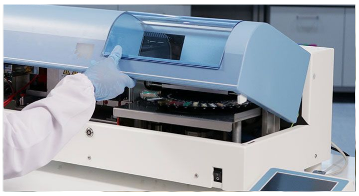
RELIABLE MERCURY ANALYSIS IN ENVIRONMENTAL SAMPLES: TOOLS, TECHNIQUES, AND BEST PRACTICES

Environmental Sample Prep Series



WEBINAR QUESTIONS

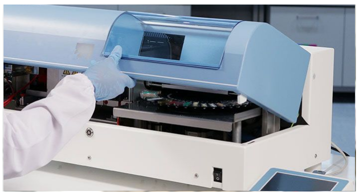
Q. Is the result obtained from the analysis referring to total mercury? Is there a way to differentiate organic mercury (methylmercury)?

A. The DMA provides results exclusively as total mercury (Hg). This is because the analytical process is based on complete thermal decomposition of the sample at high temperatures; during this combustion step, all mercury species (whether inorganic or organic) are released from the matrix. Subsequently, they are chemically converted in the catalyst into elemental mercury (Hg^0). As a result, the atomic absorption signal measured by the instrument always corresponds to total mercury, regardless of the original chemical form present in the sample.

However, determination of methylmercury using DMA is possible through a speciation approach that combines selective extraction with direct measurement. Since methylmercury is an organic mercury species commonly found in fish and seafood, it must first be separated from the sample matrix before analysis. This is necessary because solid samples cannot be directly introduced into analytical systems without prior treatment. The procedure typically involves a series of extraction steps designed to isolate organic mercury compounds from the bulk material. In particular, a double liquid–liquid extraction is commonly applied, first using an organic solvent and then a specific reagent solution to transfer methylmercury into an aqueous phase. Once extracted, the analyte can be directly quantified using the DMA, which measures total mercury in the extract. As methylmercury represents the predominant organic mercury form in food samples, the measured value can be attributed to this species.

Sample	MeHg (ppb)	Certified (ppb)	Rec (%)	RSD (n:5) (%)
DORM 4	326,81	354	92,3	2,6
TORT 3	123,54	137	90,2	3,4
IAEA 461	55,96	62,3	89,8	2,8
IAEA 470	4,92	5,22	94,3	1,9

Methylmercury results obtained using DMA and compared to CRMs values



Q. Is the DMA capable of handling liquid samples? Do you have a method suggestion?

A. The instrument can work with both liquid and solid samples In the case of water analysis, the application mainly depends on the mercury concentration present in the sample and on the type of water involved, for example whether it is wastewater, drinking water, or another kind of aqueous sample.

Generally speaking, it is possible to work with almost all types of water using a sample volume between 50 and 400 µL. Depending on the selected volume, different methods can be applied in order to optimize the analysis conditions and ensure reliable results. For liquid samples, we use quartz boats, which are particularly suitable because of their capacity (1.5 mL) and their very low memory effect, making them ideal for trace and ultratrace determinations.

In terms of sensitivity, the DMA in its Tricell configuration can be calibrated to reach very low detection levels. Fr example, it is possible to set the first calibration point as low as 0.04 ng, which allows working in the range of approximately 100–200 ppt, provided that appropriate working conditions are ensured (clean environment, optimized method, and well-maintained instrument).

Operating at such low levels requires careful handling, proper calibration strategies, and strict control of potential contamination sources to achieve consistent and accurate results.

Q. Which standard do you use for calibration?

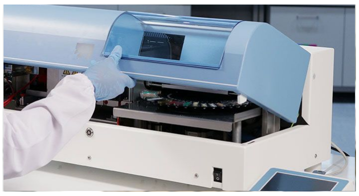
A. For calibration, we typically use certified mercury standard solutions, usually traceable to international standards (e.g., NIST). These are commonly prepared from a 1000 mg/L mercury stock solution and then diluted to the required working concentrations depending on the calibration range. All standards are prepared in an appropriate acidic matrix, typically using hydrochloric acid (around 2% v/v) to ensure stability of mercury in solution and to minimize losses due to adsorption.

It is also important to note that, since the technique is matrix-independent, it is not necessary to use CRMs or standards that replicate the sample matrix for calibration purposes.

The calibration strategy (number of points and concentration range) is then adapted based on the expected mercury levels in the samples and the selected instrument configuration.

Q. Which are the analytical benefits of using DMA over other techniques?

A. It is possible to determine mercury by other techniques, such as acid digestion followed by ICP analysis or Cold Vapors techniques. However, there are several important aspects specific to mercury that should be carefully considered before choosing those approaches.



First, mercury is highly volatile, which can lead to analyte losses during sample preparation, digestion, and even during storage if conditions are not properly controlled. This makes accurate quantification more challenging compared to less volatile elements.

In addition, mercury is well known for causing memory effects in ICP systems. It tends to adsorb onto tubing, the sample introduction system, and other internal components, resulting in long washout times and potential carryover between samples. This can negatively impact both accuracy and sample throughput.

Matrix effects and spectral interferences also need to be considered. Depending on the sample composition, matrix components can suppress or enhance the signal, while spectral overlaps may require correction strategies, adding complexity to the method development and validation.

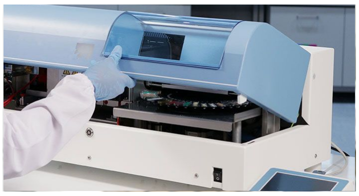
For these reasons, although digestion followed by ICP is a viable and widely used technique, direct mercury determination with DMA is often considered more robust, faster, and less prone to the issues mentioned above, especially when mercury is the primary analyte of interest.

Q. What maintenance is required? And which are the consumables?

A. Routine maintenance is generally not required, as the instrument is very robust and can operate in almost any laboratory environment. Maintenance activities are limited to the periodic replacement of consumable components after a certain number of analyses, with the replacement frequency depending on several factors such as the amount of mercury analyzed, the type of samples, and the overall instrument usage over time. The only true consumables of the system are the catalyst and the amalgamator, which are essential for proper operation and typically last more than six months under normal conditions. All other parts, including the quartz boats and the rest of the instrument, are not considered consumables, as they have a long lifetime and are usually inspected during annual maintenance. In addition, an annual maintenance check of the air compressor is recommended.

Q. How do I clean the boats?

A. The boats can be cleaned in different ways, depending on your workflow and available equipment. One option is to use the dedicated cleaning procedure available on the DMA, which typically takes around 5 minutes per cycle. This can be conveniently performed using the autosampler.



The main advantage of cleaning the boats directly on the DMA is that it allows you to immediately verify the effectiveness of the cleaning process by monitoring the signal values obtained. This is particularly useful when working at trace or ultratrace levels, where even minimal contamination can affect the results.

Alternatively, the boats can be cleaned using a muffle furnace, which is generally the faster and more efficient option when handling many boats at once. For this approach, it is sufficient to set the furnace to 600°C for metal boats and 900°C for quartz boats, with a holding time of approximately 10 minutes.

In both cases, regular and proper cleaning is essential to minimize memory effects and ensure consistent analytical performance over time, especially when working with low mercury concentrations.