P S ANALYTICAL

Application Note 060

DETERMINATION OF MERCURY IN NATURAL GAS

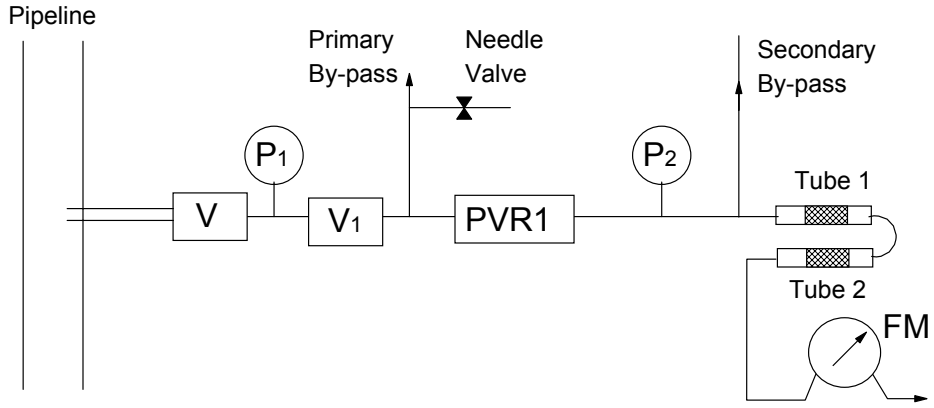
Introduction

Mercury occurs naturally in natural gas at concentrations anywhere from 0 to 200 μg m^{-3} and in addition, may be present in several forms. The presence of mercury in natural gas can have catastrophic effects on gas plants - the mercury attacks aluminium welds leading to cracking and eventually failure. Resulting in unscheduled shut-downs costing millions of dollars. As such it is imperative that the mercury be determined accurately and precisely. This application note describes instrumentation designed to allow the determination of mercury in natural gas to be carried out with excellent sensitivity, selectivity and precision.

Sampling Apparatus: PSA 10.537 PSA Off-line Sampling System.

The sampling arrangement is illustrated in Figure 1. Teflon hose braided with stainless steel was connected directly to the pipeline at line pressure. A primary by-pass was set up at a flow rate of >30 l/min using a needle valve arrangement. For sampling of export gas the waste from the primary by-pass was vented to a flare whereas for inlet gas the waste was vented to atmosphere 50 metres away from the source. The pressure was reduced using PVR1 to approximately 15 psi. To eliminate condensation of hydrocarbons and losses of mercury on stainless components during the pressure letdown PVR1 was heated to 150°C.

Figure 1 Sample Interface



Key to Figure 1

V = Isolation Valve on Pipeline
V_1 = Isolation Valve for 10.537
P_1 = Press Gauge for Pipeline
PVR1 = Heated Pressure Regulator
P_2 = Pressure Gauge prior to sampling tubes
FM = Wet Gas Flow Meter

P S ANALYTICAL
UK: Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK
Tel: +44 (0) 1689 891 211 *Fax: +44 (0) 1689 896009* *E-mail: psa@psanalytical.com*
USA: 1761 W. Hillsboro Blvd., Suite 318, Deerfield Beach, FL 33442, USA
Tel: +1 (954) 429 1577 *Fax: (954) 429 1601* *E-mail: usa@psanalytical.com*
www.psanalytical.com

The gas exiting PVR1 was then delivered to a secondary by-pass and two sampling tubes connected in series. Gold impregnated spherisorb was utilised as the adsorbent material. Previous work [1,2] has indicated that all forms of mercury are quantitatively collected on this adsorbent material. To avoid condensation of hydrocarbons on the sampling tubes a collection temperature of 140°C was utilised. The gas volume passed over the sampling tubes was measured using a wet gas flow meter and corrected for temperature and pressure.

The 10.537 is a portable off-line sampling system certified to ExDIIC T3. The system is commercially available and is shown in Figure 2. Table 1 summarises the conditions used.

Figure 2 Photograph and schematic of front panel of the 10.537

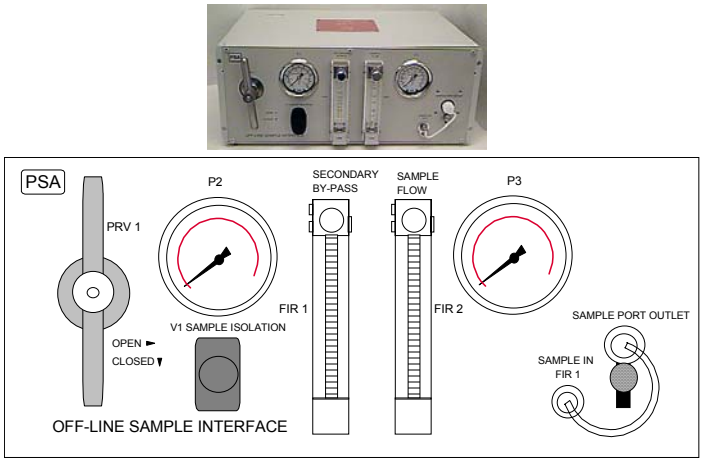


Table 1 Conditions for PSA 10.537 Off-Line Sampling Apparatus

Apparatus	:	PSA 10.537 Serial No. 007
Inlet Pressure (P1)	:	Export Gas psi Inlet Gas psi
Pressure Reduction (P2)	:	15 psi
Primary By-pass Flow Rate	:	> 30 l min^{-1}
Secondary By-pass Flow Rate	:	1.5 l min^{-1}
Sample Flow Rate	:	< 0.5 l min^{-1}
Wet Gas Flow Meter	:	Model No. DM3A Serial No. M3386 Certificate No. Z042151
Gas Temperature of Flow Meter	:	19-26°C
Vent Pressure	:	Atmospheric
Temperature of PVR1	:	150°C
Temperature of Sampling Tubes	:	140°C

P S ANALYTICAL
UK: Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK
Tel: +44 (0) 1689 891 211Fax: +44 (0) 1689 896009 E-mail: psa@psanalytical.com
USA: 1761 W. Hillsboro Blvd., Suite 318, Deerfield Beach, FL 33442, USA
Tel: +1 (954) 429 1577 Fax: (954) 429 1601 E-mail: usa@psanalytical.com
www.psanalytical.com

Mercury Analyser: PSA 10.525 Sir Galahad II

The Sir Galahad instrumentation operates on the principle of dual amalgamation coupled to atomic fluorescence spectrometry [3]. A schematic diagram illustrating the automated thermal desorption arrangement is shown in Figure 3. Prior to sampling the sampling tubes were cleaned to give a reproducible blank. Calibration was achieved using the vapour injection technique. Table 2 summarises the instrumental conditions.

Figure 3 Remote cycle of Sir Galahad

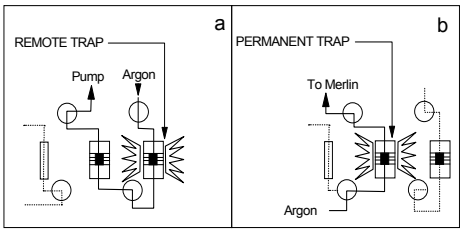


Table 2 Conditions for PSA 10.525 Sir Galahad Mk.II

Gain	:	10
Mode	:	RATIO
Zero	:	Off
Delay	:	30 secs
Vaporises	:	15 secs
Coolant	:	120 secs
Carrier Gas	:	Argon at 0.4 l min^{-1}
Coolant Gas	:	Argon (30 psi)
Cal Mode	:	Sample Volume
Stat Flush	:	30 secs
Stat Heat	:	60 secs
Stat Coolant	:	180 secs
Stat Transfer Delay	:	10 secs
Analysis Gas Control	:	None
Sample Valve Control	:	None
Analysis Window	:	x 1
Auto Over Range	:	ON

Results

The results obtained for export and inlet gas streams are reported in Table 3. Two sample points were analysed for the export gas. The gas flow rate was set to approximately 0.5 l min^{-1}. With these conditions a mean breakthrough from the first tube in series was found to be 3.94 ± 1.5% (n = 6). Each sampling point was analysed in triplicate, and in both cases the relative standard deviation was less than 4%. This illustrates the excellent reproducibility of the technique which can be obtained.

Due to the lack of time available only preliminary measurements of the inlet gas were obtained. The Sir Galahad was set up to operate for lower concentration ranges and therefore very small sample volumes had to be taken for the inlet gas streams. Two samples were collected at this site. In the first instance a flow rate of 0.25 l min^{-1} was used and no breakthrough on the sampling tubes was observed. The second sample was collected at 0.5 l min^{-1} and a breakthrough of 4.68% was observed. A mean result of 291.99 ± 65.29 $\mu g/m^3$ was obtained for the inlet gas. It is expected that the precision of the measurement would improve with optimised sampling and instrumental conditions.

P S ANALYTICAL
UK: Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK
Tel: +44 (0) 1689 891 211Fax: +44 (0) 1689 896009 E-mail: psa@psanalytical.com
USA: 1761 W. Hillsboro Blvd., Suite 318, Deerfield Beach, FL 33442, USA
Tel: +1 (954) 429 1577 Fax: (954) 429 1601 E-mail: usa@psanalytical.com
www.psanalytical.com

Table 3 Determination of mercury at inlet and export gas streams

Sample Reference	Gas Volume (l)	Tube No	ng Hg/tube	ng Hg/tube blank corrected	ng Hg/sample	µg Hg/m^3	Mean µg/m^3
Export Gas Sample Point 1	1.53 (T = 19°C)	1 2	41.88 2.897	41.38 2.293	43.673	28.54	27.89 ± 1.12
Export Gas Sample Point 1	1.53 (T = 19°C)	1 2	42.59 2.056	42.04 1.644	43.684	28.55	RSD = 4% (n = 3)
Export Gas Sample Point 1	1.53 (T = 19°C)	1 2	38.79 2.738	38.43 2.255	40.685	26.59	
Export Gas Sample Point 2	1.52 (T = 22°C)	1 2	45.20 2.182	44.83 1.305	46.135	30.35	29.77 ± 0.71
Export Gas Sample Point 2	1.51 (T = 23°C)	1 2	42.63 2.103	42.29 1.465	43.755	28.98	RSD = 2.4% (n = 3)
Export Gas Sample Point 2	1.50 (T = 25°C)	1 2	44.98 1.438	44.108 0.873	44.981	29.99	
Inlet Gas	0.10 (T = 25°C)	1 2	24.42 0.00	24.582 0.00	24.582	245.82	291.99 ± 65.29
Inlet Gas	0.198 (T = 26°C)	1 2	64.62 3.246	63.96 2.996	66.956	338.15	RSD = 22% (n = 2)

P S ANALYTICAL
UK: Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK
Tel: +44 (0) 1689 891 211Fax: +44 (0) 1689 896009 E-mail: psa@psanalytical.com
USA: 1761 W. Hillsboro Blvd., Suite 318, Deerfield Beach, FL 33442, USA
Tel: +1 (954) 429 1577 Fax: (954) 429 1601 E-mail: usa@psanalytical.com
www.psanalytical.com

Conclusions

The Sir Galahad instrument and sampling apparatus were successfully applied to the determination of mercury in natural gas. Two export sample points were analysed in triplicate. Sample points 1 and 2 gave results of 27.89 ± 1.12 μg/m^3 and 29.77 ± 0.71 μg/m^3 respectively. Sampling was achieved using two gold impregnated spherisorb adsorbents connected in series. A very small amount of breakthrough was observed (3.94 ± 1.5%, n = 6) from the first tube. The amount of breakthrough would appear to be related to the flow rate rather than a concentration effect. Lower flow rates, however, could lead to losses of mercury in the sampling apparatus. The inlet gas was also analysed but due to the lack of time only two measurements were taken. A mean result of 291.99 ± 65.29 μg/m^3 was obtained. Ideally the sampling apparatus should be left for at least one hour prior to sampling to ensure equilibrium conditions. The Sir Galahad was calibrated for a fairly low concentration range and in order to analyse the inlet gas very small sample volumes were collected. Ideally, the instrumentation should have been re-calibrated so that larger sample volumes could have been collected. The normal working range of the Sir Galahad based on a 1 litre sample volume is 0.1 ng/m^3 to 500 μg/m^3. The Sir Galahad can also use the Au/Pt gauze adsorbent if so desired, but the trapping efficiency has shown to be slightly lower with this adsorbent.

References

[1] Shafawi, A., Ebdon, L., Foulkes, M., Stockwell, P.B. and Corns, W.T.
Analyst, 1999. 124. 185-189.
Determination of Total Mercury in Hydrocarbons and Natural Gas condensate by Atomic Fluorescence Spectrometry.

[2] Dumarey, R., Dams, R. and Hoste, J.
Anal. Chem. 1985. 57. 2638.
Comparison of the Collection & Desorption Efficiency of Activated Charcoal, Silver and Gold for the Determination of Vapour Phase Atmospheric Mercury.

[3] Stockwell, P.B. and Corns, W.T.
Hydrocarbon Asia. Oct 1993. 36.
Atomic Fluorescence Technique to Analyse Mercury in Natural Gas & Petrochemicals.

P S ANALYTICAL
UK: Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK
Tel: +44 (0) 1689 891 211Fax: +44 (0) 1689 896009 E-mail: psa@psanalytical.com
USA: 1761 W. Hillsboro Blvd., Suite 318, Deerfield Beach, FL 33442, USA
Tel: +1 (954) 429 1577 Fax: (954) 429 1601 E-mail: usa@psanalytical.com
www.psanalytical.com