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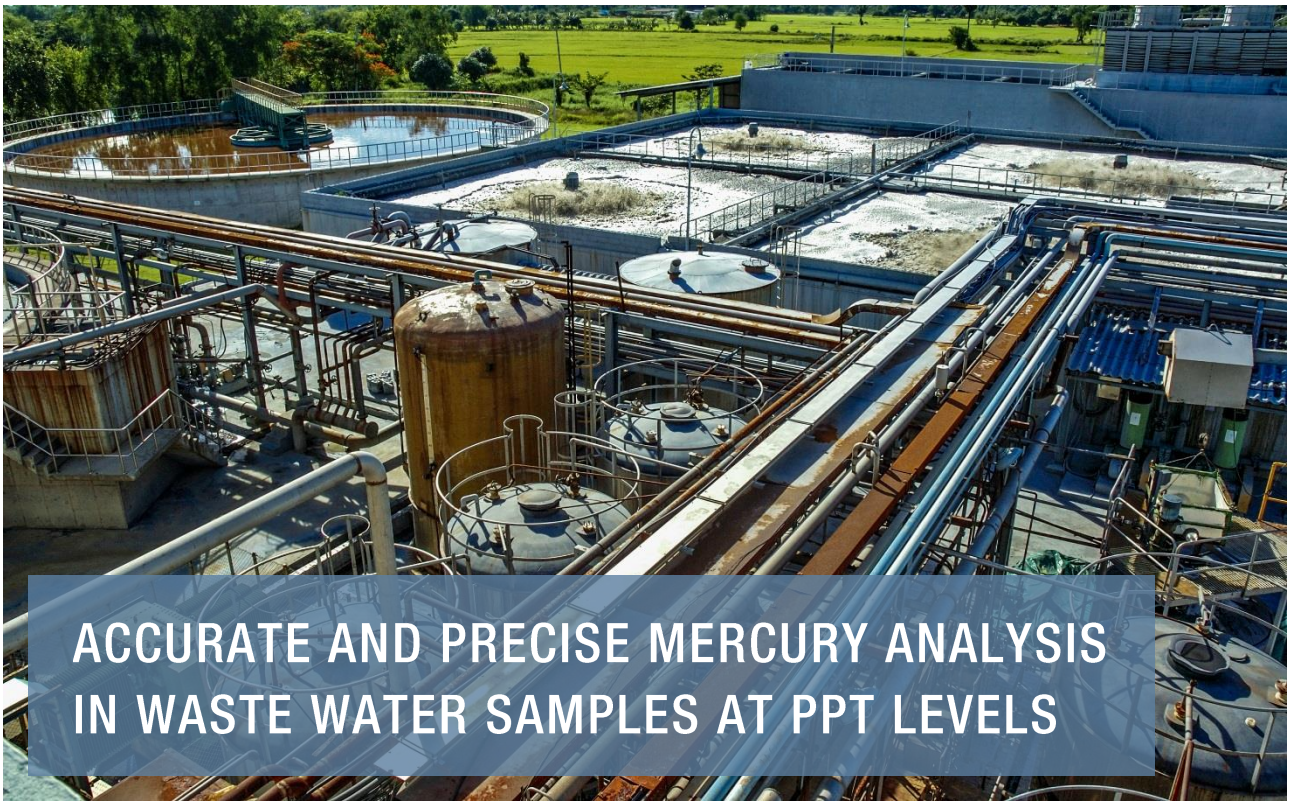

ACCURATE AND PRECISE MERCURY ANALYSIS IN WASTE WATER SAMPLES AT PPT LEVELS

Direct mercury analysis at low levels using the DMA-80 *evo* with double-beam spectrophotometer.

INTRODUCTION

Mercury is used in many industrial applications. Some of them includes conducting electricity, measuring temperature and pressure, acting as a biocide, preservative, and disinfectant, as well as being a catalyst for reactions.

Unlike some of the other pollutants, mercury cannot be eliminated, and it has high mobility; so, monitoring its levels allow to minimize harmful effects for the population. Several methods are available for mercury analysis in environmental samples like soils, waste and waste water. Most of these methods however, require elaborate preparation procedures that are labour intensive and subsequently expensive.

Direct mercury analysis, as described in EPA Method 7473, is an alternative to these methods and has been used successfully to determine total mercury in environmental samples. This technique requires no sample preparation and delivers results in as little as six (6) minutes per sample making it significantly faster than traditional wet chemistry.

Mercury is naturally present in the earth and enters the air and water streams through the burning of fossil fuels, discharge of industrial waste and use of pesticides. Companies have also discharged mercury onto their property via production by-products.

The cement industry use raw materials and fuels that often contain mercury, therefore it

is pivotal to control these materials to ensure mercury monitoring and avoid mercury emissions in the environment.
Traditional analytical methods such as Cold Vapor Atomic Absorption (CVAA) and ICP-MS both require sample preparation prior to analysis. This results in both techniques being costly, labour-intensive and subsequently, having a long turnaround time. Direct mercury analysis is a cost-effective, proven alternative to these labor-intensive, wet chemistry techniques.
Direct analysis affords the laboratory many benefits including:

- Reduced Sample Turnaround (6 min.)
- No Sample Preparation
- Reduced Hazardous Waste Generation
- Reduction of Analytical Errors
- General Cost Savings (70 % versus CVAA)

EXPERIMENTAL

INSTRUMENT

The DMA-80 *evo*, Direct Mercury Analyser, as referenced in EPA Method 7473, from Milestone was used in this study.

Figure 1 - DMA-80 evo Direct Mercury Analyzer

In this study has been used the DMA-80 double beam configuration, which allow to get better signal/ background value, ensuring high performances even at very low concentrations such as 0,1 ppb.

The DMA-80 double beam features a circular, stainless steel, interchangeable 40 position autosampler for virtually limitless throughput and can accommodate both nickel (500 mg) and quartz boats (1500 uL) depending on the requirements of the application. It operates from a single phase 110/220V, 50/60 Hz power supply and requires regular grade oxygen as a carrier gas. As the process does not require the conversion of mercury to mercuric ions, both solid and liquid matrices can be analyzed without the need for acid digestion or other sample preparation. The fact that zero sample preparation is required also eliminates all hazardous waste generation. All results, instrument parameters including furnace temperatures, are controlled and saved with easy import/export capabilities to Excel or LIMS.

PRINCIPLE OF OPERATION

Direct mercury analysis incorporates the following sequence: Thermal Decomposition, Catalytic Conversion, Amalgamation, and Atomic Absorption Spectrophotometry. Controlled heating stages are implemented to first dry and then thermally decompose a sample introduced into a quartz tube. A continuous flow of oxygen carries the Decomposition products

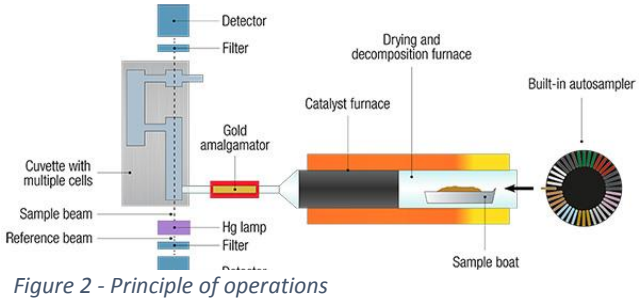

Figure 2 - Principle of operations

through a hot catalyst bed. All mercury species are reduced to Hg(0) and are then carried along with reaction gases to a gold amalgamator where the mercury is selectively trapped.

CALIBRATION

Calibration standards were prepared using a NIST traceable stock solution of 1000 ppm Hg preserved in 5 % HNO_3. Working standards of 100ppb and 1 ppm were prepared and preserved in 37% HCl and stored in amber glass vials. By injecting increasing sample volumes of standard into the quartz sample boats, calibration graphs of 0 – 1500 ng of mercury were created using aqueous standards respectively.

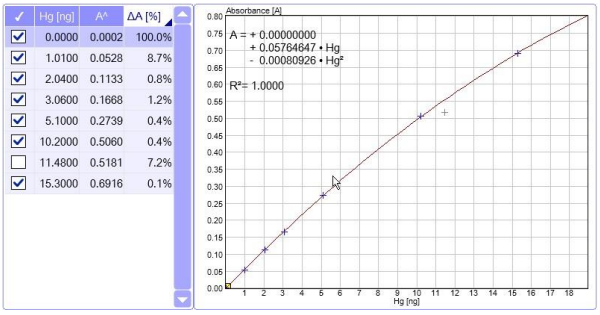

Figure 3 - High sensitivity Cell for low Hg Level

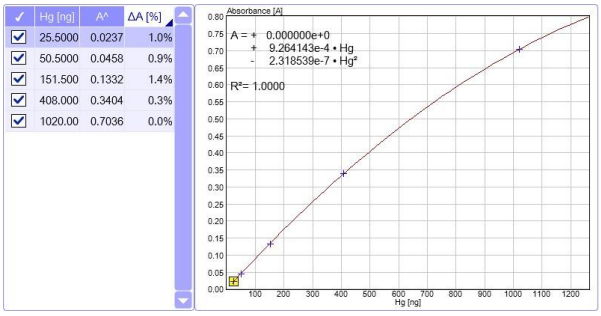

Figure 4 - Cell for high Hg level

OPERATING CONDITIONS

The DMA-80 evo's operating conditions for all analyses are shown in Table 1.

Parameter	Setting
Drying Temp/Time	90 seconds to 200°C
Decomposition Ramp	120 seconds to 650°C
Decomposition Hold	90 seconds at 650°C
Catalyst temperature	565°C
Purge Time	60 seconds
Amalgamation Time	12 seconds at 900°C
Recording Time	30 seconds
Oxygen Flow	120 ml/min

Table 1- Operating conditions

EXPERIMENTAL AND RESULTS

In this study a water sample has been spiked with 0,1 µL/L of NIST traceable stock solution of 1000 ppm Hg.

The spiked sample has been replicated five times using quartz boats.

The blank values before and after the spiked samples shown the capabilities of the DMA double beam to achieve very low background level.

Sample	Amount	Concentration
Blank	-	0.0001 µg/L
Water Sample 1st	0.5 ml	0.105 µg/L
Water Sample 2nd	0.5 ml	0.108 µg/L
Water Sample 3rd	0.5 ml	0.109 µg/L
Water Sample 4th	0.5ml	0.106 µg/L
Water Sample 5th	0.5ml	0.105 µg/L
Sample 5th + 1µg/L spike	0.5ml	1.12 µg/L
Blank	-	0.0001 µg/L

Table 2- Results

m = 0.1069 µg/kg

σ_{abs} = 0,0019 µg/kg

σrel = 1,76%

CONCLUSION

A lab analysing environmental matrices often has to analyse low concentration mercury in wastewater samples and in other matrices. This study shows how the DMA-80 double beam addresses this task along with a great ease of use and high productivity.

The double beam feature enhances the performance of the DMA-80 at very low range, such as 0,1ppb, providing great reproducibility (RSD 1.76%).

Since many years the DMA-80 *evo* has been used to determine mercury in a wide variety of environmental samples (as described in the US EPA 7473) such as waste water, soils, sediments, sludge, and wastes, today it also ensures superior performances at low range.

FURTHER READING

To learn more about mercury and other related topics, feel free to visit these websites.

EPA Method 7473
http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/7473.pdf

ASTM Method D6722-01
http://www.astm.org/Standards/D6722.htm

EPA Mercury
http://www.epa.gov/mercury/

Methyl Mercury
http://en.wikipedia.org/wiki/Methylmercury

Mercury in Fish
http://www.epa.gov/waterscience/fish/advice/mercupd.pdf

Mercury in Coal
http://energy.er.usgs.gov/health_environment/mercury/

Mercury Analysis
http://www.milestonesrl.com

About Milestone

At Milestone we help chemists by providing the most innovative technology for metals analysis, direct mercury analysis and the application of microwave technology to extraction, ashing and synthesis. Since 1988 Milestone has helped chemists in their work to enhance food, pharmaceutical and consumer product safety, and to improve our world by controlling pollutants in the environment.

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