# **Inductively Coupled Plasma Optical Emission Spectrometry**

# **Xiandeng Hou**

College of Chemistry, Sichuan University, Chengdu, China

# Renata S. Amais

Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba, Brazil

## Bradley T. Jones and George L. Donati

Wake Forest University, Winston-Salem, NC, USA

| 1 | Introduction |  |    |
|---|--------------|--|----|
| 2 | Theory       |  |    |
|   | 2.1          | Inductively Coupled Plasma Operation   | 2  |
|   | 2.2          | Inductively Coupled Plasma             |    |
|   |              | Characteristics                        | 3  |
| 3 | Sam          | ple Introduction                       | 4  |
|   | 3.1          | Nebulizers                             | 4  |
|   | 3.2          | Hydride Generation                     | 6  |
|   | 3.3          | Electrothermal Vaporization            | 7  |
|   | 3.4          | Chromatographic Couplers               | 8  |
| 4 | Tor          | ch Configuration                       | 8  |
|   | 4.1          | Radial View                            | 8  |
|   | 4.2          | Axial View                             | 9  |
|   | 4.3          | Dual View                              | 9  |
| 5 | Det          | ection of Emission                     | 10 |
|   | 5.1          | Gratings                               | 10 |
|   | 5.2          | The Photomultiplier Tube               | 12 |
|   | 5.3          | Array Detectors                        | 14 |
| 6 | Ana          | lytical Performance                    | 15 |
|   | 6.1          | Analytical Wavelength                  | 15 |
|   | 6.2          | Quantitative Methods                   | 15 |
|   | 6.3          | Analytical Figures of Merit            | 17 |
|   | 6.4          | Continuum Background and Interferences | 20 |
|   | Ack          | nowledgments                           | 21 |
|   | Abb          | previations and Acronyms               | 21 |
|   | Rela         | ated Articles                          | 22 |
|   | Ref          | erences                                | 22 |
|   | Furt         | ther Reading                           | 25 |
|   |              | 0                                      |    |

Inductively coupled plasma optical emission spectrometry (ICP OES) is a powerful tool for the determination of many elements in a variety of different sample matrices. With this method, liquid samples are injected into a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried, vaporized, and energized through collisional excitation at high temperature. The atomic emission emanating from the plasma is viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device. Single-element measurements can be performed costeffectively with a simple monochromator-photomultiplier tube (PMT) combination, and simultaneous multielement determinations are performed for up to 70 elements with the combination of a polychromator and an array detector. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regard to sample throughput and sensitivity.

# **1 INTRODUCTION**

ICP OES is one of the most powerful and popular analytical tools for the determination of trace elements in a myriad of sample types (Table 1). The term inductively coupled plasma atomic emission spectrometry (ICP AES) has also been used, but it is not recommended to prevent confusion with Auger electron spectroscopy (AES). The technique is based on the spontaneous emission of photons from atoms and ions that have been excited in a RF discharge. Liquid and gas samples may be injected directly into the instrument, while solid samples usually require extraction or acid digestion so that the analytes are present in a solution. The sample solution is converted to an aerosol and directed into the central channel of the plasma. At its core, the inductively coupled plasma (ICP) sustains a temperature of approximately 10000 K, so the aerosol is quickly vaporized. Analyte elements are liberated as free atoms in the gaseous state. Further collisional excitation within the plasma imparts additional energy to the atoms, promoting them to excited states. Sufficient energy is often available to convert the atoms to ions and subsequently promote the ions to excited states. Both the atomic and ionic excited state species may then relax to the ground state via the emission of a photon. These photons have characteristic energies that are determined by the quantized energy level structure for each type of atom or ion. Thus, the wavelength of the photons can be used to identify the elements from which they originated. The total number of photons is directly proportional to the concentration of the originating element in the sample.

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Table 1Survey of elemental application areas of ICP $OES^{(1-8)}$ 

| Categories                 | Examples of samples   |  |  |
|----------------------------|---|--|--|
| Agricultural<br>and food   | Animal tissues, beverages, feeds, fertilizers, garlic, nutrients, pesticides, plant materials, rice flour, soils, vegetables, and wheat flour   |  |  |
| Biological and clinical    | Brain tissue, blood, bone, bovine liver,<br>feces, fish, milk powder, orchard leaves,<br>pharmaceuticals, pollen, serum, and urine  |  |  |
| Geological                 | Coal, minerals, fossils, fossil fuel, ore, rocks, sediments, soils, and water   |  |  |
| Environmental<br>and water | Brines, coal fly ash, drinking water,<br>dust, mineral water, municipal wastewater,<br>plating bath, sewage sludge, slags, seawater,<br>and soil  |  |  |
| Metals                     | Alloys, aluminum, high-purity metals, iron, precious metals, solders, steel, and tin  |  |  |
| Organic                    | Adhesives, amino acids, antifreeze,<br>combustion materials, cosmetics, cotton<br>cellulose, dried wood, dyes, elastomers,<br>epoxy, lubricant, organometallic, organo-<br>phosphates, oils, organic solvent, polymers,<br>and sugars |  |  |
| Other<br>materials         | Acids, carbon, catalytic materials, elec-<br>tronics, fiber, film, packaging materials,<br>paints and coatings, phosphates, semicon-<br>ductors, and superconducting materials  |  |  |

The instrumentation associated with an ICP OES system is relatively simple. A portion of the photons emitted by the ICP is collected with a lens or a concave mirror. This focusing optics forms an image of the ICP on the entrance aperture of a wavelength selection device such as a monochromator. The particular wavelength of light exiting the monochromator is converted to an electrical signal by a photodetector. The signal is amplified and processed by the detector electronics, then displayed and stored by a personal computer.

The characteristics of the ICP as an analytical atomic emission source are so impressive that virtually all other emission sources (such as the flame, direct current plasma (DCP), laser-induced plasma (LIP), and electrical discharge) have been relegated to specific, narrowly defined application niches. Indeed, even much of the application field originally assigned to flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS) has been relinquished to the ICP. Compared to these other techniques, ICP OES enjoys a higher atomization temperature, a more inert environment, and the natural ability to provide simultaneous determinations for up to 70 elements. This makes the ICP less susceptible to matrix interferences, and better able to correct for them when they occur. In cases where sample volume is not limited, ICP OES provides limit of detection (LOD) comparable

to the ones obtained with its best competitor, GFAAS, for all but a few elements. Even for these elements, the simplicity with which the ICP OES instrument is operated often outweighs the loss in sensitivity.

## **2 THEORY**

The ICP was developed for optical emission spectrometry (OES) by Wendt and Fassel at Iowa State University in the United States, and by Greenfield et al. at Albright & Wilson, Ltd. in the United Kingdom in the mid-1960s.<sup>(1,9,10)</sup> The first commercially available ICP OES instrument was introduced in 1974. The ICP is now not only the most popular source for OES but also an excellent ion source for mass spectrometry: inductively coupled plasma mass spectrometry (ICP-MS).<sup>(11)</sup> ICP OES is a proven commercial success, and the future is still bright for ICP-based spectroscopic techniques. Detectability has been continuously and dramatically improved over the past 50 years. LODs, for example, have improved by a factor of four to six orders of magnitude for many elements. Nevertheless, research and commercial opportunities for further development of ICP OES remain active.<sup>(1,11–13)</sup>

#### 2.1 Inductively Coupled Plasma Operation

As shown in Figure 1, the so-called ICP torch is usually an assembly of three concentric fused-silica tubes. These are frequently referred to as the outer, intermediate, and inner gas tubes. The diameter of the outer tube ranges from 9 to 27 mm. A water-cooled, two- or three-turn copper coil, called the load coil, surrounds the end of the torch and is connected to an RF generator. The outer argon flow (*plasma gas*,  $10-20 \,\mathrm{Lmin}^{-1}$ ) sustains the hightemperature plasma and positions it relative to the torch outer walls and the induction coil, preventing the walls from melting and facilitating the observation of emission signals. Under these conditions, the plasma has an annular shape. The sample aerosol carried by the inner argon flow (*nebulization gas*,  $0.5-1.5 \,\mathrm{L\,min^{-1}}$ ) enters the torch central channel and helps to sustain the plasma shape. The intermediate argon flow (*auxiliary gas*,  $0-1.5 \,\mathrm{L\,min^{-1}}$ ) is optional and may serve the functions of diluting the inner gas flow in the presence of organic solvents, or pushing the plasma slightly away from the end of the central sample tube, improving the transference of energy from the plasma to the sample aerosol. The auxiliary gas plays an important role while running high total dissolved solid (TDS) samples and organic solvents. It prevents the deposition of salt and carbon particles on the torch and the preoptics.

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**Figure 1** Schematic diagram and actual photograph of an ICP assembly showing the three concentric tubes composing the torch, the RF coil, the different plasma regions, and the temperature as a function of distance from the load coil.

The ICP is generated as follows: RF power, typically 700-1500 W, is applied to the load coil and an alternating current oscillates inside the coil at a rate corresponding to the frequency of the RF generator. For most ICP OES instruments, the RF generator has a frequency of either 27 or 40 MHz. The oscillation of current at this high frequency causes the same high-frequency oscillation of electric and magnetic fields to be set up inside the top of the torch. With argon gas flowing through the torch, a spark from a Tesla coil is used to produce 'seed' electrons and ions in the argon gas inside the load coil region. These ions and electrons are then accelerated by the magnetic field and collide with other argon atoms, causing further ionization in a chain-reaction manner. This process continues until a very intense, brilliant white, teardrop-shaped, hightemperature plasma is formed. Adding energy to the plasma via RF-induced collisions is known as inductive coupling, and thus the plasma is called an ICP. The ICP is sustained within the torch as long as sufficient RF energy is applied.<sup>(1)</sup> In a cruder sense, the coupling of RF power to the plasma can be visualized as positively charged Ar ions in the plasma gas attempting to follow the negatively charged electrons flowing in the load coil (and the corresponding electric and magnetic fields), as the flow changes direction 27 (or 40) million times per second. The multitude of collisions produced in this environment gives rise to the energy transferred to the sample. No combustion reactions occur in the plasma, unless oxygen gas is introduced through the torch's intermediate channel to minimize matrix effects when analyzing high-carboncontent samples.(14)

Figure 1 shows the temperature gradient within the ICP with respect to distance from the load coil. It also gives the nomenclature for some of the different zones of the plasma as suggested by Koirtyohann et al.<sup>(15)</sup> The induction region (IR) encircled by the load coil is 'doughnut shaped' as described above, and it is the region where the inductive energy transfer occurs. This is also the region of highest temperature and it is characterized by a bright continuum emission. From the IR outward toward the tail plume, the temperature decreases. The continuum background radiation at the IR region is a result of three main processes: relaxation of excited molecular species in the plasma; electron-argon ion recombination reactions; and the Bremsstrahlung effect (electromagnetic radiation emitted when electrons are decelerated by the changing magnetic field).

An aerosol, or very fine mist of liquid droplets, is generated from a liquid sample by the use of a nebulizer. The aerosol is carried into the center of the plasma by the argon gas flow (nebulization gas) through the IR. To prevent large droplets from reaching the plasma and causing it to shut down due to decoupling, the fine mist generated by the nebulizer passes through a nebulization chamber. The aerosol then collides with the nebulization chamber walls and only the smallest of droplets continue onto the plasma, while the large ones fall into the drain. Upon entering the plasma, the droplets undergo three processes. The first step is desolvation or the removal of the solvent from the droplets, resulting in microscopic solid particulates, or a dry aerosol. The second step is vaporization or the decomposition of the particles into gaseous-state molecules. The third step is atomization or the breaking of the gaseous molecules into atoms. Finally, excitation and ionization of the atoms occur, followed by the emission of radiations from these excited species. The analytical signal is normally observed through an end-on (axial) viewing position.

#### 2.2 Inductively Coupled Plasma Characteristics

The main analytical advantages of the ICP over other excitation sources originate from its capability for efficient and reproducible vaporization, atomization, excitation, and ionization for a wide range of elements in various sample matrices. This is mainly due to the high temperature, 6000–8000 K, in the observation zones of the ICP, which is much higher than the maximum temperature of flames or furnaces (3300 K). The high temperature of the ICP also allows it to excite refractory elements and renders it less prone to matrix interferences. Other electrical-discharge-based sources, such as alternating current and direct current arcs and sparks, and the microwave-induced plasmas (MIP) also have high temperatures for excitation and ionization, but

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the ICP is typically less noisy and better able to handle liquid samples. In addition, the ICP is an electrodeless source, so there is no contamination from the impurities present in an electrode material. Furthermore, it is relatively easy to build an ICP assembly, and it is inexpensive when compared to some other sources such as a LIP. The following is a list of some of the most beneficial characteristics of the argon ICP source:

- high temperature (6000-8000 K),
- high electron density  $(10^{14} 10^{16} \text{ cm}^{-3})$ ,
- appreciable degree of ionization for many elements,
- simultaneous multielement capability (over 70 elements including P and S),
- low background emission and relatively low chemical interference,
- high stability leading to excellent accuracy and precision,
- excellent LODs for most elements  $(0.1-300 \,\mu g \, L^{-1})$ ,<sup>(16)</sup>
- wide linear dynamic range (LDR) (four to six orders of magnitude),
- applicable to refractory elements, and
- cost-effective analyses.

The majority of ICP OES routine applications utilize argon as the plasma gas. However, there are several interesting applications of mixed-gas plasmas, and even complete replacement of argon to improve the analytical figures of merit. The addition of other gases (e.g. H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, halocarbon gases, He, and other noble gases) to the composition of the auxiliary gas or the nebulization gas can improve plasma characteristics such as thermal conductivity, electron number density, and plasma temperature. Such modifications can facilitate the atomization, ionization, and excitation of elements with high excitation and ionization energies (e.g. F, Cl, Br, I, As, Se, P, and S) and enable the analysis of slurries. Even small amounts of He or O<sub>2</sub> added to the composition of plasma gas (5%) can generate significantly more energetic conditions, resulting in potentially fewer matrix effects. Temperatures and electron number densities tend to be higher for an O<sub>2</sub>-Ar plasma when compared to a conventional all-Ar plasma. For high-carbon matrices and organic solvent mixtures, adding O<sub>2</sub> to the plasma can prevent the deposition of carbon on the torch and reduce background emissions due to CN and C<sub>2</sub> bands. The main drawbacks for using mixed-gas or alternative-gas plasmas are the required modifications in the torch and/or other parts of the instrumentation, the introduction of new potential interferences, and the additional running costs associated with using different gases and mixtures.<sup>(17,18)</sup>

#### **3** SAMPLE INTRODUCTION

An introduction system is used to transport a sample into the central channel of the ICP as a gas, vapor, aerosol of fine droplets, or solid particles. The general requirements for an ideal sample introduction system include amenity to samples in all phases (solid, liquid, or gas), tolerance to complex matrices, the ability to analyze very small amounts (<1 mL or <50 mg), excellent stability and reproducibility, high transport efficiency, simplicity, and low cost.<sup>(2)</sup> A wide variety of sample introduction methods have been developed, such as nebulization, hydride generation (HG), electrothermal vaporization (ETV), laser ablation (LA), and direct sample insertion (DSI).<sup>(1,19–25)</sup> The analysis of liquid microsamples, at flow rates less than 0.1 mL min<sup>-1</sup>, is also possible.<sup>(26,27)</sup> The most popular sample introduction methods are described below.

#### 3.1 Nebulizers

Nebulizers are the most commonly used devices for solution sample introduction in ICP OES. With a nebulizer, the liquid sample is converted into an aerosol and transported to the plasma. Both pneumatic nebulizers (PNs) and ultrasonic nebulizers (USNs) have been successfully used in ICP OES. PNs make use of highspeed gas flows to create an aerosol, while the USN breaks liquid samples into a fine aerosol by the ultrasonic oscillations of a piezoelectric crystal. The formation of aerosol by the USN is therefore independent of the gas flow rate.

Only very fine droplets (about 8µm in diameter) in the aerosol are suitable for injection into the plasma. A spray chamber is placed between the nebulizer and the ICP torch to remove large droplets from the aerosol and to dampen pulses that may occur during nebulization. Thermally stabilized spray chambers are sometimes adopted to decrease the amount of liquid introduced into the plasma, thus providing stability especially when organic solvents are involved. Because of this strict droplet size selection, pneumatic nebulization becomes a very inefficient process. Only a very small fraction (less than 5%) of the aspirated sample solution actually reaches the plasma, and most of the liquid is lost down the drain in the spray chamber. Despite its drawbacks, PN retains its popularity owing to its convenience, reasonable stability, and ease of use. Efficiency may only be a concern when sample volumes are limited or measurements must be performed at or near the LOD.

Three types of PNs are commonly employed in ICP OES: the concentric nebulizer, the cross-flow nebulizer, and the Babington nebulizer (Figure 2). The concentric nebulizer is designed from fused silica. The sample

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**Figure 2** Schematic diagrams of three types of pneumatic nebulizer: (a) the concentric nebulizer; (b) the cross-flow nebulizer; and (c) the Babington nebulizer.

solution is pumped into the back end of the nebulizer by a peristaltic pump. Liquid uptake rates may be as high as 4 mL min<sup>-1</sup>, but lower flows are more common. The sample solution flows through the inner capillary of the nebulizer. This capillary is tapered so that flexible tubing from the pump is attached at the entrance (4mm outer diameter). The exit has a narrow orifice approaching 100 µm or less in inner diameter. Ar gas  $(0.5-1.5 \,\mathrm{L\,min^{-1}})$  is supplied at a right angle into the nebulizer outer tube. This tube is also tapered so that the exit internal diameter approaches the outer diameter for the sample capillary. As the Ar gas passes through this narrow orifice, its velocity is greatly increased (Venturi effect), resulting in the shearing of the sample stream into tiny droplets (Figure 2a). Concentric nebulizers have the advantages of excellent sensitivity and stability, but the small fragile fused-silica orifices are prone to clogging, especially when aspirating samples of high-salt content. Concentric nebulizers also require a fairly large volume of sample, given the high uptake rate. The microconcentric nebulizer (MCN) is designed to solve this problem. The sample uptake rate for the MCN is less than  $0.1 \text{ mL min}^{-1}$ . The compact MCN employs a smaller diameter capillary (polyimide or Teflon) and poly(vinylidene difluoride) body to minimize the formation of large droplets and to facilitate the use of hydrofluoric acid.

A second type of PN, the cross-flow nebulizer, is designed to reduce the clogging problem. In contrast to concentric nebulizers, cross-flow nebulizers use a highspeed stream of argon perpendicular to the tip of the sample capillary. Again, the sample solution is broken into an aerosol, as shown in Figure 2(b). The drawbacks



Figure 3 The Hildebrand grid nebulizer (HGN).

of the cross-flow nebulizer include lower sensitivity and potential capillary misalignment.

The third type of PN used for ICP OES is the Babington nebulizer, which allows a film of the sample solution to flow over a smooth surface containing a small orifice (Figure 2c).<sup>(28)</sup> High-speed argon gas emanating from the orifice shears the sheet of liquid into small droplets. In some cases, the liquid may be guided over the argon orifice by positioning both the orifice and the sample introduction port at the base of a V-shaped groove (Vgroove nebulizer). The essential feature of the Babington nebulizer is that the sample solution flows freely over a small aperture, rather than passing through a fine capillary, resulting in a high tolerance to dissolved solids. In fact, even slurries can be nebulized with a Babington nebulizer.<sup>(29)</sup> This type of nebulizer is the least susceptible to clogging and it can nebulize very viscous liquids.

The Hildebrand grid nebulizer (HGN) (Figure 3) may be considered a specialized version of the Babington nebulizer with many orifices. Often the nebulizer has a screw-cap design. The outer member (cap) of the nebulizer holds two parallel platinum screens or grids. The grids are separated by approximately 2mm. The inner body of the nebulizer (screw) has a single sample channel. Liquid is pumped through this channel at rates up to 1 mLmin<sup>-1</sup>. The inner body also has a circular V-groove that allows the liquid to contact the entire perimeter of the inner platinum grid. In this manner, the liquid completely wets both grids. A high-velocity stream of argon  $(1 \text{ Lmin}^{-1})$  blows through the center of the nebulizer. Often the velocity of the argon is increased by placing a sapphire crystal containing a small orifice (0.2 mm) in the center of the gas stream. The highvelocity argon forces the liquid through the tiny openings in the screens producing a fine aerosol. The HGN is characterized by clog-free operation, high efficiency, and excellent stability.

Another PN alternative to minimize clogging and improve sensitivity is based on *Flow Blurring*<sup>®</sup> hydrodynamics.<sup>(30)</sup> In these devices, similar to a concentric nebulizer, the sample solution is pumped into the

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**Figure 4** Flow Blurring<sup>®</sup> nebulizer: (a) cross-sectional diagram of the nozzle geometry, where *H* is the distance between the end of the solution capillary and the external nebulizer tube and *D* is the diameter of the exit orifice; (b) back-flow mixing region when  $\psi = 0.2$ . (Reproduced with permission from A.M. Gañán-Calvo, *Appl. Phys. Lett.*, **86**, 214101 (2005) http://dx.doi.org/10.1063/1.1931057 © 2005, AIP Publishing LLC.)

back end of the nebulizer by a peristaltic pump, and the nebulization gas is introduced perpendicularly to the liquid flow (Figure 4a). However, while nebulization in a concentric nebulizer relies on the Venturi effect, Flow Blurring<sup>®</sup> nebulizers provide a fine aerosol, with a particularly narrow-sized droplet distribution, owing to the turbulent and extremely efficient micromixing between nebulization gas and sample solution. This is achieved by forcing the nebulization gas to flow upstream into the incoming liquid solution (Figure 4b), when  $\psi < 0.25$  $(\psi = H/D)$ , where H is the distance between the end of the solution capillary and the external nebulizer tube and D is the diameter of the exit orifice). An interesting application of the Flow Blurring® technology is the possibility of developing multinebulizer systems.<sup>(31)</sup> The use of a multiple nozzle device allows for the simultaneous nebulization of different solutions (e.g. sample, standards, internal standards [ISs], and other reagents), which can enable online calibration, matrix matching, HG, and other 'in chamber' sample preparation procedures.

With the USN, sample solution is first introduced onto the surface of a piezoelectric transducer that is operated at a frequency between 0.2 and 10 MHz. The longitudinal wave, which propagates perpendicularly to the surface of the transducer toward the liquid-air interface, produces pressure that breaks the liquid into an aerosol.<sup>(32,33)</sup> The efficiency of an USN is typically between 10% and 20%. This nebulizing efficiency is greater than that of a PN, and it is independent of argon flow rate. Therefore, a slower gas flow rate can be used to transport the aerosol to the plasma, thus prolonging the residence time of the analyte in the plasma. This can result in improved sensitivity, and LODs may be lowered by a factor of 8–200, depending on the element. However, the USN is more complicated and expensive, and more susceptible to high solid loading and matrix and memory effects. The USN is not compatible with hydrofluoric acid.

While the efficiency of each type of nebulizer depends on the specific ICP OES instrument employed (and its power, gas, and flow parameters), some comparisons are possible. Table 2 compares the relative magnitude of LODs observed for 11 elements using four different nebulizers. As the USN provides the lowest LOD in each case, its value is set to 1, and the other LODs are higher by the factor listed in Table 2. Using these 11 elements as representative cases, on an average, LODs follow the trend USN < HGN < concentric < V-groove.<sup>(3,34)</sup> Various other means of nebulization have been tested with limited degrees of success.<sup>(32)</sup>

#### 3.2 Hydride Generation

HG is a very effective sample introduction technique for some elements. These elements include arsenic, bismuth, germanium, lead, antimony, selenium, tin, and tellurium. In this method, the sample in diluted acid solution is mixed with a reducing agent, usually a solution of sodium borohydride in dilute sodium hydroxide. The reaction of sodium borohydride with the acid produces hydrogen. The hydrogen then reduces the analyte metal ions to hydrides, which are gaseous at ambient temperature. The chemical reactions are shown in Equations (1) and (2).

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H \quad (1)$$

$$E^{m+} + (m+n) \operatorname{H} \to \operatorname{EH}_n + \operatorname{mH}^+$$
(2)

where *E* is the hydride-forming element of interest.

The advantages of the HG technique include the following:

• physical separation of the analyte from possible matrix interfering concomitants;

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| Element | Wavelength (nm) | USN <sup>a</sup> | HGN | Concentric | V-groove |
|---------|-----------------|------------------|-----|------------|----------|
| Ag      | 328.1           | 1                | 9   | 9          | 17       |
| Al      | 396.2           | 1                | 3   | 10         | 14       |
| As      | 193.7           | 1                | 6   | 4          | 8        |
| Cd      | 226.5           | 1                | 2   | 8          | 19       |
| Со      | 228.6           | 1                | 3   | 6          | 11       |
| Cr      | 267.7           | 1                | 3   | 7          | 11       |
| Cu      | 324.8           | 1                | 4   | 12         | 25       |
| Mn      | 267.6           | 1                | 7   | 8          | 12       |
| Ni      | 231.6           | 1                | 2   | 3          | 6        |
| Pb      | 220.4           | 1                | 7   | 5          | 9        |
| Zn      | 213.9           | 1                | 4   | 6          | 8        |
| Average |                 | 1                | 5   | 7          | 13       |

**Table 2** Relative ICP OES LODs observed using different nebulizers<sup>(3,34)</sup>

<sup>a</sup>The relative LOD is the ratio of the LOD using a given nebulizer to the LOD for the USN.

- higher efficiency than conventional pneumatic nebulization;
- preconcentration of the analyte for better LODs;
- capability for inorganic and/or organic speciation; and
- ease of automation when used with flow injection techniques.

On the other hand, several disadvantages of this technique may include the following:

- interference from those contaminants that reduce HG efficiency;
- slow reactions, necessitating hydride trapping before introduction;
- critical control of experimental conditions such as pH and reagent concentrations; and
- extra influential factors, such as the oxidation state of the analyte of interest.

Table 3 shows a comparison of LODs for the hydridegenerating elements determined by ICP OES using HG or conventional nebulization techniques. The values for HG-ICP OES in Table 3 are the best LODs cited in Nakahara's review paper.<sup>(19)</sup> Compared with conventional pneumatic nebulization techniques, LODs achieved by the HG technique are enhanced by a factor between 10 and 1000, depending on the element.

## 3.3 Electrothermal Vaporization

ETV has also been used to solve problems associated with pneumatic nebulization. Graphite furnaces or other electrothermal devices, such as carbon rods, carbon cups, graphite boats, graphite tubes, tungsten coils, and other metal filaments, have been used in research laboratories to electrothermally vaporize a liquid or solid sample for introduction into the ICP.<sup>(20,21,35–37)</sup> Other vaporization methods, such as arc/spark vaporization and

**Table 3**LODs observed by hydride generation, HG-ICP $OES^{(1,19)}$ 

| Elements | $\begin{array}{c} LOD \\ by HG \\ (\mu g L^{-1}) \end{array}$ | LOD by<br>conventional<br>nebulization<br>$(\mu g L^{-1})$ | Ratios<br>(conventional/<br>HG) |
|----------|---|--|---------------------------------|
| As       | 0.03  | 20   | 667                             |
| Bi       | 0.06  | 20   | 333                             |
| Ge       | 0.3   | 20   | 67                              |
| Pb       | 1.0   | 10   | 10                              |
| Sb       | 0.07  | 10   | 143                             |
| Se       | 0.04  | 50   | 1250                            |
| Sn       | 0.2   | 30   | 150                             |
| Те       | 0.04  | 10   | 250                             |

LA/vaporization, have also been used as a means for sample introduction in ICP OES. Even the ICP itself has been used to vaporize samples into a second ICP for analytical measurements.<sup>(38)</sup> In a typical experiment, a low current is applied to the ETV to remove the sample solvent. A small portion of the sample is then vaporized by the device through the application of a high current. An optional 'ash' step may be used to remove some of the matrix before the analyte vaporization step. The resulting dense cloud of the analyte vapor is then efficiently swept into the center of the plasma by a flow of argon gas.

A commercial graphite furnace designed for atomic absorption spectrometry (AAS) is most frequently used in ETV-ICP OES. The major advantage of ETV as a means of sample introduction is that the transportation efficiency is dramatically improved over a PN, from less than 5% to over 60%. Consequently, the LODs are improved by at least an order of magnitude. Some difficult-to-analyze samples, those with high TDSs, for example, can be introduced by the ETV. However, as these devices are generally not of a continuousflow nature, the ICP instrument has to be capable of

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recording transient signals. In addition, the simultaneous multielement capability of the system could be limited owing to this transient nature of signals. Furthermore, when graphite material is used for the ETV, carbide formation could be a problem for some elements, resulting in lowered sensitivity and memory effects for refractory elements.

In an attempt to eliminate the problems associated with graphite, metal filaments have been employed for ETV-ICP OES. For example, a tungsten coil from a commercial slide projector bulb can be used to vaporize liquid samples before their introduction into the ICP.<sup>(35,39)</sup> A small volume, typically  $10-20\,\mu$ L, of sample solution is delivered to the tungsten coil and dried at low current. Then, a higher current is applied to atomize the sample from the coil. The vapor is then rapidly introduced into the plasma as a dense plug by a flow of argon/hydrogen gas. The LODs are typically improved by 100–1500 times compared with pneumatic nebulization. These LODs are comparable to those obtained by GFAAS, but with the capability of simultaneous multielement measurement and at a low cost. A tungsten loop has also been used as an in-torch vaporization (ITV) means for sample introduction to the ICP, and the operation can possibly be automated.<sup>(20)</sup> These approaches still share some of the other disadvantages associated with graphite furnace ETV, and commercial systems have not yet appeared.

#### 3.4 Chromatographic Couplers

The combination of the separation power of chromatography and the detection power of atomic emission spectroscopy results in many advantages. One of the primary advantages of chromatography over conventional sample introduction is the ability to obtain speciation information.<sup>(40,41)</sup> When used as a detector for chromatographic methods, the ICP offers good sensitivity, wide LDR, and multielement detection capability. The multielement capability of the ICP, in turn, enhances the performance of chromatographic methods. Both gas chromatography (GC) and high-performance liquid chromatography (HPLC) can be coupled with ICP OES.<sup>(42-46)</sup> Compared with HPLC, however, the GC-ICP coupling is less common because the analytical performance of ICP OES is often not adequate for the typical non-metalcontaining analytes separated by GC. Undoubtedly, GC-ICP OES is still useful in the analyses of volatile organometallics, as demonstrated in the determination of methylmercury species.<sup>(47)</sup> The successful combination of these two techniques is realized through the use of chromatographic couplers. Fortunately, most of the interface systems currently in use are relatively inexpensive and easy to construct, and they require few, if any, modifications to commercial ICP OES instruments.

Direct connections between the end of the HPLC column and the nebulizer suffer from poor transport efficiency and low tolerance to many of the organic solvents commonly employed in mobile phases for HPLC, particularly when a PN is used. To improve the transport efficiency and to minimize the influence of organic solvents on the stability of the ICP, USNs, water-cooled thermospray chambers, and glass-frit nebulizers have been utilized for sample introduction in HPLC-ICP OES. The solvent load on the plasma can also be decreased by aerosol thermostating, by adding oxygen gas into the plasma composition, increasing the incident RF power, using a condenser, or using a micro-HPLC column.

Other major sample introduction methods, such as thermospray, DSI, and LA, have also been used for ICP OES.<sup>(22,23,48–52)</sup> Each of these has its advantages and disadvantages. For example, LA can be used to vaporize any solid sample into the ICP.<sup>(22,53,54)</sup> In this case, no sample preparation is required, which usually results in improved LODs. On the other hand, LA generally has poor reproducibility, relatively high cost, and issues associated with calibration.

## **4 TORCH CONFIGURATION**

The atomic emission from the plasma, as shown in Figure 1, is sampled for spectrometric measurements. Two configurations may be employed for observing emission from the ICP. One is referred to as a *radial* or *side-on viewing of the plasma* and the other is known as an *axial* or *end-on viewing of the plasma* (Figure 1). A third viewing mode is the combination of these two basic modes and is known as *dual view*. These are all commercially available, and each of them has advantages and disadvantages.

## 4.1 Radial View

The radial view is the classical operation mode for ICP OES. With radial viewing, the plasma is operated in a vertical orientation, and the analytical zone is observed from the side of the plasma. This mimics the classical viewing orientation for atomic emission from a flame. Radial viewing constrains the observation volume to the distance through the diameter of the plasma. As this path length is limited, sensitivity is also limited, and so are the effects of potential spectral and background interferences. The radial view orientations than the axial view orientation, which results in improved analytical precision. The radial view also suffers from less matrix effects, as analytical signals from specific optimal regions of the plasma can be collected.

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#### 4.2 Axial View

With the axial view, the emission signal is observed from the end of the plasma (usually in a horizontal position). The axial view provides better LODs than the radial view.<sup>(55)</sup> This may be attributed to the longer viewing path available down the axis of the plasma. Thus, a better sensitivity and a 5- to 10-fold improvement in the LODs can be achieved. The disadvantages of the axial view include the increased potential for spectral interference and matrix-induced interferences. Moreover, self-absorption effects can be quite severe because the observations are made through the much cooler tail plume of the plasma. These effects can be significantly reduced by use of a shear gas,<sup>(56)</sup> or an appropriate cooled-cone optical interface, which displaces the tail plume from the optical path, thus reducing the self-absorption (Figure 1). However, both strategies present disadvantages associated to the additional consumption of gas or the reduced capacity of handling samples with high amounts of dissolved (or suspended) solids. On the other hand, spectral

interferences may be either corrected or minimized by improving spectral resolution, using an alternate analytical line with less or no interference, or by applying an interelement correction (IEC) factor.<sup>(1)</sup>

#### 4.3 Dual View

In cases of very complicated sample matrices having a wide range of elemental concentrations, the axial view may be inadequate. Several commercial instruments combine the axial and radial view configurations into a single unit, known as *dual view*. This dual view system allows the user to optimize the appropriate configuration for the type of sample without the expense of two separate ICP OES systems.<sup>(1)</sup> Dual view instruments are usually built to be either axially or radially-optimized, with the other plasma view orientation working at a compromise condition. In any case, reflective surfaces or periscopes are required to enable signal collection from both view orientations.<sup>(12)</sup> Conventional dual view instruments require at least two sequential readings of the sample to cover both axial and radial plasma views. Depending on



**Figure 5** Schematic diagram of the synchronous vertical dual view configuration. Emitted radiations from axial and radial plasma views synchronously converge onto the dichroic spectral combiner and are transmitted to the polychromator. (Reproduced with permission from Ref. 57. O Agilent Technologies<sup>®</sup>, 2014.)

*Encyclopedia of Analytical Chemistry*, Online © 2006–2016 John Wiley & Sons, Ltd. This article is © 2016 John Wiley & Sons, Ltd. This article was published in the *Encyclopedia of Analytical Chemistry* in 2016 by John Wiley & Sons, Ltd. DOI: 10.1002/9780470027318.a5110.pub3 the instrument design, up to four readings are necessary, which deteriorates the analytical throughput.

Alternatively, a dichroic spectral combiner can be used to select and combine radiations from both views, allowing specific emission wavelengths to be reflected and transmitted to the detector.<sup>(57)</sup> The synchronous vertical dual view configuration (Figure 5) allows for the determination of elements at high concentration levels (e.g. macronutrients) simultaneously to those at trace levels. The simultaneous acquisition enables faster analysis and less consumption of argon than other dual view configurations.

## **5 DETECTION OF EMISSION**

#### 5.1 Gratings

ICP OES is characterized by remarkably rich spectra. For example, the 70 elements most commonly determined by the method give rise to at least 70000 total emission lines in the 200- to 600-nm wavelength range. A consequence of this high density of spectral information is the need for high resolving power. The low-resolution dispersive systems typically employed with atomic absorption spectrometers will not suffice. Spectral interferences occur in this case even if only a small number of concomitant elements are present at moderate concentrations in the sample. Much higher resolution is desirable in ICP OES, with spectral bandpass ( $\Delta \lambda_s$ ) of 0.01 nm or lower, if possible. Traditionally, this degree of resolution has been accomplished using plane grating monochromators with large focal lengths (f=0.5 m or more).

Figure 6 depicts a plane-ruled grating. The normal to the grating surface (N) is shown as a dashed line. A light ray incident to the grating approaches at angle  $\alpha$ , measured with respect to N. The diffracted ray leaves the grating surface at angle  $\beta$ . Parallel rays striking the grating on different adjacent groove facets travel a different distance before reaching a common position beyond the grating. If the difference in distance traveled is a multiple of the wavelength of the light ( $\lambda$ ) incident upon the grating surface, then the rays undergo constructive interference. Otherwise, destructive interference occurs. Relatively simple geometrical considerations result in the grating formula shown in Equation (3):

$$d(\sin \alpha + \sin \beta) = m\lambda \tag{3}$$

Equation (3) shows the relationship between  $\alpha$ ,  $\beta$ , the groove spacing (*d*), the wavelength of light ( $\lambda$ ), and the order of diffraction (*m*). The order of diffraction may take any integer value including zero. At zero order,



**Figure 6** Diagram of the plane-ruled grating. *N* is the normal to the grating surface,  $\alpha$  the angle of incidence measured with respect to *N*,  $\beta$  the angle of diffraction measured with respect to *N*, and *d* the width of a single groove.

all wavelengths undergo constructive interference at the same diffraction angle, and the grating works as a mirror. In the first order, one particular wavelength undergoes constructive interference at the angle  $\beta$ , which corresponds to the specular reflection angle for rays incident at angle  $\alpha$ . This wavelength is called the *blaze wavelength* for the grating, and it is determined by the angle at which the grooves are cut with respect to the surface of the grating. A grating is most efficient at its blaze wavelength. Typically, a grating may have efficiency as high as 70% at its blaze wavelength is 70% of the intensity that would be measured at the specular reflectance angle for a polished mirror of the same coating and material as the grating.

Normally, when a plane grating is employed, the angle of incidence is nearly 0, so  $\sin \alpha$  approaches 0. In this case, the grating formula may be further reduced, as shown in Equation (4):

$$\sin \beta = \frac{m\lambda}{d} \tag{4}$$

The angular dispersion of the grating  $(d\beta/d\lambda)$  may be found, as shown in Equations (5) and (6), by taking the derivative of both sides of the above equation with respect to  $\lambda$ :

$$(\cos\beta)\frac{\mathrm{d}\beta}{\mathrm{d}\lambda} = \frac{m}{d} \tag{5}$$

$$\frac{\mathrm{d}\beta}{\mathrm{d}\lambda} = \frac{m}{\mathrm{d}\cos\beta} \tag{6}$$

The angular dispersion, therefore, increases with larger order, smaller groove spacing, or larger  $\beta$ . Angular dispersion may be converted to linear dispersion along

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the exit focal plane of the monochromator by simply multiplying by the focal length (f) of the monochromator. The spectral bandpass  $(\Delta \lambda_s)$  in wavelength units is then determined by dividing the slit width of the monochromator by the linear dispersion. So  $\Delta \lambda_s$  gets smaller (higher resolution) for larger f, larger order, larger  $\beta$ , smaller d, and smaller slit width. A typical plane grating is operated in the first order. The groove density of the grating might be as high as  $3600 \,\mathrm{grooves}\,\mathrm{mm}^{-1}$ , so the groove spacing (d) might be as small as 0.0003 mm. Therefore, assuming  $\beta$  is 45° and the slit width is  $25 \,\mu$ m, a monochromator with a focal length of 500 mm provides a spectral bandpass of 0.01 nm. Such a system effectively isolates most ICP emission lines. However, simultaneous multielement determinations are not performed effectively with such a system. The focal plane for this type of monochromator is 5-cm long at best, so the entire spectral window is approximately 20 nm in width. Unless the analytes of interest exhibit emission lines within 20 nm of one another, the wavelength must be scanned to detect multiple elements. So, two other optical approaches have become more popular for simultaneous determinations: the concave grating placed on a Rowland circle and the echelle grating coupled with a prism ordersorting device.

Shortly after designing his grating ruling engine in 1881, Rowland first conceived the idea of ruling gratings on a spherical mirror of speculum metal.<sup>(58)</sup> The most important property of such a concave grating was also observed by Rowland. If the source of light and the grating are placed on the circumference of a circle, and the circle has a diameter equal to the radius of curvature of the grating, then the spectrum is always brought to a focus on the circle. Hence, the focal 'plane' is curved and of considerable length (Figure 7). In this case, one entrance slit is placed on the circle for introduction of the source radiation, and multiple exit slits may be placed around the circle at the analytical wavelengths of interest. Thus, Rowland's circle is ideally suited for multielement ICP emission spectrometry. A further advantage of the Rowland geometry is the elimination of the need for any collimating or focusing lenses or mirrors. A Rowland circle spectrometer with the same groove density, slit width, and focal length as the plane grating system described above provides similar spectral bandpass but with a much larger spectral window.

The Paschen-Runge arrangement shown in Figure 7 is the basis of the commercial *optimized Rowland circle alignment* (ORCA) system. The configuration, with 32 line array detectors, a sealed polychromator filled with Ar, and no focusing lenses, mirrors, or prisms, allows for low stray light levels, high resolution and high sensitivity in the UV and vacuum ultraviolet (VUV) region. The ORCA system has a larger footprint than traditional



**Figure 7** The Paschen-Runge mounting of a concave grating on a Rowland circle. The grating, entrance slit, and focused images of the diffracted wavelengths are all positioned on the perimeter of the circle. *N* is the grating normal.

echelle-based instruments. On the other hand, it provides uniform resolution over a wide spectral region.<sup>(13)</sup>

A second approach to carrying out high-resolution, multielement determinations is based on the echelle grating, which is a coarsely ruled grating, typically having a groove density of 70 grooves mm<sup>-1</sup>, so d = 0.014 mm. The increase in spectral bandpass due to the increase in dis overcome by operating the grating in higher orders (m=25-125) and using steeper angles of diffraction  $(\beta > 45^{\circ})$ . Figure 8 demonstrates how the steeper sides of the groove facets are used with the echelle grating. If the steep sides of the grooves are blazed such that specular reflectance occurs when  $\alpha = 60^{\circ}$  and  $\beta = 50^{\circ}$ , then each wavelength exhibits a peak in grating efficiency at a particular order as determined by the grating formula. For example, for the 70 grooves  $mm^{-1}$  grating described above, the order of maximum efficiency  $(m_{\text{max}})$  occurs as shown in Table 4. The efficiency of the grating for a given wavelength at its optimum order can be as high as 65%. This level of efficiency is typically attained across the free spectral range for a given order. The free spectral range  $(\Delta \lambda_f)$  is defined as the range of wavelengths over which no overlap from adjacent orders occurs and is given by Equation (7):

$$\Delta\lambda_{\rm f} = \frac{\lambda}{m+1} \tag{7}$$

As indicated in Table 4,  $\Delta \lambda_f$  is very small for large values of *m*. Obviously, then, severe spectral overlap occurs with an echelle grating. The overlap does not simply involve adjacent orders, but all orders

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**Figure 8** Diagram of the echelle grating. *N* is the normal to the grating surface,  $\alpha$  the angle of incidence measured with respect to *N*, and  $\beta$  the angle of diffraction measured with respect to *N*. The light is incident to the steeper sides of the groove facets and approaches the grating at nearly grazing angles (62°); *d* is the width of a single groove.

**Table 4** The order of maximum efficiency and the free spectral range at that order for an echelle grating having 70 grooves mm<sup>-1</sup>, angle of incidence ( $\alpha$ ) of 60°, and blaze angle ( $\beta$ ) of 50°

| $\lambda$ (nm) | $m_{\rm max}$ | $\Delta\lambda_{f}\left(nm\right)$ |
|----------------|---------------|------------------------------------|
| 200            | 117           | 1.7                                |
| 250            | 93            | 2.7                                |
| 300            | 78            | 3.8                                |
| 350            | 67            | 5.2                                |
| 400            | 58            | 6.7                                |

are dispersed in multiple layers along the same focal plane. This overlap is corrected most often with an order-sorting prism. This prism is placed between the echelle grating and the focal plane (Figure 9). The prism is positioned so that it disperses the light in a direction perpendicular to the direction of dispersion of the grating. As a result, the focal plane has wavelength dispersed in the horizontal direction and order sorted in the vertical direction. The free spectral range (and the region of maximum efficiency) has a roughly triangular shape centered horizontally on the plane (Figure 10). An echelle spectrograph often provides a spectral bandpass nearly 10 times smaller than that of a typical grating monochromator with a similar focal length. In addition, the echelle system provides high efficiency at many wavelengths rather than a single blaze wavelength. Finally, both the high efficiency and superior resolution are available over a very broad spectral window. As



**Figure 9** Schematic diagram of an echelle spectrograph. (Adapted from the schematic diagram of the Prodigy ICP provided by Teledyne Leeman Labs, Inc., Hudson, NH.)

a result, the echelle configuration is the predominant optical arrangement in modern ICP OES instruments.<sup>(59)</sup>

Oxygen gas strongly absorbs radiation in the VUV (100-200 nm) region of the electromagnetic spectrum. Elements such as As, Br, C, Cl, P, and S present strong emission lines in this region and almost no analytically significant emission line above 200 nm. Thus, to enable detections of these analytes in normal atmospheric air conditions, the entire path length from the plasma to the detector is purged with an inert gas. The most common choices are N<sub>2</sub> and Ar, which depend not only on the analytical performance but also on the cost. The optics can also be evacuated, which is more expensive and can negatively affect the price of the instrument.<sup>(60)</sup> An alternative is to seal the entire polychromator and fill it with Ar, as in the previously described ORCA system.<sup>(13)</sup>

#### 5.2 The Photomultiplier Tube

Figure 11 is a schematic representation of the PMT. Like its predecessor, the vacuum phototube, the heart of the PMT consists of two electrodes sealed in a fused-silica envelope. The cathode has a relatively large surface area, usually in the shape of a vertical, hollow 'half cylinder'. The cathode is made from a photoemissive material such as an alkali metal oxide. The anode is simply an electron collection wire or grid. Unlike the phototube, however, the PMT has up to 14 secondary emission dynodes placed between the cathode and the anode. Typically, the anode is fixed to the ground potential and the dynodes are at potentials that are successively more negative, by about 100 V/dynode. The potential of the cathode is typically -1000 V.

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**Figure 10** Diagram representing the two-dimensional focal plane provided by the echelle spectrograph (a). The triangle-shaped free spectral range is the region of highest grating efficiency. The distance between adjacent vertical lines is 1 nm, and the beginning ( $\lambda_1$ ) and ending ( $\lambda_2$ ) wavelengths depicted by the lines are listed for each order. Only 1 out of every 10 orders is shown for clarity. An actual negative image collected during the aspiration of tap water (b) shows atomic emission lines as dark spots against a white background. Close inspection reveals the different orders as faint horizontal lines across the image, with the roughly triangular shape of the free spectral range. An image for distilled-deionized water (c) may be subtracted from the tap water image resulting in a background-subtracted image (d). The region of interest may be enlarged so that emission lines from Ca, Mg, and Si in the tap water may be identified (e).

A photon generated in the ICP and passing through the wavelength selection device may pass through the fusedsilica envelope of the PMT, through a baffle-type grill, and strike the photocathode. If the energy of the photon is higher than the work function of the photocathode material, then an electron may be ejected from the cathode (photoelectric effect). The fraction of photons with energy greater than the work function that actually produce a photoelectron is called the *quantum efficiency of the photocathode*. The quantum efficiency may be as high as 0.5, and it depends on the photocathode material and the wavelength. A plot of quantum efficiency versus wavelength is called the *spectral response curve* for the



**Figure 11** Cross-sectional and front views of a side-on PMT. In the cross section, two types of dynodes are depicted: curved (outer) and flat (inner). The outside surfaces of the curved dynodes are seen in the front view.

PMT. The spectral response curve is usually supplied by the manufacturer.

Once an electron has been ejected by the photocathode, it is accelerated toward the first dynode. Upon impact, the first dynode releases x secondary electrons (where x is typically between 2 and 5). This process continues at each dynode, with each electron impact imparting xnew secondary electrons. So, by the time that the pulse generated by a single photon reaches the anode it has been greatly multiplied, and hence the name *multiplier phototube* or *PMT*. The gain, *G*, for a PMT can be defined as shown in Equation (8):

$$G = x^n \tag{8}$$

where *n* is the number of dynodes. The gain depends on the voltage across the PMT and it may be as high as  $10^8$ . One of the best features of the PMT is that the gain is acquired with almost no increase in noise. Thus, the PMT is ideally suited for the detection of small analytical signals against a relatively dark background, as is the case near the LOD in high-resolution atomic emission spectrometry.

Usually the *entrance aperture*, as defined by the grill on the PMT, is very large compared to a single resolution element at the focal plane of a monochromator. This disparity is corrected by placing a mechanical slit on the focal plane in front of the PMT. The width of this slit then defines the range of wavelengths ( $\Delta\lambda_s$ ) that are allowed to strike the PMT. Sequential detection of multiple elements can be accomplished by changing the grating angle in a conventional monochromator, thus scanning the wavelengths that are detected. A second approach is to move the PMT rapidly along the focal curve of

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a Rowland circle spectrometer. Such a spectrometer may have several prealigned exit slits along the focal curve, each corresponding to a particular element (Figure 7). A still more efficient method for sequential multielement determinations involves the echelle polychromator (Figure 9). A mask with many slits, each corresponding to a different element, may be placed on the two-dimensional focal plane. The PMT is held in a mechanical arm that quickly positions the detector at the appropriate x-y coordinates for a given element. This design allows very fast sequential determinations by 'wavelength hopping' or direct reading rather than scanning linearly through all wavelengths to reach a select few. One commercial instrument using this design is called a *direct reading echelle (DRE) ICP instrument*.

Simultaneous multielement determinations may be performed with multiple PMTs, but such designs quickly become limited by the size of the PMTs and the geometry of the polychromator. Multiple PMTs may be positioned either along the focal curve of a Rowland circle spectrometer or along the exit plane of an echelle polychromator. Solid-state detectors, with their relatively small size and intrinsic multielement nature, are usually more effective for simultaneous determinations.

## 5.3 Array Detectors

Charge transfer devices (CTDs) include a broad range of solid-state silicon-based array detectors.<sup>(61)</sup> They include the charge injection device (CID) and the charge-coupled device (CCD). The CCD has found extensive use in nonspectroscopic devices such as video cameras, bar code scanners, and photocopiers. With the CTDs, photons falling on a silicon substrate produce electron-hole pairs. The positive electron-holes migrate freely through the p-type silicon semiconductor material, while the electrons are collected and stored temporarily by an array of metal oxide semiconductor (MOS) capacitors (Figure 12). Each MOS capacitor is composed of a small metal electrode and a thin layer of insulating SiO<sub>2</sub> material on top of the p-type silicon substrate. A positive potential is applied to the metal electrode, so the electrons generated in a given region are trapped just below the insulating layer. Each MOS capacitor (or pixel) has a width in the 5- to 50- $\mu$ m range and a height that may be as large as 200  $\mu$ m. A two-dimensional array of pixels is easily prepared by proper placement of the metal electrodes. Such arrays may vary in size, even beyond 4000 pixels on an edge. The CCD differs from the CID mainly in the readout scheme. The CCD is read out in a sequential charge-shifting manner toward the output amplifier. The CID, on the other hand, may be read out in a nondestructive manner by shifting charge between adjacent electrodes, and then shifting it back again. The CID thus benefits from quick



**Figure 12** Cross-sectional diagram of two adjacent pixels in a CCD detector.

random access, even during long integration periods. In CID-based devices, charges can be measured even during signal collection. Thus, integration time can be adjusted to avoid blooming (charge spill from one pixel to one of its neighbors) and improve the detector's dynamic range. Because charges in each pixel are measured and recorded separately in a CID, background and spectral interference correction can be carried out after the measurement. In addition, both intense and weak signals can be recorded simultaneously at the most adequate signal-to-noise (S/N) conditions for each case.

Spectroscopic applications of CTDs have been hampered by the physical mismatch between the relatively small surface area of the detector and the large, sometimes two-dimensional, focal plane associated with polychromators. This mismatch may be overcome, however, and one commercial ICP spectrometer employs a CID detector having more than 250 000 pixels positioned on an echelle focal plane.

Alternative approaches have been successful with the CCD detector. In one case, a group of several CCD arrays are arranged around a circular optical system (CIROS) based on a Rowland circle design. Rather than monitoring discrete wavelengths, as is the case with the multiple PMT Rowland circle systems, the CIROS system provides total wavelength coverage from 120 to 800 nm, with resolution on the order of 0.009 nm.

A second multiple CCD array detector has been available commercially. This detector, called a *segmented array charge-coupled device detector* (*SCD*), employs over 200 small subarrays of 20–80 pixels each.<sup>(61)</sup> The subarrays are positioned along the two-dimensional focal plane of an echelle spectrograph. The position of each subarray corresponds to one of the 236 most prominent ICP emission lines of the 70 most commonly determined ICP elements. This design allows for discrete wavelength determinations as seen with the multiple PMT designs, but it also provides additional spectral information around

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the vicinity of each emission line without exhaustively recording data at all wavelengths.

Another approach to correcting the mismatch between conventional imaging CTD arrays and the focal plane of an echelle spectrometer is to specifically design a CTD array to exactly match the spectrometer image. $^{(3,62)}$ This process, called *image-mapping the detector* or *large* format programmable detection, is available in a couple of commercial products. One device called the VistaChip consists of a series of 70 diagonalized linear arrays (DLAs) of pixels that are designed to exactly match the individual diffraction orders present in the focal plane of the echelle spectrometer. The 70 DLAs correspond to orders 19-88, and the length of an individual DLA is set to match the free spectral range for the corresponding order. In this manner, continuous wavelength coverage is provided across the range 167-363 nm, and selected coverage is provided in the range 363–784 nm where the diffraction orders are wider than the selected width of the detector (although no atomic emission lines of relevance miss the detector). The overall dimensions of the VistaChip are  $15 \text{ mm} \times 19 \text{ mm}$ , and a total of 70 908 pixels are packed inside the 70 DLAs. Other commercial CTD detectors are now as large as  $27 \text{ mm} \times 27 \text{ mm}$ , and any wavelength point on the chip may be accessed, from 160 to 1100 nm.<sup>(3)</sup> As a result of this broad spectral coverage, the combination of echelle polychromator and CTD has become the system of choice for ICP OES.<sup>(59)</sup>

## 6 ANALYTICAL PERFORMANCE

#### 6.1 Analytical Wavelength

The ultraviolet and visible regions (160–800 nm) of the electromagnetic spectrum are most commonly used for analytical atomic spectrometry. In ICP OES, the number of elements that can be determined is related to the wavelength window that can be covered by the optical system. With current echelle-CTD combinations, this entire spectral window may be surveyed simultaneously (Figure 10). For the tap water sample image in Figure 10(b), note the relative crowding of the emission lines in the visible region (in the bottom third of the image). In this negative image, individual emission lines due to elements in the sample appear as dark spots against a white background. Many of these spots may also arise from Ar emission lines and hence are clustered in the visible region. In addition, the continuum emission from the plasma is relatively intense in the visible region, as evidenced by the gray shading across this region. These emission signals arising from the background may be effectively corrected by subtracting a blank: the image of a distilled-deionized water sample (Figure 10c). The resulting corrected spectrum (Figure 10d) shows only those lines due to the elements present in the tap water but not in the blank. Upon expansion of the region of interest marked by a rectangle in Figure 10(d), one may identify the metals of interest in the sample (Figure 10e). In this case, multiple lines are observed for both Mg and Ca. As a rule of thumb, in the absence of significant interferences, wavelengths above 500 nm are employed when alkali metals need to be determined, whereas wavelengths below 190 nm or even below 160 nm are employed when elements such as chlorine, bromine, nitrogen, or arsenic must be determined. There are several criteria for selecting the specific analytical lines for analysis. First, the wavelengths must be accessible by both the dispersive system and the detector. Second, the wavelengths must exhibit signal levels appropriate for the concentrations of the respective elements in the sample. Third, the wavelengths selected must be free from spectral interferences. When this is not possible, emission lines whose intensities can be corrected to account for spectral interferences should be chosen. Fourth, if internal standardization is used, it may be preferable to match the analyte ion lines with an IS ion line and analyte neutral atom lines with an IS neutral atom line. Most modern instruments offer several wavelength suggestions for each element, and they are capable of simultaneously monitoring multiple lines for a single element to reduce the potential for interference.

#### 6.2 Quantitative Methods

The external calibration (EC) method using aqueous standard solutions is easily employed in ICP OES. Aqueous stock solutions for single elements or aqueous mixtures containing multiple elements are available from several commercial vendors. In addition, stock solutions may be prepared in the laboratory with little difficulty.<sup>(63)</sup>

In those cases where the analytical signal is noisy owing to variations such as small changes in solution flow rates, gas flow rates, or plasma position, the IS method may be employed. The IS element may just as easily be added to each solution by the analyst. The choice of the IS element is critical. The element should not be present in the sample of interest, should not interfere spectrally with any of the analytes of interest, and, in the best case, should have physical and chemical properties similar to those of the analyte.<sup>(64)</sup> The perfect IS element experiences the same matrix effects and spectral background as the analyte. In practice, many IS elements are suitable, and published analytical procedures may offer a suite of choices for a given analyte. In some cases, a single IS could be effective for a large number of different analyte elements.<sup>(65)</sup> This approach is most successful under robust ICP conditions: high ICP power (~1.5 kW)

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**Figure 13** ICP OES spectrum of a solution containing  $60 \ \mu g \ L^{-1}$  Pb and  $100 \ \mu g \ L^{-1}$  Cu.

and low nebulization gas flow rate (~0.6 L min<sup>-1</sup> Ar).<sup>(66)</sup> The procedure is straightforward. One simply adds the IS element with a constant concentration to each standard and sample solution to be analyzed. For example, a Pb calibration curve in the range of  $0-100 \,\mu g \, L^{-1}$  may be constructed by preparing five Pb standard solutions spanning this concentration region, each containing  $100 \,\mu g \, L^{-1}$  Cu. The Pb emission line at 217.0 nm may be monitored along with a nearby Cu emission line at 216.5 nm (Figure 13). If spectra such as this are collected for each solution, a plot of the raw Pb signals generate the calibration points depicted by the black diamonds in Figure 14. If, on the other hand, those same Pb signals are divided by the emission signal for Cu in each spectrum, a better linear fit is observed (circles in Figure 14). When



**Figure 14** Internal standard correction for a Pb calibration curve. The fit using the raw Pb emission signal (diamonds) is greatly improved when ratioed to the signal measured for a given amount of Cu  $(100 \,\mu g \, L^{-1})$  added to each sample (circles). The same Pb ICP OES emission signals were used in each case.

the curves are scaled to the same magnitude, note that the slopes are nearly identical, as, in theory, the IS plot is equivalent to the raw plot divided by a constant. In this example, not only is the linear fit improved but also the S/N ratio for the individual measurements is increased by nearly a factor of 10.

In extreme cases, where the sample matrix actually affects the slope of the calibration curve, the standard additions (SA) method should be employed.<sup>(67-69)</sup> It is also possible to combine IS and SA to improve both accuracy and precision in ICP OES determinations. The internal standard additions (ISA) method has been used to analyze urine samples by ETV-ICP OES after simple 1:1 dilution with water.<sup>(70)</sup> The urine sample was divided into five separate 1-mL aliquots. Increasing amounts of a Cd standard solution were added to the five aliquots, resulting in a series of solutions having 0, 2.5, 5.0, 7.5, and  $10.0 \,\mu g \, L^{-1}$  added Cd. Each solution was also spiked with  $1 \mu g L^{-1}$  Bi as an IS, and the final volume was made up to 2 mL with water. No further sample preparation was employed, and the ETV-ICP OES signals from Cd (diamonds) and Cd/Bi ratio (circles) are plotted in Figure 15. Note that the IS correction is necessary to improve the fit such that an accurate x intercept may be determined. The value for the x intercept is  $-1.1 \,\mu g \, L^{-1}$ , and thus the original urine sample was found to contain  $1.1 \pm 0.2 \,\mu g \, L^{-1}$  Cd. Analysis of the same sample by GFAAS following microwave acid digestion gave a value of  $1.3 \pm 0.5 \,\mu g \, L^{-1} \, Cd.^{(70)}$ 

Standard dilution analysis (SDA) is another calibration alternative that is faster and as accurate and precise as SA.<sup>(71)</sup> Only two calibration solutions are required in SDA. Solution 1 contains 50% sample and 50% of a standard reference solution containing the analytes and an IS. Solution 2 has 50% sample and 50% blank. As Solution 1 is introduced into the ICP OES, the continuously monitored analyte and IS signals increase until they reach a stable plateau. Solution 2 is then added to the same tube containing Solution 1 and many calibration points are generated as dilution takes place (Figure 16). Because the amount of sample never changes (both Solutions 1 and 2 contain each 50% sample), only the standard is diluted; hence the name SDA. This matrixmatching effect contributes to improved accuracies, and the presence of an IS minimizes signal fluctuations due to variations in solution flow rates, gas flow rates, or plasma positioning.(71,72)

The SDA calibration curve is built by plotting the analyte-to-IS signal ratio  $(S_A/S_{IS})$  on the *y*-axis and the reciprocal of the IS concentration  $(1/C_{IS})$  on the *x*-axis (Figure 16b). Equations (9)–(12) show the mathematical approach to the SDA strategy. The analytical signal  $(S_A)$  arises from both the sample (sam) and the reference standard (std), while the IS signal  $(S_{IS})$  comes from the

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**Figure 15** Standard additions curves for the determination of Cd in urine by ETV-ICP OES. The *x*-axis represents the concentration of Cd added to separate 1 mL aliquots of a urine sample. Each sample was also spiked with  $1 \mu g L^{-1}$  Bi. The diamonds (a) represent the raw Cd signal and the circles (b) include internal standard correction using the ratio of the Cd and Bi emission signals. The urine sample was found to contain  $1.1 \mu g L^{-1}$  Cd using the internal standard. Without the internal standard, the amount found (*x* intercept) was zero.

reference standard only. These signals are related to the respective concentrations by the calibration curve sensitivities (m):  $S_A = m_A C_A$  and  $S_{IS} = m_{IS} C_{IS}$ . The ratio between analyte and IS signals will then be

$$\frac{S_{\rm A}}{S_{\rm IS}} = \frac{m_{\rm A}C_{\rm A}}{m_{\rm IS}C_{\rm IS}} = \frac{m_{\rm A}(C_{\rm A}^{\rm sam} + C_{\rm A}^{\rm std})}{m_{\rm IS}C_{\rm IS}}$$
$$= \frac{m_{\rm A}C_{\rm A}^{\rm sam}}{m_{\rm IS}C_{\rm IS}} + \frac{m_{\rm A}C_{\rm A}^{\rm std}}{m_{\rm IS}C_{\rm IS}}$$
(9)

If  $S_A/S_{IS}$  is the dependent variable (y-axis) and  $1/C_{IS}$  is the independent variable (x-axis), the slope and intercept of this calibration curve will be

$$Slope = \frac{m_A C_A^{sam}}{m_{IS}}$$
(10)

Table 5Average recoveries (%) for Cr, Cu, and Fedetermined in five different matrices by ICP OES and EC, IS,SA, or SDA

| ,       |              |              |            |            |
|---------|--------------|--------------|------------|------------|
| Analyte | EC           | IS           | SA         | SDA        |
| Cr      | $110 \pm 21$ | $116\pm7$    | $103\pm13$ | $102\pm5$  |
| Cu      | $116 \pm 18$ | $123 \pm 12$ | $95 \pm 7$ | $97 \pm 3$ |
| Fe      | $112\pm29$   | $118\pm15$   | $105\pm14$ | $103\pm5$  |

Results are the combined mean  $\pm 1$  standard deviation (n = 15) for red wine, mouthwash, cola soft drink, HNO<sub>3</sub> 40% v v<sup>-1</sup>, and water spiked with 10 mg L<sup>-1</sup> of each analyte.<sup>(71)</sup>

Intercept = 
$$\frac{m_{\rm A}C_{\rm A}^{\rm std}}{m_{\rm IS}C_{\rm IS}}$$
 (11)

Finally, the analyte concentration in the sample is calculated by rearranging Equations (10) and (11):

$$C_{\rm A}^{\rm sam} = \frac{\rm Slope}{\rm Intercept} x \frac{C_{\rm A}^{\rm std}}{C_{\rm IS}}$$
(12)

When compared to the traditional methods of EC, IS, and SA, the SDA method provides improved accuracy and precision, as shown in Table 5 for Cr, Cu, and Fe determined by ICP OES.<sup>(71)</sup> In this example, samples of red wine, mouthwash, cola soft drink, HNO<sub>3</sub> 40% v v<sup>-1</sup>, and water were spiked with 10 mg L<sup>-1</sup> of each analyte. The results are shown as average recoveries for all matrices combined.

#### 6.3 Analytical Figures of Merit

For ICP OES, the analytical figures of merit include the number of elements that can be determined, selectivity, reproducibility, long-term stability, susceptibility to matrix interferences, LOD, and accuracy.<sup>(73)</sup> The number of elements that can be measured by ICP OES is often more than 70 out of a total of 92 naturally occurring elements, as listed in Table 6. Routine determination of 70 elements can be accomplished by ICP OES at concentration levels below  $1 \text{ mg } \text{L}^{-1}$ . As can be seen from Table 6, almost all naturally occurring elements, with the exception of hydrogen, oxygen, fluorine, and inert gases, can be determined by ICP OES. The elements that are not usually determined by ICP OES fall into three basic categories. The first one includes those elements that occur either as trace contaminants in the argon gas used in the ICP OES (C from CO<sub>2</sub>), constituents of the sample solvent (C, O, H), or as contaminants from the environment or atmosphere (N, for example). The second category encompasses those elements that require high excitation energy, such as the halogens. However, these elements could be determined with poor LOD. The third category is the family of short-lived

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**Figure 16** Typical standard dilution analysis signal profiles for (a) Cr, Cu, Fe, and V and (b) the corresponding SDA calibration curves.

 Table 6
 List of elements that can be determined by ICP OES

| Alkaline and alkaline earth              | Lanthanides and actinides                                       | Transition metals   | Others   |
|--|---|---|--|
| Li, Na, K, Rb, Cs, Be, Mg,<br>Ca, Sr, Ba | Ce, Pr, Nd, Sm, Eu, Gd, Tb,<br>Dy, Ho, Er, Tm, Yb, Lu, Th,<br>U | Sc, V, Ti, Cr, Mn, Fe, Co,<br>Ni, Cu, Zn, Y, Nb, Zr, Mo,<br>Ru, Th, Pd, Ag, Cd, La, Hf,<br>Ta, W, Re, Os, Ir, Pt, Au,<br>Hg | B, C, N, Al, Si, P, S, Cl, Ga,<br>Ge, As, Se, Br, In, Sn, Sb,<br>Te, I, Tl, Pb, Bi |

radioactive elements that are commonly determined by  $\gamma$ -ray spectrometry.<sup>(1)</sup>

Selectivity is important to minimize the spectral overlap interferences resulting from elements with rich-line emission spectra (tungsten, cobalt, niobium, molybdenum, tantalum, and rare earth elements) and to improve the signal-to-background ratio (SBR).<sup>(73)</sup>

Selectivity is largely decided by the practical resolution of the wavelength dispersive system of the ICP OES instrument. High selectivity is usually achieved with a sacrifice in sensitivity and the wavelength coverage range. For the best commercial ICP OES instruments, a resolution of less than 5 pm is possible.<sup>(73)</sup>

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The LODs of ICP OES are generally in the microgram per liter range. The LOD is usually defined as the *analyte concentration* that produces an analytical signal equivalent to three times the standard deviation observed for several measurements (e.g. 20) of a blank solution.<sup>(74)</sup> Another definition of LOD for ICP OES determinations is related to the SBR of the analyte line at a given concentration, c, and the relative standard deviation (RSD) of the background, RSD<sub>B</sub>, as shown in Equations (13) and (14):<sup>(16,75)</sup>

or

$$LOD = \frac{3 \times c \times RSD_B}{SBR}$$
(13)

$$LOD = 3 \times RSD_B \times BEC$$
 (14)

In this case,  $\text{RSD}_{\text{B}} = S_{\text{B}}/I_{\text{B}}$ , where  $S_{\text{B}}$  and  $I_{\text{B}}$  are the standard deviation and the mean intensity for the blank (n = 16);  $\text{SBR} = I_{\text{Net}}/I_{\text{B}}$ , where  $I_{\text{Net}}$  is the analyte's mean net intensity for concentration *c* and  $I_{\text{B}}$  the mean intensity for the blank (n = 16); and the background equivalent concentration, BEC = c/SBR.

The LOD is determined, therefore, by the sensitivity of the measurement and the noise level (or stability) of the ICP OES instrument. The high degree of stability of an ICP was identified when Greenfield et al.<sup>(10)</sup> first used it for analytical atomic spectrometry. For the best ICP OES instruments, a long-term stability of less than 1% RSD has been achieved.<sup>(73)</sup> The atomic emission signals from the ICP are larger than those from other sources, such as a flame. This occurs because the high-temperature and inert-argon environment of the ICP leads to more efficient atomization, ionization, and excitation. In fact, the temperature of the ICP is so high that the largest signals are usually from ionic lines. There are many other factors that may influence LOD, such as nebulizer type, view mode, and sample matrix.<sup>(16,76)</sup> Table 7 shows representative ICP OES LODs obtained for 27 different elements.<sup>(3)</sup> LODs using an axially viewed plasma are typically better than those observed by radial viewing by a factor of 5-10<sup>(1)</sup> as shown in Table 7. Table 8 shows LODs for ETV-ICP OES in comparison with those of GFAAS. LODs for many elements by ETV-ICP OES are better than, or equivalent to, those achieved by GFAAS.<sup>(77,78)</sup> Notice that some elements that cannot be determined by GFAAS can be measured by ICP OES.

Often the BEC is also used to check instrumental performance in ICP OES. The BEC is defined as the *concentration of a solution* that results in an analyte emission signal equivalent in intensity to that of the background emission signal at the measurement wavelength. The BEC can be used as an indicator of relative sensitivity for an emission line. An unusually

**Table 7** LODs ( $\mu$ g L<sup>-1</sup>) observed for ICP OES using a concentric nebulizer with different viewing modes<sup>(3)</sup>

| Element | Wavelength (nm) | Radial view | Axial view |
|---------|-----------------|-------------|------------|
| Ag      | 328.07          | 1           | 0.4        |
| AĨ      | 396.15          | 1           | 0.2        |
| As      | 193.70          | 12          | 3          |
| В       | 249.77          | 2           | 0.1        |
| Ba      | 455.40          | 0.1         | 0.01       |
| Be      | 313.04          | 0.06        | 0.04       |
| Ca      | 317.93          | 2           | 0.6        |
| Cd      | 226.50          | 0.7         | 0.2        |
| Со      | 228.62          | 2           | 0.3        |
| Cr      | 267.72          | 1           | 0.1        |
| Cu      | 324.75          | 0.7         | 0.2        |
| Fe      | 259.94          | 0.7         | 0.1        |
| Κ       | 766.49          | 10          | 0.8        |
| Mg      | 279.55          | 7           | 0.01       |
| Mn      | 267.61          | 0.3         | 0.02       |
| Мо      | 202.03          | 1           | 1          |
| Na      | 589.00          | 1           | 0.08       |
| Ni      | 231.60          | 2           | 0.4        |
| Р       | 177.43          | 30          | 10         |
| Pb      | 220.35          | 5           | 1          |
| Sb      | 206.83          | 9           | 3          |
| Se      | 196.03          | 20          | 4          |
| Si      | 288.16          | 10          | 0.8        |
| Sr      | 407.77          | 0.05        | 0.03       |
| Tl      | 190.86          | 20          | 2          |
| V       | 292.40          | 0.9         | 0.07       |
| Zn      | 213.86          | 0.7         | 0.09       |

high BEC often indicates problems with the efficiency of the sample introduction system.

The LDR of calibration curves for ICP OES is usually four to six orders of magnitude wide, starting from the LOD on the low-concentration side. These LDRs are significantly larger than the two to three orders of magnitude observed for competing techniques such as AAS and arc/spark OES. The wide LDRs in ICP OES translate into simple preparation of calibration curves. Very often, a couple of standards together with a blank solution is enough to produce an accurate calibration. Multiple sample dilutions are seldom needed before the analysis.

In general, the accuracy of the ICP OES technique gets poorer as the analyte concentration approaches the LOD. For semiquantitative analysis (accuracy  $\pm 10\%$ ), the analyte concentration should be at least five times higher than the LOD. For accurate quantitation ( $\pm 2\%$ ), the concentration should be 100 times greater than the LOD. At this concentration level, the precision is typically better than 1% RSD. This precision is considered sufficient for most trace element determinations. Better precision can be achieved, if necessary, by sacrificing analysis speed or with a more complex instrumental design. The concept of limit of quantitation (LOQ) has

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Table 8 LODs (pg) for ETV-ICP OES compared with those of  $\mbox{GFAAS}^{(2,77,78)}$ 

| Elements | ETV-ICP OES | GFAAS   |
|----------|-------------|---------|
| Ag       | 1           | 0.5     |
| Al       | 0.5         | 4       |
| As       | 60          | 20      |
| Au       | 10          | 10      |
| Ba       | 0.3         | 10      |
| Be       | 1           | 1       |
| Bi       | 200         | 10      |
| В        | 4           | NA      |
| Ca       | 150         | 5       |
| Cd       | 1           | 0.3     |
| Со       | 12          | 1       |
| Cu       | 2           | 1       |
| Er       | 34          | 300     |
| Eu       | 12          | 10      |
| Fe       | 10          | 2       |
| Ga       | 10          | 10      |
| Ge       | 10          | 20      |
| Hg       | 4           | 100     |
| In       | 20          | 5       |
| Κ        | 1200        | 2       |
| Li       | 2           | 5       |
| Lu       | 54          | 4000    |
| Mg       | 0.1         | 0.4     |
| Mn       | 0.3         | 1       |
| Мо       | 7           | 4       |
| Na       | 400         | 5       |
| Ni       | 27          | 10      |
| Р        | 100         | 3000    |
| Pb       | 4           | 5       |
| Pt       | 25          | 50      |
| Rb       | 2800        | 5       |
| Re       | 100         | NA      |
| Ru       | 95          | 40      |
| Sb       | 100         | 20      |
| Sc       | 17          | 40      |
| Se       | 450         | 20      |
| Si       | 100         | 40      |
| Sn       | 20          | 20      |
| Sr       |             | 2       |
| Te       | 50          | 10      |
| Ti       | 6           | 100     |
| TI       | 300         | 10      |
| Ũ        | 3           | 2.411.0 |
| v        | 6           | 20      |
| Ŵ        | 160         | NA      |
| Ŷ        | 25          | NA      |
| Yh       | 18          | 4       |
| Zn       | 0.6         | 1       |

NA, not available.

been defined as *a concentration* for which the precision, expressed as RSD, would be below a given threshold, for instance, 10% or 5%.<sup>(79)</sup> A 5%-based LOQ normally occurs at concentrations approximately 10 times greater than the LOD (based on three standard deviations).

#### 6.4 Continuum Background and Interferences

The ICP spectrum includes argon emission lines and a continuum background emission that covers the entire wavelength region used in ICP OES. This emission continuum may or may not be related to spectral interferences. It is mainly a result of radiation emitted by decelerating electrons (Bremsstrahlung effect) and by recombination reactions  $(M^+ + e^- \rightarrow M + h\nu)$ , where M<sup>+</sup> can be any ion, but primarily represents argon species). These phenomena are responsible for the plasma continuum background emission in the visible and UV regions, respectively. Although not generally significant, molecular emission bands from species generated in the plasma by aqueous solutions and atmosphere gases (e.g. OH, N2<sup>+</sup>, NH, NO, and CN) also contribute to the background continuum. The introduction of matrices that cause plasma cooling also affects background intensity. On the other hand, more severe effects may be observed when introducing high-carbon-content matrix samples and organic-solvent-containing mixtures into the plasma. Relatively high molecular emission from species such as C<sub>2</sub> (Swan band), CN (violet), and CH can significantly impact the background signal intensity and represent potential spectral interferences for determinations above 300 nm.<sup>(14,80)</sup> Because the intensity of the background continuum is proportional to the square of the electron number density  $(n_e^2)$ , the optimization of instrumental parameters such as RF applied power and nebulization gas flow rate can minimize potential interfering effects.

Among all commonly used analytical atomic spectrometry techniques, ICP OES is probably the one with the fewest number of interferences. The argon plasma is inert when compared to the chemical reactivity of a flame. In addition, the high temperature of the plasma helps to reduce chemical interferences. The temperature is high enough to break down most species into atoms or ions for excitation and subsequent emission. In contrast, in a lowtemperature flame, chemical interferences can be a severe problem. For example, a small amount of aluminum will interfere with the determination of calcium in flame AAS. On the other hand, no such chemical interference is observed in ICP OES even at aluminum concentrations 100 times higher than what would have been a problem for FAAS. However, chemical interferences do exist in ICP OES. Sometimes higher RF applied power and/or lower nebulization argon flow rates are used to minimize these effects. One particular type of chemical interference is the so-called easily ionized element (EIE) effect. The EIEs are those elements that have low ionization potentials, such as alkaline elements. High concentrations of EIEs can suppress or enhance emission signals, depending on the analyte species. One way to reduce the EIE effect is to dilute the sample solution to the point that the EIE effect

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is not measurable. Sometimes, higher RF applied power or mathematical correction may be used to compensate for EIE interference. Instrumental conditions such as slit width, viewing height, and viewing volume can be chosen to minimize interference and to optimize emission signal collection in either axial or radial configuration.<sup>(81)</sup>

The most common interference problem in ICP OES is spectral interference (also referred to as background interference). Ironically, this type of interference arises because of the multielement nature of the plasma. As the ICP is capable of exciting almost any element that is introduced into the plasma, spectra are likely to be rich, especially for highly complex and concentrated samples. The solution to the spectral interference problem, as discussed previously, is the use of high-resolution spectrometers. However, some spectral overlap may still exist even with the best commercial system. In these cases, advanced background correction techniques are employed or a different analytical wavelength for the element(s) of interest is chosen. Spectral interferences can be classified into four categories: simple background shift, sloping background shift, direct spectral overlap, and complex background shift. The simple background shift is defined as *a shift in background intensity* that is essentially constant over a given wavelength range on either side of the analytical line. The background may shift up or down. There are two approaches to deal with this background problem. The first is to select a different analytical line at a wavelength with no background interference. The second is to correct for the background by measuring it somewhere near, but not falling on, the profile of the analytical line of the analyte element. Two background correction points, one on each side of the profile of the analytical line, are used to correct for the *sloping* background shift. This means that the average signal measured at the two points is subtracted from the total signal measured at the analytical line. In the worst case, direct spectral overlap occurs. This can be corrected if the magnitude of the interference is known as a function of the concentration of the interfering element. A correction factor can be calculated and used to correct the signal measured at the analyte wavelength. This can be best achieved by making simultaneous measurements of both the signal at the analyte wavelength and at a different wavelength for the interfering element. This method is referred to as the concentration ratio method or IEC method. The basic requirement is that the concentration of the interfering element can be accurately measured at another wavelength. With advanced detector systems, all spectral lines are present, so IEC is possible. A complex background shift is a shift in a background intensity that varies significantly on both sides of the analytical line. This is usually caused by the occurrence of a number of intense, closely spaced emission lines nearby, and perhaps

directly overlapping the analyte wavelength. In this case, a different analytical wavelength should be chosen if possible.<sup>(1)</sup>

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### **ABBREVIATIONS AND ACRONYMS**

| AAS     | Atomic Absorption Spectrometry       |
|---------|--------------------------------------|
| BEC     | Background Equivalent Concentration  |
| CCD     | Charge-coupled Device                |
| CID     | Charge Injection Device              |
| CIROS   | Circular Optical System              |
| CTD     | Charge Transfer Device               |
| DCP     | Direct Current Plasma                |
| DLA     | Diagonalized Linear Array            |
| DRE     | Direct Reading Echelle               |
| DSI     | Direct Sample Insertion              |
| EC      | External Calibration                 |
| EIE     | Easily Ionized Element               |
| ETV     | Electrothermal Vaporization          |
| FAAS    | Flame Atomic Absorption Spectrometry |
| GC      | Gas Chromatography                   |
| GFAAS   | Graphite Furnace Atomic Absorption   |
|         | Spectrometry                         |
| HG      | Hydride Generation                   |
| HGN     | Hildebrand Grid Nebulizer            |
| HPLC    | High-performance Liquid              |
|         | Chromatography                       |
| ICP     | Inductively Coupled Plasma           |
| ICP-MS  | Inductively Coupled Plasma Mass      |
|         | Spectrometry                         |
| ICP OES | Inductively Coupled Plasma Optical   |
|         | Emission Spectrometry                |
| IEC     | Interelement Correction              |
| IR      | Induction Region                     |
| IS      | Internal Standard                    |
| ISA     | Internal Standard Additions          |
| ITV     | In-torch Vaporization                |
| LA      | Laser Ablation                       |
| LDR     | Linear Dynamic Range                 |

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| LIP  | Laser-induced Plasma                  |
|------|---------------------------------------|
| LOD  | Limit of Detection                    |
| LOQ  | Limit of Quantitation                 |
| MCN  | Microconcentric Nebulizer             |
| MIP  | Microwave-induced Plasma              |
| MOS  | Metal Oxide Semiconductor             |
| OES  | Optical Emission Spectrometry         |
| ORCA | Optimized Rowland Circle Alignment    |
| PN   | Pneumatic Nebulizer                   |
| PMT  | Photomultiplier Tube                  |
| RF   | Radiofrequency                        |
| RSD  | Relative Standard Deviation           |
| SA   | Standard Addition                     |
| SBR  | Signal-to-background Ratio            |
| SCD  | Segmented Array Charge-coupled Device |
|      | Detector                              |
| SDA  | Standard Dilution Analysis            |
| TDS  | Total Dissolved Solids                |
| USN  | Ultrasonic Nebulizer                  |
| VUV  | Vacuum Ultraviolet                    |
|      |                                       |

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