Sampling and determination of mercury in liquid and gaseous hydrocarbons

Mercury may be found in the volatile (gas), non-volatile (liquid) and particulate phases of hydrocarbons, and may be present in both inorganic and organic forms.

Sampling oils and gases for subsequent mercury determination is not straightforward since mercury has an affinity for the internal surface of many types of sampling vessels particularly aluminium resulting in anomalously low values for mercury content when the samples are analysed.

For this reason, sampling equipment used in service for the determination of mercury must be either coated to prevent absorption of mercury or 'conditioned' prior to sampling. Conditioning may be achieved by repeated use of a vessel to sample a particular well or pipeline. In time, contact with the sample neutralises the active sites on the internal surfaces of the vessel, so that it no longer adsorbs mercury. However, this takes time and until equilibrium has been reached the analytical data obtained will almost certainly be erroneously low.

The alternative to conditioning is to use sample vessels that are manufactured with an inert coating on the internal surface. However, it is important to verify the integrity of the coating prior to sampling using calibration gases to ensure no losses are occurring.

Which types of sample vessels can be used and what type of samples can be analysed ?

Depending on the available sampling points, samples may be single phase in nature i.e. gases, gas condensates and oils. Alternatively the samples may be multi-phase in nature, under high pressure and also contain associated water.

The inert coating is ideal for stainless steel surfaces, which covers the vast majority of sample vessels. Aluminium vessels will adsorb mercury from the sample regardless of any pre-treatment. Aluminium is therefore not suitable for collecting samples for subsequent mercury determination.

QA & QC

Expro's analytical data services is an accredited laboratory (UKAS/NAMAS testing station no.1880) and all reagents, instruments and personnel involved in the procedures above are controlled under the UKAS quality system. Whilst the determination of mercury in oil and gas is not an accredited method, the procedures are fully documented in-house and records of sampling equipment suitability checks carried out are retained for the purposes of traceability. This includes details of initial tests to determine the suitability of vessels, and records of the reagents used and performance checks carried out.

Sampling

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 form correct use of sampling points and protocol for sampling into conditioned or coated vessels 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.

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Sampling of single-phase products

Single-phase samples of gases and liquids can be taken directly into conditioned/coated vessels. 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.

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.

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 Determination

Determination of mercury can be achieved using a variety of techniques. Expro's analytical data services 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's analytical data services can determine mercury in gases;

i. 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.

ii. 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)

iii. For gases that contain minimal benzene Expro's analytical data services uses specialised atomic absorption equipment that allows direct measurement using atomic absorption.

All of the above analysis can be carried out offshore if required.

Hydrocarbon liquids

Mercury is determined by combustion in oxygen and final detection by atomic absorption. This method is based on UOP 938 (and ASTM D6722). This methodology can be conducted offshore if required.

Residual/associated water

Mercury is determined by combustion in oxygen and final detection by atomic absorption. This method is based on EPA 7472. This methodology can be conducted offshore if required.

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Particulates

Previous work at Expro's analytical data services has shown that particulates recovered from produced oil and gas samples can contain relatively high levels 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 by total combustion in oxygen using a Leco 254 total mercury analyser. By using a combination of acid digestions, it is often possible to obtain some basic information on the mercury species present in the solid material.

Multi-phase samples

For multi-phase samples the gas is passed through the liquid absorber train described above to remove inorganic/metallic mercury and also organic mercury. This may be carried out by simply allowing the cylinder to de-gas down to atmospheric pressure and room temperature. Alternatively it can be controlled at any given temperature or pressure to mimic plant separation conditions. 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.

Summary of Services Provided

- Expro's analytical data services can provide on-site sampling and analysis for a variety of sample types (gases, oils, water and process chemicals).
- If analysis onsite/offshore is not possible, samples can be taken into treated vessels which minimise losses of mercury during transit.
- Expro's analytical data services will provide all necessary equipment for sampling purposes.
- Expro's analytical data services will liaise with all operators involved with sampling to evaluate suitability of sampling points and sampling procedure to ensure sample integrity.
- The methodology is suitable for single and multi-phase samples including those where there is only a minor liquid component.
- Expro's analytical data services can provide interpretation on quantities of mercury detected and the impact on the process.