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**Committee D02 on Petroleum Products and Lubricants
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**INTERLABORATORY STUDY ON THE DETERMINATION OF
MERCURY IN CRUDE OILS BY ATOMIC SPECTROSCOPIC
METHODS: ASTM D7622 & ASTM D7623**

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Importance of mercury in crude oil (and other fossil fuels such as coal) is well-known based on the toxicity of mercury and its compounds to the environment and humans. A vast literature exists on its effects on the ecosphere. Although routinely analyzed in many oil refinery laboratories, until now a standardized test method was lacking in the ASTM literature for crude oils.

Over the years, a number of different instrumental methods have been used to quantitatively determine total mercury as well as its species in a variety of fossil fuel matrices. Some of the methods which have been standardized by ASTM are summarized in Table 1 below. There are a number of other techniques available for such work besides those mentioned in this Table.

Table 1
ASTM Standard Test Methods for Determination of Mercury in
Fossil Fuels

ASTM #	Matrix Analyzed	Analytical Technique
D 5954	Natural Gas	Gold-Amalgamation + CVAAS
D 6350	Natural Gas	Gold Amalgamation + AFS
D 3684	Coal	Oxygen Bomb Combustion +AAS
D 6414	Coal	Acid Extraction or Wet Oxidation + CVAAS
D 6722	Coal	Combustion + Gold Amalgamation + CVAAS
D 7482	Crude Oil	Sampling, Storage and Handling of Hg Samples
*	Crude Oil	Gold Amalgamation + CVAAS (NIC)
*	Crude Oil	Gold Amalgamation + CVAAS (Lumex)
*	Crude Oil	AFS

(*) In various stages of ASTM standardization process.

Based on the widely used techniques in the industry, two standard test methods have been developed in this work. Both are based on the cold vapor atomic spectrometry. The two methods are based on the instruments provided by two vendors – Nippon and Lumex.

Nippon Method

This method is based on the use of Nippon Instrument Corporation, Osaka, Japan's (NIC) mercury analyzer capable of measuring from 0.1 to 10,000 ng Hg/mL. In this method, a sample is decomposed by heating at about 700°C and collecting the mercury vapors as gold amalgam. After collection, the amalgam is heated and the mercury is re-amalgamated on a second collector. Upon completion of this two step gold amalgamation procedure, the mercury is liberated by heating the collector to 700°C. The vaporized mercury is carried to an absorption cell with a pure carrier gas and detected by the CVAAS technique. Aqueous mercury chloride standards are used. Based on the limited

data available, a repeatability of 0.2 and 3 ng/mL was obtained at mercury levels of 0.8 and 47 ng/mL.

Lumex Method

A method similar to the NIC method described above but without using the gold amalgamation procedure and using Zeeman AAS instead of CV-AAS is proposed by Ohio Lumex for their instrument. The use of Zeeman correction obviates the need for amalgamation by avoiding the matrix-induced interferences. There are other differences between the NIC and Ohio Lumex instruments.

In the Zeeman AAS method, controlled heating following thermal decomposition of the analysis sample in air is used to liberate the mercury. The sample is placed into the sample boat, which is inserted in the first chamber of the atomizer, where the sample is heated at a controlled temperature of 300 – 500°C. The mercury compounds are evaporated and partially dissociated forming elemental mercury vapor. Mercury and all decomposition products are carried to the second chamber of the atomizer heated to about 700 – 750°C. Mercury reduction takes place on the surface of the heating nichrome coil; thus no catalyst is needed. In this step, mercury compounds are totally dissociated and the organic matrix of the sample is burnt out. Continuously flowing air carries mercury and other combustion products through an absorbance cell heated up to 750°C positioned in the light path of a double-wave cold vapor Zeeman AAS instrument. The mercury resonance line 253.7 nm is split into several components, one of those falling within the mercury absorbance line (analytical line) profile and another one lying outside (reference line). The difference between the intensities of these compounds is proportional to the number of mercury atoms in the analytical cell. Absorbance peak area or peak height is a function of the mercury concentration in the original sample being analyzed.

This ILS was organized under the aegis of ASTM Committee D02.SC 3, and was principally conducted by Kishore Nadkarni and David Hwang (Chevron Energy Technology Company).

A list of laboratories and the equipment they used is given in Table 2. These included laboratories from several oil companies and several commercial service laboratories. Some laboratories used both Nippon and Lumex instruments and provided two sets of results. Some others, however, at the end did not return the results.