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An Overview

ICP emission spectrometry (ICP-OES) is one of the most important techniques of instrumental elemental analysis. It can be used for the determination of approximately 70 elements in a variety of matrices. Thanks to its versatility and productivity it is used in many different applications, and nowadays it carries the basic workload in many routine laboratories.

This book gives an introduction to the basic principles of ICP emission spectrometry and provides some background information as well as practical hints to the user. This knowledge should enable the reader to appreciate the possibilities and limitations of this analytical technique in order to use it in an optimal way.

Throughout the text, you will find complementary information, which is indicated by a frame around the text. Symbols indicate the type of information given:

🛠 Practical tips
ⓘ Additional information
📖 Complementary theory

1.1 Features of ICP-OES

The heart of an ICP emission spectrometer is the plasma, an extremely hot "gas" with a temperature of several thousand Kelvin. It is so hot that atoms and mainly ions are formed from the sample to be analyzed. The very high temperature in the plasma destroys the sample completely, so the analytical result is usually not influenced by the nature of the chemical bond of the element to be determined (absence of chemical interference). In the plasma, atoms and ions are excited to emit electromagnetic radiation (light). The emitted light is spectrally resolved with the aid of diffractive optics, and the emitted quantity of light (its intensity) is measured with a detector. In ICP-OES, the wavelengths are used for the identification of the elements while the intensities serve for the determination of their concentrations.

Since all elements are excited to emit light in the plasma simultaneously, they can be determined simultaneously or very rapidly one after another. Consequently, the analytical results for a sample can be obtained after a short analysis

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time. The time needed for the determination depends on the instrument used and is of the order of a few minutes. The fact that all the elemental concentrations are determined in one analytical sequence and not by measuring one series of samples for one element, another series for another element, and so on usually makes the technique attractive with respect to speed.

Samples analyzed are normally liquids, occasionally solids, and (quite rarely) gases. For the determination of an element, no specific equipment (such as the lamp used in atomic absorption spectrometry) is needed. As a rule, one only needs a calibration solution of the element to be analyzed and a little time for method development. Hence, an existing analytical method can easily be extended to include another element. This makes ICP emission spectrometry very flexible.

ICP-OES has a very large working range, typically up to six orders of magnitude. Depending on the element and the analytical line, concentrations in the range from less than µg/L up to g/L can be determined. Time-consuming dilution steps are therefore rarely needed, which considerably increases the analysis throughput.

Particularly in environmental analysis, the working ranges for many elements correspond to the concentrations normally found in the samples, and this is one of the reasons why this technique is widely used in environmental applications; about half of all users of ICP-OES use it in these or related areas.

Because of the widespread use of this technique in environmental applications, there are a number of standards and regulations that apply. The most important of these are ISO 11885 [1] and EPA Method 200.7 [2]. Moreover, ICP-OES is used in a variety of other applications, such as metallurgy and the elemental analysis of organic substances.

Plasma was first described as an excitation source for atomic spectroscopy in the mid-1960s [3–6], and the first instrument appeared in research laboratories a decade later. After a further 10 years the technique was commercialized [7–9]. At first slowly, but then at an increasing rate, ICP emission spectrometers were introduced into routine laboratories. During the same period, the instruments were refined to make them more user friendly [10]. Since the early 1990s, ICP-OES has become the "workhorse" in the modern analytical laboratory [11, 12]. These years also brought a number of significant improvements, most importantly the use of solid-state detectors [13].

1.2 Inductively Coupled Plasma Optical Emission Spectrometry – the Name Describes the Technique

As a rule, the technique is referred to as ICP or ICP-OES. The latter is the abbreviation for **i**nductively **c**oupled **p**lasma **o**ptical **e**mission **s**pectrometry. The complete name describes or implies the analytic features of this technique: "**Plasma**" describes an ionized gas at very high temperatures. The energy necessary to sustain the plasma is transferred electromagnetically via an induction coil. This method of energy transfer is found in the first part of the name of the technique: "**Inductively coupled** plasma."

The sample to be analyzed is introduced into this hot gas. As a rule, all chemical bonds are dissociated at the temperature of the plasma, so that the analysis is independent of the chemical composition of the sample. The atoms and ions are excited in the plasma to emit electromagnetic radiation ("light"), which mainly appears in the ultraviolet and visible spectral range. The **emission** of light occurs as discrete lines, which are separated according to their wavelength by diffractive optics and utilized for identification and quantification.

Spectrometry is a technique for quantification that uses the emission or absorption of light from a sample. Its goal is the determination of concentrations and differs from qualitative analysis by spectra, which is commonly referred to as spectroscopy [14].

As a rule, in ICP emission spectrometry there is a linear relationship between intensity and concentration over more than 4–6 decades. This intensity concentration function depends on a number of parameters, some of which are unknown. Hence, there is a need for empirical proportionality factors. Consequently, in ICP emission spectrometry, these factors have to be determined before the analysis (calibration). One assumes that the slope of the calibration functions does not change between standards and the samples. It is an important prerequisite to ensure good accuracy of the analytical results to prove that this is actually the case. Instrument performances as well as method development have a large influence on this, which can be challenging at times.

Since all atoms and ions emit light simultaneously, ICP-OES is a typical representative of a sample-orientated multielement technique. This means that the results for the elements in one sample are measured in one step, unlike the element-orientated mode of operation where all samples are examined for one element. After all the samples have been analyzed for the first element, they are then measured in a new series for the next element. A typical representative of the element-orientated mode of operation is classical atomic absorption spectrometry. The advantages of the sample-orientated mode of operation for routine analysis are obvious, since the sample is characterized very quickly.

ⓘ ICP, ICP-OES, ICP-AES, ICP/AES, ICP emission spectrometry, ICP ES: What is the correct name for this technique?

The variety of names for this technique reminds one of the tower of Babel. Which version should one follow? We will try to throw some light on this while attempting to trace the origin of the terms used:

Let us start with "ICP," the abbreviation for "inductively coupled plasma." This is widely accepted. Everyone agrees to use this abbreviation, at least in written communications.

However, the abbreviation "ICP" alone is no longer sufficient as a clear identification of the technique since a similar technique, ICP-MS (ICP mass spectrometry), exists. To distinguish these from each other, it is recommended to add "OES" or "MS" to the abbreviation "ICP" in order to clearly specify which technique is meant. "ICP" should rather be understood as a generic term for both techniques.

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The abbreviation “OES” is the short form for “**o**ptical **e**mission **s**pectrometry” and has been around for many decades. Originally, it was used in connection with excitation by spark or glow discharge long before inductively coupled plasma was used analytically. Since plasma only represents another excitation source, it makes sense to stay with the abbreviation “OES.”

Sometimes one finds the name “atomic emission spectrometry” or “AES.” Typically, this version is used by users and manufacturers who in many cases have worked with “atomic absorption spectrometry” (AAS) before. The use of the term “atomic” is plausible to some extent since ICP-OES as well as AAS and ICP-MS are categorized under the group name “atomic spectrometry.” However, the reference to “atoms” is misleading in a way since most particles in the plasma are ions (Table 2.2).

Complications could also arise from the fact that the abbreviation “AES” stands for “Auger Electron Spectroscopy.” Since this is a completely different technique, it is not likely that there would be confusion. However, in order to be sure, it seems wise not to use the abbreviation “AES” for “emission spectrometry.”

The light can be diffracted only by optical means. Therefore, it is redundant to include the term “optical.” The term “optical emission” is a tautology similar to “cold ice” or “wet water.” For this reason, ISO 12235 [15] suggests dropping the “O” (and “A”) completely. The author follows this logic. This leads to the fact that in addition to the abbreviations “OES” and “AES” there would be yet another form “ES.” The likelihood of confusion between these terms increases, so throughout this book “OES” will be used.

In a few rare cases, a slash “/” is used to connect “ICP” and “OES.” However, to the author’s knowledge there is no international norm or regulation that suggests the use of a slash. For the sake of clarity, the use of a slash should therefore cease.

1.3 Distribution of ICP-OES

The first applications of ICP-OES were in metallurgy; however, environmental analysis was the driving force leading to its widespread use in routine laboratories. In addition, the technique is used for a variety of other areas of element determination, as shown in Figure 1.1.

With respect to geographical distribution, nearly half of all the instruments in operation worldwide are located in North America. Germany is the next biggest market, with more than 10%, while Japan and the Netherlands have fewer than 10% of the installed instruments. Australia, China, Britain, and France have shares in the small percentage range.

1.4 Related Techniques for Elemental Analysis

Atomic absorption spectrometry (AAS) [16, 17] was the standard analytical technique for elemental analysis until a few years ago. Classical AAS is a

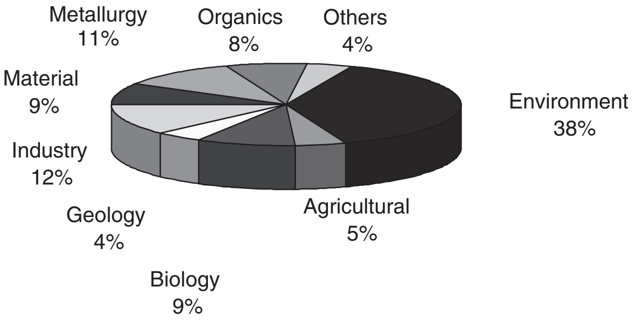

Figure 1.1 Use of ICP-OES in different application areas in Germany. Similar patterns can be found in most other countries of the world.

single-element technique. AAS uses the absorption of light by atoms that originate from the sample and are in resonance with the light emitted by a specific element lamp. The greater the number of the atoms in the light beam, the higher the absorption, and this is used to measure the concentration. As a rule, the working range is about two orders of magnitude. Flames, furnaces (mainly made of graphite), or quartz cuvettes with chemical reduction reactions (hydride and cold vapor techniques) as sampling systems serve as an atomizing source. Furnaces and chemical reactions typically yield very good limits of detection. The furnace will typically modify the sample, so in a way it serves also for sample preparation, which is a great advantage of this specific technique. This is especially important in clinical applications.

High-resolution continuum source AAS (HR-CS AAS) uses a xenon lamp rather than a multitude of single element lamps [18]. The use of a xenon lamp allows the determination of all elements in a sample simultaneously. Thus, the risk of spectral interferences is increased. Using high-resolution optics compensates for this effect.

Atomic fluorescence spectrometry (AFS) makes use of the fluorescence that is emitted by atoms in all directions after excitation [19]. Because the detection can be done off-axis from the light beam used to excite the atoms, very low background emission is typical for AFS, unlike AAS and OES. In principle, because of this fact, very low limits of detection are achievable. There are only a few commercial AFS instruments in use, and these are mostly used for the analysis of hydride-forming elements and Hg. The possibility of using fluorescence with an ICP as an excitation source [20] has not been pursued further.

As in ICP-OES, plasma is used in **ICP mass spectrometry** (ICP-MS). Here, the ions formed in the plasma are used for quantification. The separation of the ions is carried out (fast) sequentially with a quadrupole (resolution 1 amu) or sector field (resolution of 300–10 000 amu with a typical instrument setting of 4000 amu) or simultaneously using the time-of-flight principle (TOF). The great advantage of ICP-MS consists in its detection power, which is especially high for the high-resolution instruments (if they are operated in a low resolution mode). A greater concentration of dissolved substances in the sample solution may cause clogging of the interface between the plasma and the high-vacuum section of the mass spectrometer. Therefore, the excellent detecting power cannot always be converted to overall better limits of quantification in the sample because in many cases, the samples must be very highly diluted prior to aspiration into an ICP-MS instrument.

An alternative to high-resolution ICP mass spectrometers to eliminate interferences is the use of reaction or collision cells. These transform either interfering ions or shift the analyte ion to a compound ion that is free from interferences.

In a **direct current plasma** (DCP) [21], the sample is introduced into a direct current arc. There it is excited to emit light. The region of the arc besides the electric current sustaining the plasma is viewed for quantification. A three-electrode plasma has a cathode and two anodes (Figure 1.2). The sample aerosol is introduced via an injector between the two anodes. The analysis with DCP is very susceptible to excitation interference, particularly by easily ionizable elements. In addition, molecular bands will often interfere [22].

A **microwave-induced plasma** (MIP) [24] uses He as the plasma gas. This enables much higher excitation temperatures to be obtained, so that nonmetals are excited particularly well. The MIP is highly subject to matrix influences, even water. Therefore, it is preferably used for the analysis of gases. The combination with electrothermal vaporization works very well [25], as does the quantification of hydrides. MIP is an ideal detector for gas chromatography [26–28].

In the year 2011, an instrument based on **microwave plasma** using nitrogen as operating gas was commercially introduced. It uses an air-cooled magnetron similar to the ones used in kitchen microwave ovens. The magnetron produces a magnetic field, which produces a rotational symmetric plasma, similar to an ICP. This plasma reaches a temperature of about 5000 K [29]. Like in ICP-OES, a torch is used. The applications are similar to flame atomic absorption spectrometry [30].

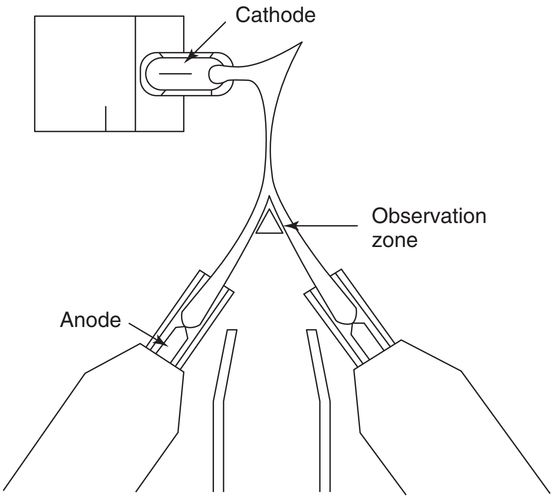

Figure 1.2 Schematic representation of a three-electrode direct current plasma. Source: Adapted from [23].

The plasma temperature of a **capacitively coupled microwave plasma** (CMP) [31] is very low (below 5000 K) [32]. Therefore, excitation interference is quite pronounced. It has been replaced by ICP-OES.

Glow discharge optical emission spectrometry (GDOES) uses the light emitted from a glow discharge formed between a hollow cathode and a sample anode in a reduced-pressure argon atmosphere [33]. Argon cations are formed, which are accelerated in the direction of the negatively charged solid sample. When they hit the surface, atoms from the surface are released and excited. The light from these atoms is used for quantification. GDOES is a technique for surface analysis of electrically conductive materials. Since the composition of the surface has a great influence, a correction must be applied, but this is only successful if all components are known [34].

In **spark optical emission spectrometry** (SOES) [35–37] part of the material from a metal sample is vaporized with an electric spark. It is further atomized and ionized. The emission during the excitation that takes place is used for quantification. SOES is a fast method to check the composition of metals [38]. Particularly compact instruments are in use as mobile spectrometers.

Laser-induced plasma spectrometry ([LIPS], also laser-induced breakdown spectroscopy [LIBS]) [39], is a relatively new technique of solid sampling [40]. The irradiation of a solid sample with a laser [41, 42] will cause an immediate transfer of the material into the plasma phase. The radiation emitted from this plasma is used directly for quantification. Since the duration of such an emission signal is very short [43], array spectrometers are typically used in LIPS. Lasers operating in the UV range are preferred since the absorption of lower wavelengths is better than that of wavelengths in the visible or infrared region [44]. Both the radiation of the laser to the sample for the generation of the plasma and the radiation emitted can be transferred by fiber optics. Therefore, this technique is particularly attractive for the direct online analysis of unapproachable sample material, such as that in nuclear plants [45] or the Mars exploration [46].

The irradiation of a sample with X-rays triggers the fluorescence of the atoms and ions. Here the lower electron shells (K and L) are excited. The fluorescence emitted is used for qualitative and quantitative analysis in **X-ray fluorescence** (XRF) [47]. In wavelength-dispersive XRF, several dispersive crystals are used to cover the frequency range. In energy-dispersive instruments, the separation is carried out in the detector, which converts the different energies of radiation into electric current or voltage. XRF is used successfully for the analysis of solid samples, especially for large number of samples with small matrix composition changes. The determination of light elements is problematical in XRF. Mutual interference of the elements requires calibration with well matrix-matched standards and advanced processing of intermediate results.

In **total-reflection X-ray fluorescence spectrometry** (TXRF) [48], a liquid sample is placed on a quartz plate and dried. This plate is then placed in the beam of the X-ray at a very flat angle so that it is totally reflected. Directly above and normal to this primary beam, a detector (Si [Li]) measures the fluorescence. TXRF is particularly suitable for determining elements with an atomic number of >11 in very low concentrations in small volumes.

1.5 Terms

The element to be determined is called the **analyte**. Its concentration can be in different ranges. If its concentration in the sample is at least 10%, then it is a **main component**. If its concentration is between 10% and 0.01% it is a **minor component**. A component with a lower concentration is called a **trace**. The accuracy and reproducibility normally depend on the magnitude of the concentration to be analyzed. As a rule, only very small deviations are tolerated for main and minor components (typically up to about 1%), while in trace analysis greater tolerances (up to 10% and sometimes even more) are accepted.

The tolerances consist of a statistical part, the **reproducibility** of the measurement, which is usually given as standard deviation of the measurement (e.g. intensity in c/s) or in concentration units of the transformed result (e.g. concentration in mg/kg). The reproducibility is frequently also termed the **precision**, although the term is sometimes used in a different context encompassing accuracy and reproducibility. Furthermore, error tolerances include the deviation from the true value, which is referred to as the **accuracy**. It can be determined only on synthetic samples, since true values for real samples cannot be known. However, some well-characterized samples, which were examined by a number of renowned laboratories and evaluated following strict statistical rules, the **standard reference materials** (SRMs), exist. The concentration values given in the certificates of these SRMs are generally accepted as “true” values. Quite frequently, the deviations of the measurements from those of the SRMs are used for the determination of the accuracy.

In many cases, the analysis is influenced by the sample components. The sum of all the components of a sample is called the **matrix**. The matrix components may cause an analytical error. This is called **interference**. Since analytical errors are not only linked to the measurement with the ICP instrument itself but are also caused by the complete analytical process, which includes sampling, storage, pretreatment, and measurement, to name the most important ones, the overall error of the analysis is greater than the measurement tolerances. This concept leads to the idea of the **uncertainty**. The determination of this quantity is quite complex, so that it is very rarely carried out.

The **sensitivity** is the slope of the calibration function, or expressed mathematically, the first derivative of the calibration function [49].

Although not permitted in any standard, the concentration descriptor “parts per million” (ppm) still is quite widespread. Its main disadvantage is that this “unit” does not unambiguously describe whether the concentration refers to particles, mass, or volume. Therefore, units such as “mg/L” or “mg/kg” are to be preferred.