

# The determination of Mercury in Liquefied Petroleum Gas - a comparison of sampling techniques

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## Introduction

Knowledge of the mercury content in petrochemicals is extremely important. Mercury is highly toxic, is of environmental concern and can cause significant damage to petrochemical plants which can force unscheduled shutdowns. Regular monitoring of mercury levels in process streams is required to confirm the performance of mercury removal units and compliance with product specifications.

High levels of mercury are commonly found in hydrocarbon streams. In most cases, mercury tends to preconcentrate in the lighter liquefied gas fractions such as liquefied petroleum gas (LPG). LPG is a mixture of C<sub>3</sub> and C<sub>4</sub> compounds, primarily propane and butane, and is pressurised to maintain it in the liquid phase to facilitate storage and transport and vaporised when used.

The mercury concentration in LPG is typically measured by atomic spectroscopy methods, following vaporisation of a representative sample. Various sampling techniques are available, based on either vaporising a representative sample in the field or collecting a liquid sample in a sample bomb and vaporising a sub-sample in the laboratory.

This poster compares two sampling options based on offline determination of mercury by amalgamation-atomic fluorescence spectrometry (AFS) following vaporisation of a representative sample. Both alternatives are based on the ISO6978 and ASTM 6350 methods for the determination of mercury in natural gas.

## Field Vaporisation Approach

In this approach, the liquid sample is vaporised in the field using a heated pressure regulator and sampled onto Amasil™ tubes. The sample tubes are then returned to the laboratory for analysis.

Sampling was achieved using the PSA 10.547 Offline Sample Interface, shown in Figure 1. The unit was specifically designed to operate in hazardous areas (Zones 1 or 2) and is Ex d IIC T3 rated. This enabled samples to be collected close to the process line to minimise lag time and the potential for contamination or losses. The system included provision for a primary bypass (at process pressure) and a secondary bypass downstream of the heated vaporising regulator to ensure the sample point and sampling line was well flushed and a representative sample available. The gas phase sample flowed over two Amasil™ sampling tubes in series, where mercury in the sample was collected by amalgamation onto gold. The tubes are heated by an Ex d heater to at least 10° C above the dew point of the sample to prevent condensation of hydrocarbons. Different sample volumes were collected to ensure that no matrix interference was encountered.

If a liquid-phase bypass is not available, careful attention is required to ensure adequate flushing of sample take off valves and sample lines for LPG samples without requiring long pre-sampling conditioning periods: (i) without the use of additional equipment, the primary bypass flow achievable was low, to prevent freezing when the liquefied stream flashes; and (ii) for a given bypass flow, the effective flowrate of the liquefied sample in the lines was much lower than for a gas-phase sample stream. For example; if a 15 m (50 ft) stainless steel braided Teflon sample line and typical sampler set up are used; the lag time is 11 min with no primary bypass, falling to 75 sec if a vapour primary bypass of 10 sL min<sup>-1</sup> is provided.

Following sampling, the sample tubes were analysed by dual amalgamation-AFS using the PSA 10.525 Sir Galahad, shown schematically in Figure 2.

Figure 3 shows typical data for repeated analysis of a mixed LPG stream at an offshore location in SE Asia over 5 days. A high flow bypass was used. The average concentration observed over the test campaign was 1143 µg Sm<sup>-3</sup> with a standard deviation of 165 µg Sm<sup>-3</sup> (n=36). This is approximately 600 µg kg<sup>-1</sup> (ppb w).

Figure 1 PSA 10.547 Offline Sample Interface

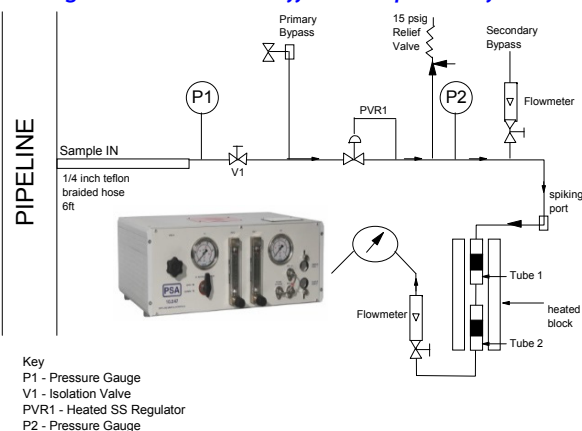


Figure 2 PSA 10.525 Sir Galahad

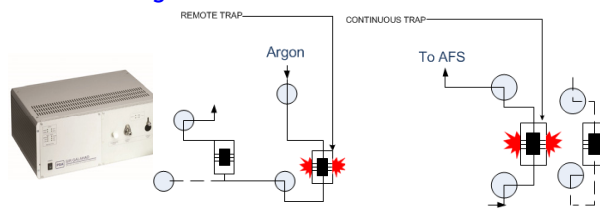
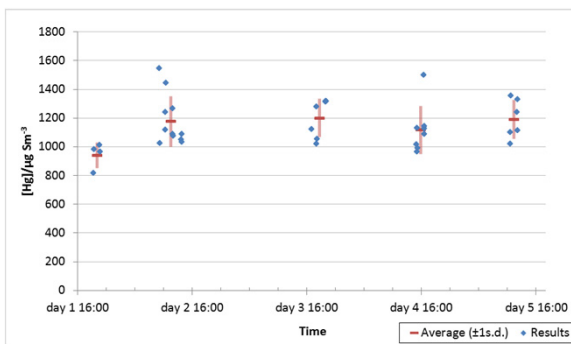


Figure 3 Results trend for repeated sampling of a mixed LPG stream (no MRU)



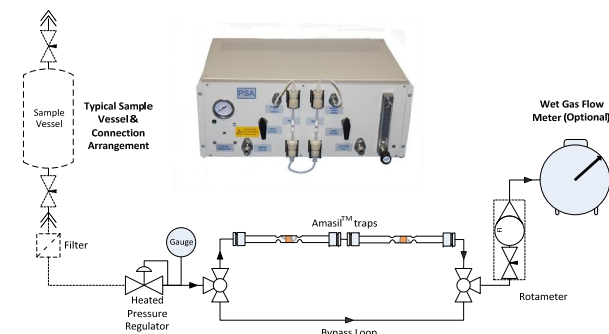
## Laboratory Vaporisation Approach

In this approach, a liquefied sample is collected in a sample bomb in the field and returned to the laboratory for analysis. In the laboratory, the sample is vaporised using a heated pressure regulator and mercury in the sample collected onto Amasil™ tubes for analysis.

In the field, a PTFE-lined or SilcoNert-coated sample bomb is filled with pressurised sample. To ensure a representative sample is collected, the sample point must be well conditioned and well-flushed. The sample is then taken to the laboratory for analysis.

The sample bomb is then connected to the PSA 20.630 Liquefied Gas Sampling System (Figure 4) where a low flow rate is vaporised by a heated pressure regulator. The gas phase sample flows over two Amasil™ sampling tubes in series, where mercury in the sample was collected by amalgamation onto gold. The tubes are not heated as the ambient temperature in a laboratory is typically more than 10° C above the dew point of the sample. Following sampling, the sample tubes are analysed by dual amalgamation-AFS using the PSA 10.525 Sir Galahad, as for the Field vaporisation approach. The system can also be configured to sample the vaporised gas directly onto the Amasil™ trap in the Sir Galahad.

Figure 4 PSA 20.630 Liquefied Gas Sampling System



## Discussion

Both sampling approaches offer a sensitive and accurate method of determining mercury in LPG by amalgamation AFS. They offer detection limits of <1 ng Sm<sup>-3</sup> and by varying the sample volume collected and utilising the linear dynamic range of 7 orders for the AFS detector can achieve an upper working range of 3000 µg Sm<sup>-3</sup>.

The field vaporisation approach enables samples to be collected over a longer period of time, providing results which represent the average concentration over several hours whereas the lab. vaporisation approach provides results for a short time period.

The field vaporisation approach requires Ex d apparatus and longer time in the field for sample collection, particularly if extensive sample point/sample line conditioning is required whereas the lab. vaporisation approach uses simpler equipment and is more likely to use an existing well-flushed sample point. It is important however to ensure that the sample bombs used are well cleaned or dedicated to a single sample point to avoid contamination during sample transfer.