INDUSTRY REPORT

DMA-80 *evo* | ENVIRONMENTAL

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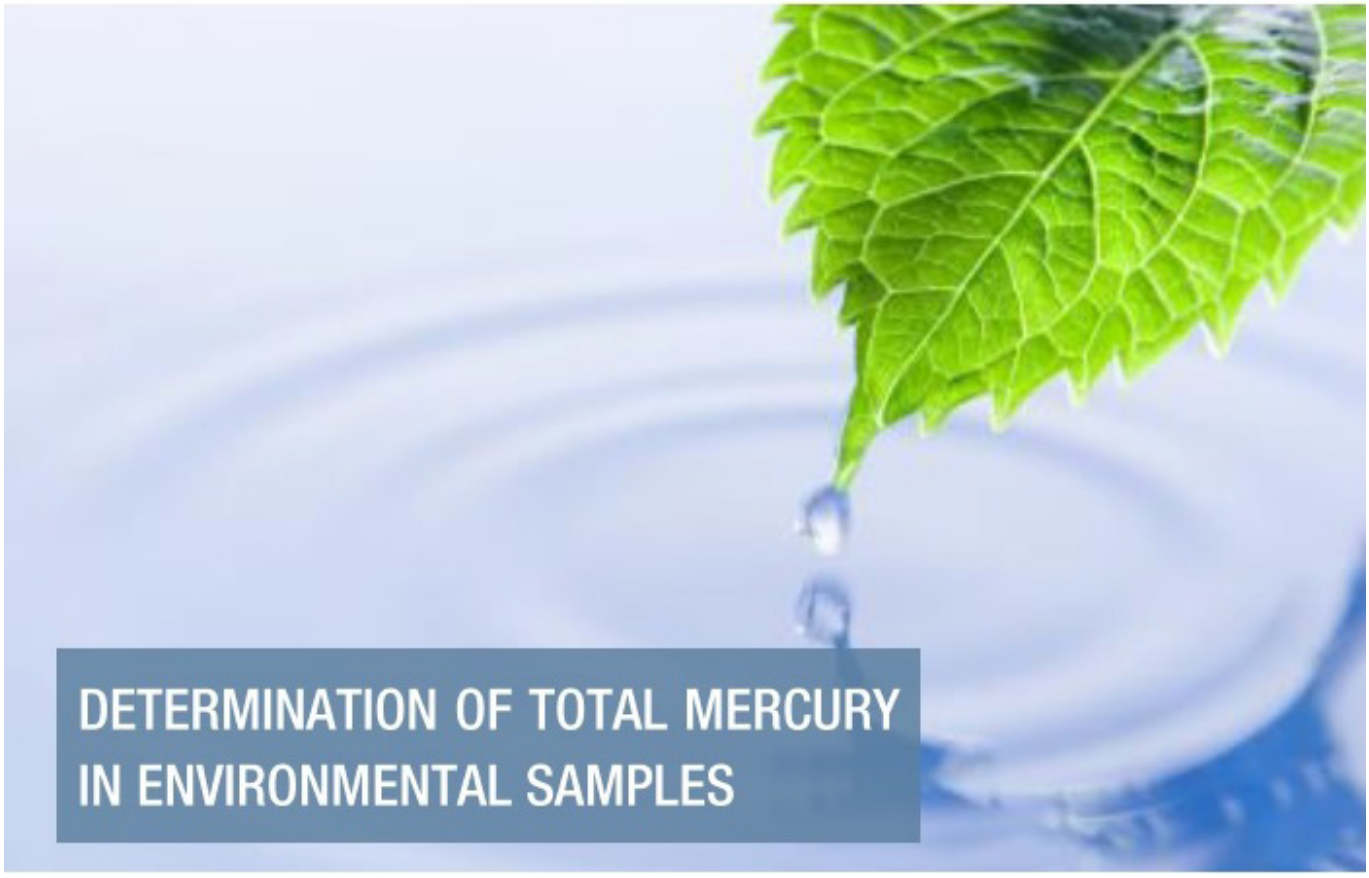

Determination of Total Mercury in Environmental Samples Utilizing Direct Analysis for Mercury Detection in Soil, Sediment, and Waste Water Samples

| SUMMARY

As more emphasis is placed on the monitoring of mercury emissions, both private and public institutions are looking at characterizing soil, sediments and waste water samples. Contaminated soil has to be excavated and remediated, or depending on the level of contamination, disposed of as hazardous waste. Several methods are available for mercury analysis in environmental samples like waste water and soil. 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 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.

| INTRODUCTION

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. Now, with more emphasis being placed on the monitoring of this neurotoxin, both private and public institutions are looking at characterizing the soil, sediment and waste water, on their property.

Contaminated soil has to be excavated and remediated, or depending on the level of contamination, disposed of as hazardous waste. Several methods exist for the determination of mercury in environmental samples. 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

Figure 1 Milestone's DMA-80 evo

The DMA-80, Direct Mercury Analyzer, as evidenced in EPA Method 7473, from Milestone Srl (www.milestonesrl.com) was used in this study.

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 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.

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 sample introduced into a quartz tube.

A continuous flow of oxygen carries the decomposition products through a hot catalyst bed where halogens, nitrogen, and sulphur 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.

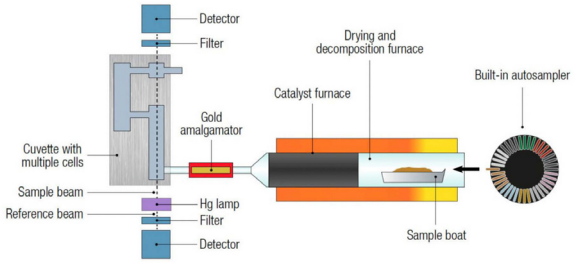

Figure 2 An Internal Schematic of Milestone's DMA-80 evo.

EXPERIMENTAL DISCUSSION

The goal of this study was to evaluate the effectiveness of the DMA-80 to analyse both soil and ground water samples – two vastly different matrices. All soil and water samples were obtained from an independent contract laboratory that had already analysed the samples via CVAA. For this study, the soil and water samples were analysed at various weights in the nickel and quartz sample boats respectively

CALIBRATION

Calibration standards were prepared using a NIST traceable stock solution of 1000 ppm Hg preserved in 5% HNO_3. Working standards of 100 ppb 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 – 20 ng (Figure 3) and 20 – 500 ng (Figure 4) of mercury were created using the 100 ppb and 1 ppm standards respectively.

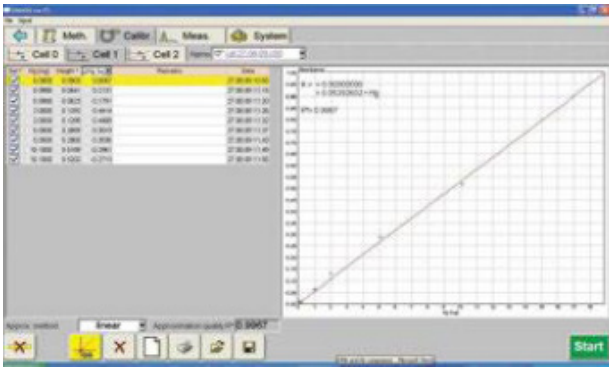

Figure 3 0 ng – 20 ng Calibration Graph for ultra-level

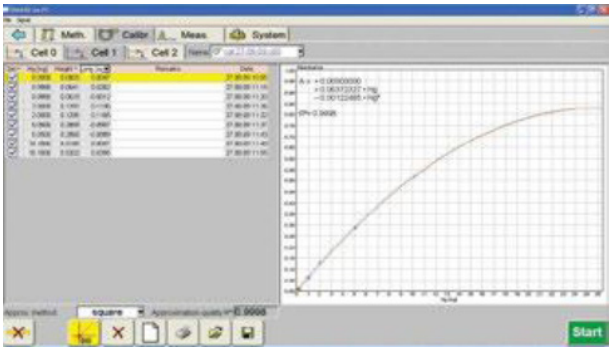

Figure 4 20 ng – 1000 ng Calibration Graph for low to mid-level analysis (ppb, ppm)

| 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 650 °C
Decomposition Hold	90 seconds at 650 °C
Catalyst Temp	565 °C
Purge Time	60 seconds
Amalgamation Time	12 seconds at 900 °C
Recording Time	30 seconds
Oxygen Flow	120 mL/min

Table 1 Analysis Operating Parameters

| RESULTS

Table 2 shows the results for all samples analysed on the DMA-80. The far column indicates the results previously obtained via CVAA. All sample results were within satisfactory range of previous analyses. The slight discrepancy in the soil sample results can be attributed to using smaller sample sizes which leads to samples being inhomogeneous.

Sample	Concentration (µg/Kg)	Contract Laboratory (µg/Kg)
0,2 (µg/Kg)	0,211	0,205
1 (µg/Kg)	0,915	1,05
5 (µg/Kg)	4,72	5,04
10 (µg/Kg)	9,717	10,3
ICV (5 µg/Kg)	5,446	5,2
blank	0,01	0,03
LCS (5 µg/Kg)	5,773	5,1
soil	0,663	0,9
soil	5,092	5
soil	0,535	0,63
CCV (5 µg/Kg)	5,765	5,5

Table 2 Unknown Environmental Samples on DMA-80 vs Contract Laboratory

In addition to the unknown environmental samples, NIST 2709 San Joaquin Soil, a matrix matched Standard Reference Material (SRM) was periodically analysed.

Sample	Concentration (µg/Kg)	Certifield (µg/Kg)
LCS (5 µg/Kg)	5,541	5,9
Soil	398,013	520
Soil	7684,281	6590
Soil	8408,259	7630

Table 2 Unknown Environmental Samples on DMA-80 vs Contract Laboratory (Part II)

Sample	Concentration (mg/Kg)	Certified (mg/Kg)
NIST 2709	1,378	1,40 ± 0,08
NIST 2709	1,404	1,40 ± 0,08
NIST 2709	1,406	1,40 ± 0,08
NIST 2709	1,404	1,40 ± 0,08
NIST 2709	1,424	1,40 ± 0,08

Table 3 Summary of results of QA/QC analysis

| CONCLUSION

All results obtained on the DMA-80 were in good agreement with the previous CVAA results. The DMA-80, direct mercury analyser, successfully analysed five replicates of the NIST 2709 SRM. Similar success can be expected when analysing other soil and sludge-type samples. As previously mentioned, a possible reason for the discrepancy in Table 2 can be sample homogeneity. All the liquid standard results were within their expected range. The DMA-80 is a fast, reliable alternative to wet chemistry techniques. No sample preparation enables quick sample turnaround which enable higher throughput for environmental contract laboratories.

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 http://www.milestonesrl.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

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

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

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