



## FAST AND DIRECT MERCURY ANALYSIS IN THE CEMENT INDUSTRY

### Mercury analysis of raw materials and alternative fuels in the cement industry using DMA-80 *evo* direct mercury analyzer

#### INTRODUCTION

In the cement industry limestone and other mineral components are burned to form clinker, which is then ground and mixed with certain additives to form the final product: cement.

To provide the necessary heat for the production process, different type of fuels are used. Due to the mercury content of the raw materials as well as of the fuels, the production of cement clinker results in mercury emissions.

Since the cement industry uses a wide variety of raw materials, fuels and alternative fuels, there is a growing demand of fast, flexible and easy to use mercury analysis procedures, overcoming the limitation of the

conventional approach which involve sample preparation steps and wet chemistry.

Direct mercury analysis, is an alternative to these methods and has been used successfully to determine total mercury in large variety of samples. This technique doesn't require sample preparation and it delivers results in as little as six (6) minutes per sample, making it significantly faster than traditional mercury analysis.

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.

The cement industry uses 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 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 Analyser, as referenced in EPA Method 7473, from Milestone was used in this study.



Figure 1 - DMA-80 *evo* Direct Mercury Analyzer

The DMA-80 *evo* 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 analysed 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 through a hot catalyst bed.

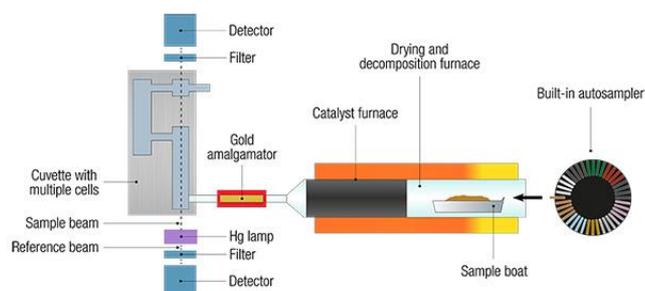


Figure 2 - Principle of operation



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<sub>3</sub>. 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 – 1500 ng of mercury were created using aqueous standards respectively.

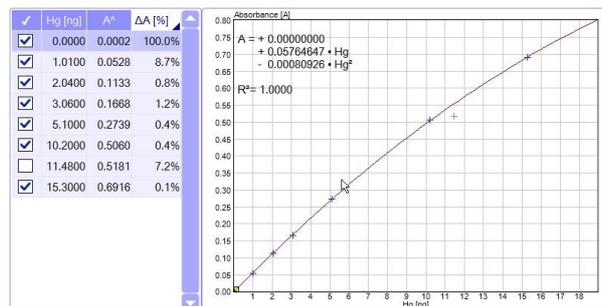


Figure 3 - High sensitivity Cell for low Hg Level

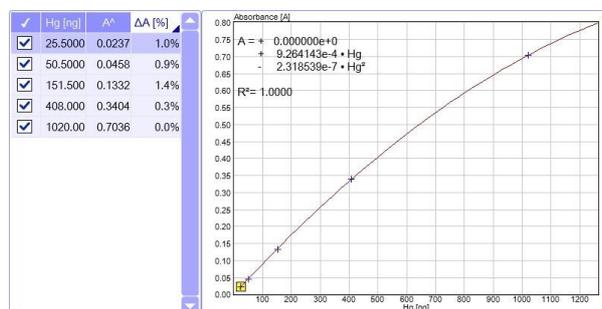


Figure 4 - Cell for high Hg level

### 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, multiple samples and CRM, typically used as raw material or fuels in the cement industry, have been tested. The below table reports the results for all samples, blanks and CRM.

Sample name	Weight	Concentration µg/kg
Blank	-	0.0011
Coke	0.059 g	0.83
Coke	0.052 g	0.90
Coke	0.046 g	0.79
Blank	-	0.0051
Coal	0.06 g	32.9
Coal	0.059 g	29.12
Coal	0.062 g	30.56
Blank	-	0.0037
Limestone	0.109 g	10.2
Limestone	0.109 g	10.21
Limestone	0.101 g	9.96
Blank	-	0.0023
NIST 2691	0.105 g	59.1

Table 2- Results

### Reference Material NIST 2691:

Coal Fly Ash

Hg certified value → 57.8 ± 4.3 µg/kg



## CONCLUSIONS

The cement industry demand for mercury determination growth in the last years. Since the source of mercury in this industry is related to the process and the materials used, the interest to find a cost-effective and easy to use method for mercury determination in various matrices dramatically increased. This study shows how the direct mercury analyzer address this task and provide reliable and accurate data for a wide range of matrices. In addition, it also demonstrates the ease of use and effectiveness of the direct mercury determination procedure, providing a very rugged and reliable method.

## 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/](http://energy.er.usgs.gov/health_environment/mercury/)

Mercury Analysis  
<http://www.milestonesrl.com>

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