Mercury in the Environment
Which technique is best for me?

Environmental Monitoring

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Publication

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Mercury Toxicity

The toxic nature of mercury is been well documented and has resulted in the development of various techniques and instrumentation for measuring this life-threatening element. Mercury is a neurotoxin that rapidly bioaccumulates and can cause major health problems, and even death, in small quantities and is considered as one of the top ten chemicals of public health concern by the World Health Organization. Chronic exposure at low levels is known to affect the nervous, digestive and immune systems as well as the lungs, kidneys and eyes with fetuses and breast feeding babies susceptible to developmental effects.

Mercury is a naturally occurring element found in air, water and soil and all humans are exposed to low levels of mercury through natural weathering of rock and volcanic activity. Mercury release through human activity is mainly from the burning of coal, waste incinerators and mining. It exists in various forms including the elemental or metallic form, the inorganic form as in mercury salts, and the organic form with methylmercury being the most toxic.

Once in the environment, inorganic mercury can be converted to the more toxic methylmercury form by bacteria. It bioaccumulates in fish and shellfish with large predatory fish including shark, mackerel, tuna and sword fish often recording high levels. Exposure in the womb can result from a mother's consumption of fish and shellfish, adversely affecting a baby's growing brain and nervous system. Breastfeeding infants are particularly susceptible, especially in communities with a high intake of seafood, as methylmercury is excreted into the mother's milk. Other forms of organic mercury such as ethylmercury, sometimes used as a preservative in vaccines and pharmaceuticals, are said to pose no health risk as they are quickly broken down by the body and do not accumulate. Even so, many actions are being taken to reduce or eliminate mercury from mercury-containing products that include batteries, dental amalgam, lamps, electrical equipment, thermometers, pharmaceuticals and cosmetics.

Properties of Mercury

The chemical and physical properties of mercury are both a blessing and a curse. The only metal to exist as a liquid at room temperature, its highly volatile nature can increase the likelihood of mercury loss during sample preparation, especially in open vessel digestions. Furthermore, adsorption to container walls and sample introduction components can complicate analyses due to possible carry-over into successive samples. Conversely, this makes possible the direct determination of ultra-trace mercury concentrations in many environmental and food samples using cold vapor techniques, whereby mercury is reduced to its atomic state and thus forming mercury vapor that can then be measured with either absorption, fluorescence or emission techniques. Direct analysis of solid samples is also possible and mercury's ability to amalgamate with metallic gold also allows for enrichment, further lowering the limits of detection.

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The introduction of ICP-MS has advanced the multi-element capability of spectroscopy techniques with the ability to detect even lower concentration of many more elements than previously possible. The high ionization potential and large number of naturally occurring isotopes with abundances below 30 % results in a lower sensitivity for mercury compared to many other elements measured by ICP-MS. Although, the absence of interferences means detection limits at sub parts-per-trillion are achievable. Speciation techniques including HPLC coupled to ICP-MS also allows for the separation of inorganic and organic mercury species, including toxic methyl mercury.

Regulating Mercury

In October 2013, the European Union (EU) signed the Minamata Convention on Mercury, thereby committing to the ratification and implementation across the EU. The new regulations set strict limitations on the use, export and disposal of mercury in products in the European Union, covering mainly batteries and accumulators, electrical and electronic equipment and measuring devices containing mercury for use by the general public. It also prohibits any future uses of mercury in new products and industry unless environmental and health benefits are demonstrated and there are no mercury-free alternatives. The Commission also prohibits the manufacture and use of five phenylmercury compounds from 10 October 2017.

It also addresses the issue of dental amalgam, the second biggest intentional use of mercury in the EU. The Commission has investigated its use and potential health impacts as well as possible alternative tooth fillings. Opinions formulated following investigation into the issue clearly indicate that significant negative impacts of dental amalgam on health are not proven, but there may be situations where the release of dental amalgam into waters may risk increasing pollution and endanger the quality of water. The regulation restricts its use to the encapsulated form and demands the use of separators by dentists.

The determination of both total mercury and methylmercury concentrations in environmental samples such as natural waters and soils is important in environmental risk assessment. Although, mercury in drinking-water is considered to be a minor source of exposure except in circumstances of significant pollution. In October 2000, the EU Water Framework Directive was formerly adopted, including mercury and its compounds. As of July 2013, the Environmental Quality Standards define the maximum allowable concentration of 0.05 µg/L for primary substances and other pollutants, with limits of quantification in fresh water and waste water of 0.015 µg/L and 0.5 µg/L, respectively.

In seafood, methylmercury is the chemical form of most concern and can make up more than 90 % of the total mercury in fish and shellfish. Provisional tolerable weekly intake of methylmercury as recommended by the joint Food and Agriculture and World Health Organizations is 1.6 µg/kg body weight per week. Due to the long range transport properties of mercury, the exposure of the environment and people living within in the EU cannot be reduced to an acceptable level through domestic policies alone. Co-ordinated international action is therefore needed to address the mercury problem in a globally effective manner.

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Comparison of Techniques

Analytik Jena offers a broad range of products that cover a vast array of methods, standards and limits defined by the numerous Agreements, Directives, Actions, Priorities, Commissions and Conventions dedicated to the determination of mercury in water, soil, sediment and sludge, plants, fertilizer, fish and shellfish, food, fuels, materials and so on. This includes an extensive portfolio of elemental techniques including Atomic Absorption, ICP-Optical Emission and ICP-Mass Spectrometers as well as a range of dedicated and optional cold vapor mercury analyzers.

Analytik Jena's mercur series are a cost effective, fully-automated and dedicate mercury analyzer range that offer exceptional ultra-trace detection capability using cold vapor in either atomic absorption or fluorescence modes. Atomic fluorescence offers an order of magnitude improvement on detection limits to sub part-per-trillion levels (<ng/L or ppt) with the option of enrichment via amalgamation with gold (mercur PLUS series) to go even lower. While atomic absorption offers improved matrix tolerance for more complex samples. The mercur DUO offer the best of both worlds. The selectivity of the technique specific to mercury provides exceptional performance and superior detection limits while the simplicity of the technique, combined with complete automation ensures fast and easy operation.

Though classical atomic absorption and ICP optical emission systems are capable of measuring a broad range of elements, they do not provide very good direct determination of mercury. Optional flow injection accessories, with cold vapor determination of mercury from mid-to-low ppt levels, extend the capability of these multi-element techniques. A separate, inter-changeable sample introduction system is necessary and can increase user complexity. The modular design of Analytik Jena's hydrEA and hydride accessories for the novAA®, ZEEnit, contrAA® and PlasmaQuant® range of AAS and ICP-OES systems make them simple to install, quick to optimize and easy to operate.

As mercury can be volatilized from practically all compounds at temperatures above 400 °C, it's possible to determine mercury by directly heating solid samples and enriching by amalgamation on gold mesh. The technique works for many samples if the enrichment step is preceded by a carefully matched, heated oxidation catalyst. The reason is that the matrix components must be oxidized when the mercury is expelled, otherwise the collector would be immediately and irreversibly damaged. Alternatively, Analytik Jena's exclusive Direct Solid Sampler allows for the direct analysis of solid samples, including dried fish, milk powder, sediment and soil on the novAA®, ZEEnit and contrAA® series of graphite furnace AAS. As a result, sample preparation times are shorter and less sample handling means the potential for contamination is reduced.

ICP Mass Spectrometers have gained popularity over the past decade and typically provide interference-free determination of mercury at sub-part-per-trillion levels. The PlasmaQuant® MS from Analytik Jena provides true multi-element measurement of up to 75 elements, including mercury, within a single analysis. While mercury carry-over from the exposure to solutions with very high mercury concentrations is of concern, washout times have significantly improved through more efficient sample handling techniques. Advances in autosampler technology, including dual rinse stations and switching valve accessories, greatly reduce cross contamination between samples by minimizing sample contact time with tubing.

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Summary

The detrimental effect of mercury on the environment, within the food chain and to humans is a challenge we all face today. Only through a concerted, international effort will we be able to eliminate this threat. Analytik Jena is playing its role by offering a comprehensive range of products that meet and exceed the stringent regulatory requirements defined by the relevant government and international agencies. With a range of dedicated mercury analyzers that cater to all international standards, an exclusive direct solid sampler combined with either the novAA®, contrAA® and ZEEnit series of AAS to the latest PlasmaQuant® series of ICP-OES and ICP-MS, Analytik Jena offers a broad range of solutions and brings a vast amount of experience to help overcome this global challenge.

Table 1. Comparison of Techniques

Technique	Product Name	Hg Limit of Detection	Linear Dynamic Range (Decades)
Mercury Analyzer (Absorption)	mercur AA mercur AA PLUS	5 ng/L 0.5 ng/L	3 3
Mercury Analyzer (Fluorescence)	mercur mercur PLUS	0.5 ng/L 0.1 ng/L	5 5
Mercury Analyzer (Absorp/Fluores)	mercur Duo mercur Duo PLUS	As defined above	As defined above
Direct Solid AAS	Graphite furnace AAS models with Direct Solid Sampler	10-50 µg/kg	3
Cold Vapor AAS (Flame)	Flame AAS models with Hydride accessory Flame AAS models with Hydride + Enrichment (PLUS)	40 ng/L 4 ng/L	3
Cold Vapor AAS (Furnace)	Graphite furnace AAS models with HydrEA accessory Graphite furnace AAS models with HydrEA + Enrichment (PLUS)	40 ng/L 4 ng/L	3
Cold Vapor ICP-OES	PlasmaQuant® 9000 with HS PQ Pro hydride accessory	3 ng/L	6
ICP-MS	PlasmaQuant® MS	0.3 ng/L	10

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Table 2. Strengths and Limitations of each technique

Technique	Strengths	Limitations
Mercury Analyzer (Absorption)	Selective Hg determination with optional enrichment for ultra-trace Hg detection.	Linear dynamic range
Mercury Analyzer (Fluorescence)	Superior detection limits and linear dynamic range compared absorption technique	Susceptible to matrix interferences
Mercury Analyzer (Absorp/Fluores)	Combination of both absorption and fluorescence techniques	As defined above
Direct Solid AAS	Direct analysis solid samples eliminating the need for sample digestion	Not suitable for all matrices and suitable solid calibrants are required
Cold Vapor AAS (Flame)	Multi-element capability of flame AAS with optional ultra-trace Hg determination	Requires inter-changeable cold vapor accessory
Cold Vapor AAS (Furnace)	Multi-element capability of graphite furnace AAS with optional ultra-trace Hg determination	Requires inter-changeable cold vapor accessory
Cold Vapor ICP-OES	Multi-element capability of ICP-OES with optional ultra-trace Hg determination	Requires inter-changeable cold vapor accessory
ICP-MS	Multi-element measurement including Hg to sub ppt detection limits	Extensive linear dynamic range although limited by carry-over

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