INTRODUCTION

▼ General
This book is intended as a guide to analysts in the selection of techniques and instrument settings for practical flame spectroscopy. Although the techniques and settings quoted will give satisfactory results for the majority of determinations, it is impossible in the space of this book to provide for all contingencies. Consequently, where analytical circumstances differ appreciably from those indicated in the book, appropriate changes in operating conditions may be required. Throughout the book, emphasis had been placed on practical applications and no attempt has been made to provide a complete theoretical background. Readers seeking a more thorough theoretical treatment of the subject are referred to the many text books currently available—see ‘General references’ later in this section.

Also, while every effort has been made to ensure the validity of the published material in this book, analysts should satisfy themselves that the written procedures and operating conditions, (and the results obtained from these) are valid.

▼ Safety aspects
Some warning messages will appear in the text. These are used when failure to observe instructions or precautions could result in injury or death.

Note, however, that many chemicals used in the preparation of samples and standards in this text are potentially hazardous. If you are in any doubt over the correct handling procedures for any material, you should consult an appropriate reference on the subject.

You should also observe the warning on the inside of the front cover of this book, and refer to reference 8 (at the end of this section).

Other points to note are:
1. A flame should never be left unsupervised.
2. Build-up of salt or carbon deposits on a burner should never be allowed to continue unchecked.

Refer also to Varian instrument operation manuals for details of required safety practices.

▼ Reagents and apparatus
The purity of reagents may determine the accuracy of the analysis and all reagents should therefore be of the highest purity available.

Prior to any analysis all reagents and equipment should first be checked for the element of interest by carrying out a blank determination.

All apparatus for trace analysis should be thoroughly soaked in dilute nitric acid and rinsed several times with distilled water prior to use. It is recommended that a full set of new apparatus be put aside expressly for use in trace analysis, thus minimizing any possibility of contamination.

PTFE and plastic volumetric vessels are available and should be used in preference to glass whenever hydrofluoric acid or strong caustic solutions are to be handled.

▼ Sample preparation
The sample to be analyzed can be brought into solution by a number of means

- acid attack
- alkali fusion and subsequent acid attack
- dissolution in solvent

Whichever procedure is used, it is essential to ensure that no analyte element is lost and that a clear, stable solution is obtained.

When carrying out dissolution it is advisable to avoid adding components likely to cause severe interference. For example, in the alkali fusion of tantalum ores, potassium should not be used since it will form highly refractory potassium fluorotantalate.

Where interferences are severe, or the concentration being determined is very low, chemical separation or pre-concentration may be necessary. In atomic absorption analysis this is generally achieved by solvent extraction.

Solvent extraction can also be used to remove a major element and reduce the overall solution concentration. In iron and steel analysis, ketone or ester extraction from strong hydrochloric acid solution removes iron almost quantitatively, and trace elements can be determined in the aqueous layer. This eases the requirements for matrix matching of standards.

When choosing a solvent for organic extraction, avoid using aromatics such as benzene, or highly volatile halogen solvents such as carbon tetrachloride and chloroform. Apart from their hazardous nature, these types of solvent will create severe flame disturbance.

The ketone and ester solvents have been found to possess the most suitable properties for use in premix burner systems. Methyl isobutyl ketone, diisobutyl ketone and ethyl acetate are the solvents most commonly used because of the wide range of metals which can be chelated and extracted with a high degree of efficiency.

Detailed methods for solvent extraction of metals can be found in the literature.

When working with any aqueous-organic system it is good practice to subject the standards to the same extraction procedure as the samples. This automatically compensates for the slight solubility of solvents in water, the extraction efficiency involved (which is rarely 100%), and any metallic impurities in the solvent.
Standard preparation

Stock solutions for atomic absorption spectrometry (as 1000 μg/mL) are readily available for a wide range of elements from commercial suppliers. Alternatively, standards may be prepared from the solid. Wherever possible, metals and metal oxides are to be preferred in the preparation of standards. This enables the analyst to dissolve them so that samples and standards will contain identical elements and hence minimize any chemical or physical interference effects. Only concentrated standards (above 1000 μg/mL) should be held in storage. Working standards should be diluted from standard stock solutions only when needed.

At low concentrations (less than 10 μg/mL) solutions have been found to deteriorate quite quickly because of adsorption on the walls of the container. Similarly, standard addition solutions can be prepared containing all of the required elements. This will avoid multiple splitting of the sample for individual elements and reduce the amount of time spent in preparing standards.

Before weighing, standard materials should be treated to ensure that they are in a standard state.

Metals: Wash with acetone and ether to remove any oil layers. Remove any oxide coating by abrasion with emery cloth or by acid pickling and drying.

Oxides: Dry at 110°C for two hours. If necessary, heat to elevated temperatures to remove bound water.

Compounds: Equilibration at constant water content, or drying at 110°C for two hours to remove any water.

For more detailed information the reader is advised to consult the many texts on classical chemical analysis.

Matrix effects

(a) Precipitation

Inaccurate results are commonly caused by precipitation of the element of interest. Examples of this are: the hydrolysis of silicon and tin compounds, and the formation of insoluble chlorides and sulfates.

(b) Physical properties of standard and sample

For a given flow of support gas, the amount of sample aspirated by the nebulizer and the proportion which reaches the flame are dependent on the physical properties of the solution—viscosity, surface tension, density, solvent vapor pressure. To avoid differences in the amount of sample and standard which reach the flame, it is necessary that the physical properties of sample and standard be matched as closely as possible. If this cannot be done, the method of standard additions must be employed.

Chemical interferences

The formation of ground state atoms can be inhibited by two general forms of chemical interferences. These are:

(a) Incomplete dissociation of compounds

(b) Ionization

(a) Incomplete dissociation of compounds

The most common form of this interference is the formation in the flame of such refractory compounds as calcium phosphate and potassium fluorotantalate. Such interferents form compounds which are not completely dissociated at the temperature of the flame and hence prevent the formation of neutral ground state atoms.

When establishing an analytical technique, use the following method to check for chemical interference:

(i) Prepare a set of solutions of varying interferent levels.

(ii) Take absorbance readings for each solution.

(iii) Plot the results as shown.

It will be noted that in region B, small variations in interferent level will cause large changes in the absorbance of the analyte element. Because this is analytically undesirable, the analyst should use a sample treatment procedure which will avoid operating in region B.

Where interference is encountered, the following procedure for optimization of the flame stoichiometry is recommended:

Prepare two calibration standards having the same analyte element concentration—one being prepared in distilled water and the other in a synthetic matrix corresponding to the sample material.

Light the flame and measure the absorbance of both solutions. Adjust the burner position for maximum absorbance with the synthetic matrix solution, and adjust the fuel flow until the absorbance of both solutions is identical, or as close as possible. This procedure will provide optimum flame stoichiometry and minimize the effects of interference to yield improved accuracy and precision.
If interference is still present and cannot be compensated for, then 4 means of overcoming it are possible:

(1) Use a higher temperature flame

Where compounds are insufficiently dissociated in the cooler flames, a high temperature flame such as nitrous oxide-acetylene can frequently supply sufficient thermal energy to cause complete dissociation. For example, calcium interference on aluminium can be overcome by using the nitrous oxide-acetylene flame to dissociate the refractory calcium aluminate found in cooler flames.

(2) Extract the analyte element

Where the interference assumes serious proportions, it is sometimes possible to extract the analyte element into an organic medium. When choosing a chelating agent it is unnecessary to ensure high selectivity; it is only necessary to ensure that the interferent and analyte are separated. For example, potassium interference on tantalum can be avoided by extracting tantalum as the fluoride complex into methyl isobutyl ketone, thus preventing the formation of refractory potassium fluorotantalate.

(3) Extract the interferent

It is often possible to remove the interferent by organically extracting it from solution. A highly specific and quantitative extraction is not always necessary. For example, in the determination of trace metals in iron ores, the excess iron can be extracted into isobutyl acetate as the chloride complex. This allows trace analysis to be carried out on the aqueous solution free of bulk iron.

(4) Use of releasing agents

The formation of some refractory compounds can be prevented by adding an excess of another element which will combine with the interferent in preference to the analyte. This will remove the interference. For example, in calcium determinations, lanthanum or strontium nitrate can be added to solutions containing phosphorous. This will allow calcium to be determined in an air-acetylene flame without interference due to the formation of calcium phosphate.

(b) Ionization

High temperature flames such as nitrous oxide-acetylene may cause appreciable ionization of the analyte element. The alkali and alkaline-earth metals are more susceptible to ionization than the transition elements.

To control ionization of the analyte it is necessary to add a suitable cation having an ionization potential lower than that of the analyte. The addition of readily ionized elements such as sodium, potassium and cesium at concentrations between 2000 and 5000 µg/mL creates an excess of electrons in the flame and effectively suppresses ionization of the analyte.

When investigating ionization levels, it is recommended that a graph be plotted of suppressant concentration against analyte absorbance as shown.

From the graph a concentration of ionization suppressant should be chosen such that minor changes in suppressant concentration have no effect on the analyte absorbance.

Some typical ionization potentials are:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ionization potential eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>6.0</td>
</tr>
<tr>
<td>Ba</td>
<td>5.2</td>
</tr>
<tr>
<td>Be</td>
<td>9.3</td>
</tr>
<tr>
<td>Ca</td>
<td>6.1</td>
</tr>
<tr>
<td>Cs</td>
<td>3.9</td>
</tr>
<tr>
<td>K</td>
<td>4.3</td>
</tr>
<tr>
<td>Mg</td>
<td>7.6</td>
</tr>
<tr>
<td>Na</td>
<td>5.1</td>
</tr>
<tr>
<td>Sr</td>
<td>5.7</td>
</tr>
<tr>
<td>Tb</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Typical degrees of ionization are:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration µg/mL</th>
<th>% Ionization Air-acetylene</th>
<th>% Ionization Nitrous oxide-acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>100</td>
<td>–</td>
<td>10</td>
</tr>
<tr>
<td>Ba</td>
<td>30</td>
<td>0</td>
<td>88</td>
</tr>
<tr>
<td>Be</td>
<td>2</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>Ca</td>
<td>5</td>
<td>3</td>
<td>43</td>
</tr>
<tr>
<td>Mg</td>
<td>2</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Sr</td>
<td>5</td>
<td>13</td>
<td>84</td>
</tr>
<tr>
<td>Tb</td>
<td>15</td>
<td>–</td>
<td>20</td>
</tr>
</tbody>
</table>

It should be noted that the degree of ionization will vary with the concentration of the analyte element. When using more concentrated solutions (as for example when operating on alternative wavelengths), ionization may not present a serious problem.

▼ Nebulizers

The nebulizer and glass bead can be set to achieve the desired analytical performance dictated by your sample type. For example, they may be set to achieve a high absorbance signal, or to accommodate high dissolved solids sample solutions. Refer to the appropriate Varian documentation for details. Organic solvents also have specific nebulizer requirements.
Organic solvents

(a) Adjustable nebulizer
When an organic solvent is analyzed by flame atomic absorption spectrometry, it effectively contributes extra fuel to the flame. It is recommended that an adjustable nebulizer is used for aspiration of organic solvents, and that the uptake rate be limited to about 1-2 mL/min depending upon the solvent.

(b) Spray chamber
When organic solvents are used regularly, it is recommended that the organic solvent spray chamber assembly is used. Refer to the latest Varian documentation for details.

Observe safety practices when using flammable organic solvents. Refer also to Varian instrument operation manuals.

Recommended instrument parameters

Working conditions (fixed)
The conditions listed will provide optimum performance for dilute aqueous solutions.

If chemical interference is known to be present then it may be necessary to use the hotter nitrous oxide-acetylene flame in order to eliminate interferences and obtain optimum conditions for precision and accuracy. With some elements, the flame stoichiometry can greatly affect the analytical signal. It is therefore desirable to examine the effect of flame conditions (or stoichiometry) on the signal. An oxidizing flame is one with low acetylene content, while a reducing flame has a relatively high acetylene content. Reducing flames become luminous due to the excess amount of carbon.

Working conditions (variable)
The upper limit of the working range concentration will give about 0.8 to 1.0 absorbance. The lower limit of the working range is about 10 times the defined detection limit. This range may be altered by burner rotation in order to avoid dilutions.

The alternative wavelengths shown have been selected to give a variety of working ranges. In some cases other analytical lines are available. However, the sensitivities are no better than the listed lines and the latter have been preferred because of the relatively better signal strength and spectral purity. The slit width indicates the spectral band width expressed in nanometers.

General references