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Application Note 009

COMPARISON DATA FOR SIR GALAHAD AND POTASSIUM PERMANGANATE ABSORPTION

The international standard ISO 6978 specifies two methods, A and B, for the determination of total mercury in natural gas [1].

Method A prescribes sampling at atmospheric pressure using absorption in potassium permanganate solution followed by cold vapour atomic absorption spectrometry. The lower detection limit is 0.5 µg m^{-3} for a sampling time of 2 hours. Aromatic hydrocarbons may interfere. If aromatic hydrocarbons are present then method B is recommended.

Method B prescribes sampling at atmospheric or higher pressure using adsorption of mercury on silver/gold followed by desorption and subsequent analysis by flameless atomic absorption spectrometry. The lower detection limit is 0.3 µg m^{-3} at a minimum pressure of 3 Mpa (30 bar) and for a sampling time of 2 hours.

The Sir Galahad instrumentation essentially uses the principles of method B, the difference being adsorption of mercury on gold spherisorb columns and analysis by atomic fluorescence spectrometry. The lower limit of detection is 0.01 ng m^{-3} for a sampling time of 2 hours [2, 3].

Method A is normally recommended for natural gases with a high mercury content while method B is preferred for lower concentrations. The atomic fluorescence approach, however, is more linear and therefore suitable for both high and low concentrations.

Principle

Method A Determination of mercury by absorption into potassium permanganate.

The gas is passed through a gas washing bottle filled with potassium permanganate - sulphuric acid solution (1% m/V KmnO4 / 25% v\v H_2SO_4), The mercury present in the gas is oxidised to mercury (II) ions. The excess permanganate is reduced by hydroxylamine-hydrochloride solution and the mercury (II) ions are reduced by tin (II) chloride solution to form elemental mercury which is transferred to an atomic absorption spectrometer. Calibration is achieved using aqueous standards.

Method B Determination of mercury using a Sir Galahad.

The gas is passed through a silica tube containing gold spherisorb at 0.5 $lmin^{-1}$. All the mercury species in the gas are quantitatively trapped by the gold. The sampling tube is then introduced to the Sir Galahad instrument via the STAT furnace head. The tube is heated to 900°C to release mercury whilst passing a stream of argon. The mercury vapour is transferred to a second gold spherisorb trap. The second trap is heated to 900°C to release mercury which is transferred and detected by atomic fluorescence spectrometry. Calibration is achieved using a vapour injection technique [4].

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Comparison Data

Three natural gas samples were collected. These were analysed by the two methods described and the results obtained are shown in Tables 1 & 2.

Table 1 Potassium Permanganate Absorption

Sample	Vol of Gas (litres)	Sampling Time (min)	Mercury (μgm^{-3})	Mercury (ppm)
1	24.4	30	108.7	0.013
2	47.6	60	71.9	0.009
3	71.9	90	*	*

* Bubblers over saturated.

Table 2 Sir Galahad Method

Sample	Vol of Gas (litres)	Sampling Time (min)	Mercury (μgm^{-3})	Mercury (ppm)
1	0.513	1	118.6	0.014
2	0.997	2	78.1	0.010
3	4.747	10	37.5	0.005

Summary and Conclusions

Two international standard methods have been applied to the analysis of natural gas samples.

The first method using potassium permanganate absorption followed by cold vapour atomic absorption spectrometry has relatively long sampling times. After absorption of mercury from the natural gas the sample still has to be prepared for analysis by CV-AAS. This method is subject to interference from aromatic hydrocarbons which are frequently present in natural gas samples.

The second method using the Sir Galahad instrument is an amended international standard which reduces the sampling time by thirty times. The analysis procedure involves no chemical pretreatment and takes only 5 minutes. Furthermore the procedure is completely automated and suitable for on-line measurements.

The agreement between the two techniques is excellent. One further advantage of the Sir Galahad instrument is that it is suitable for both high and low concentrations.

References

1) ISO 6978, Draft, Natural Gas - Determination of Mercury at high and low pressure.
2) Stockwell, P.B., Rabl, P. and Paffrath, M. 1991, Process control and quality, 1, 293-298.
3) Stockwell, P.B. and Corns, W. T. 1993, Hydrocarbon Asia, 36-41.
4) Ebdon, L., Corns, W.T., Stockwell, P.B. and Stockwell, P.M. 1989, Journal of Automatic Chemistry, 11, 247-253.

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