

Sampling and determination of mercury for the oil and gas industry

Services provided

- Determination of mercury in gas, condensate / oil and water during well test operations
- Evaluations of the mercury content of new wells tying in to existing facilities
- Determination of mercury in process gases and liquids
- Determination of mercury in process chemicals (e.g. amine, glycol, caustic)
- Mass balance of mercury across a plant process, monitoring feed, process and final products
- Evaluation of mercury removal bed performance
- Atmospheric monitoring during plant shutdown
- Speciation of mercury on gases, oil, condensate and water
- Advice on occupational exposure limits and control measures
- Bespoke reports tailored to suit customer requirements

Oil production yields a complex, multiphase fluid, which is subject to variations in (among others) temperature, pressure, phase, pH and redox potential as it passes through the production system. The chemistry of mercury in this system is not fully understood, but it is known that some mercury species can partition into different phases of the produced fluids as conditions change.

In a typical reservoir the mercury is present principally as metallic Hg (Hg0), but can react to form HgS (solid precipitate), and sometimes Hg2+ (soluble ionic mercury) during production and processing.

Mercury may be found in the produced volatile (gas) and non-volatile (liquid) phases of hydrocarbons. The predominant form of mercury found in the gas fraction is metallic mercury (Hg0). The predominant forms of mercury found in condensate and oil are mercuric sulphide (HgS) and metallic mercury (Hg0) although for some fields ionic mercury (Hg2+) may be the prevalent species in the oil.

Mercury compounds found in crude oil and their relative solubility's and abundances

Formula	Name	Boiling Point °C	Solubility in H ₂ O at 25 °C	Solubility in Alkane at 25 °C	Relative Abundance in Natural Gas	Relative Abundance in Condensate	Relative Abundance in Crude Oil
Hg ⁰	Elemental/Metallic	357	50 ppb	2 ppm	> 90%	0-100%	0-100%
(CH ₃) ₂ Hg	Dimethylmercury	93	< 1 ppm	completely	< 1%	< 1%	< 1%
HgCl ₂	Mercuric chloride	302	70g/L	~ 20 ppm	0%	10-50%	10-50%
Hg ₂ Cl ₂	Mercurous chloride	Subl 400	~ 2 ppm	unknown	0%	unknown	unknown
HgS	Mercuric sulphide	Subl 583	Insoluble	Insoluble	0%	0-100%	0-100%
CH ₃ HgCl	Methylmercuric chloride	unknown	> 10g/L	1000 ppm	0%	< 1%	< 1%

Processing of gas and oil that are rich in mercury can be problematic and needs to be monitored and managed on an ongoing basis. The three major areas for concern resulting from mercury are Liquid Metal Embrittlement (LME), catalytic poisoning and environmental issues.

Mercury forms amalgams with other metals particularly aluminium and has the potential to cause corrosion of welds, cryogenic components, aluminium based heat exchangers, compressor seals/stems/seats and pump shafts made from copper alloys.

There have been some widely publicised incidents where mercury corrosion has caused catastrophic failures leading to plant shutdowns and in one unfortunate case resulted in several fatalities.

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In the downstream processing of gas and oil, mercury can cause premature failure of catalytic beds. If not monitored and controlled correctly a plant contaminated with mercury can lead not only to worker exposure during planned plant shutdowns but also environmental release of mercury.

As a consequence of the issues arising from the presence of mercury, even at trace concentrations, it is common to find mercury specifications imposed on pipelines and feedstocks to gas plants, refineries and petrochemical plants. Historically specifications applied to gases only, however strict stipulations are now being imposed increasingly on liquids. Some refiners are now starting to impose limits on feedstocks in the single ppb range and more commonly there is an impact on the “price per barrel” of oil for oils contaminated with mercury.

For fields with a high mercury concentration it may be necessary to incorporate a mercury removal system into the production/process design. The absorbents used in mercury removal systems typically remove metallic mercury only. It is for this reason (as well as environmental and operator exposure issues) that some oil companies need to identify what species of mercury are present.

Sampling

Ideally, where possible, determination of mercury in gases, condensates and oils should be carried out at source (at the well site or processing facility).

It is possible to use sampling containers that are coated to reduce losses of mercury but this is a secondary choice to analysis onsite. It is well documented that, with time, mercury can precipitate from the gas as mercuric sulphide after reaction with sulphur compounds. Thus, time delays caused by the necessity to transport samples back to an onshore laboratory may result in mercury reacting to form other species, resulting in erroneous speciation data (although total mercury concentrations for stabilised liquid samples taken in glass containers should remain unaffected).

Sampling equipment used to capture samples for subsequent determination of mercury must be coated to minimise absorption of mercury. It is important to verify the integrity of the coating prior to sampling using mercury calibration gas to ensure no significant losses are occurring.

Location of sampling points within the process system should be considered in order to obtain appropriate samples. For example assessment of feeds into a pipeline system should be sampled subsequent to any separation and processing (e.g. glycol dryer) and immediately prior to entry into the system.

It is essential that the correct procedure for operation of sampling points is followed along with the use of suitable sampling vessels in order to obtain representative, repeatable data. Any deviation from correct use of sampling points and protocol for sampling may result in erroneous data.



Suitability of sampling points

It is important that sampling points being used are either in frequent use or have had all pipes fittings and valves conditioned for mercury sampling. It is often the case that this is not possible, particularly at offshore installations and in these circumstances, sampling points with the minimum length sampling line should be used. Ideally, a sample point should be such that it is possible to place a flow-through sampling vessel in-line, which will allow the sampling line and vessel to be flushed prior to collection of sample. If the sample point design does not allow flushing in this manner, then the provision of evacuated sampling vessels should be employed. The sampling line should be free from any copper, brass and aluminium fittings and the vessel inlet should be connected to the sampling point with “hard” fittings only, i.e. no flexible hoses. A flexible hose can however be used on vessel outlet.

Sampling of single-phase products

Single-phase samples of gases can be collected in gas bags or conditioned/coated vessels and liquids can be taken directly into acid washed glass bottles. Ordinarily for liquid samples, a minimum of 5 mL is required whilst for gas samples, the minimum volume is typically 10 L. However, exact volume requirements are dictated by the limit of quantification required; consultancy and advice regarding minimum sample volumes will be given prior to commencement of sampling. Analysis should be conducted as soon as possible after sampling.

Sampling of multi-phase products

The distribution of mercury within individual phases needs to be considered for multi-phase samples. If the requirement is for total mercury in the whole sample, this is achieved by determining mercury in each phase present (gas, liquid hydrocarbon, water and solid) and then calculating total mercury found in the whole sample. If there is a requirement to determine mercury in individual phases then a sampling protocol should be adopted such that each phase is isolated at the time of sampling. This is particularly important for wet and sour multi-phase samples, as previous work has shown that it is possible for mercury to partition from the gas phase into the liquid phase, during sample transit to the laboratory (precipitating as HgS).

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Sampling at source onto gold sand traps

This sampling procedure collects mercury from a known volume of gas onto a gold trap by amalgamation. The mercury collected onto the gold traps can then be determined using a variety of analysers. This methodology is particularly suitable for single-phase gaseous samples but is not suitable for multi-phase samples.

Mercury analysis

Determination of mercury can be achieved using a variety of techniques. Expro use a number of mercury analysers; the selection of which depends on sample matrix, sampling procedure, limit of quantification and customer requirements and specifications.

Hydrocarbon gases

There are three ways in which Expro can determine mercury in gases:

- Mercury is trapped from a known volume of gas using a gold sand trap and subsequently determined in the trap using either atomic fluorescence or atomic absorption (e.g. ISO 6978). This is the most common approach adopted by Expro.
- For gases that contain minimal benzene Expro uses specialised atomic absorption equipment that allows direct measurement using atomic absorption.
- A known quantity of gas is passed through an absorber train. The first absorber contains potassium permanganate solution, which removes inorganic/metallic mercury. The second absorber contains free bromine solution to remove organic mercury species. Mercury is then determined in these solutions by atomic absorption.

Hydrocarbon liquids

Mercury is determined by combustion in oxygen and final detection by atomic absorption. This method is based on ASTM D7623. This methodology can be conducted offshore if required.

Water samples

Mercury is determined by combustion in oxygen and final detection by atomic absorption. This method is based on EPA 7473.

All analysis described for gases and liquids can be conducted offshore / onsite.

Particulates

Previous work at ADS has shown that particulates recovered from produced oil and gas samples can contain relatively high concentrations of mercury, however the total mass of particulate found is usually low. It is possible to determine mercury in particulate directly by combustion in oxygen and final detection by atomic absorption, however it is often necessary to filter the particulate and perform a high-pressure microwave digestion. Mercury is then determined in the digested solution.

Multi-phase samples

For multi-phase samples the gas is flashed off and mercury is trapped as described above for gases. The remaining liquid and solid phases are recovered from the vessel and mass/volume is recorded. Mercury is then determined on each individual fraction as described above. As well as reporting mercury concentrations found in each fraction, the total mercury present in the whole sample may also be calculated.

Mercury speciation

As a standard practice Expro offer a service of analysing liquid samples after allowing settling (for at least 24 hours) and after shaking. The settled analysis indicates how much soluble mercury is present, the shaken analysis indicates how much total mercury is present (includes any fine particulates). Previous work by our laboratory has shown that mercuric sulphide (HgS) is the predominant form of mercury found in the particulate portion of produced oil and water.

Where required the following mercury speciation can be conducted either in the laboratory or offshore / onsite as required:

Gases	Metallic (elemental) mercury Organic mercury
Condensates	Volatile mercury Soluble ionic mercury Soluble non-ionic mercury Particulate mercury
Black oils	Volatile mercury Soluble mercury Particulate mercury
Water	Volatile mercury Soluble ionic mercury Soluble non-ionic mercury Particulate mercury

Typical analytical approach

The following represents a typical approach to mercury determinations in oil industry samples

- Determine mercury in the gas using gold sand trap methodology
- Determine mercury on the pressurised or stabilised oil (soluble and total)
- Determine mercury in the water (total Hg if only a small quantity of water is present, on settled and shaken if a large quantity of water is present).
- If the concentration of mercury in the gas and/or the oil are found to be relatively high, then speciation analysis should be considered.

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