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Heavy Metals Monitoring

Technologies and methods for analysis and monitoring - from industrial waste to environmental samples

Monitoring heavy metals has never been more in the spotlight. Recent regulation and legislation are set to keep it that way. This article outlines the impact heavy metals can have on human health and the environment and goes on to provide an insight into the wide range of analytical techniques available to the analysts involved in monitoring heavy metals today.

The beneficial properties of heavy metals have been appreciated for many centuries. The Romans, for example, used lead to improve the taste of wine and food - a habit that almost certainly resulted in high rates of gout and sterility within the ranks of the Roman elite. However, it wasn't until the industrial revolution that the production of heavy metals began to increase exponentially, and since then these elements have been put to a multitude of uses.

The potential toxicity of heavy metals has also been well documented throughout history. For instance, while the Romans thought their low level dietary exposure to lead was harmless, they were fully aware that the lead miners they depended on suffered acute poisoning.

Today, it is understood that exposure to heavy metals can seriously affect human health, causing developmental problems, cancer, organ damage, autoimmune and other disorders. Heavy metals are also a major environmental pollutant, capable of causing severe damage to ecosystems. Globally, heavy metal pollution affects millions of people and in some places it is becoming worse. Given the extent of the problem, governments worldwide are taking action to strictly limit the amount of potentially toxic heavy metals that can be released into the environment. >

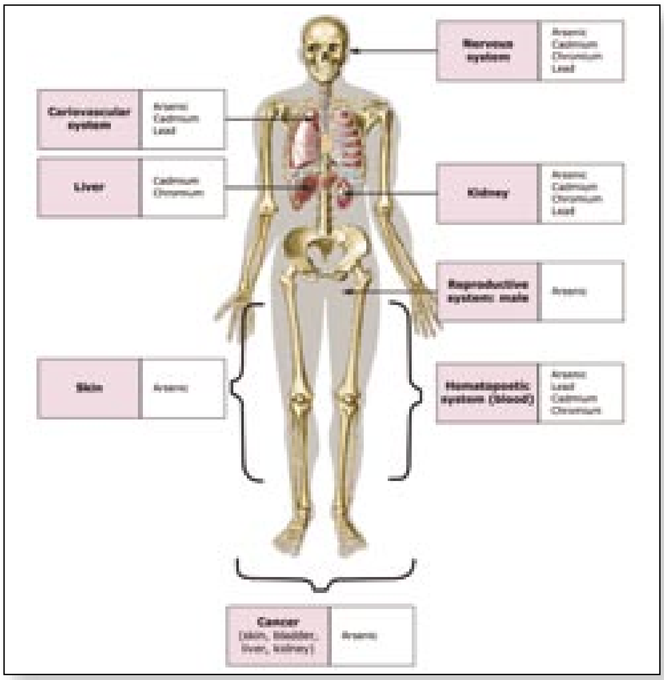

Figure 1: Primary organs affected following ingestion of certain heavy metals

Defining the problem

The term heavy metal is so commonplace in scientific literature that it is perhaps surprising that there is no universally accepted definition. A 2001 survey revealed that definitions can be divided broadly into those that are based on atomic weight, atomic number, other chemical properties, and toxicity[1]. Health and environmental legislation often specifies the heavy metals to which it applies, but this leads to inconsistency as, inevitably, different regulatory bodies classify different elements as heavy metals.

> "for the purposes of this article, the term heavy metal will refer to metals and semimetals (such as arsenic) that are associated with contamination and potential toxicity"

This definition generally includes the elements: lead, copper, nickel, cadmium, platinum, zinc and mercury.

A risk to the environment and human health

Potential toxic exposure to heavy metals arises in diverse circumstances, including environmental, therapeutic and industrial. Exposure patterns range from chronic, low level, such as exposure to lead paint; or acute high dose exposure, either small scale such as a child swallowing a mercury battery, or large scale such as accidental contamination of a water supply[1].

Entering the body by ingestion, inhalation or absorption through the skin or mucous membranes, metals are stored in the soft tissues. Once absorbed, heavy metals compete with other ions and bind to proteins, causing impaired enzymatic activity and potentially damaging many organs throughout the body.

The type of damage depends very much on the metal and the kind of exposure. For example cadmium, exposure to which occurs mainly through food crops grown on contaminated soils, accumulates in the kidneys and is implicated in a range of kidney diseases[2]. It may also have important carcinogenic effects and there is a reasonable chance it is genotoxic[3]. While mercury, which is found mainly as elemental and methyl mercury, is particularly harmful to foetal and embryonic nervous systems, causing learning difficulties, poor memory and shortened attention spans[4]. Methyl mercury is also classified as a possible human carcinogen by the International Agency on the Risks of Cancer. The major human exposure route is via ingestion, particularly from certain types of fish.

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Sources

Trace metals exist naturally in the environment. Problems occur when their concentrations are greatly increased. Heavy metals enter the environment - land, water and air - in a variety of ways, including from operational and former extractive mines, untreated sewage, traffic and combustion by-products. Once in the environment, metals can be transported considerable distances from their source. For example most of the mercury found in high concentrations in the Florida Everglades has travelled on trade winds from Europe and Africa.

Current situation

Of the heavy metals released from various products and processes, cadmium, lead and mercury are of greatest concern to human health, because of their toxicity, potential to cause damage at low concentrations, and ability to bio-accumulate[2]. In Europe, for example, significant progress has been made in reducing emissions to air of these metals: between 1990 and 2004 the total of these anthropogenic emissions in the European region decreased for all the three metals - for lead by about 84%, cadmium 47% and mercury 44%[3]. >

Another example where the situation has improved vastly is for lead in gasoline. In the U.S. for instance, during the 1970s, researchers found that combustion of leaded gasoline had become the primary source of lead in the environment. Therefore, the U.S. Environmental Protection Agency promoted legislation to ban lead in gasoline, and since then concentrations of lead in blood, a key indicator of exposure to lead, have declined significantly. In young children, the median concentration of lead in blood decreased by 85 percent from 1976 to 1999-2000[4].

However, on a global scale the picture is less encouraging. The accumulation of toxic heavy metals in the environment is actually increasing due to human activity. In particular, mining operations and heavy industry in the developing world is leading to the accumulation of high concentrations of toxic heavy metals in rivers and lakes[5].

A further area of concern is in dealing with waste from computer and IT equipment, one of the categories of waste undergoing the most rapid growth worldwide. Such refuse can release lead, mercury and cadmium into the environment. Improper disposal of computer equipment is causing severe problems. In the worst cases, waste has ended up in poorly managed facilities, such as the group of waste sites in Guiyu, south-eastern China, which became the focus of international attention in 2002. At Guiyu, imported computer waste was being picked apart by hand, alongside rivers and fields, creating significant health and environmental risks.

Legislation and regulation

Regulatory organizations across the world are involved in making environmental policies to reduce the harmful impacts of heavy metals.

> "given that heavy metals cross between land, water and air, and can travel huge distances, legislation often requires a cross-media and trans-national approach"

The latest major legislation, which came into force on 1st July 2006, is the European Union's (EU) stringent new rules on electrical and electronic equipment in relation to its composition and the levels to which it should be recycled. The Restriction of Hazardous Substances (RoHS) directive limits the use of certain hazardous materials in electrical and electronic equipment; and The Waste Electrical and Electronic Equipment (WEEE) directive will prevent the generation of waste from electrical and electronic equipment and reduce the disposal of such waste by encouraging reuse and recycling.

The directives seek to avoid or limit the use of specific heavy metals and other hazardous substances - namely, lead, cadmium, mercury, hexavalent chromium, and polybrominated biphenyl and polybrominated diphenyl ether. The sales and marketing of any new electrical and electronic equipment containing more than the agreed levels of these substances is now banned from the EU.

Around the world similar directives are being introduced, including electronic waste recycling legislation in the U.S., often referred to as California RoHS. Japan introduced legislation similar to WEEE in 1998 and RoHS is being adopted in China. Throughout Asia, especially where exports of electronic products to the EU represent an important share of foreign trade, countries have been quick to respond to the challenges of WEEE and RoHS.

> "there are many methods available for analysis: some based on emission or absorption of electromagnetic energy or radiation, with others based on the chemical interaction of heavy metals"

Regulating emissions

Dealing with waste is just one aspect of the problem. The United Nations has addressed the emission of heavy metals with the 1998 Aarhus Protocol on Heavy metals. It targets cadmium, lead and mercury and obliges parties to reduce their emissions for these metals. The Protocol aims to cut emissions from industrial sources (iron and steel industry, non-ferrous metal industry), combustion processes (power generation, road transport) and waste incineration. It lays down stringent limit values for emissions from stationary sources and requires the phasing out of leaded fuel. It also introduces measures to lower heavy metal emissions from other products, such as mercury in batteries, and proposes the introduction of management measures for other mercury-containing materials. The EU ratified the Aarhus protocol on behalf of its member states in 2001 and at the time of writing, a total of 36 countries had signed up to the protocol.

Methods of analysis

Given the potential for heavy metals to cause damage to health and the environment, accurate and precise monitoring is essential to ensure safety regulations are being met.

Emission or absorption of electromagnetic energy or radiation

Atomic Absorption (AA) spectroscopy

The energy source of an AA spectrometer emits resonance line radiation. The instrument's detector measures the level of absorption from a sample, which is fed as an aerosol and vaporized. Analyte concentration is determined from this. The most advanced instruments have more than one channel for simultaneous determination of several elements.

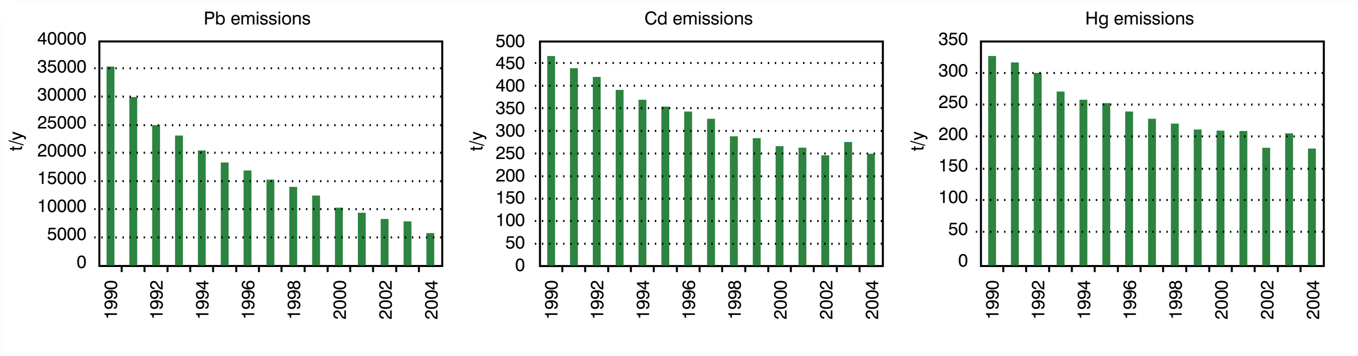

Figure 2: Total anthropogenic emissions of lead, cadmium and mercury in the EMEP region in the period 1990-2004 according to the official data combined with expert estimates

Inductively Coupled Plasma (ICP) - Atomic Emission Spectrometry (AES)/Mass Spectrometry (MS)

ICP uses very high temperature plasma, sustained with a radiofrequency electric current, that efficiently desolvates, vaporizes, excites and ionizes atoms. ICP is coupled with MS or AES: ICP as the method of ionisation, with MS or AES as the method of identification and detection of ions. Both methods are highly sensitive and since all atoms in a sample are excited at once, they can be detected simultaneously.

X-ray fluorescence spectroscopy (XRF)

XRF spectrometry is a non-destructive technique used to identify and determine the concentrations of elements present in solid, powdered and liquid samples. There are two basic types:

Wavelength Dispersive XRF (WDXRF)

In WDXRF spectrometry, the polychromatic beam emerging from a sample surface is dispersed into its monochromatic constituents by an analyzing crystal. The wavelength for any measured line is calculated from the crystal parameters and diffraction angle. Simultaneous WDXRF spectrometers use one or more detectors placed at defined angles for different elements. Sequential WDXRF spectrometers turn the crystal and measure the spectrum sequentially.

Energy Dispersive XRF spectrometry (EDXRF)

An EDXRF spectrometer works on the principle that the pulse height of the detector signal is proportional to the X-ray photon energy, which is correlated with the wavelength. Fluorescence photons from the sample hit the detector directly. Elements and their concentrations are identified by counting pulses at different energy levels. A multichannel analyzer enables simultaneous photon counting at different energies.

Fluorescence spectrophotometry

Fluorometers measure the amount of fluorescent radiation produced by a sample when exposed to monochromatic radiation. Light is collected at 90 degrees from the incident beam and detected with photomultipliers or photodiodes. Fluorometers are often used for continuous flow measurements but are also used for single samples – either in the laboratory or in the field.

Instrumental neutron activation analyses (NAA)

NAA measures gamma rays emitted by a sample when irradiated in the neutron flux of a research reactor. Elemental composition is determined by the identification of characteristic gamma ray energies associated with different isotopes. If the number of gamma rays emitted over time is compared to that of irradiated calibration standards, quantitative data can also be obtained.

Chemical interaction of heavy metals

Ion chromatography

Ion chromatography is used for the analysis of common anions and cations in aqueous solutions. Ion-exchange resins separate atomic or molecular ions based on their interaction with the resin. Samples must be aqueous solutions and may require filtration or dilution. For solid samples, ions are extracted from the sample with water. Most ion chromatography instruments use two mobile phase reservoirs containing buffers of different pH, and a programmable pump that can change the pH of the mobile phase during the separation.

Chemical testing kits

A number of kits are available for analyzing samples containing heavy metals, including colorimetric and titrimetry kits. Colorimetric kits are portable and simple to use but provide only limited information, such as an indication as to whether a particular pollutant may be present. Titrimetry kits, which work on the principles of titration, are a routinely used field method. However, they are time consuming if several samples require measurement.

Other methods

There are other techniques available, based on the electrical interaction of heavy metals, such as Voltammetry and Amperometric cell sensor techniques. There are also biological techniques, including bio-assessment and toxicity testing. Bio-assessments are expert interpretations of the health of an ecosystem, generally used to identify the existence of an ecological risk and determine whether data collection is needed. Toxicity tests rely on specific organisms and their biological response to contaminants. >

Bench-top EDXRF instrument and high-performance WDXRF system - Courtesy of PANalytical

Choosing the right technique

The best method to use depends very much on the application. For simple and inexpensive screening, biological assessment or chemical kits may be appropriate. To meet the demands of current environmental legislation, however, an approach that can measure heavy metals at low detection limits is needed. For this, the best methods include ICP, XRF, AA spectrometry and ion-chromatography. NAA also provides very accurate analysis, but it has major limitations - following analysis a sample remains radioactive for many years, and there is also the need for a nuclear reactor. This makes the technique expensive and since the introduction of newer methods, NAA has declined in popularity.

Fluorescence spectrophotometry offers detection limits in the ppb range but is less favoured for environmental monitoring because sample preparation is time consuming and the cost per analysis is fairly high. Ion-chromatography offers very low detection limits and rapid sample processing. It is ideal for fast analysis of anions at ppb levels, although aqueous analysis solutions must be prepared beforehand. This method also generates a liquid waste that requires disposal.

Elemental analysis in the environmental field has traditionally been dominated by solution techniques, such as AA spectrometry and ICP. ICP is becoming the more popular of the two because of its sensitivity and capacity to measure quantities of multiple ions simultaneously.

An emerging solution

XRF, a technique widely used in many areas of industry and research, is rapidly gaining popularity for heavy metals monitoring. This is happening for several reasons: in contrast with other analytical techniques, XRF benefits from simple, essentially hazard-free, sample preparation (only XRF and NAA can operate with both solids and liquids, with no need to extract solid samples to a liquid phase). It is non-destructive, very rapid and - compared to ICP, AA spectrometry and ion-chromatography - is inexpensive in terms of cost per analysis.

Furthermore, in today's climate of strict legislation it is clear that environmental protection requires the analysis of highly diverse material types and element concentrations. One of the key strengths of XRF spectrometry is its ability to deal with such diversity:

- *XRF supports analysis in a wide range of applications including geology, agriculture, use of fossil and secondary fuels, industrial emissions monitoring, recycling, catalyst production, electronics and electrical appliance manufacture and many others*
- *Samples of almost any form, such as solid pieces, pressed powders, loose powders, granules and liquids, can be placed directly into the XRF instrument with little or no pre-treatment*
- *Analysis can be conducted on a wide variety of materials, including plastics, polymers, metals, brass, solder and wire*
- *Calibrations cover wide dynamic concentration ranges (sub-ppm to %)*

A range of XRF instruments is available, from simple hand-held units through bench-top EDXRF instruments to high performance WDXRF instruments. Many such instruments are now developed specifically to address the heavy-metal analysis requirements of various environmental applications, with options such as 'standardless' software to enable analysis of a wide variety of sample types and physical forms with a single calibration.

Conclusion

With a clear consensus that heavy metals have a major impact on human health and the environment, and strict legislation in place in most parts of the world aimed at addressing growing issues in this area, the monitoring of heavy metals has become vital for many industries. A diverse range of analytical methods is available and many aspects need to be considered when deciding which will provide the best characterization and quantification for a particular application. ■

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