



# Overview of Most Commonly Used Analytical Techniques for Elemental Analysis

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Element determination and quantification in liquid and solid samples is a topic of great interest in many fields. Usually, environmentally important elements are present at very low concentrations (trace and ultra-trace levels) and therefore the use of sensitive instrumental analytical techniques is mandatory. At present a wide range of analytical techniques for elemental analysis are available in the market. Each of these techniques has its advantages and drawbacks and thus, few laboratories rely only on one of these analytical methods but often use complementary combinations of them. This article gives an overview of the most commonly used analytical techniques (atomic spectroscopy and X-ray fluorescence spectrometry) for element analysis of liquid and solid samples. Special attention is given to current instrumentation and the advantages and limitations of each configuration mode are shown. The performance of the discussed analytical techniques discussed is also compared in the last section of the article.

## Elemental Analysis of Solid Samples

### • Atomic Spectroscopic Techniques

One of the drawbacks of most atomic spectroscopic techniques (including flame absorption atomic spectroscopy (FAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS)) for the analysis of solid samples is that the market for these types of instruments offers principally instrumentation that is initially dedicated to the analysis of liquid samples and therefore, solid samples have to be brought into solution before analysis by means of a previous chemical pre-treatment. Sample dissolution is often a tedious and time-consuming step in the analytical procedure that limits sometimes its use in some applications (i.e. elemental analysis of siliceous samples which are difficult to be dissolved).

Graphite furnace atomic absorption spectroscopy (GFAAS), also known as thermal atomic absorption spectroscopy (ETAAS), is mostly the only variant of atomic spectroscopy that allows the analysis of solid micro samples. However, its use for this purpose has been traditionally limited due to the sequential character of the determination of elements as well as the impossibility of determining non-metals such as sulphur. Recent advances in the development of high-resolution continuum sources have promoted the commercialisation of AAS systems which enable a fast simultaneous and sequential multi-element analysis. Figure 1 gives a graphical view of the high-resolution continuum source graphite furnace atomic absorption spectrometer (contrAA 600) supplied by Analytik Jena AG. Apart from being used for the determination of metals, this system also allows the determination of non-metals such as phosphorus, sulphur and halogens. This novel AAS spectrometer has been used for elemental analysis of solid and liquid samples in different fields including environment, material sciences, clinical chemistry, medicine, pharmacy, etc. Taking into account the micro analytical capability of the graphite furnace technique, another interesting application is the elemental analysis and characterisation of nanomaterials and mass-limited solid samples.

### • X-ray Fluorescence Spectrometry

X-ray emission analysis methods, based on the emission of characteristic X-rays by the analytes when a target is irradiated with an energetic radiation like an exciting X-ray beam, have since long been used widely for the determination of major, minor and trace elements in an extensive range of solid samples in different fields. In addition to the multi-element character and wide dynamic working range, the possibility to analyse solid samples with minimum sample preparation is one of the major advantages of X-ray fluorescence spectrometry (XRF). Using XRF, solid powders can be prepared as pressed pellets reducing the use of chemicals and time in sample preparation. In Table 1, as an example, several specific solid sample treatment procedures for XRF analysis in some biological, environmental and industrial fields are presented. The published literature on this topic is rather extensive and a more complete description of the sample preparation procedures and applications may be found in some earlier books and reviews (see the reference section). During the last decade, noticeable development was made in the instrumental aspects of X-ray spectrometry. This progress includes, for instance, considerable improvements in the design and production of detectors and X-ray optics. All this has resulted in a wide variety of instrumentation becoming available today since the first modern commercial X-ray spectrometer was introduced into the market at the end of the 1940s. It is difficult to make a unique classification of XRF techniques, because, depending on the detection system mode, the geometry of the optical path and the spectrometer size, we can find several different instrument configurations. In Figure 2, a tentative classification taking into account these facts is proposed.

Usually, XRF spectrometers are divided into two main categories depending on the fundamentals of the detection system: wavelength detection systems (WDXRF) and energy dispersive systems (EDXRF).



Figure 1. Graphical view of the high-resolution continuum source graphite furnace atomic absorption spectrometer (contrAA® 600) supplied by Analytik Jena AG (Source: <http://www.analytik-jena.de>)

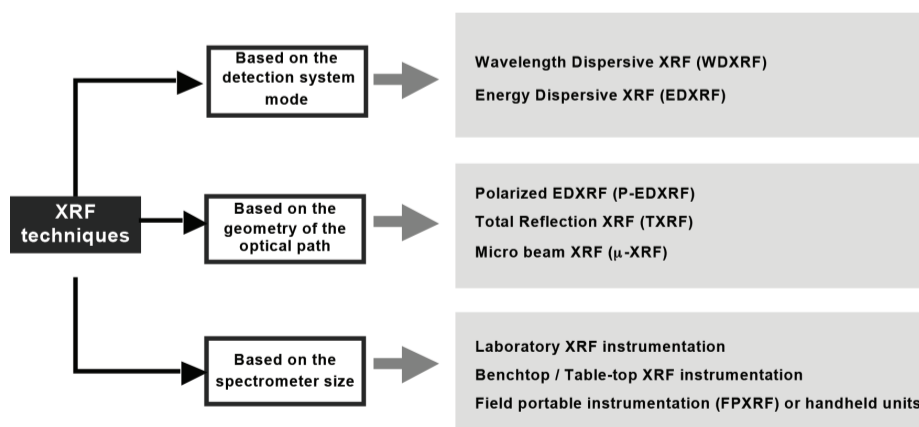


Figure 2. Classification of instrumental configurations in XRF techniques

WDXRF employs diffraction by a dispersing system (crystal or multilayer) to separate the characteristic wavelengths emitted from the sample. In contrast, EDXRF spectrometers use the proportional characteristics of a photon detector to separate the characteristic photons emerging from the sample in terms of their energies. The characteristics of the two configurations differ mostly in their relative sensitivities and the way in which data are collected and presented. In general, a WDXRF system is about one order of magnitude more sensitive than EDXRF instrumentation. However, an EDXRF spectrometer measures all elements within its range at the same time, whereas a WDXRF system identifies only elements for which it is programmed. The selection of the most suitable

Table 1. Specific solid sample treatment procedures for XRF analysis in some biological, environmental and industrial fields

Type of Sample	Sample Preparation Procedure	
Biological	<b>Vegetation</b>	- Oven-drying ( $T \leq 60^\circ\text{C}$ ) or freeze-drying - Grinding to obtain a fine powder - Pelletizing (using different sample amounts / binders)
	<b>Biological tissues</b>	- Freeze-drying → pulverization → pelletizing
Environment	<b>Soil/sediment</b>	- Oven-drying - Grinding to obtain a fine powder - Pelletizing (using different sample amounts / binders) or fused bead preparation (determination of light and major elements)
	<b>Aerosol and dust</b>	- Drawing a large air volume through a filter - Analysis of the loaded filter
Industrial	<b>Automotive catalysts</b>	- Grinding to obtain a fine powder - Pelletizing using wax as a binder
	<b>Food (powder milk)</b>	- Grinding to obtain a fine powder - Pelletizing (using different sample amounts / binders)
	<b>Pharmaceutical (solid)</b>	- Homogenization of the powder - Pelletizing (usually the addition of a binder is not necessary)
	<b>WEEE (*)</b>	- Method-1: Homogenization → pulverization → pelletizing

(\*) WEEE: Waste electrical and electronic equipment

configuration is based on the requirements for a given purpose. WDXRF is used almost exclusively for routine, high-throughput analyses when there is a great need for fast accurate analysis, and where flexibility is of little importance. Therefore such systems are widely used, for example, in quality assurance for industrial routine analyses or to determine the major and minor elements in geological specimens. EDXRF systems lack somewhat in energy resolution compared with WDXRF systems but have the capability to display information on all elements present in the sample at the same time, which makes EDXRF instrumentation ideal for general troubleshooting problems in many application fields. EDXRF has been particularly effective, inter alia, in the alloy industry, forensic science and the environmental field.

Depending on the set up (geometry) of the basic components of the spectrometer, one has also differently configured XRF systems. For instance, in polarised-EDXRF instrumentation (P-EDXRF), the X-ray optical path between the X-ray source, the sample and the detector is not limited to one plane, like in conventional EDXRF systems, but involves three dimensional optics (3D optics). The main advantage of this geometry is that scattered tube radiation cannot reach the detector because of polarisation and thus the sensitivity and limits of detection for minor and trace elements are better than those achieved with common 2D EDXRF systems. This fact is particularly interesting in the analysis of organic solid samples as can be seen in Figure 3.

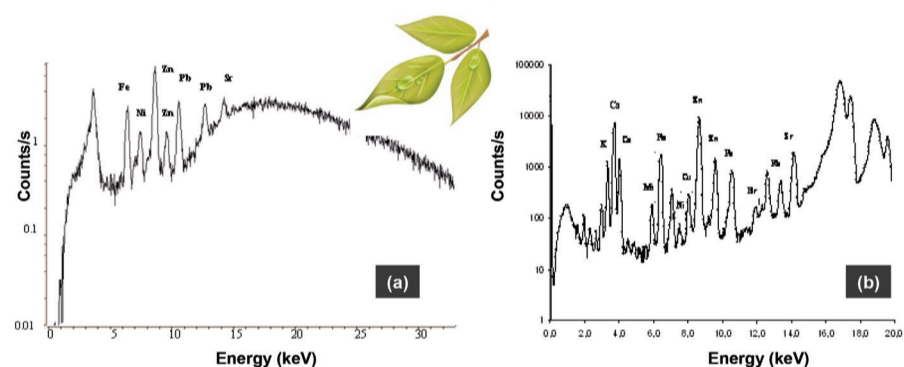


Figure 3. Basic spectra obtained in the analysis of a leaf sample using (a) an EDXRF spectrometer and (b) a P-EDXRF spectrometer

On the other hand, in total reflection XRF (TXRF) systems, the primary beam strikes a sample on a very flat support at a very small angle ( $\leq 0.1^\circ$ ) compared with conventional EDXRF systems ( $\sim 45^\circ$ ) and that results in a low penetration depth of the exciting beam. Due to the inherent surface sensitivity of TXRF, since its development, this technique has been primarily used for controlling contamination of silicon wafers in the semiconductor industry and for trace element analysis of small quantities ( $\mu\text{L}$ - $\mu\text{g}$ ) of liquid and solid samples deposited on a reflective carrier (usually a quartz reflector).

Finally, in some XRF spectrometers, a focusing optic device is introduced between the X-ray source and the sample in order to focus the incident radiation into a small spot on the sample in the micrometre and sub-micrometre size scale. Originally, micro X-ray analysis systems were largely restricted to X-ray techniques using excitation by accelerator charged-particle beams, but significant advances in focusing optics (mostly the development of polycapillary lenses) have promoted the development of micro beam XRF ( $\mu\text{-XRF}$ ) instrumentation employing (conventional) X-ray tubes as the source of primary radiation. Nowadays,  $\mu\text{-XRF}$  is an indispensable tool in many disciplines (including: industrial, environmental, cultural, and forensic) in order to get information on the element distribution at the micrometre and sub-micrometre scale.

Over the last few decades, most of the published XRF analyses were performed using large-scale instruments with high-power X-ray tubes, which demanded water-cooling systems and liquid-nitrogen cooled detectors. However, in recent years, the development of ceramic low-power X-ray tubes (maximum power  $\sim 50\text{ W}$ ) and silicon drift detectors (SDDs), that do not require cooling media and gas consumption to operate, has promoted the development of benchtop or table-top XRF instrumentation (both EDXRF and WDXRF) in low-cost compact designs. These improvements in X-ray excitation and detector systems coupled with technological development in batteries and microprocessors have led to the fast growing and wide adoption of field-portable or handheld units (FPXRF). These devices allow almost point-and-shoot ease of use and have proven especially useful in

art and solid waste studies due to the possibility to analyse objects that cannot be transported to the laboratory.

Additional and more detailed information on the state-of-the art of XRF instrumentation for chemical analysis can be found in a former published article in Petro Industry News (see the reference list).



Figure 4. Graphical view of the bench-top dual-view ICP-OES spectrometer (Optima 8x00 ICP-OES spectrometers) supplied by Perkin Elmer (Source: <http://www.perkinelmer.com>)

## Elemental Analysis of Liquid Samples

### • Atomic spectroscopic techniques

Despite the fact that AAS continues at present to be a well-established technique in the elemental analysis field, its use for water sample analysis is limited mostly due to the sequential character of the determination of the elements which significantly increases the analysis time. For this reason, atomic emission spectrometers using inductively coupled plasma as excitation source (ICP-OES) are preferred instead, as they allow the simultaneous determination of a variety of elements over a wide dynamic concentration range. This technique is widely used as the official analysis method according to ISO standards and also supports analysis in many different fields including research and development, automated analysis for production control and water-quality monitoring for environmental management. The recent technological advances in plasma technology and optical systems have led to an improvement of the sensitivity and limits of detection for trace analysis as well as a reduction of the argon consumption and thus the operating costs. According to an ICP cost calculator program supplied by SPECTRO Analytical Instruments, considering 8 operating hours per day, the operating costs of most newest ICP systems (including optic purge gas consumption, plasma operation gas consumption and electricity consumption) is around 5000 euro per year. An additional advantage is also the compact dimensions of such systems as it can be seen in Figure 4. Today most manufacturers of ICP-OES spectrometers worldwide provide bench-top systems at a reasonable price. In Table 2, a summary of some ICP-OES spectrometers currently available on the market is presented.

Table 2. Examples of reduced-size ICP-OES spectrometers and quadrupole based ICP-MS systems currently available on the market (List of manufacturers in alphabetic order).

Instrument	Type of ICP System	Manufacturer	Website
Agilent Technologies	ICP-OES ICP-MS	700 Series 7700e, 7700x, 7700x, 7900	<a href="http://www.chem.agilent.com">www.chem.agilent.com</a>
Bruker	ICP-MS	aurora M90 aurora Elite	<a href="http://www.bruker.com">www.bruker.com</a>
Perkin-Elmer	ICP-OES ICP-MS	Optima™ Series NexION 300	<a href="http://www.perkinelmer.com">www.perkinelmer.com</a>
Thermo Scientific	ICP-OES ICP-MS	iCAP™ 7200 iCAPQ	<a href="http://www.thermoscientific.com">www.thermoscientific.com</a>

If extremely low limits of detection (at microgram/nanogram per litre level) or isotopic analysis of different elements present in a sample is required, then ICP-MS systems are preferred. The unequivocal separation of analyte ions from spectral interferences is a prerequisite for accurate and precise elemental analysis when using such instrumentation. High mass resolution spectrometers (magnetic sectors) are commonly used for this purpose. However, these systems are quite expensive and they are not widely available for most analytical laboratories. Recent technological advances (development of innovative interfaces and reaction/collision cells among others) have promoted the improvement of the benefits of quadrupole-based ICP-MS systems which are affordable and easy-to-use for trace and ultra-trace elemental analysis. In Table 2, a summary of some quadrupole-based ICP-MS spectrometers currently available on the market is displayed.

### • X-ray Fluorescence Spectrometry

The analysis of liquid samples by conventional XRF instrumentation usually implies a high X-ray scatter background resulting in detection limits in the mg/L range which are not satisfactory for most applications. Therefore, in most of studies related to the analysis of liquid samples by XRF techniques, a preconcentration procedure is carried out before the analysis. Taking into account that XRF operates best on solid samples, gives optimal sensitivity and accuracy for thin homogeneous targets and offers sufficient spectral resolution for assessing several elements simultaneously, multi-elemental preconcentration procedures leading to solid thin targets will be ideal. Many preconcentration methods for the analysis of liquid samples by X-ray spectrometric techniques have been developed in the last decades. A comprehensive overview on this subject can be found elsewhere (see Reference list). As an example, in Figure 5 the benefits of using a preconcentration procedure for the determination of trace amounts of Cd in sea water samples by P-EDXRF is displayed.

As discussed in the previous section, TXRF systems can also be used for trace element analysis of



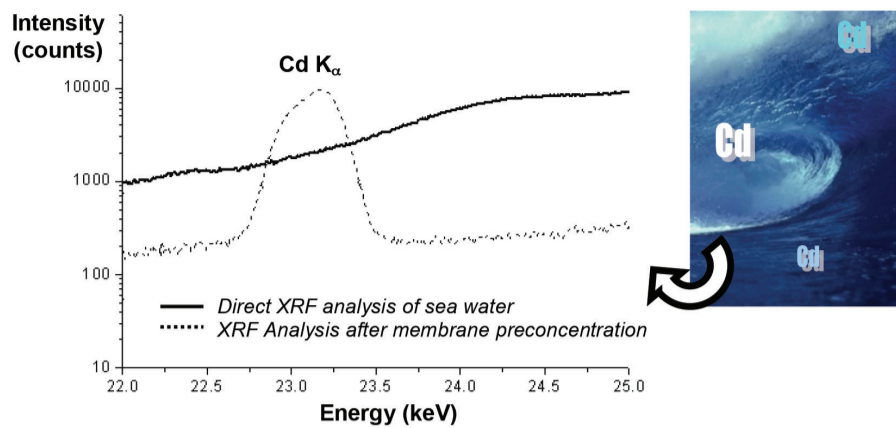


Figure 5. Comparison between spectra obtained for the direct analysis of a water sample containing 600 µg L<sup>-1</sup> of Cd and after a membrane preconcentration step. (Epsilon 5 HE-P-EDXRF spectrometer, PANalytical).

small quantities (µL) of liquid samples deposited on a reflective carrier. The TXRF system makes use of the fact that, at very low glancing angles, the high background that would generally occur due to scatter from the sample support is absent. Because the background is so low, concentrations in the range of several µg L<sup>-1</sup> can be measured in aqueous samples without recourse to preconcentration. However, when dealing with the analysis of complex water samples (i.e., sea water) a special preparation method has to be applied to separate the suspended matter and to remove the salt content prior to the measurement.

### Comparative Performance of Analytical Techniques

In order to select the best elemental analytical technique for a given purpose, in addition to the limits of detection and multi-elemental capability, other analytical parameters and budgetary considerations are of significance. In Table 3, information on this topic is displayed for the analytical techniques aforementioned. In fact, there is no universal analytical technique useful for the determination of the whole periodic table in all type of samples. Each of these techniques has its advantages and drawbacks and thus, few laboratories rely on only one of these analytical methods, but often use compatible combinations of them.

Table 3. Analytical characteristics and budgetary consideration for analytical techniques used for elemental analysis.

	FAAS	ETAAS	ICP-OES	ICP-MS	XRF
Sample throughput	10-15 s (per element)	3-4 min (per element)	6-60 element (per minute)	2-5 min (all elements)	10-15 min (all elements)
Dynamic range	10 <sup>3</sup>	10 <sup>2</sup>	10 <sup>5</sup>	10 <sup>5</sup> - 10 <sup>8</sup>	10 <sup>4</sup> - 10 <sup>6</sup>
Precision	<10 %	1-10 %	1-5 %	<5 %	1-10 %
Interferences Spectral	Very few	Very few	Many	Few	Few
Chemical (matrix)	Many	Very many	Very few	Some	Some
Sample amount	mL	µL-µg	mL	mL	mg-g
SemiQ information	No	No	Yes	Yes	Yes
Isotopic analysis	No	No	No	Yes	No
Ease of use	Very easy	Moderate	Easy	Moderate	Easy
Automatisation	No	Yes	Yes	Yes	Yes
Capital costs	Low	Medium	High	Very High	Medium/High
Running costs	Low	Medium	High	Very High	Low
Cost per element analysis	Low	High	Medium	Medium	Low/Medium

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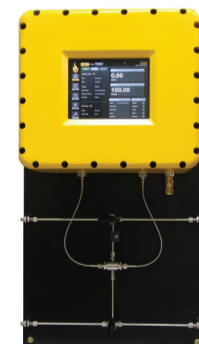
PAC IRIS Software has numerous plugins (PAC instruments it connects to) including the Herzog OptiDist, ISL PMD 110, Herzog HVM472, ISL VIDA, and many more. All IRIS plugins include a results section to view previously completed tests, a run control section that displays real-time instrument data, a reports section to print reports, a LIMS connection to automatically transfer data, and an online manager to allow web-based control of the software and remote data access. Some plugins have more advanced features including the ability to start a test, to define upper and lower limits and targets, to define the test results from a sample test as a standard to compare to other test results, or for users to modify units of the instrument parameters.

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