Determination of Mercury in Liquid Hydrocarbons using Direct Mercury Analyzer Milestone DMA-80

Summary

Mercury is released into the environment during the refining process, and from the combustion of refinery products such as gasoline and diesel fuel. Direct contributions from refining activities are small. The refining sector's contribution to global mercury emissions is 0.1% of the total global mercury releases to air and water.
It is important to note that mercury can accumulate in refining equipment even when good operating practices and feed stock controls are implemented.
The common analytical methods used for the analysis of petrochemical samples are UOP 938-00 (UOP, 2000), or a newer ASTM standard method, D7623-10 (ASTM, 2010).
Analytical techniques for detecting mercury have improved in recent years, but it is important to note that the most common analytical tests report the total concentration of mercury, not the concentration of individual species. This is particularly true for the trace mercury concentrations that exist within the hydrocarbon streams in a refinery.

Introduction

One common test method can be described as a four-step process: (**1**) converting all forms of mercury to elemental mercury; (**2**) capturing the elemental mercury via a reaction with a gold film; (**3**) releasing the mercury from the gold film via heating; and (**4**) measuring the total mercury that is emitted.

Although mercury concentrations are less than 2 parts per billion (ppb) in most crudes, mercury has the potential to accumulate and cause operational issues in refining facilities. It is then fundamental to monitor it to ensure operator's protection and instruments' safety from the environmental impact that mercury pollution could generate.

- **UOP 938-10 (Universal Oil Products)**
Total Mercury and Mercury Species in Liquid Hydrocarbons

- **ASTM D7623-10**
Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption

Milestone Srl is proactive in the Petrochemical field participating to the ASTM D02 meetings on Petroleum Products and Lubricants. Milestone suggest the use of the DMA-80 instrument (Direct Mercury Analyzer) to address these issues.

The DMA-80 Principle of operation is fully in compliance with the UOP and ASTM methods.

Instrumentation

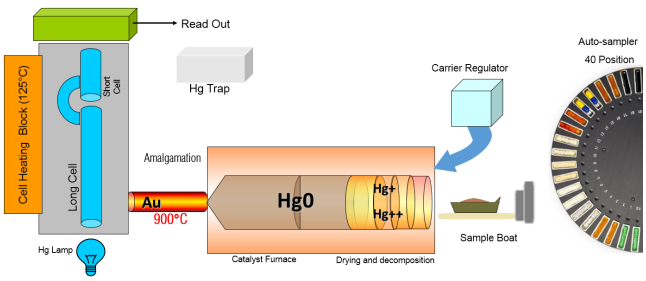
The DMA-80, Direct Mercury Analyzer, from Milestone (www.milestonesrl.com) was used in this study (Figure 1).

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

The DMA-80 features a circular, stainless steel, interchangeable 40 positions 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.



(Figure 2). An internal Schematic of Milestone's DMA-80

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.

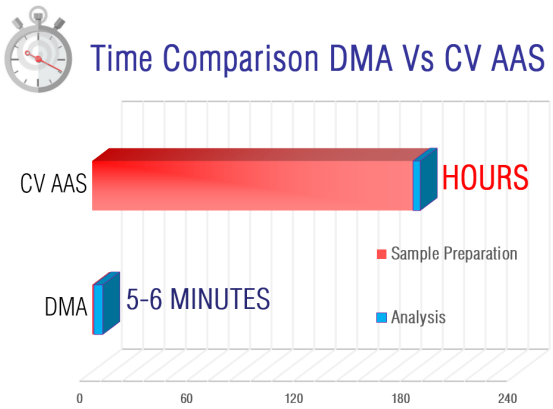
The amalgamator is subsequently heated and releases all trapped mercury to the single beam, fixed wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury content.

The main benefits of direct mercury analysis include:

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

Time per Analysis

The total time to perform a single run is only 6 minutes. No sample preparation and not wet chemistry.



Experimental discussion

To test the efficiency of the DMA-80, one crude oil available certified material NIST 2722 was used to verify the accuracy and the stability of the instrument.

The Crude oil samples are analyzed from different refinery in different countries.

The aim of the tests is to determine the mercury following the UOP-938 method.

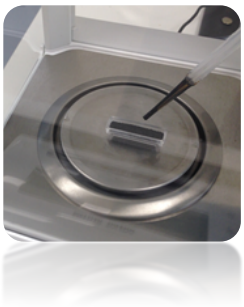
* Samples has been named (Crude Oil1, Crude Oil2, Crude Oil3, Crude Oil4)

Calibration

The DMA can be calibrated using aqueous standards or Standard Reference Materials (SRM).
The DMA-80 used for this experiment had a tri-cell spectrophotometer and covered a dynamic range 0.001-1500ng Hg. Each cell was calibrated using different volumes and different concentration prepared from a Nist traceable 1000mg/L stock solution.

Operating Conditions

The sample is injected into the DMA boat using a syringe, along with the additive prepared earlier. It is important to weight the Crude oil sample using an analytical balance.



The DMA-80's operating conditions for all analyses are shown in Table 1.
- DMA-80 Tricell + Milestone Air Compressor or Air cylinder
- Required additives UOP938 e ASTM:

Additive B: Aluminum Oxide
Additive M: Calcium Hydroxide + sodium carbonate

The additives must be pre-treated in a muffle furnace at 600°C for 2 hours. This step eliminates mercury from additives.

DMA-80 Parameter (UOP)	Settings
Temperature of sample heating furnace	950°C
Temperature of decomposition furnace element	850°C
Pre-heating temperature of mercury collector	150°C
Hg collector temperature	700°C
Carrier gas	Dry purified air
Amalgamation time	12 seconds
Recording time	60 seconds

Table.1

Results

The results of the standard reference materials (SRM's) are shown in the table below. All results were within 10% of the certified value. (Table 2)

Calibration Control Check

Sample	Concentration	Certified
NIST 2722	**0.121** µg/Kg	0.129 µg/Kg
NIST 2722	**0.135** µg/Kg	0.129 µg/Kg
NIST 2722	**0.125** µg/Kg	0.129 µg/Kg
NIST 2722	**0.129** µg/Kg	0.129 µg/Kg
NIST 2722	**0.140** µg/Kg	0.129 µg/Kg

Table 2. Crude Oil (Heavy Sweet) SRM2722

After the Certified Material's control check, different Crude Oil samples have been analyzed following the UOP-938 with DMA-80 Tricell. (Table 3).

All samples have been analyzed in five replicates.

	Crude Oil1 µg/Kg	**Crude Oil2 µg/Kg**	**Crude Oil3 µg/Kg**	**Crude Oil4 µg/Kg**
1	0.35	0.86	1.02	0.42
2	0.37	0.97	0.92	0.51
3	0.46	0.81	1.14	0.59
4	0.39	0.89	1.10	0.49
5	0.41	0.79	0.89	0.46
	RSD 10.65%	RSD 8.25%	RSD 10.75%	RSD 12.85%

Table 3. Crude Oil samples + RSD calculated from DMA-80.

Control Check (+1µg/Kg Standard solution spike)

	Crude Oil1 µg/Kg	**Crude Oil2 µg/Kg**	**Crude Oil3 µg/Kg**	**Crude Oil4 µg/Kg**
1	1.50	1.95	2.21	1.70
2	1.48	2.08	2.02	1.65
3	1.35	1.75	2.34	1.29
4	1.30	1.90	1.98	1.39
5	1.39	2.12	2.39	1.40
	RSD 6.06%	RSD 7.56%	RSD 8.42%	RSD 12.02%

Table 4. Crude Oil Samples spiked with 1µg/Kg in order to verify the accuracy of the results.

Time to time a Calibration Control Check was performed in order to demonstrate the accuracy of the instrument in the short term stability.

Conclusion

Evaluating the results obtained, we can state that the DMA-80 is a completely technical in compliance with UOP-938 and ASTM D-7623-10 methods for the determination of mercury in hydrocarbon samples.

About 70% of the crude oil produced in the world contains a mercury concentration less than 2 µg/Kg.

The Hg concentration of samples used for this test, are representative for the most types of crude oil samples.

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

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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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