduction | |
| 769.9 nm | 2× | |
| 404.4 nm | 200× | |
| 407.7 nm | 200× | |

| Flame details | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 1.1 - 1.3 |
| Signal | 0.8 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity.
2. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of caesium, to the sample and standard solutions.
3. High concentrations of mineral acids slightly depress the response.
 - Match all solutions for acid content for maximum accuracy.

| Furnace details | |
|--------------------------|-------------------------------------|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2500 |
| Modifier | none recommended |
| Signal | 20 µL of 0.6 µg/L gives about 0.1 A |

1. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
2. Potassium has a high risk of contamination.
 - Take particular care when preparing solutions.

| Praseodymium | | Pr |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 59 | |
| Atomic mass | 140.9077 | |
| Primary wavelength (nm) | 495.1 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 100% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 20 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 495.1 | |
| Secondary wavelength | Sensitivity reduction | |
| 492.5 nm | 2.3× | |
| 513.3 nm | 1.5× | |
| 473.7 nm | 2.3× | |
| 502.7 nm | 2.5× | |
| 504.6 nm | 4× | |
| 491.4 nm | 5× | |
| 503.3 nm | 6× | |

Flame details

| | |
|------------------------|--------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 2000 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to the sample and standard solutions.

Furnace details

| | |
|--------------------------|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |

1. Praseodymium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.

| Rhenium | Re |
|-----------------------------|-----------------------|
| Atomic no. | 75 |
| Atomic mass | 186.2 |
| Primary wavelength (nm) | 346.1 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 4.8 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | 346.1 |
| Secondary wavelength | Sensitivity reduction |
| 345.2 nm | 2.4× |
| 346.5 nm | 1.5× |

Flame details

| | |
|------------------------|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 500 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. Large excesses of aluminium, calcium, iron, lead, manganese, and potassium depress the response.
 - Match all solutions for these species if they are present.

Furnace details

| | |
|--------------------------|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |

1. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
2. This element is very insensitive.
 - Instrumental and performance data are limited.

| Rhodium | | Rh | |
|-----------------------------|--|-----------------------|--|
| Atomic no. | | 45 | |
| Atomic mass | | 102.9055 | |
| Primary wavelength (nm) | | 343.5 | |
| Bandpass (nm) | | 0.5 | |
| Lamp current | | | |
| normal use | | 75% | |
| best sensitivity | | 50% | |
| best precision | | 100% | |
| Performance | | | |
| flame characteristic conc. | | 0.08 mg/L | |
| furnace characteristic mass | | 15 pg | |
| Emission wavelength (nm) | | 346.0 | |
| Secondary wavelength | | Sensitivity reduction | |
| 365.8 nm | | 5× | |
| 369.2 nm | | 1.7× | |
| 339.7 nm | | 2.5× | |
| 370.1 nm | | 8× | |
| 350.7 nm | | 4× | |
| 328.1 nm | | 10× | |

| Flame details | |
|------------------------|--------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.1 |
| Signal | 8 mg/L gives about 0.4 A |

- The response is affected by most anions.
 - Match all solutions for anion content and type.
 - Sulphate gives the best sensitivity.
- Other platinum group metals interfere.
 - Add uranium or lanthanum (1% m/V) as a releasing agent.

| Furnace details | |
|--------------------------|------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1300 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | 20 µL of 20 µg/L gives about 0.1 A |

- Background absorption and scatter are common.
 - Use background correction.
- Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.

| Rubidium | | Rb |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 37 | |
| Atomic mass | 85.4678 | |
| Primary wavelength (nm) | 780.0 | |
| Bandpass (nm) | 1.0 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 100% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.02 mg/L | |
| furnace characteristic mass | 1.0 pg | |
| Emission wavelength (nm) | 780.0 | |
| Secondary wavelength | Sensitivity reduction | |
| 794.8 nm | 2.5× | |
| 420.2 nm | 100× | |
| 421.6 nm | 250× | |

| Flame details | |
|------------------------|-----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 2 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. Aluminium depresses the response.
 - Add 0.5% m/V of calcium to all solutions to reduce this effect.

| Furnace details | |
|--------------------------|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2700 |
| Modifier | none recommended |
| Signal | 20 µL of 1.2 µg/L gives about 0.1 A |

1. Emission effects can occur.
 - Use the reduced height bandpass setting.

| Ruthenium | Ru |
|-----------------------------|-----------------------|
| Atomic no. | 44 |
| Atomic mass | 101.07 |
| Primary wavelength (nm) | 349.9 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 100% |
| best sensitivity | 100% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.8 mg/L |
| furnace characteristic mass | 20 pg |
| Emission wavelength (nm) | 349.9 |
| Secondary wavelength | Sensitivity reduction |
| 379.9 nm | 2× |
| 392.6 nm | 10× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 1.2 - 1.4 |
| Signal | 80 mg/L gives about 0.4 A |

- The response is affected by platinum, rhodium, tungsten, and molybdenum.
 - Match all solutions these species if they are present.
- Other platinum group metals interfere.
 - Add uranium or lanthanum (1% m/V) as a releasing agent.

Furnace details

| | |
|--------------------------|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2650 |
| Modifier | none recommended |
| Signal | 20 µL of 25 µg/L gives about 0.1 A |

- Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
- Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.

| Samarium | | Sm |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 62 | |
| Atomic mass | 150.40 | |
| Primary wavelength (nm) | 429.7 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 100% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 2.4 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 476.0 | |
| Secondary wavelength | Sensitivity reduction | |
| 472.8 nm | 2× | |
| 476.0 nm | 1.4× | |
| 520.1 nm | 1.6× | |
| 478.3 nm | 2.1× | |
| 511.7 nm | 2.4× | |
| 458.2 nm | 2.7× | |
| 528.3 nm | 100× | |

| Flame details | |
|---|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 250 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> 1. Ionization causes an interference. <ul style="list-style-type: none"> • Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |

| Furnace details | |
|---|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |
| <ol style="list-style-type: none"> 1. Samarium forms a stable nitride. <ul style="list-style-type: none"> • Use argon, not nitrogen, as the inert furnace gas. 2. Emission effects can occur. <ul style="list-style-type: none"> • Use the reduced height bandpass setting. • Carefully check the furnace alignment. 3. There are no interferences from up to 100 times excess amounts of the other rare earths. 4. Oxidizing acids depress the response. <ul style="list-style-type: none"> • Use hydrochloric acid for sample preparation. | |

| Scandium | Sc |
|-----------------------------|-----------------------|
| Atomic no. | 21 |
| Atomic mass | 44.9559 |
| Primary wavelength (nm) | 391.2 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.13 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | 402.0 |
| Secondary wavelength | Sensitivity reduction |
| 408.2 nm | 6× |
| 390.8 nm | 1.2× |
| 402.4 nm | 1.4× |
| 402.0 nm | 1.8× |
| 327.0 nm | 4× |
| 405.5 nm | 12× |
| 327.4 nm | 15× |

| Flame details | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 15 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
2. The response is affected by large excesses of fluoride.
 - Match all solutions for this species.

| Selenium | Se |
|-----------------------------|-----------------------|
| Atomic no. | 34 |
| Atomic mass | 78.96 |
| Primary wavelength (nm) | 196.0 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 80% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.33 mg/L |
| furnace characteristic mass | 10 µg |
| vapor characteristic conc. | 0.7 µg |
| Emission wavelength (nm) | 196.0 |
| Secondary wavelength | Sensitivity reduction |
| 204.0 nm | 3× |
| 206.3 nm | 12× |
| 207.5 nm | 50× |

| Flame details | |
|--|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 3.8 - 4.2 |
| Signal | 40 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> 1. The Slotted Tube Atom Trap with an argon/hydrogen flame improves the characteristic concentration to 0.08 mg/L. 2. The Nitrous oxide/acetylene flame reduces or eliminates many interferences. | |

| Furnace details | |
|--------------------------|---|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 300 (no modifier) 1000 (with modifier) |
| Atomize temperature (°C) | 2300 |
| Modifier | 20 µg of nickel as nickel nitrate |
| Signal | 20 µL of 13 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.

| Vapor details | |
|-------------------------------|--|
| Measurement delay (seconds) | 40 - 50 |
| Carrier gas flow (mL/min) | 150 - 250 |
| Pump speed (RPM) | 30 40 |
| EC90 furnace temperature (°C) | 900 |
| Reductant | 0.5 - 1.0% m/V sodium borohydride solution stabilized with 0.5% m/V of sodium hydroxide. |
| Acid reagent | 50%v/v (5M) hydrochloric acid |
| Signal | 16 µg/L gives about 0.1 A |

1. Only Se(IV) can be reduced to the hydride.
 - Reduce Se(VI) to Se(IV) by heating at 80-100°C with 4M hydrochloric acid.
2. Mercury, gold, copper, nickel, platinum, palladium, and iron cause major interferences.
 - Use thiosemicarbazide or 1,10-phenanthroline as masking agents .
 - or-
 - Use 5 - 7M hydrochloric acid to form stable chlorocomplexes.

| Silicon | Si |
|-----------------------------|-----------------------|
| Atomic no. | 14 |
| Atomic mass | 28.086 |
| Primary wavelength (nm) | 251.6 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 1.3 mg/L |
| furnace characteristic mass | 21 pg |
| Emission wavelength (nm) | 251.6 |
| Secondary wavelength | Sensitivity reduction |
| 250.7 nm | 2.6× |
| 251.4 nm | 3.4× |
| 252.9 nm | 3.4× |
| 252.4 nm | 3.8× |
| 221.7 nm | 4.5× |
| 221.1 nm | 10× |

Flame details

| | |
|------------------------|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.5 - 5.0 |
| Signal | 150 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1300 |
| Atomize temperature (°C) | 2600 |
| Modifier | none recommended |
| Signal | 20 µL of 25 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Silicon has a high risk of contamination.
 - Take particular care when preparing solutions.
 - Use plastic vessels, and avoid the use of glassware.

| Silver | Ag |
|----------------------------------|-------------------------------|
| Atomic no. | 47 |
| Atomic mass | 107.868 |
| Primary wavelength (nm) | 328.1 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.025 mg/L |
| furnace characteristic mass | 1.0 pg |
| Emission wavelength (nm) | 328.1 |
| Secondary wavelength 338.3 nm | Sensitivity reduction 2.0× |

| Flame details | |
|------------------------|-------------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 2.5 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 40%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.12 mg/L.
3. Large excesses of aluminium, thorium, permanganate, iodate, and tungstate depress the response.
 - Match all solutions for these species if they are present.

| Furnace details | |
|--------------------------|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 450 |
| Atomize temperature (°C) | 1100 |
| Modifier | none recommended |
| Signal | 20 µL of 1.3 µg/L gives about 0.1 A |

1. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
2. Silver halides are insoluble, and will precipitate from solution.
 - Avoid the use of halide acids or salts.
 - Check for halide contamination of vessels and reagents.

| Sodium | | Na | |
|-----------------------------|--|-----------------------|--|
| Atomic no. | | 11 | |
| Atomic mass | | 22.9898 | |
| Primary wavelength (nm) | | 589.0 | |
| Bandpass (nm) | | 0.2 | |
| Lamp current | | | |
| normal use | | 75% | |
| best sensitivity | | 75% | |
| best precision | | 100% | |
| Performance | | | |
| flame characteristic conc. | | 0.004 mg/L | |
| furnace characteristic mass | | 0.22 pg | |
| Emission wavelength (nm) | | 589.0 | |
| Secondary wavelength | | Sensitivity reduction | |
| 330.3 nm | | 300x | |
| 589.6 nm | | 2x | |

| Flame details | |
|------------------------|----------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 0.5 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 50%.
2. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

| Furnace details | |
|--------------------------|----------------------------------|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 1100 |
| Atomize temperature (°C) | 2000 |
| Modifier | none recommended |
| Signal | 20 µL of 0.25 µg/L gives about A |

1. Emission effects can occur.
 - Use the reduced height bandpass setting.
2. Sodium has a high risk of contamination.
 - Take particular care when preparing solutions.
 - Use plastic vessels, and avoid the use of glassware.

| Strontium | | Sr |
|-----------------------------|--|-----------------------|
| Atomic no. | | 38 |
| Atomic mass | | 87.62 |
| Primary wavelength (nm) | | 460.7 |
| Bandpass (nm) | | 0.5 |
| Lamp current | | |
| normal use | | 75% |
| best sensitivity | | 75% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 0.017 mg/L |
| furnace characteristic mass | | 2 pg |
| Emission wavelength (nm) | | 460.7 |
| Secondary wavelength | | Sensitivity reduction |
| none | | |

| Flame details | |
|--|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.0 - 4.4 |
| Signal | 1.6 mg/L gives about 0.4 A |
| 1. Ionization causes an interference. | |
| • Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |

| Furnace details | |
|--|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | 20 µL of 2.5 µg/L gives about 0.1 A |
| 1. Emission effects can occur. | |
| • Use the reduced height bandpass setting. | |

| Tantalum | Ta |
|----------------------------|-----------------------|
| Atomic no. | 73 |
| Atomic mass | 180.94 |
| Primary wavelength (nm) | 271.5 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 100% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 5.0 mg/L |
| Emission wavelength (nm) | 474.0 |
| Secondary wavelength | Sensitivity reduction |
| 277.6 nm | 2× |
| 260.9 nm | 2× |
| 255.9 nm | 2.5× |
| 293.4 nm | 2.5× |
| 269.8 nm | 2.8× |
| 275.8 nm | 3× |

Flame details

| | |
|------------------------|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 500 mg/L gives about 0.4 A |

1. Iron and hydrofluoric acid enhance the response.
 - Match all solutions for these species.

| Tellurium | | Te | |
|-----------------------------|--|-----------------------|--|
| Atomic no. | | 52 | |
| Atomic mass | | 127.60 | |
| Primary wavelength (nm) | | 214.3 | |
| Bandpass (nm) | | 0.5 | |
| Lamp current | | | |
| normal use | | 75% | |
| best sensitivity | | 75% | |
| best precision | | 100% | |
| Performance | | | |
| flame characteristic conc. | | 0.2 mg/L | |
| furnace characteristic mass | | 4.8 pg | |
| vapor characteristic conc. | | 0.46 µg | |
| Emission wavelength (nm) | | 238.3 | |
| Secondary wavelength | | Sensitivity reduction | |
| 225.9 nm | | 8× | |
| 238.5 nm | | 50× | |

| Flame details | |
|--|---------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 20 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> 1. The Slotted Tube Atom Trap improves the characteristic concentration to 0.08 mg/L. 2. The response is affected by large excesses of calcium, copper, silicon, sodium, zinc, and zirconium. <ul style="list-style-type: none"> • Match all solutions for these species. | |

| Furnace details | |
|--------------------------|---|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 400 (no modifier) 1000 (with modifier) |
| Atomize temperature (°C) | 2300 |
| Modifier | 20 µg of nickel as nickel nitrate |
| Signal | 20 µL of 6 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.

| Vapor details | |
|-------------------------------|--|
| Measurement delay (seconds) | 40 - 50 |
| Carrier gas flow (mL/min) | 150 - 250 |
| Pump speed (RPM) | 30 - 40 |
| EC90 furnace temperature (°C) | 900 |
| Reductant | 0.5 - 1.0% m/V sodium borohydride solution stabilized with 0.5% m/V of sodium hydroxide. |
| Acid reagent | 50% v/v (5M) hydrochloric acid Signal 10 µg/L gives about 0.1 A. |
| Signal | 10 µg/L gives about 0.1 A |

1. Only Te(IV) can be reduced to the hydride.
 - Reduce Te(VI) to Te(IV) by heating at 80-100°C with 4M hydrochloric acid.
 - Note that some commercial standards are supplied containing telluric acid (Te(VI)).
2. Iron, copper, nickel, platinum, palladium, and cobalt cause major interferences.
 - Use 5 - 7M hydrochloric acid to form stable chlorocomplexes.

| Terbium | | Tb |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 65 | |
| Atomic mass | 158.9524 | |
| Primary wavelength (nm) | 432.7 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 6.6 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 431.9 | |
| Secondary wavelength | Sensitivity reduction | |
| 410.6 nm | 3× | |
| 431.9 nm | 1.2× | |
| 390.1 nm | 1.5× | |
| 406.2 nm | 1.8× | |
| 433.9 nm | 1.8× | |

| Flame details | |
|---|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 700 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> 1. Ionization causes an interference. <ul style="list-style-type: none"> • Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |

| Furnace details | |
|--|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |
| <ol style="list-style-type: none"> 1. Terbium forms a stable nitride. <ul style="list-style-type: none"> • Use argon, not nitrogen, as the inert furnace gas. 2. Emission effects can occur. <ul style="list-style-type: none"> • Use the reduced height bandpass setting. 3. Oxidizing acids depress the response. <ul style="list-style-type: none"> • Use hydrochloric acid for sample preparation. 4. Excess amounts of base metals and other rare earths interfere. <ul style="list-style-type: none"> • Match all solutions for these species. | |

| Thallium | | Tl |
|-----------------------------|--|-----------------------|
| Atomic no. | | 81 |
| Atomic mass | | 204.37 |
| Primary wavelength (nm) | | 276.8 |
| Bandpass (nm) | | 0.5 |
| Lamp current | | |
| normal use | | 75% |
| best sensitivity | | 50% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 0.25 mg/L |
| furnace characteristic mass | | 6.3 pg |
| Emission wavelength (nm) | | 535.1 |
| Secondary wavelength | | Sensitivity reduction |
| 377.6 nm | | 2.5× |
| 238.0 nm | | 6.5× |
| 258.0 nm | | 25× |

| Flame details | |
|------------------------|---|
| Flame type | Air/acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 25 mg/L gives about 0.4 A |
| 1. | The Slotted Tube Atom Trap improves the characteristic concentration to 0.1 mg/L. |
| 2. | No serious interference effects have been reported for the determination of thallium. |

| Furnace details | |
|--------------------------|--|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 700 |
| Atomize temperature (°C) | 1200 |
| Modifier | none recommended |
| Signal | 20 µL of 7.5 µg/L gives about 0.1 A |
| 1. | Background absorption and scatter are common. <ul style="list-style-type: none"> • Use background correction. |

| Thulium | Tm |
|-----------------------------|-----------------------|
| Atomic no. | 69 |
| Atomic mass | 168.9342 |
| Primary wavelength (nm) | 371.8 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.13 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | 371.8 |
| Secondary wavelength | Sensitivity reduction |
| 375.2 nm | 5× |
| 410.6 nm | 1.5× |
| 374.4 nm | 1.8× |
| 409.4 nm | 1.8× |
| 418.8 nm | 3× |
| 420.4 nm | 10× |
| 341.0 nm | 15× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.2 - 4.6 |
| Signal | 15 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |

1. Thulium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.
4. Excess amounts of base metals interfere.
 - Match all solutions for these species.
5. Other rare earths do not interfere at up to 100× excess.

| Tin | Sn |
|-----------------------------|-----------------------|
| Atomic no. | 50 |
| Atomic mass | 118.69 |
| Primary wavelength (nm) | 224.6 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 75% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.5 mg/L |
| furnace characteristic mass | 18 µg |
| vapor characteristic conc. | 0.38 µg |
| Emission wavelength (nm) | 284.0 |
| Secondary wavelength | Sensitivity reduction |
| 300.9 nm | 7× |
| 286.3 nm | 1.5× |
| 235.5 nm | 2× |
| 270.7 nm | 2.5× |
| 303.4 nm | 3.5× |
| 254.7 nm | 5.5× |
| 219.9 nm | 6× |
| 233.5 nm | 7× |
| 266.1 nm | 30× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 50 mg/L gives about 0.4 A |

1. The Slotted Tube Atom Trap used with an air/hydrogen flame improves the characteristic concentration to 0.2 mg/L.
2. Ionization in the Nitrous oxide/ acetylene flame causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.
3. Few other serious interferences have been reported in this flame.

Furnace details

| | |
|--------------------------|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 800 |
| Atomize temperature (°C) | 2300 |
| Modifier | 100 µg of ascorbic acid -or- 50 µg of ammonium nitrate -or- 50 µg of magnesium nitrate |
| Signal | 20 µL of 20 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Phosphoric, sulphuric, perchloric and hydrochloric acids depress the response.
 - Use nitric acid.
 - or-
 - Match the acid content and type for all solutions.

Vapor details

| | |
|-------------------------------|--|
| Measurement delay (seconds) | 40 - 60 |
| Carrier gas flow (mL/min) | 150 - 250 |
| Pump speed (RPM) | 30 - 40 |
| EC90 furnace temperature (°C) | 900 |
| Reductant | 0.5 - 1.0% m/V sodium borohydride solution stabilized with 0.5% m/V of sodium hydroxide. |
| Acid reagent | 5.0% v/v (0.5M) hydrochloric acid |
| Signal | 12.5 µg/L gives about 0.1 A |

1. The acid concentration is important for tin determinations.
 - Typically, the optimum acid concentration in the sample will be around 0.5% v/v, but this should be optimized for each type of sample.
2. Copper and iron cause major interferences.
 - Use oxalic acid or 1,10-phenanthroline as masking agents.

| Titanium | | Ti |
|-----------------------------|--|-----------------------|
| Atomic no. | | 22 |
| Atomic mass | | 47.90 |
| Primary wavelength (nm) | | 365.4 |
| Bandpass (nm) | | 0.5 |
| Lamp current | | |
| normal use | | 75% |
| best sensitivity | | 75% |
| best precision | | 100% |
| Performance | | |
| flame characteristic conc. | | 0.57 mg/L |
| furnace characteristic mass | | 50 pg |
| Emission wavelength (nm) | | 399.0 |
| Secondary wavelength | | Sensitivity reduction |
| 375.3 nm | | 2× |
| 374.1 nm | | 2.5× |
| 399.0 nm | | 2.5× |
| 364.3 nm | | 1.1× |
| 320.0 nm | | 1.2× |
| 363.6 nm | | 1.2× |
| 337.2 nm | | 1.3× |
| 319.2 nm | | 1.8× |
| 334.2 nm | | 1.8× |
| 335.5 nm | | 2.0× |

Flame details

| | |
|------------------------|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.7 |
| Signal | 50 mg/L gives about 0.4 A |

- Large excesses of fluoride, aluminium, and iron enhance the response.
 - Match all solutions for these species.
- Many minor interferences from the transition metals occur.
 - Add 0.1% m/V of iron to all solutions.
- Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1500 |
| Atomize temperature (°C) | 2850 |
| Modifier | none recommended |
| Signal | 20 µL of 40 µg/L gives about 0.1 A |

- Titanium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
- Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.

| Tungsten | | W |
|-----------------------------|-----------------------|----------|
| Atomic no. | 74 | |
| Atomic mass | 183.85 | |
| Primary wavelength (nm) | 255.1 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 4.3 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 400.9 | |
| Secondary wavelength | Sensitivity reduction | |
| 400.9 nm | 2.5× | |
| 268.1 nm | 1.8× | |
| 272.4 nm | 1.8× | |
| 294.4 nm | 1.8× | |
| 294.7 nm | 1.9× | |
| 283.1 nm | 2.5× | |
| 289.6 nm | 2.7× | |
| 297.6 nm | 4× | |
| 430.2 nm | 10× | |

| Flame details | |
|------------------------|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 500 mg/L gives about 0.4 A |

1. Large excesses of iron depresses the response.
 - Match all solutions for this species.
2. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

| Uranium | U |
|-----------------------------|-----------------------|
| Atomic no. | 92 |
| Atomic mass | 238.029 |
| Primary wavelength (nm) | 356.7 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 100% |
| best sensitivity | 100% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 50 mg/L |
| furnace characteristic mass | n/a pg |
| Emission wavelength (nm) | 544.8 |
| Secondary wavelength | Sensitivity reduction |
| 351.5 nm | 2.5× |
| 358.5 nm | 0.7× |
| 394.4 nm | 2.5× |
| 348.9 nm | 3× |

Flame details

| | |
|------------------------|--------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 5000 mg/L gives about 0.4 A |

1. Large excesses of iron, cobalt, nickel, lead, and aluminium depress the response.
 - Match all solutions for these species.
2. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

| Vanadium | | V |
|-----------------------------|-----------------------|----------|
| Atomic no. | 23 | |
| Atomic mass | 50.9414 | |
| Primary wavelength (nm) | 318.5 | |
| Bandpass (nm) | 0.5 | |
| Lamp current | | |
| normal use | 75% | |
| best sensitivity | 75% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 0.34 mg/L | |
| furnace characteristic mass | 16 pg | |
| Emission wavelength (nm) | 437.9 | |
| Secondary wavelength | Sensitivity reduction | |
| 306.6 nm | 3× | |
| 306.1 nm | 2.8× | |
| 305.6 nm | 3.2× | |
| 437.9 nm | 4.5× | |
| 320.2 nm | 6.4× | |
| 385.6 nm | 6.5× | |
| 390.2 nm | 6.5× | |

| Flame details | |
|--|------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 40 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> Large excesses of aluminium and titanium enhance the response. <ul style="list-style-type: none"> Match all solutions for these species. Ionization causes an interference. <ul style="list-style-type: none"> Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |

| Furnace details | |
|---|---------------------------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2750 |
| Modifier | 50 µg of magnesium nitrate |
| Signal | 20 µL of 20 µg/L gives about 0.1 A |
| <ol style="list-style-type: none"> Vanadium forms a stable nitride. <ul style="list-style-type: none"> Use argon, not nitrogen, as the inert furnace gas. Vanadium is very involatile. <ul style="list-style-type: none"> Use high ash temperatures to remove all the matrix. Background correction may not be needed if all the matrix has been removed. All inorganic acids influence the response. <ul style="list-style-type: none"> Match all solutions for acid type and content. | |

| Ytterbium | Yb |
|-----------------------------|-----------------------|
| Atomic no. | 70 |
| Atomic mass | 173.04 |
| Primary wavelength (nm) | 398.8 |
| Bandpass (nm) | 0.5 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.035 mg/L |
| furnace characteristic mass | 2.6 pg |
| Emission wavelength (nm) | 398.8 |
| Secondary wavelength | Sensitivity reduction |
| 246.5 nm | 5× |
| 346.4 nm | 3× |
| 267.2 nm | 5× |

Flame details

| | |
|------------------------|-----------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Stoichiometric |
| Fuel flow rate (L/min) | 4.0 - 4.4 |
| Signal | 4 mg/L gives about 0.4 A |

1. Ionization causes an interference.
 - Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions.

Furnace details

| | |
|--------------------------|--|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2600 |
| Modifier | none recommended |
| Signal | 20 µL of 3.0 µg/L gives about 0.1 A |

1. Ytterbium forms a stable nitride.
 - Use argon, not nitrogen, as the inert furnace gas.
2. Emission effects can occur.
 - Use the reduced height bandpass setting.
 - Carefully check the furnace alignment.
3. Oxidizing acids depress the response.
 - Use hydrochloric acid for sample preparation.
4. Excess amounts of base metals interfere.
 - Match all solutions for these species.
5. Other rare earths do not interfere at up to 100× excess.

| Yttrium | | Y |
|-----------------------------|-----------------------|----------|
| Atomic no. | 39 | |
| Atomic mass | 89.9059 | |
| Primary wavelength (nm) | 410.2 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 100% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 1.7 mg/L | |
| furnace characteristic mass | 13,000 pg | |
| Emission wavelength (nm) | 597.2 | |
| Secondary wavelength | Sensitivity reduction | |
| 362.1 nm | 2.2× | |
| 407.7 nm | 1.2× | |
| 412.8 nm | 1.2× | |
| 414.3 nm | 2.2× | |

| Flame details | |
|--|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.2 - 4.5 |
| Signal | 170 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> Ionization causes an interference. <ul style="list-style-type: none"> Add an ionization buffer, such as 0.2% m/V of potassium, to all solutions. | |

| Furnace details | |
|--|---|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1000 |
| Atomize temperature (°C) | 2500 |
| Modifier | none recommended |
| Signal | 20 µL of 15,000 µg/L gives about 0.1 A |
| <ol style="list-style-type: none"> Yttrium forms a stable nitride. <ul style="list-style-type: none"> Use argon, not nitrogen, as the inert furnace gas. Emission effects can occur. <ul style="list-style-type: none"> Use the reduced height bandpass setting. Carefully check the furnace alignment. Oxidizing acids depress the response. <ul style="list-style-type: none"> Use hydrochloric acid for sample preparation. | |

| Zinc | Zn |
|----------------------------------|--------------------------------|
| Atomic no. | 30 |
| Atomic mass | 65.37 |
| Primary wavelength (nm) | 213.9 |
| Bandpass (nm) | 0.2 |
| Lamp current | |
| normal use | 75% |
| best sensitivity | 50% |
| best precision | 100% |
| Performance | |
| flame characteristic conc. | 0.01 mg/L |
| furnace characteristic mass | 0.22 pg |
| Emission wavelength (nm) | 213.9 |
| Secondary wavelength 307.6 nm | Sensitivity reduction 4000× |

| Flame details | |
|------------------------|-------------------------------|
| Flame type | Air/acetylene |
| Flame chemistry | Lean |
| Fuel flow rate (L/min) | 0.9 - 1.2 |
| Signal | 1.0 mg/L gives about 0.4 A |

1. The 100 mm slot burner improves the sensitivity by about 50%.
2. The Slotted Tube Atom Trap improves the characteristic concentration to 0.004 mg/L.
3. The response is depressed by large excesses of silicon.
 - Match all solutions for this species.

| Furnace details | |
|--------------------------|---|
| Cuvette type | Electrographite |
| Ash temperature (°C) | 700 |
| Atomize temperature (°C) | 1100 |
| Modifier | 100 µg of magnesium nitrate |
| Signal | 20 µL of 0.25 µg/L gives about 0.1 A |

1. Background absorption and scatter are common.
 - Use background correction.
2. Zinc has a high risk of contamination.
 - Take particular care when preparing solutions.

| Zirconium | | Zr |
|-----------------------------|-----------------------|-----------|
| Atomic no. | 40 | |
| Atomic mass | 91.22 | |
| Primary wavelength (nm) | 360.1 | |
| Bandpass (nm) | 0.2 | |
| Lamp current | | |
| normal use | 100% | |
| best sensitivity | 100% | |
| best precision | 100% | |
| Performance | | |
| flame characteristic conc. | 4.5 mg/L | |
| furnace characteristic mass | n/a pg | |
| Emission wavelength (nm) | 360.1 | |
| Secondary wavelength | Sensitivity reduction | |
| 301.2 nm | 1.8× | |
| 303.1 nm | 1.5× | |
| 352.0 nm | 1.6× | |
| 354.8 nm | 1.6× | |
| 298.5 nm | 2× | |

Flame details

| | |
|---|-------------------------------|
| Flame type | Nitrous oxide/ acetylene |
| Flame chemistry | Rich |
| Fuel flow rate (L/min) | 4.3 - 4.8 |
| Signal | 500 mg/L gives about 0.4 A |
| <ol style="list-style-type: none"> The response is affected by ammonium, chloride, fluoride, sulphate, iron, and nickel. <ul style="list-style-type: none"> Match all solutions for these species. | |

Furnace details

| | |
|--|------------------|
| Cuvette type | Coated or ELC |
| Ash temperature (°C) | 1200 |
| Atomize temperature (°C) | 2800 |
| Modifier | none recommended |
| Signal | not available |
| <ol style="list-style-type: none"> Zirconium forms a stable nitride. <ul style="list-style-type: none"> Use argon, not nitrogen, as the inert furnace gas. Emission effects can occur. <ul style="list-style-type: none"> Use the reduced height bandpass setting. Carefully check the furnace alignment. | |

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