

Standard methods used for mercury analysis in the oil and gas industry

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Abstract. Mercury is a contaminant found in a variety of hydrocarbons and non-hydrocarbon streams in the oil and gas industry. Quantification of mercury is an integral part to protect processing units especially those with aluminium components and to safeguard personnel from unwanted exposure to mercury. Although mercury is one of the many impurities in oil and gas, its impact is diverse, and this drives the need to adequately quantify the amount of mercury in the process stream as a first line of defence and to make informed decisions on mitigation. The various types of standard methods available for mercury analysis are listed and classified in this literature based on sample phase for hydrocarbon and non-hydrocarbon samples. Different types of mercury analysis such as total mercury, mercury grouping and mercury speciation are also briefly explored to determine which is best for intent of use. Measurement techniques involving different detectors and their respective detection limits are listed with specific attention provided to atomic absorption and atomic fluorescence. The diverse adoption of various mercury analysis across the hydrocarbon value chain will need to be fit for purpose and meet the analytical requirements of the test conducted.

1 Introduction

1.1 Mercury

Mercury is the 80th element listed in the periodic table of elements. Its atomic symbol is noted as 'Hg' with the atomic number of 80 and has an average atomic mass of 200.59. It is found in the transition metals group and sits closely beside the noble metals (gold, platinum, silver and palladium). Mercury readily forms an amalgam with gold and platinum [1] and can be desorbed by heating the amalgam up to 700°C [2]. This feature has been exploited for numerous modern applications such as the creation of dental amalgams and mercury traps for capturing mercury in gas.

Despite being toxic, mercury has seen many uses in industrial, domestic and health applications. In 2004, these include the broad spectrum use of mercury in the chloro-alkali industry, use of mercury in electrical and electronic devices, production of measurement and control devices, batteries, fluorescent lighting, dental amalgams and other applications [3]. It has also been reported that a derivative of mercury known as thiomersal is used in manufacturing vaccines for children [4]. However, consumers are now moving away from mercury based products due to higher awareness on its toxicity.

1.2 Mercury in the Oil & Gas Industry

Mercury is a naturally occurring contaminant which exist in trace quantities in natural gas, natural gas condensates and crude oil. Mercury deposits are often associated with geological plate boundaries, fold belts, and areas with volcanic or hydrothermal activity [5]. Belts of mercury lie across the surface of the planet and it is clear these belts appear to be associated with the boundaries between existing or ancient tectonic plates. It is reported that the largest mercury deposits in the world are located above areas in which plate subduction has occurred in combination with a degree of volcanic activity [6]. It is observed that mercury most commonly occurs in crude oil that is derived from wells that are located at or near current or historically active plate boundaries. Figure 1 shows the global location of mercury belts and mercury mines [6].

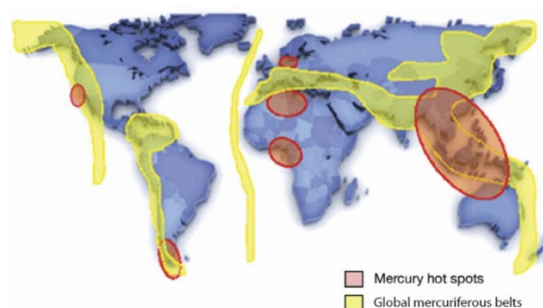


Fig. 1. Global locations of mercury belts and mercury mines

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Mercury exist indigenously in many of the hydrocarbons that are processed around the world. The concentration of mercury however varies from region to region and the concentration also differs between the gas and liquid fractions. Table 1 shows data of mercury concentration in gas and liquid collected from various parts of the world [7,8].

Table 1. Global estimates of mercury levels in gas and liquid hydrocarbons

Location	Mercury Concentration	
	Gas ($\mu\text{g m}^{-3}$)	Liquids ($\mu\text{g kg}^{-1}$)
Europe	100 – 150	-
South America	50 – 120	50 – 100
Gulf of Thailand	100 – 400	400 – 1200
Africa	80 – 100	500 – 1000
Gulf of Mexico (USA)	0.02 – 0.4	-
Overthrust Belt (USA)	5 – 15	1 – 5
North Africa	50 – 80	20 – 50
Malaysia	1 – 200	10 – 100
Indonesia	200 – 300	10 – 500
Middle East	1 – 9	0.8

There have been a number of incidences resulting in loss of human life and extensive facilities damage with regards towards the detrimental effects of mercury. In 1973, a catastrophic failure of aluminium heat exchangers occurred at the Skikda liquefied natural gas plant in Algeria [9]. Results of an investigation determined that a combination of mercury and water temperatures around 0°C caused corrosion in aluminum tubes constructed of aluminum alloy 6061 [5]. After the Skikda incident, similar corrosion issues were discovered in the gas gathering system of the Groningen field in Holland. CO₂ was initially thought to be the reason, but later investigations indicated the cause was mercury contained in the produced gas, in concentrations ranging from 0.001 to as high as 180 $\mu\text{g/m}^3$ [9]. This was then followed by another incident at Moomba gas plant (Australia) where an explosion had occurred on New Year's Day in 2004. The cause of the explosion was an inlet manifold and a related flange weld which had both failed after corrosion by mercury. This led to the release of mercury and a cloud of flammable gases such as methane, ethane, propane and butane [10].

The detrimental effects of mercury towards hydrocarbon processing facilities can be observed through two (2) major types of mercury corrosion. These are amalgam corrosion and a phenomenon known as Liquid Metal Embrittlement (LME). Metals capable of forming an amalgam with mercury suffer from the former type. If an oxide layer is formed on a metal surface, it becomes protected from amalgam corrosion. However, if the protective layer is damaged in the presence of liquid mercury, the metal quickly becomes reactive again with air or water. LME involves the diffusion of mercury into the grain boundaries of a metal and results in cracks

developing along the grains. Unlike amalgam corrosion, LME does not require the presence of water or air and, once initiated, it progresses very rapidly. This type of corrosion affects a broad range of materials, including aluminum and copper-based alloys [11]. Mercury has also been reported to poison catalyst [12,13] and fouling of equipment [5]. Most often the impact of mercury are observed in gas processing where mercury deposits in cryogenic equipment and in numerous cases cause the failure of cold boxes [1]. In order to manage the mercury concentration in process streams and to protect downstream processing equipment, mercury removal units (MRU) are used. There exist a variety of adsorbents developed specifically for mercury removal in various matrices including natural gas, liquid streams, refined products and water. These sorbents function by reacting with mercury (or a mercury compound) to a chemical form (HgS, HgI₂ or amalgam) that is insoluble in the matrix and chemically inert towards components of the process stream [1].

There are regulations in place to limit the discharge of mercury to the environment. This provides a form of governance to curb excessive discharge of mercury which can harm the environment. Every oil and gas producer operating process facilities are required by law to abide to these requirements or incur a hefty fine and risk damaging their reputation at the same time. In Malaysia, the discharge of mercury effluent is governed by the Environmental Quality Act (EQA) 1974 [14].

2 Standard Test Methods for Mercury Analysis

2.1 Importance of utilizing standard test methods

The importance of accurate and precise results associated with quantification of mercury is of great interest in the oil and gas industry. There have been many standard test methods related to the analysis of mercury published by international testing fraternities like the American Society for Testing and Materials (ASTM), the International Organization for Standardization (ISO) and the United States Environmental Protection Agency (USEPA) and American Public Health Association (APHA). There are also in-house methods which are widely used and are accepted globally, for example test methods developed by Universal Oil Products (UOP) and other organization's alike.

The main objective to establish test methods are to standardize methods of laboratory testing to reduce uncertainty in analysis and increase confidence between the producer and customer. Since both parties use a standard test method, any discrepancies or queries can quickly be investigated for rectification. False positive and false negatives result which arise from unreliable or substandard testing practices can impact the sales of

petroleum feed stocks or petroleum products as they are perceived to deviate from their required specifications. This in turn can cause the refinery or petrochemical plant to incur huge monetary losses or deprive them of a lucrative opportunity to sell their feedstock or product for a higher price. For example, feedstock and petroleum products tainted with mercury depreciate in value and are sold at a discounted price [5,6].

Although there are many international standard test methods available for mercury analysis, there still exist many opportunities for method development and method validation work to bridge the gaps which exist between these standards. These gaps exist because of the diverse properties of hydrocarbon samples which significantly differ depending on their origin and geological formation [5]. Development of new test methods which have spawned throughout the years have also been driven by the cooperation between oil and gas entities and instrument manufacturers, for example the development of ASTM D6350. One of the most challenging problems associated with analysis of mercury is the complexity of the sample matrix and the losses of mercury incurred during sample preparation [15], assuming the samples collected are representative. Unrepresentative samples further complicate the quantification of mercury and increases the possibility of error [16].

2.2 Types of mercury analysis methods

The types of mercury analyses comprise of total mercury, mercury grouping and mercury speciation as depicted in the figure below.

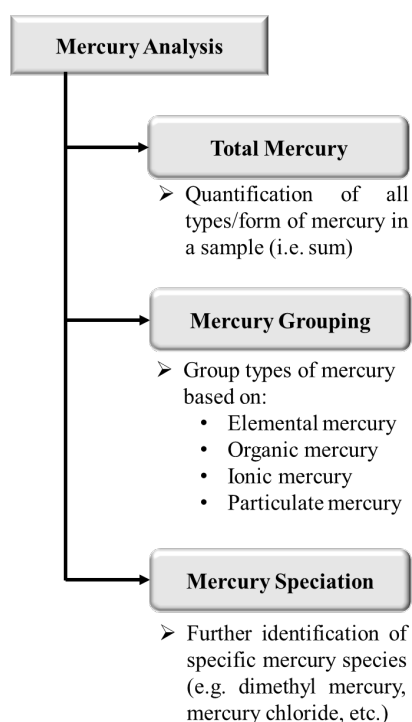


Fig. 2. Classification of mercury analysis

Total mercury analysis is one of the most common type of analysis applied in the Oil and Gas industry. It involves quantification of all forms of measurable mercury within a particular hydrocarbon or non-hydrocarbon matrix. Prior to analysis, the sample would first be filtered to remove any form of particulate matter or solids from the sample. This is commonly done as best practice for liquid samples to ensure only soluble mercury is quantified. Should there be a need to determine mercury content in the separated solid, a separate analysis can be performed.

Mercury grouping and speciation analysis on the other hand seek to classify the presence of different types of mercury in a particular sample, with the advantage of speciation being able to identify in further detail the types of mercury species present within the sample.

Mercury grouping enables the analyst to identify the main types of mercury species in a sample. This means classifying mercury presence as elemental mercury, organic mercury, ionic (inorganic) mercury and particulate mercury. It does not identify the exact species of mercury for example dimethyl mercury or methyl mercury, which are both examples of organic mercury.

Mercury speciation is a detailed analysis focused to determine the presence of certain mercury species in a particular sample. The presence of organic mercury species such methyl mercury and dimethyl mercury can be identified in samples such as condensate and water. This involves subjecting the mercury species to elution at different resident times through a column (either by Gas chromatography or High Performance Liquid Chromatography) followed by converting them sequentially to elemental mercury and detection. Detectors such as an Atomic Fluorescence spectrometer can be used. Commercial analytical equipment is available for mercury speciation. One major challenge of mercury speciation is the prohibited use of certain organic mercury standards (or Certified Reference Material) for calibration purposes due to their known toxicity.

A common challenge associated with mercury analyses is identifying which type of analysis to be performed. The answer relies on the intent and purpose of the analysis and what information the analyst seeks to obtain. For example, it is adequate to conduct analysis of total mercury for monitoring of Mercury Removal Unit (MRU) performance, while design of a suitable MRU system can consider the distribution (i.e. grouping) of mercury in the feed to be treated, and development of mercury adsorbents may consider conducting mercury speciation to better improve mercury abatement capabilities of the adsorbent.

There is a myriad of available standard methods applicable for mercury analysis. It is up to the analyst to

identify which will be suitable and fit-for-purpose in line with the objective of the testing to be conducted. Hence this will also extend to a suitable means to collect the sample for the said analysis. Here the methods for mercury analysis are further classified based on their matrix, being in hydrocarbon or non-hydrocarbon samples in various mediums (gas, liquids and solid).

2.3 Test methods for analysis of mercury in various matrices

The oil and gas industry prides itself in the quality of products and stringency of analysis it performs. There are numerous test methods that have been developed to quantify mercury in a variety of sample matrices. These matrices can be classified into three (3) main groups which are gas, liquid and solid. Each group can then be further divided into two (2) subgroups which are hydrocarbon and non-hydrocarbon samples. In addition, samples can exist in high pressure (> 1 atm) or ambient pressure (1 atm). Figure 3 shows the common standard test methods associated with mercury analysis which are commonly used in the oil and gas industry.

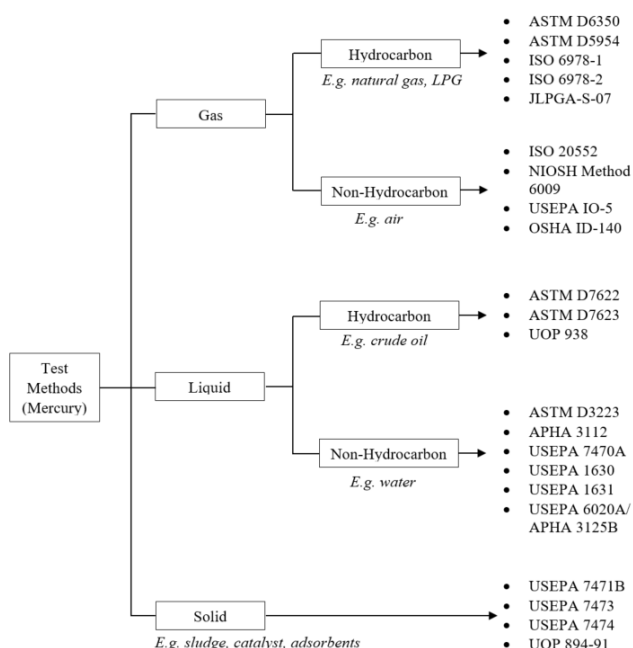


Fig. 3. Various types of standard methods used for mercury measurement

The use of these diverse methods are used in upstream and downstream activities. However, their contributions are more profound in downstream related activities to meet sales specifications. A certificate of quality (COQ) or equivalent is produced together with each batch of petroleum products to ensure the product meets all specified requirements [17]. These test methods are also used by laboratories together with ISO 17025 to ensure competence of testing and calibration performed using standard methods, non-standard methods, and laboratory-developed methods. For example, ASTM D6350 is used to ensure customers that sampling and

analysis of mercury in natural gas was performed based on the stipulated techniques required. As for downstream activities, many of the analytical activities performed involve evaluation and characterization of raw hydrocarbons from reservoirs, monitoring impurities in process streams and other related applications. The application of downstream analytical methods for upstream analysis work well, but only to a certain extent due to the complexity of sample matrix, high pressures and the content of contaminant found in raw hydrocarbons [16].

There are also other test methods available for quantification of mercury in other matrices such as flue gas and stack gas. These methods are related to the measurement of mercury from combustion sources such as the burning of coal and emission from incinerators. For example, ASTM D6784 is used to analyze elemental, oxidized, particle-bound and total mercury in flue gas. This method is also known as the Ontario Hydro method. Another example is USEPA Method 101A used to analyze particulate and gaseous mercury emissions from sewage sludge incinerators.

Mercury can be collected much easier in natural gas compared to condensate. This is because the matrix of condensate is more complex compared to natural gas. Hence requires pretreatment or conversion step prior to analysis. There are mainly two (2) approaches which are wet-chemistry and thermal conversion [18]. In a wet-chemistry conversion system, a digestion/extraction (via oxidation) step is carried out prior to a reducing step. A strong oxidizing agent (e.g. Aqua Regia) is added to the sample followed by addition of a reducing agent (e.g. SnCl_2). The digestion/extraction techniques used for the determination of total mercury in gas condensates sample are inefficient, with efficiency depending upon the species present and the complexity of the matrix [15]. Due to effects of corrosion, frequent reagent replenishment requirements, interferences from other species/elements, this method has given way to a less laborious and reproducible approach utilizing thermal conversion [18].

Thermal conversion approach involves vaporizing the hydrocarbon sample (i.e. condensate) to a temperature at or above the highest boiling point of the heaviest component in the condensate matrix in the presence of an inert gas. The inert gas can be either purified nitrogen or purified argon. The vaporized sample is then channeled through a mercury trap where mercury will be absorbed. It is known that mercury species are efficiently absorbed onto gold-coated materials and platinum group metals via amalgamation [19]. The utilization of this characteristic as means of removing the interfering matrix prior to release and measurement suggest an improved approach to total mercury determination and has been studied [15].

2.4 Measurement techniques for mercury

The quantification of mercury in hydrocarbons which include natural gas and condensate are challenging due to the very low concentrations involved, the high volatile nature of mercury and the complexity of the sample matrix [15]. This requires that either a large sample volume or highly sensitive detector or both are used to quantify mercury [7]. There are a variety of analytical methods which are available for measurement of mercury at trace and ultra-trace levels. Table 2 shows some of these methods and their detection limits [7].

Table 2. Detection techniques and detection limits for the measurement of mercury

Analytical instrument	Detection limit
X-ray fluorescence	10 ng
Neutron activation	2 ng
Gold film	0.5 ng
Differential pulse voltammetry	0.04 ng
Cold vapour atomic absorption (CV-AAS)	0.01 ng
Cold vapour atomic fluorescence (CV-AFS)	0.0001 ng
Inductively coupled plasma- mass spectrometry (ICP-MS)	0.001 ng
Inductively coupled plasma- atomic emission spectrometry (ICP-AES)	50 ng/ml

Atomic absorption and atomic fluorescence spectroscopy methods are most widely used for mercury analysis. Both are used interchangeably depending on the requirement of the detection limit. Most often AFS is used for trace and ultra-trace analysis, whereas AAS is mainly used for trace level analysis. The use of either method is dependent on the analyst requirements or may already be specified by a test method. Majority of test methods available utilize AAS compared to AFS. Table 3 shows the distribution between AAS and AFS technique as specified by particular test methods related to mercury analysis.

Table 3. AAS and AFS test methods for measurement of mercury

Spectroscopy Technique	Test methods
AAS	ASTM D5954, ASTM D7622, ASTM D7623, ASTM D3223, ASTM D6784, ISO 6978-1, ISO 6978-2, ISO 20552, UOP938, UOP 894, USEPA 7470A, USEPA 7471B, USEPA 7473, USEPA 7474, USEPA 101A, NIOSH Method 6009, OSHA ID-140, APHA 3112, JLPGA-S 07
AFS	ASTM D6350, ASTM D6784, ISO 6978-1, ISO 6978-2, ISO 20552, USEPA IO-5, USEPA 1630, USEPA 1631, JLPGA-S 07

Majority of test methods written utilize AAS compared to AFS. This has to do with AAS reliability in quantifying mercury in the ppb and ppm range of concentration, which fall within the average concentration range of mercury measured in hydrocarbons. AAS also uses filtered air as the carrier gas compared to inert gas required for AFS which translates to lower operating costs. AFS on the other hand outperforms AAS with higher sensitivity towards mercury. It has a wider range of detection compared to AAS, being able to measure mercury from the ppt to ppm range of concentration. Nonetheless, there are test methods which provide analysts options of either using AAS or AFS to quantify total mercury.

2.5 Modification of standard test methods for specific intent and purpose

Although most types of mercury analysis will have an associated standard test method which defines the process, there are occasions where custom analysis would be required to suit a specific intent. Often available standard test methods will be used as a guide with some variations introduced in the procedure or different type of sample might be used, leading to a deviation from the purpose and content of the method. In this instance, it is up to the analyst to make an educated judge should the modified method be fit for purpose. A method validation can be conducted to ensure fit for purpose of the modified method and steps to quantify uncertainty in the analytical measurement can also be conducted. Guidelines such from resources such as EURACHEM [20] and equivalent can be used. Depending on the type of analysis, the entire process can be laborious albeit the outcome will enable the new validated method to be used with a high level of confidence and be relevant as long as it remains fit for purpose.

3.0 Conclusion

The analysis of mercury in either hydrocarbon or non-hydrocarbon samples will depend on the complexity of the matrix and its phase, either gas, liquid or solid. Importance of accurate, precise and reliable analysis of mercury stems from the impact it has towards process units, and health and safety. There are different standard test methods available for most analysis required by the Oil and Gas industry which most utilize either AAS or AFS detectors to quantify mercury. Three main types of mercury analysis are total mercury, mercury grouping and mercury speciation. Each providing the analyst different depths and detail of information. It is up to the analyst to identify which type of analysis would bring the most value, as each will differ in complexity and cost, with total mercury analysis being the most basic. However, not all available standard test methods would suit a particular purpose due to the highly diverse tests required throughout the hydrocarbon value chain. A method validation can be conducted to ensure fit for purpose of the modified method and steps to quantify

uncertainty in the analytical measurement can also be conducted.

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