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THE DETERMINATION OF TOTAL MERCURY IN FISH & BIOLOGICAL TISSUES

The Determination of Total Mercury in Fish & Biological Tissues Using Direct Analysis for Mercury Detection

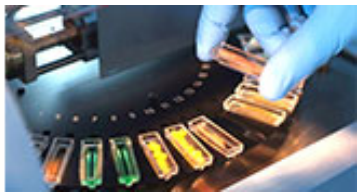
| SUMMARY

The effects of mercury exposure continue to remain a focal point of both public and private institutions. Through overexposure to this neurotoxin, fetuses and infants can exhibit various symptoms ranging from brain damage and mental disability to problems with coordination. In an attempt to make the general public more aware o the effects of overexposure, various advisories have been initiated on local fisheries. Several methods are available for mercury analysis in fish. However, most of these methods require elaborate preparation procedures that are labor-intensive and subsequently expensive. Direct mercury analysis, as described in EPA Method 7473, is an alternative to these methods and has been successfully used to determine total mercury in fish and other biological tissues.

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 techniques.

| INTRODUCTION

Mercury is naturally present in the earth and enters the air and water through the burning of fossil fuels, discharge of industrial waste and use of pesticides. Through this redistribution, it accumulates in fish and other biological tissues. Methyl mercury, its organic form, binds to proteins in the muscle and cannot be removed by trimming, skinning or cooking. By eating



large quantities of fish and seafood, humans can expose themselves to harmful levels of this neurotoxin.

Several methods exist for the determination of mercury in fish and biological tissues. 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, labor-intensive and subsequently, having a long turnaround time. Direct mercury analysis, as described in EPA Method 7473, 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 Minutes)
- 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 Analyzer from Milestone was used in this study, as referenced in EPA Method 7473.

The DMA-80 evo features a circular, stainless steel, interchangeable 40-position autosampler for virtually limitless throughput and can accommodate both nickel (500 mg) and quartz boats (1500 µL) 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.

Figure 1 Milestone's DMA-80 evo

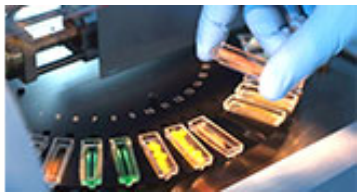
Since the process does not require the conversion of mercury to mercuric ions, both solid and liquid matrices can be analyzed without the need for acid digestion or other sample preparation. The fact that zero sample preparation is required also eliminates all hazardous waste generation.

All results and instrument parameters, including furnace temperatures, are controlled and saved with easy export capabilities to Excel or LIMS.

PRINCIPLE OF OPERATION

Direct mercury analysis incorporates the following operating 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 through a hot catalyst bed where halogens, nitrogen, and sulfur oxides are trapped. 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. All non-mercury vapors and decomposition products are flushed from the system by the continuous flow of gas. The amalgamator



is subsequently heated and releases all trapped mercury to the double beam, fixed wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury content.

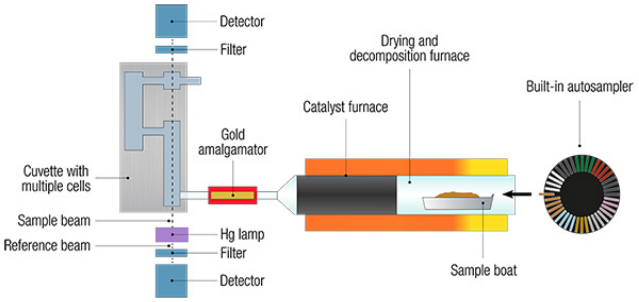


Figure 2 An Internal Schematic of Milestone's DMA-80 evo.

EXPERIMENTAL DISCUSSION

The data presented in this paper was obtained on-site at a customer laboratory while doing a live demonstration.

Originally prepared and analyzed via CVAA, the samples were reanalyzed on the DMA-80 *evo*. Samples were thawed and placed at varying weights into nickel sample boats, then loaded into the autosampler for analysis.

CALIBRATION

Calibration standards were prepared using a NIST traceable stock solution of 1000 ppm Hg preserved in 5% HCl.

Working standards of 100 ppb and 1 ppm were prepared and preserved in 0.5% HCl and stored in amber glass vials.

By injecting increasing sample volumes of standard into the quartz sample boats, calibration graphs of 0 – 20 ng (Figure 3) and 20 – 500 ng (Figure 4) of mercury were created using the 100 ppb and 1 ppm standards respectively.

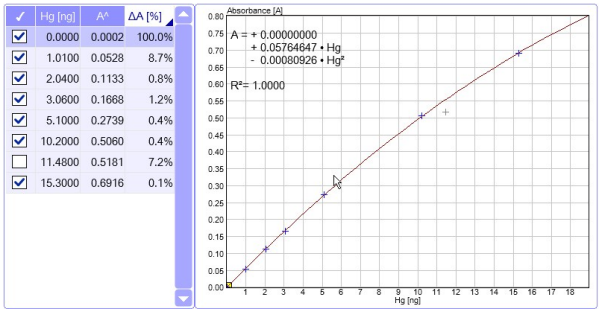


Figure 3 - 0 ng – 20 ng Calibration Graph for ultra-low level

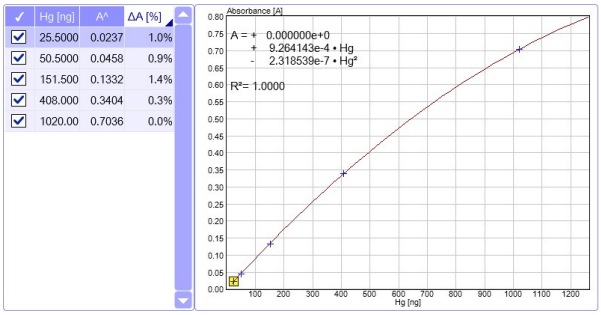


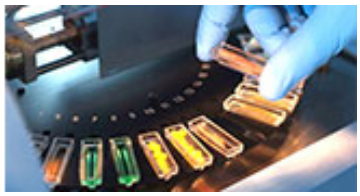
Figure 4 - 20ng – 1000 ng Calibration Graph for low to midlevel

| 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 660 °C
Decomposition Hold	90 seconds at 660 °C
Catalyst Temp	600 °C
Purge Time	60 seconds
Amalgamation Time	12 seconds at 900 °C
Recording Time	60 seconds
Oxygen Flow	120 mL/min

Table 1 Analysis Operating Parameters



RESULTS

Table 2 shows all the results obtained during the analysis. All unknown results were in excellent agreement with their previous (ICP-MS/CVAA) determination.
Results on standard reference materials (SRM's) analyzed throughout the analysis were also within their expected certified values.

Sample	CVAA/ICP-MS (ppm)	Measured	Recovery (%)
DORM-3	0.382	0.377	98.7
Fish III	0.279	0.266	95.2
Fish II	3.786	3.608	95.3
Fish I	4.774	4.358	91.3
DORM-2	4.64	4.384	94.5

Table 2 Mercury Concentrations and Percent Recoveries

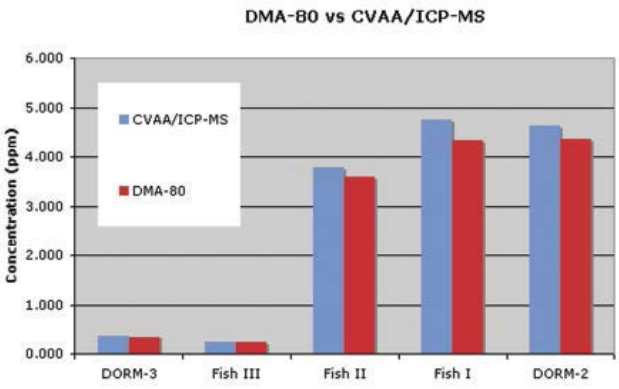


Figure 5 DMA-80 vs. CVAA/ICP-MS

| CONCLUSION

The results of the DMA-80 *evo* direct mercury analyzer were in excellent agreement with the results previously obtained on ICP-MS/CVAA (Figure 5). The DMA-80 *evo* is a fast, accurate and reliable alternative to wet chemistry techniques. No sample preparation is required resulting in sample turnaround within 6 minutes without any hazardous waste generation.

FURTHER READING

Please visit our Hg info center for complete access to application notes, technical papers, as well as links to valuable resources for mercury testing. Go to www.milestonesci.com.

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/