Determination of Total Mercury in Fish & Biological Tissues

Using Direct Analysis for Mercury Detection

Summary

The effects of over-exposure to mercury continue to remain a focal point of both public and private institutions. Through over-exposure to this neurotoxin, fetuses and infants can exhibit various symptoms ranging from brain damage and mental retardation to problems with coordination. In an attempt to make the general public more aware of affects of over-exposure, various advisories have been initiated on local fisheries.

Several methods are available for mercury analysis in fish. Most of these methods however, 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 used successfully 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, it's organic form, binds to proteins in the muscle and cannot be removed by trimming, skinning or by 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)

Instrumentation

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

Figure 1. Milestone's DMA-80 Direct Mercury Analyzer

The DMA-80 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 export capabilities to Excel or LIMS.

Principles 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 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 single beam, fixed wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury content.

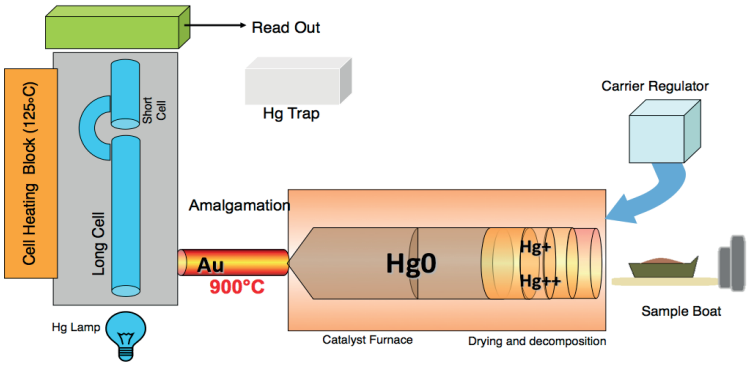

Figure 2. An Internal Schematic of Milestone's DMA-80.

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.
Samples were defrosted and placed, at varying weights into nickel sample boats and 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 – 1500 ng (Figure 4) of mercury were created using the 100 ppb and 1 ppm standards respectively.

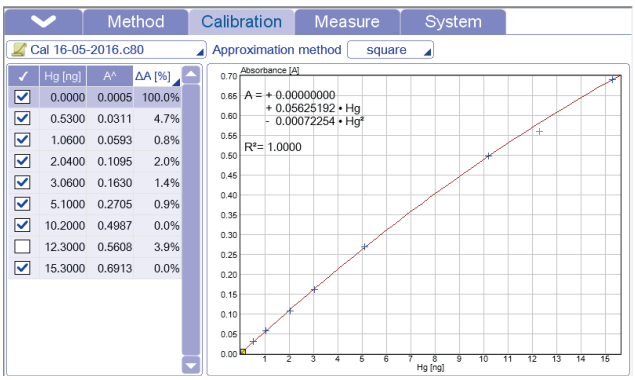

Figure 3. 0 ng – 20 ng Calibration Graph for ultra-level analysis (ppt; ppb)

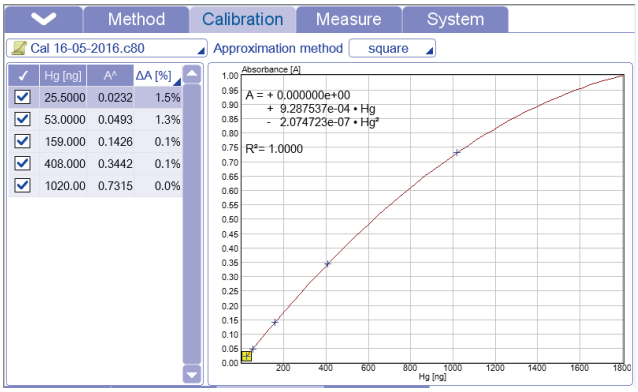

Figure 4. 020ng – 1500 ng Calibration Graph for low to mid-level analysis (ppb; ppm)

Operating Conditions

The DMA-80'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 the results were in excellent agreement with their previous (ICP-MS/CVAA) results.

Sample	Concentration DMA-80 (µg/Kg)	Contract Lab CVAA/ICP (µg/Kg)
Standard 1 (µg/Kg)	0.955	1.15
Standard 5 (µg/Kg)	4.82	4.7
Standard 10 (µg/Kg)	9.85	10.9
ICV (10 µg/Kg)	10.12	9.98
Blank	0.01	0.03
LCS (5 µg/Kg)	5.3	4.65
Sword Fish (1)	1732.01	1629.65
Sword Fish (2)	561.35	550.54
Sword Fish (3)	235.63	229.54
CCV (5 µg/Kg)	5.765	5.5
Anchovy (1)	122.01	115.36
Anchovy (2)	26.6	36.5
Anchovy (3)	95.2	81.77
Control Check (50 µg/Kg)	48.58	47.52
Shrimps (1)	39.25	34.99
Shrimps (2)	74.88	71.37
Shrimps (3)	55.12	46.33

Table 2. Fish Samples on DMA-80 vs Known Concentrations

Results on standard reference materials (SRM's) analyzed throughout the analysis were also in excellent agreement with their certified values.

Sample	Concentration DMA-80 (mg/Kg)	Certified (mg/Kg)
DORM-4	0.398	0.410 ± 0.055
DORM-4	0.395	0.410 ± 0.055
DORM-4	0.392	0.410 ± 0.055
DORM-4	0.394	0.410 ± 0.055
DORM-4	0.401	0.410 ± 0.055

Table 3. Summary of results of QA/QC analysis (DORM-4)
RSD 0.89%
Mean: 0.396 mg/Kg
SD: 0.0035

Sample	Concentration DMA-80 (mg/Kg)	Certified (mg/Kg)
BCR 463	2.73	2.85 ± 0.16
BCR 463	2.70	2.85 ± 0.16
BCR 463	2.71	2.85 ± 0.16
BCR 463	2.71	2.85 ± 0.16
BCR 463	2.77	2.85 ± 0.16

Table 4. BCR 463 Tuna Fish Certified Material
RSD 1.03%
Mean: 2.72 mg/Kg
SD: 0.0027

Conclusion

All results obtained on the DMA-80 were in excellent agreement with the results previously obtained on ICP-MS/CVAA. The system successfully analyzed five replicates of the DORM-4 SRM and BCR 463 SRM.
The DMA-80 provides a fast, accurate and reliable alternative to wet chemistry techniques. No sample preparation is required meaning results are obtained within six minutes. This is ideal for laboratories looking for quick turnaround of their in-house samples.

Further Reading

Please visit our Hg info center for complete access to application notes, technical papers, as well as links to valuable resouces for mercury testing.

Go to http://www.milestonesrl.com/mercury

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/fi sh/advice/mercupd.pdf

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

About Milestone

Our full suite of Microwave Sample Prep productivity tools is backed by over 50 patents and 29 years of industry expertise. Milestone is committed to providing safe, reliable and flexible platforms to enhance your productivity. Over 20,000 customers worldwide look to Milestone to improve their metals digestions, organic extractions, mercury analyzers or synthetic chemistry processes.

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