

A vertical photograph of a bright blue sky with scattered white clouds, positioned on the left side of the page.

Elemental Analysis of Airborne Particles

Evaluating XRF, ICP-OES, and ICP-MS Analytical Technologies

Introduction

Air pollution is a continuous concern of industries, governments, and populations worldwide. Particularly the harmful health effects of the exposure to heavy metals such as lead, arsenic, or cadmium absorbed into particulate matter, carried through the air, and introduced into the lungs and body are within focus.

These particles are principally generated by processes such as combustion. Monitoring and analysis of the elements present in these airborne particles is performed by a variety of organizations, - by industry, environmental protection agencies, as well as research institutes and testing laboratories for

environmental and occupational health and safety.

Fortunately, modern laboratory-grade spectrometric analyzers are available that can handle the necessary analyses. They provide accurate, efficient airborne elemental particle identification and measurement. This paper explains several of the methodologies commonly employed for these applications — focusing on ED-XRF, ICP-OES, and ICP-MS technologies — and describes the desirable attributes of suitable analyzer models for each.

Growing Regulations

Over recent decades, science has linked pollution by fine particles to increased incidence of health problems ranging from breathing difficulties to heart disease, premature births, and several forms of cancer. Beyond the general dangers of any particulate matter (PM), metal particles can pose specific problems. For instance, lead can cause neurological disorders.

Increasing regulatory scrutiny and tightening requirements add urgency to implementing systematic, accurate air monitoring efforts.

Detection and measurement of immissions — particles present or received — require monitoring air quality in widespread areas. They're typically performed by governmental regulators and environmental research institutes. Detection and measurement of emissions — particles put out — require monitoring the air quality of point sources, such as vehicles or the smokestacks of incinerators, chemical or steel plants, and so on. They're usually performed by testing laboratories, on behalf of companies that must fulfill regulatory fiat limiting exposures for surrounding populations, or for employees.

This paper focuses on airborne particle analysis technologies carried out on a discontinuous basis, sample by sample, via laboratory-grade ICP or XRF instruments. Analysis of air filters often concentrates on monitoring regulatory

limit values for certain metals (such as lead, cadmium, arsenic, and nickel) and particulate matter (PM) in the air. These limit values vary by industry, as regulations vary by region or country.

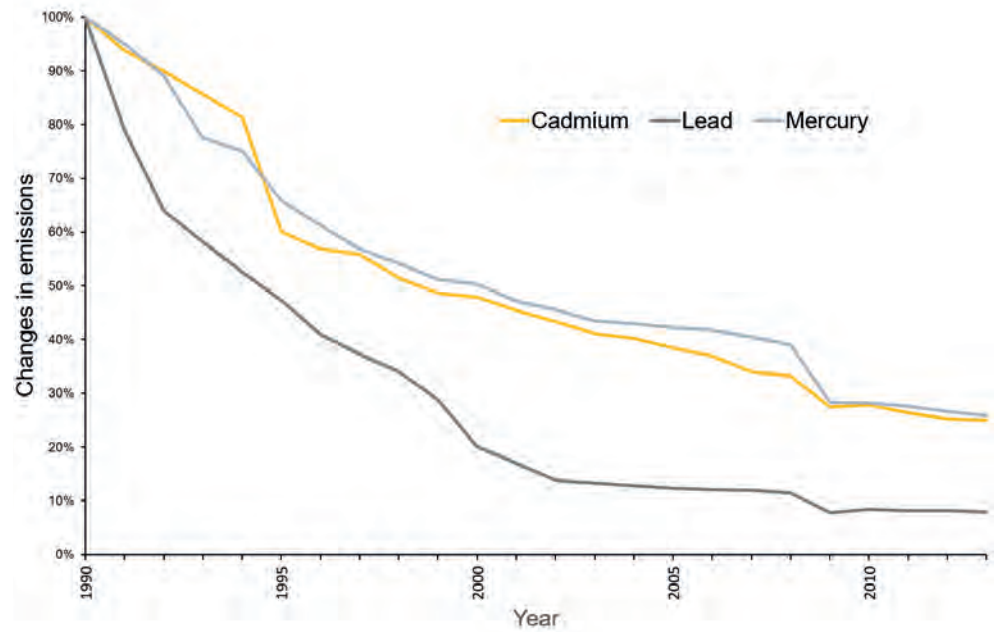
In contrast, some monitoring, such as for mercury in coal-fired power plants and other industrial facilities, is mandated to be performed continuously and online. Such monitoring systems for mercury are typically based on atomic fluorescence spectrometry. As per international guidelines the offline analysis of ambient air is mainly done by discontinuous measurements using cold vapor atomic fluorescence or cold vapor atomic absorption spectrometry. Please note that the measurement of mercury using ICP and XRF technologies is also possible, adding a small amount of stabilizing reagents like gold for sample preparation for ICP.

Figure 1 shows the positive effects of monitoring, analysis, and control over the time period. Figure 2 exhibits recent amounts of remaining problematic emissions. Mercury, generally determined using atomic fluorescence spectrometry, is not included within the scope of this white paper.

European Union

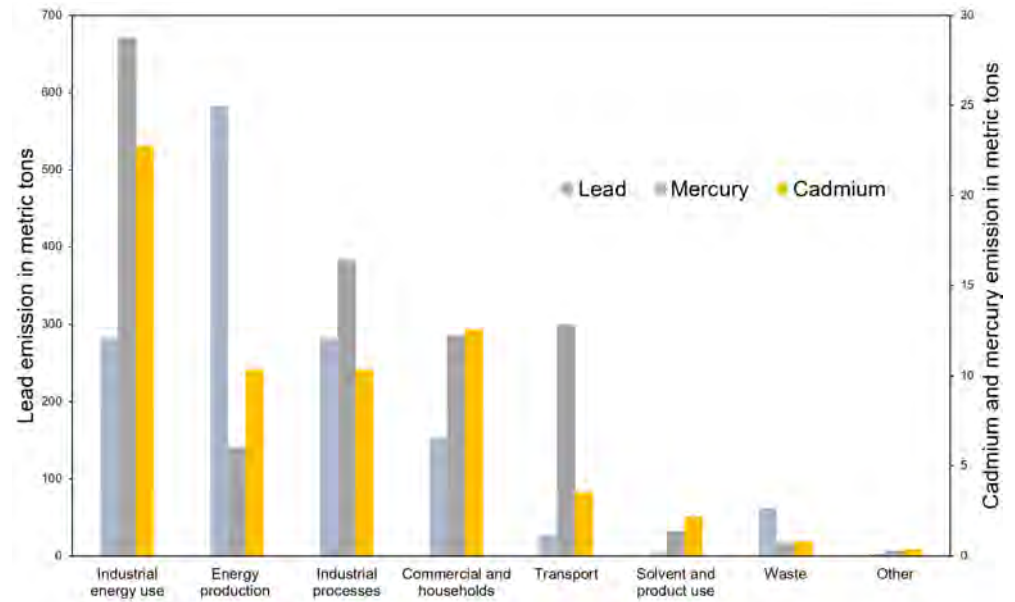
The EU air quality directive 2008/50/EC describes the monitoring of air — on an immission basis as well as at specific emission sources — principally for lead, mercury, arsenic, cadmium, and nickel. Other directives such as

Figure 1: Trends in emissions of selected heavy metals (Europe, 1990-2013)*



* European Environmental Agency, 2015

Figure 2: Emissions of selected heavy metals (Europe 2013, by sector)*



* European Environmental Agency, 2015

Germany's Technical Instructions on Air Quality Control (German Engineers Association/VDI standards) depict further monitoring parameters. To perform air quality analysis, existing EU standards primarily call for instruments based on ICP technologies. Additional analytical methods (such as ED-XRF) may be used where they can prove to give results equivalent to the reference method.

United States

The USA's Clean Air Act and subsequent rules call for monitoring of hazardous air pollutants such as mercury and lead, listing several designated references and equivalent methods. Organizations such as the National Institute for Occupational Safety and Health (NIOSH) describe parameters and analysis methods. For air quality analysis, several US standards — such as the Environmental Protection Agency's Inorganic Method Compendium (EPA IO-3.3) — require instruments based on either ICP or XRF technologies.

Asia

Standards vary across the region. "Green regulations" requiring air monitoring are proliferating where industrial development continues to increase. Some regulations describe the use of older solutions such as flame AAS or photometric technologies. But ICP technologies are already well represented in government standards, and acceptance of XRF technology is growing.

China: The GB 3095-2016 standard describes air monitoring of the heavy metals, lead, cadmium, arsenic, mercury, and chromium.

India: Indian National Ambient Air Quality Standards (NAAQS) describe the monitoring of arsenic, lead, and nickel (as well as PM and other gases).

Modern Technologies

A number of spectrometric technologies have been applied to airborne particle analysis and monitoring over the years. Each has displayed varying pluses and minuses. As demand for this analytical task has increased, technologies have evolved and improved.

Atomic absorption spectrometry (AAS) was once commonly employed for air filter analysis. While often still the most affordable solution per initial purchase price, AAS may suffer from limitations including low dynamic range, chemical interferences, sequential operation (and associated relatively low throughput), safety risks when left unattended, recurring lamp replacement expenses, and the need for frequent recalibration. Thus other technologies have increasingly replaced it.

Photometers were also used fairly frequently. But these suffer several disadvantages, such as low accuracy for high concentrations, the necessity of more extensive sample preparation, and the lack of simultaneous screening for all targeted elements. With the advent of the better technologies shown below,

photometric analyzers are probably more suitable for measuring alkali metals than the toxic heavy metals most of interest in air particle analysis.

Today, the most commonly used technology for analysis of airborne particles is probably one of two inductively coupled plasma (ICP) techniques. Depending on desired detection limits — and whether local regulations demand a specific choice — these are inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) instruments.

Finally, XRF spectrometers are increasingly popular — especially energy dispersive X-ray fluorescence (ED-XRF) models.

Most suppliers specialize in one or two of these technologies. A few manufacturers, such as SPECTRO Analytical Instruments — a leader in design and manufacture of instruments for environmental analysis — can provide all three.

Table 1 shows advantages and disadvantages of each spectrometer type, followed by a detailed discussion.

Table 1: Comparing Technologies

	ED-XRF (SPECTRO XEPOS)	ICP-OES (SPECTROBLUE TI)	ICP-MS (SPECTRO MS)
Acquisition Costs	\$\$	\$	\$\$\$
Annual Operating Costs	Low	Moderate	Moderate
Sample Preparation	Not required; non destructive	Filter digestion required; destructive	Filter digestion required; destructive
Calibration/Standardization	Only recalibration required, typically once per month/quarter	Daily, as required	Daily, as required
Measurement Speed	15 – 30 minutes (as needed) per sample	3 minutes per sample	3 minutes per sample
Space Requirements	Benchtop	Benchtop	Floor model
Detectable Elements	Na – U	Li – U (except C, N, O)	Li – U (except C, N, O), each isotope
Test Methods	EPA IO-3.3, VDI 2267-12, CPCB-NAAQS*	EN 14385, EPA IO-3.4, VDI 2267-1 & -14, CPCB-NAAQS*	EN 14385 & 14902, EPA IO-3.5, VDI 2267-1, CPCB-NAAQS*
Typical Limits of Detection	Parts per million (ppm)	Parts per billion (ppb)	Parts per trillion (ppt)

*Central Pollution Control Board – National Ambient Air Quality Standards

Sample Taking

A number of spectrometric technologies have been applied to airborne particle analysis and monitoring over the years.

Each has displayed varying pluses and minuses. As demand for this analytical task has increased, technologies have evolved and improved.

Sample Preparation

ICP-OES, ICP-MS, AAS, and photometric analyses all require sample preparation. Filters are placed in vials or other containers, and are mixed with digestion reagents (usually nitric acid plus hydrofluoric acid or hydrogen peroxide).

The resulting liquid with suspended solids is then heated on hotplates, in a microwave digestion system or in hot blocks for extended times, until the particles are digested. After appropriate dilution the sample can then be introduced into the analyzer.

By contrast, XRF analysis requires no such lengthy pretreatment. The loaded filters themselves are simply placed into an analyzer's appropriately sized sample cup. (If required, filters may first be cut to size.) This provides rapid results and noticeable ease of use.

After calibration — with liquid standards for ICP, or available reference filters with XRF — analysis can begin according to the given instrument's method.

ED-XRF Technology

How ED-XRF works

Energy-dispersive X-ray fluorescence (ED-XRF) instruments identify and quantify the elements present in a substance as follows: A sample is subjected to X-rays emitted from a high-intensity X-ray tube. Some energy is absorbed by the atoms of elements in the sample. These excited atoms then emit X-ray fluorescent signals — along a spectrum of energies characteristic of the elements present. All element-specific signals are measured simultaneously, using a fixed, energy-dispersive semiconductor detector.

The radiation intensity of each elemental signal is proportional to the concentration of the element in the sample. This signal is processed in a multichannel analyzer, and the measured spectra are used to determine intensities. Concentrations are calculated using a calibration based on measurements of samples with known composition.

ED-XRF advantages and disadvantages

Modern ED-XRF analyzers are increasingly utilized for airborne particle analysis. For most uses, they are often now regarded as the easier and quicker solution when compared to ICP technologies.

ED-XRF instruments allow nondestructive sampling plus relatively fast, simple sample preparation, without the need

for preheating or chemical digestion. This enables quick analysis — even by relatively inexperienced laboratory personnel — while minimizing the risks of contamination or element loss. ED-XRF also offers lower operating costs compared to ICP. It uses no expensive argon gas, consumes less electricity, and needs fewer supplies.

Thus the latest ED-XRF analyzers can provide fast, precise, accurate, and economical solutions.

Some limitations of traditional ED-XRF technology made it difficult or impossible for these analyzers to measure certain heavy metals such as cadmium. They simply couldn't muster sufficiently low detection limits. However, scientists and manufacturers have made improvements to ED-XRF

methodology and to some instruments. So for the most advanced units, limits of detection and analytical capabilities using ED-XRF have caught up with — and may now even surpass — regulatory requirements.

For contract environmental and industrial laboratories, local regulations may prescribe which technology must be used. When it comes to research laboratories, which typically are free of regulations mandating particular technologies, some prefer the nondestructive analysis offered by ED-XRF. Others are looking for trace elements or high-volume use, and often prefer ICP-OES or ICP-MS.

In terms of disadvantages, note that only quite advanced ED-XRF units offer analysis of heavy metals. Many models utilizing traditional ED-XRF technology still lack sufficient detection limits for certain elements of interest: principally cadmium.

Modern ED-XRF analyzers are probably most suitable for smaller laboratories or other operations that require modest volumes of air particle analysis to be performed quickly and easily. Larger laboratories with heavy air particle analysis loads requiring the highest throughput may instead consider ICP-OES models.

Superior ED-XRF solutions

The SPECTRO XEPOS ED-XRF spectrometer's groundbreaking design



SPECTRO XEPOS ED-XRF spectrometer

provides accurate, precise, reliable analysis of airborne particle samples. It's optimized for analysis of heavy metals and all other relevant elements found in those samples.

The instrument is suitable for air particle analysis of industrial emission sources, as well as in ambient air monitoring. But SPECTRO XEPOS also delivers

outstanding analytical performance for analysis of soils and sludges, making it an increasingly popular all-round solution for environmental analysis.

Like other ED-XRF instruments, it performs nondestructive sampling with rapid, simple sample preparation — no preheating or digestion needed. But unlike others, it features an innovative 50 W / 60 kV X-ray tube, an improved high-count rate detector, and unique adaptive excitation technology. So it can furnish previously impossible sensitivity boosts of up to 10X over previous models, optimized to target element groups of the user's choice.

This makes it an analyzer that can actually deliver limits of detection low enough (down to less than one part per million) for heavy metals — until now, beyond the reach of ED-XRF technology.

SPECTRO XEPOS also accommodates users who choose to prioritize speed over utmost precision. It can dramatically cut measurement times while still maintaining precision levels comparable to traditional ED-XRF spectrometers. And it achieves unprecedented affordability with strategies such as low-volume helium purging for light elements in liquids and powders, and a vacuum system for solids.

Additionally, SPECTRO XEPOS is one of the few ED-XRF instruments from any supplier that offers a factory-installed method specifically for airborne particle analysis.

Element	LOD (3 σ) [ng/cm ²]
Al	1
As	0.4
Ca	0.6
Cd	4
Cl	1
Co	1.8
Cr	0.5
Cu	2.8
Fe	7
K	2
Mg	3
Mn	0.7
Ni	3
P	1
Pb	2.1
S	1
Sc	0.6
Si	1
Ti	0.6
V	0.6
Zn	1.9

Table 2: Typical limits of detection for air filter analysis, measured on SPECTRO XEPOS

Altogether, the SPECTRO XEPOS ED-XRF analyzer provides high resolution and sensitivity, reduced measurement times, low detection limits, low consumables use, and good long-term stability for exceptional quality of the analysis of airborne particles.

ICP-OES Technology

How ICP-OES works

Inductively coupled plasma optical emission spectrometry (ICP-OES) instruments are optimized for the detection of trace amounts of metals. ICP-OES technology relies on atomic/ionic emission, breaking down a sample within a high-temperature (typically up to 10,000° C) argon plasma to generate atoms and ions. Sample elements emit a characteristic number of specific spectral lines with different wavelengths when excited within the plasma. Emitted light is resolved into these separate lines by optical components such as diffraction gratings; the light is finally directed onto a detector array that quantifies light intensities at these different wavelengths.

As with ED-XRF analyzers, the radiation intensity of each elemental signal is proportional to the concentration of the element in the sample. This signal is processed and the measured spectra are used to determine intensities. Concentrations are calculated using an empirical calibration.

ICP-OES advantages and disadvantages

The toxic heavy metals of most concern for airborne particle analysis are well within the limits of detection for these analyzers — a critical advantage when trace amounts of elements must be analyzed. Additionally, a good ICP-OES spectrometer can conduct a high number of sample analyses in relatively short time. This technology may prove the ideal choice for larger laboratories that require the highest throughput, and that may conduct occasional air particle analyses as part of a larger menu of analytical tasks.

Note that ICP-OES is destructive of the sample. It also requires sample preparation with heating and digestion. And compared to XRF instruments, it incurs higher operating costs for argon, power, reagent supplies, and more.

Also, most (but not all) ICP-OES analyzers rely on a conventional optical approach, utilizing two-dimensional detector arrays and diffraction gratings of the echelle type. Unfortunately, this technology can suffer from lower light throughput and stray light, plus interferences and overlaps especially in line-rich spectra. For certain elements in certain circumstances, these can diminish overall analyzer sensitivity, resolution, and stability.

Finally, there are still ICP-OES instruments which operate on a sequential basis: having to analyze each element in a sample one at a time. Such

instruments lack the ability to capture the entire spectrum with each analysis. This handicap can further increase analysis times. It also prevents users from archiving complete data for later study and/or regulatory compliance proof.

Superior ICP-OES solutions

The SPECTROBLUE ICP-OES analyzer is a relatively compact, midrange solution that sets a new benchmark of performance for routine laboratory

analysis — ideal in settings such as environmental testing labs. That high performance is combined with simple operation, low maintenance, and great affordability.

Users can choose from three SPECTROBLUE models, each employing a different plasma view. The unique axial interface version, SPECTROBLUE EOP, provides high sensitivity and detection limits for superior analysis of trace elements in air filters. The SPECTROBLUE SOP radial interface version offers precise performance at higher sample concentrations (such as when analyzing major elements in metal alloys). And the SPECTROBLUE TI twin interface version automatically performs both axial and radial viewing of the plasma. This optimizes linearity and dynamic range, and can effectively eliminate the easily ionizable element (EIE) effect — while enabling high-sensitivity measurement of toxic elements (such as lead, cadmium, and arsenic) in environmental samples.

It also avoids a common ICP-OES shortcoming. Unlike conventional echelle-based optical technology, SPECTROBLUE uses an innovative Optimized Rowland Circle Alignment (ORCA) design. Avoiding two-dimensional detectors, ORCA polychromator systems take advantage of modern linear detector performance. They incorporate arrays of charge coupled device (CCD) linear detectors optimally fitted to the focal curve. Using

Element	λ [nm]	LOD (3 σ) [$\mu\text{g/L}$]
Al	167.078	0.05
As	189.042	2.21
Ba	233.527	0.13
Be	234.861	0.04
Cd	226.502	0.18
Co	228.616	0.19
Cr	267.716	0.31
Cu	324.754	0.57
Fe	259.941	1.50
Mg	279.553	0.04
Mn	257.611	0.07
Mo	281.615	1.00
Ni	231.604	1.45
Pb	220.353	1.42
Sb	217.581	2.79
Sn	189.991	1.19
Sr	421.552	0.04
V	311.071	0.63
Zn	206.200	0.13

Table 3: Typical limits of detection for air filter analysis, measured using a SPECTROBLUE-TI in axial mode

curved mirrors, with a concave grating arrangement optimized to limit light loss during diffraction, results in sensitivity and uniform resolution over a wide spectral range, plus exceptional stability.

Unlike ICP-OES models, which operate on a sequential basis, SPECTROBLUE analyzes the entire relevant emission spectrum of a sample using two simultaneous measurements. This provides high-speed analysis. It's also critical when users wish to archive a complete record of airborne particle analyses for later study, or for proof of regulatory compliance — allowing later screening for elements that weren't initially analyzed.

Finally, SPECTROBLUE offers advantages such as a top-of-the-line generator for

utmost stability; innovative UV-PLUS recirculating gas purification technology to eliminate expensive argon purging of the optical system; and a breakthrough OPI-AIR air-cooled interface that avoids costly, complicated water cooling.

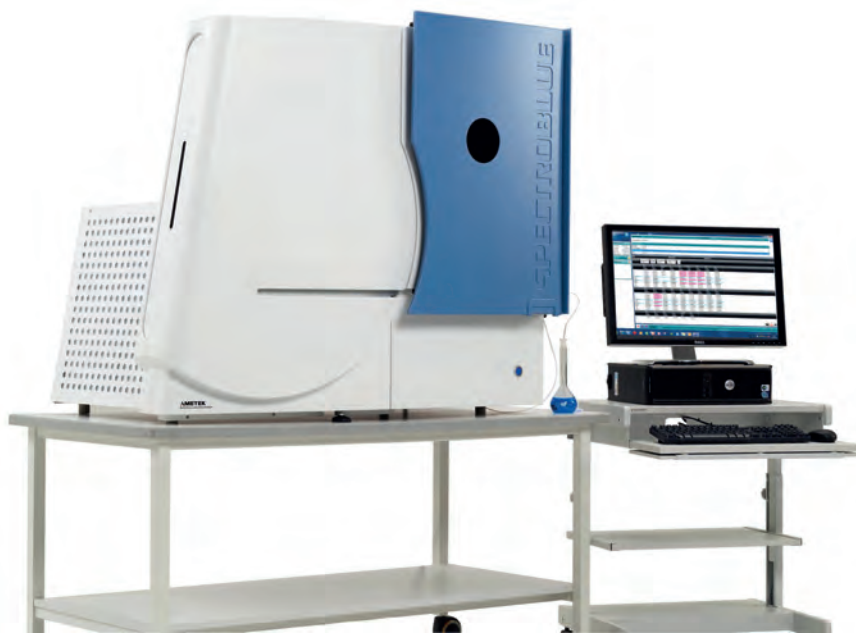
ICP-MS Technology

How ICP-MS works

Mass spectrometers utilize several different ionization techniques. For inorganic mass spectrometric analysis, as airborne particle analysis, users mostly rely on inductively coupled plasma mass spectrometry (ICP-MS).

In an ICP-MS instrument, sample components are atomized and ionized via a high-temperature plasma. The generated atom ions are sampled from the plasma through an interface, and accelerated. In a magnetic sector field model (like the SPECTRO MS instrument featured below), the ions are then deflected by electrostatic and magnetic fields in the analyzer section. The lower the mass of each ion (specifically, the smaller its mass-to-charge ratio), the greater its deflection. The various deflected ions are recorded by a detector. The system can identify which isotopes are present in the sample by their specific deflection in the analyzer fields.

(Note that quadrupole model ICP-MS instruments operate somewhat differently: accelerated ions are



SPECTROBLUE ICP-OES analyzer

subjected to electromagnetic fields oscillating among four rods. The mass-to-charge ratio of each ion determines its trajectory. Fully sequential, a QMS lets pass only one m/z-ratio to the detector, and different isotopes are determined by “scanning” the quadrupole fields.)

ICP-MS advantages and disadvantages

In a significant advantage, most ICP-MS analyzers demonstrate at least 10X the sensitivity of ICP-OES units, with much better limits of detection for elements of interest in airborne particle analysis.

However, most ICP-MS systems perform sequential analysis only. They must

analyze for each isotope one at a time, which naturally leads to longer total analysis times. The long time required to capture and record the entire mass spectrum typically forbids to do so, leading to gaps in the record. Note that a few newer ICP-MS analyzers don’t suffer from this limitation; see below.

ICP-MS is destructive of the sample. It’s also the most expensive of the technologies considered here. Typical instruments may cost approximately twice as much as ED-XRF models for initial purchase, and their greater operating costs include digestion reagents, etc.

Superior ICP-MS solutions

Compared to ICP-OES models, the SPECTRO MS ICP mass spectrometer offers higher sensitivity — by factors from 10X to 1000X — for air particle environmental samples, depending on the element being detected. The result is greater headroom for routine analytical tasks. These advantages make the SPECTRO MS ideal for the analysis of toxic trace elements in air.

Like several other SPECTRO analyzers, this instrument offers truly simultaneous measurement. Unlike most ICP-MS models, which operate on a sequential basis, SPECTRO MS analyzes the entire relevant mass spectrum from lithium to uranium at the same time. This capability can be extremely useful when users wish to archive a complete record for later study, or for proof of regulatory

Element	Isotope	LOD (3 σ) [$\mu\text{g/L}$]
Al	27	0.07
As	75	0.02
Ba	138	0.002
Cd	111	0.005
Co	59	0.01
Cr	52	0.02
Cu	63	0.02
Fe	54	0.7
Mg	24	0.10
Mn	55	0.02
Mo	98	0.006
Ni	60	0.03
Pb	208	0.002
Sr	88	0.003
V	51	0.02
Zn	66	0.04

Table 4: Typical limits of detection for air filter analysis, measured using the SPECTRO MS

compliance — allowing later screening for elements and isotopes that weren't initially analyzed.

In this fundamental step from sequential to simultaneous measurement, not only are precision and accuracy improved, but measuring time per sample is greatly reduced.

The heart of the SPECTRO MS analyzer's technological innovation is the combination of a double-focusing Mattauch-Herzog sector field mass spectrometer with a novel planar detector that is able to simultaneously

record the complete mass to charge dispersed ion beam. This detector uses the direct charge detection principle, with 4800 channels to cover all relevant isotopes at once. So the entire mass spectrum is always recorded "at a single glance," and then stored.

The unit's outstanding productivity results from excellent throughput, reliability, and ease of use. The SPECTRO MS is used primarily by larger testing laboratories and environmental labs that can take advantage of its superior capabilities.

Conclusion

Several analytical methodologies address the growing needs of industry and regulators for analysis of airborne particles. Most instrument suppliers specialize in one or two of the applicable technologies; SPECTRO Analytical Instruments on the other hand provides a comprehensive product portfolio.

With care to select modern analyzers that exhibit the right technological innovations and features, users can obtain airborne particle analysis that's rapid, reliably, accurate, and surprisingly affordable.



SPECTRO MS ICP-MS analyzer

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