

Determination of total mercury in hydrocarbons and natural gas condensate by atomic fluorescence spectrometry

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A new and simple technique for the determination of total mercury in gas condensate was developed which eliminates the use of chemicals/additives and complicated digestion procedures. The determinations are carried out by vapourisation of the samples at 400 °C with adsorption of mercury species on a gold trap (Amasil) maintained at 200 °C. The trap is then heated at 900 °C to release metallic mercury, which is determined by atomic fluorescence spectrometry. The mercury recoveries from seven species, dimethylmercury (DMM), diethylmercury (DEM), diphenylmercury (DPM), methylmercury chloride (MMC), ethylmercury chloride (EMC), phenylmercury chloride (PMC) and mercury(II) chloride (MC) spiked individually into gas condensate were found to be in the range 80–100%. The mercury recoveries for mixtures of the seven species added in equal amounts to gas condensate were in the range 88–97%. For Conostan mercury standard added to the condensate, the recovery was 88%. The instrumental precision from 10 measurements of a toluene control was 4% RSD. For three mercury species, DEM, MC and EMC, added to condensate, the precision was between 2 and 5% RSD ($n = 10$). The limit of detection ($3\sigma_{n-1}$ criterion) for the procedure was calculated to be 180 pg Hg in toluene and 270 pg in condensate. For three mercury species added to a condensate sample, the absolute detection limits were 270 pg Hg for DEM, 450 pg Hg for MC and 630 pg Hg for EMC. Total mercury measurements in five real condensate samples from two sites at different stages of production covered the range 7–50 ng ml⁻¹ with uncertainties in the range 4–7% RSD. The total mercury concentration of two commercial heavy gas oil samples were found to be 22.2 ± 0.6 µg ml⁻¹ with RSD 3% ($n = 4$) and 2.3 ± 0.1 µg ml⁻¹ of mercury with RSD 3% ($n = 7$).

Background

Mercury occurs naturally in trace amounts in natural gas and natural gas condensate.^{1–4} Although it is difficult to generalise, the typical mercury concentration in natural gas and natural gas condensate is between 1 and 200 µg m⁻³. Mercury in natural gas condensate could be present in various forms (elemental, organometallic and inorganic salt), depending on the origin of the condensates.⁵

Knowledge of the total mercury content and the different species present in natural gas condensate is extremely important. First, mercury in most forms is highly toxic and, particularly when present as the organomercury species, is a cause of great environmental concern. Second, the damage caused to industrial plants, particularly petrochemical plants, by the presence of mercury species can be financially crippling especially when unscheduled shut-downs are forced.

The implication of the effect of mercury in natural gas was not reported until 1973, when a catastrophic failure of an aluminium heat exchanger occurred at the Skikda liquefied natural gas plant in Algeria.^{4,6} Subsequent investigations determined that mercury corrosion caused the failure. The source of mercury, however, was in debate.^{4,7} After similar plant failures in both western and far eastern gas fields, the full mercury problem was realised together with the multi-million pound cost implications.

A recent paper⁸ defined the problem: 'At present it is not well known in which chemical forms mercury is present in natural gases and gas condensates and, in addition, methods for the determination of total mercury concentrations must be regarded to be of unproven reliability due to lack of adequate standard reference materials and poor accuracy'.⁹ While a number of workers have recently addressed this problem in terms of the speciation,^{9,10} there is still a need for the development of

reliable quantitative approaches to total mercury determination in such samples.

Current practices for the determination of total mercury in condensate are based on treatments and digestion with oxidising solutions^{7,8,11,12} or high temperature reaction with air or oxygen prior to determination by a spectrometric detector.^{8,13} These methods of treatment require large amounts of reagents and procedures which are often complicated and time consuming, increasing the risk of analytical errors and deteriorating detection limits through high and variable blank levels.^{7,8} Most recently, a dedicated analyser for the determination of mercury in naphtha has been developed.¹³

Unlike the gas condensate samples, the determination of total mercury in natural gas itself can be carried out accurately to very low detection limits by collecting the species on special gold impregnated silica traps. The mercury species adsorbed on the gold trap can be released by heating to high temperatures (about 900 °C) and is then swept through into a commercially available atomic fluorescence detector by argon gas.^{14,15} However, trapping by this method has some restrictions. In the presence of heavier hydrocarbons and wet conditions, the collection efficiency of the adsorbent may be affected. It was reported that adsorption efficiencies could be sustained quantitatively by keeping the trap (Au/Pt) at a temperature of 80 °C to prevent condensation on the amalgamating surface. It was reported that elemental mercury was collected with 100% efficiency. However only 50% dimethylmercury was recovered from the gas matrix.^{7,8}

In this work, we sought to utilise the excellent sensitivity of atomic fluorescence spectrometry (AFS), using a readily available commercial system, for determining mercury whilst addressing the matrix interference and species-dependent recovery problems highlighted above. In particular, this paper reports an investigation of elevated trap temperatures, which

has proved successful for natural gas, and a commercially available trap of Amasil to overcome matrix interferences. It was also hoped that this procedure would overcome the variable recoveries often reported for different mercury species in hydrocarbon samples.

Experimental

Reagents

The organomercury compounds dimethylmercury (DMM) and diethylmercury (DEM) were obtained from Stream Chemicals (Newbury Port, MA, USA), methylmercury chloride (MMC), ethylmercury chloride (EMC) and phenylmercury chloride (PMC) from Johnson Matthey (Royston, Hertfordshire, UK), diphenylmercury (DPM) from Aldrich (Gillingham, Dorset, UK) and mercury(II) chloride (MC) from Merck (Poole, Dorset, UK).

Stock standard solutions (1000 mg dm^{-3}) of DMM, DEM and DPM were prepared by dissolving the compounds in toluene (HPLC grade, Rathburn, Walkerburn, UK). For MMC, EMC, PMC and MC these were first dissolved in small amounts of propanol ('AnalaR' grade, Merck) and diluted to volume with toluene. All solutions were stored at 4°C and freshly prepared weekly. Working standard solutions were prepared daily prior to analysis.

Procedure

Known mercury species were spiked individually at different concentrations (measured as mercury) in condensate and control samples (condensate or toluene). An accurately measured volume of sample (0.25 ml) was injected using a gas tight syringe (Dynatech Precision, Baton Rouge, LA, USA) into a specially constructed vapourisation chamber held at 400°C . Normally 5–10 min were required to vaporise the sample completely. The vapour generated was continuously swept by argon gas, at between 300 and 400 ml min^{-1} , through to a heated gold sand-trap (Amasil; PS Analytical, Orpington, Kent,

UK) maintained at 200°C . The sample matrix (paraffins, aromatics, naphthanes) was consequently carried in its vapour phase away from the trap and directed to a waste collector. The mercury adsorbed on the Amasil trap was then released as elemental mercury by heating to about 900°C and swept through to an atomic fluorescence detector (Merlin; PS Analytical). Recovery experiments based on the standard additions technique, together with condensate sample analyses (various condensate fractions, oils, *etc.*), were performed.

Instrumentation

A schematic diagram of the instrumentation is shown in Fig. 1.

Adsorption trap system. The adsorption trap module (PS Analytical) consists of a gold coated medium (Amasil) within a silica tube surrounded by a Nichrome heating wire. This tube is retained within a specially designed cooling chamber. The trap was positioned within a small oven (Kenwood, Hampshire, UK) maintained at $200 \pm 5^\circ\text{C}$.

Vaporisation chamber. The chamber consists of a 250 ml three-necked, round-bottomed flask and an electrothermal heating mantle ($400 \pm 10^\circ\text{C}$). The separate necks were connected to a heated trap line, an argon purge gas line and a third was fitted with a double septum for sample introduction by an injection technique. The top part of the chamber was insulated to reduce heat loss. The tubing from the chamber to the gold sand-trap was maintained at 200°C by heating tape to prevent any condensation of the vaporised sample before it reached the trap.

Valve switching sequences. Control switching of the purging, cooling and carrier gas lines was performed by a computer driven Galahad system (PS Analytical).

Filter installation. To improve baseline stability and prevent trace organic material entering the detector system, a special filter was inserted into the gas line prior to the detector.

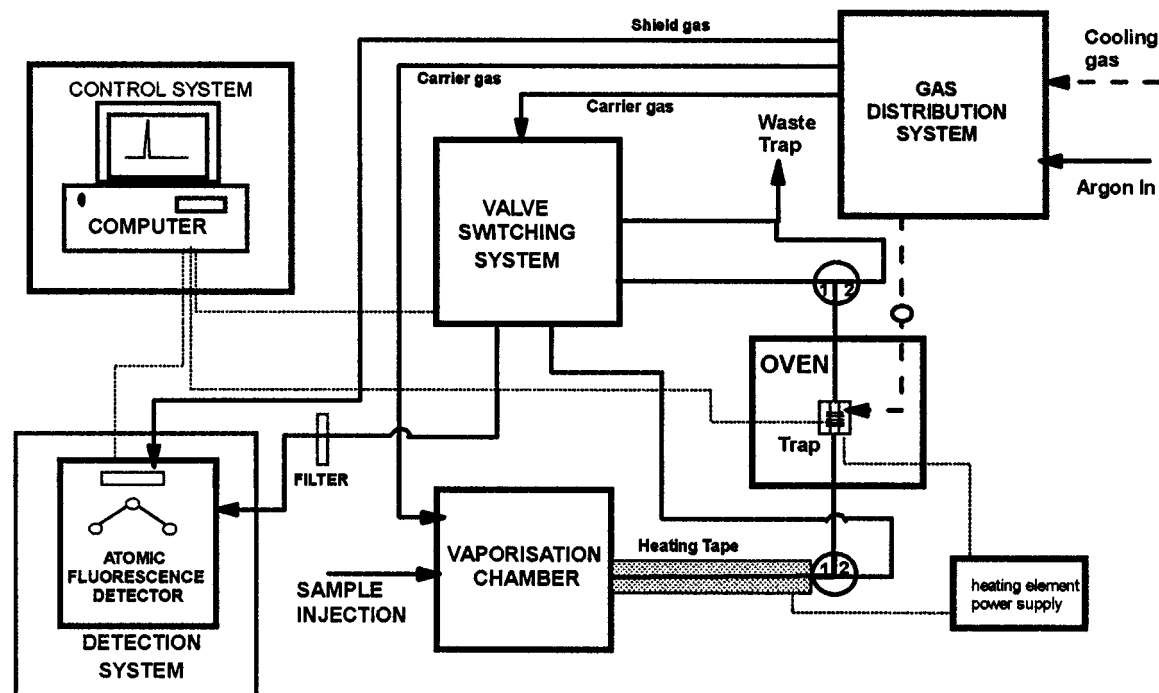


Fig. 1 Schematic diagram of instrumental set-up for determination of total mercury in condensate.

filter, which comprises two ashless, No. 1 filter-papers in a demountable holder (Whatman, Maidstone, UK) did not affect the performance of the calibration or any subsequent analysis. This was changed every 50 runs or earlier if found to be necessary.

Calibration

Calibration was based against elemental mercury for all species. The calibrations relied upon the knowledge that at a fixed temperature, the saturated vapour pressure of mercury is known and a fixed volume of vapour will contain a known quantity of mercury. This volume was injected and adsorbed on the Amasil trap and then re-vaporised into the detector where the peak response was measured. Once the values of temperature and volume are known, the absolute quantity of mercury adsorbed on the trap can be calculated.¹⁶

The use of elemental mercury to calibrate also served as another species which can be present in gas condensate.⁵

A summary of the general operating conditions used in all mercury analyses is given in Table 1.

Results and discussion

Performance characteristics of the trap system

The stability of mercury adsorbed on the Amasil trap was evaluated by carrying out calibrations at room temperature and 200 °C. The results, shown in Fig. 2, indicate that at 200 °C the mercury calibration is both stable and quantitative.

The performance of the trap in holding the mercury species (bleed-off effects) at 200 °C was investigated. The sample (0.25 ml), containing 20 ng ml⁻¹ of a mercury species, was vaporised and swept through the trap using an argon gas flow (350 ml min⁻¹) using various collection times from 5 min to 1 h. The results showed that no significant bleeding occurred up to 30 min (96–103% recovery) and the trap was capable of holding the mercury species at 200 °C. Longer time periods gave

Table 1 Summary of operating conditions

Condition	Value
Vaporisation chamber temperature	400 °C
Vaporisation time	5–10 min
Argon carrier flow rate for vaporisation	300–400 ml min ⁻¹
Argon flow rate for detector	500 ml min ⁻¹
Detector sheath gas flow rate	250 ml min ⁻¹
Gold trap flushing time	30 s
Gold trap vaporisation time	15 s
Gold trap vaporisation temperature	900 °C
Gold trap cooling period	2 min

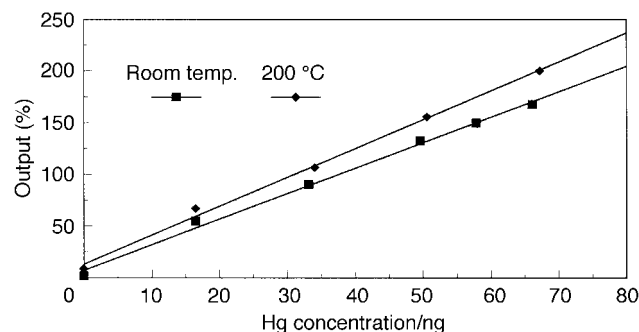


Fig. 2 Stability of calibration curve with temperature.

increased recoveries owing to the contribution from the very low mercury content of the argon carrier gas being trapped.

It was observed that the traps did not suffer from memory effects and that the lifetime of a trap was also improved because of the higher trapping temperatures employed (200 °C).

Recovery performance of DMM and DPM added to toluene

The total mercury content of a toluene sample (control) was determined. The sample was vaporised at 400 °C and the vapour trapped at 200 °C prior to desorption for mercury determination by the AFS detector. The analyses were conducted by injecting different sample volumes *via* the septum into the vaporisation chamber. The mercury content in the toluene blank was found to be 2.0 ± 0.3, 2.4 ± 0.2 and 3.4 ± 0.4 ng ml⁻¹ for volumes of 0.1, 0.25 and 0.5 ml, respectively (not corrected for the mercury contribution from the sweep gas). DMM and DPM (50 ng ml⁻¹ as Hg), when spiked into toluene and when different volumes were injected, indicated that the recovery was reduced by about 20% if the sample injected was increased from 0.25 to 0.5 ml.

A volume of 0.25 ml was chosen for three reasons: (i) representative sampling improved precision, (ii) 85–90% recovery for the species was obtained and (iii) to match the sensitivity of the system without saturating the gold trap sites with matrix during adsorption (competitive exclusion). This recovery effect, which was dependent on the sample volume injected, was removed when a double sized gold trap was employed. Up to 1.0 ml of sample gave the same recovery for the species as that of a 0.25 ml injection. These results are shown in Fig. 3. It is important to note that the increase in sample volume requires a longer vaporisation period, hence a longer trapping time is needed. A correction for the mercury present in the argon carrier gas must therefore be made alongside any solvent blank contribution.

Recoveries for mercury species added to condensate samples

The recovery of mercury species spiked into 'real' gas condensate samples was evaluated. Two commercial gas condensate samples labelled GC1 and GC2, light gas condensates from different sites, were used. The final boiling-points were in the range 250–270 °C. As with the toluene sample, the vaporisation temperature used was 400 °C, which

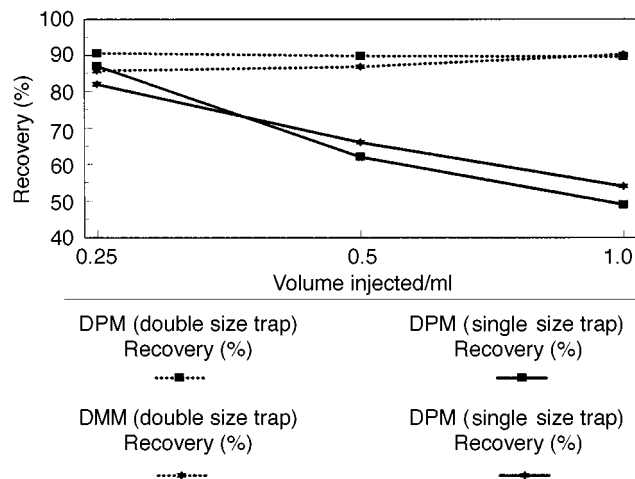


Fig. 3 Comparison of recovery performance between single and double sized traps for different sample volumes injected.

was found to be sufficient to vaporise the sample completely within 5 min.

Seven species of mercury, DMM, DEM, MMC, EMC, DPM, PMC and MC, were spiked individually at different concentrations, 10, 30 and 50 ng ml⁻¹ (as Hg), into real gas condensates. For each experiment the total mercury content of the condensate samples was determined to be used for correction in the recovery experiments.

The results for different concentrations of mercury species spiked into condensates are given in Table 2. Considering the nature of the condensates, which are a very complex mixture of volatile hydrocarbons, the recoveries are mainly > 80% with many above 90%. For each given species, the linearity of the recovery data, in the concentration range covered, was better than $r^2 = 0.99$. The total mercury recoveries for a mixture of the seven species added in equal quantities, *i.e.*, 10, 30 and 50 ng ml⁻¹, are also given in Table 2. These recoveries were in the range 88–97%.

Precision of the experimental procedure

To determine the precision of the experimental procedure, the total mercury content in (i) toluene, (ii) a commercial condensate (GC3), and (iii) a condensate (GC3), with three representative mercury compounds added at the 10 ng ml⁻¹ Hg level, *i.e.*, EMC acting as an organohalide mercury species, DEM as an organomercury species and mercury(II) chloride as an inorganic mercury species, were analysed 10 times for each species.

The mercury content for the toluene (0.25 ml injected) was 6.4 ± 0.2 ng ml⁻¹. For the condensate GC3 alone, the mercury value was 7.45 ± 0.34 ng ml⁻¹. The relative standard deviations (RSDs) for the analyses were 3.7 and 4.8%, respectively.

For the condensate GC3 spiked with 10 ng ml⁻¹ (as Hg) of the three species, the total mercury content was determined as 17.55 ± 0.35 ng ml⁻¹ (EMC), 17.28 ± 0.62 ng ml⁻¹ (DEM) and 18.04 ± 0.86 ng ml⁻¹ (MC), with RSDs between 2 and 5%. It is of note that the recoveries for these spiking experiments with condensate were 101, 98 and 106%, respectively (RSD between 4 and 7%).

Conostan mercury standard

For the determination of mercury in oil and similar petroleum products, a suitable mercury standard, which allowed addition techniques, was employed. Conostan mercury standard is an alkylaryl dithiocarbamate mercury compound (Hg-S bonded) dissolved in white base (paraffin) oil. This species was spiked 10 times into condensate GC3 at the 10 ng ml⁻¹ level. The recovery was $88 \pm 5\%$.

Table 2 Summary of recovery performance

Mercury species added	Recovery $\pm s$ (%)		
	10 ng ml ⁻¹	20 ng ml ⁻¹	30 ng ml ⁻¹
DPM	74 \pm 12	74 \pm 2	77 \pm 0
DMM	111 \pm 13	119 \pm 14	105 \pm 9
MC (1)	80 \pm 18	98 \pm 13	89 \pm 8
MC (2)	123 \pm 8	98 \pm 17	98 \pm 3
EMC (1)	90 \pm 19	86 \pm 2	—
EMC (2)	108 \pm 15	129 \pm 2	119 \pm 5
EMC (3)	92 \pm 5	81 \pm 5	77 \pm 5
MMC	102 \pm 4	92 \pm 5	92 \pm 8
PMC	77 \pm 13	92 \pm 6	99 \pm 5
DEM	113 \pm 8	92 \pm 6	99 \pm 5
Equal mixture	90 \pm 5 ^a	88 \pm 2 ^a	97 \pm 1 ^a

^a Total recovery where concentration stated is for each component.

Detection limits

The detection limits that can be obtained with the proposed method depend to some extent on the complexity of the condensate sample, *i.e.*, the volatility of both the condensate and the mercury species in the sample, together with the effect of any matrix sample condensing on the trap. The absolute detection limits for the method (based on three times the standard deviation and a 0.25 ml volume sample injection) were 180 pg for toluene and 270 pg for GC3 condensate. For three different mercury species added to the GC3 condensate, the absolute detection limits were 270 pg for DEM, 450 pg for MC and 630 pg for EMC. When based on the system alone, without sample introduction but monitoring the carrier gas (argon), the absolute limit of detection was reduced to 11 pg ($n = 6$).

Total mercury measurements of commercial condensate

Five types of natural gas condensate, obtained from several sources, were analysed for total mercury. The results indicate that the concentration of the mercury is independent of location and type of condensate. The total mercury concentrations of the condensate samples GC1–5 together with the precisions are given in Table 3. The RSDs for the analyses are in the range 4–7% for a 0.25 ml manual sample injection.

Table 3 Total mercury content of commercial condensate samples

Sample	Test No.	Concentration/ng ml ⁻¹	Mean $\pm s$ /ng ml ⁻¹	RSD (%)
GC1	1	23.3	22.3 \pm 1.4	6
	2	22.5		
	3	21.9		
	4	21.5		
	5	19.9		
	6	21.3		
	7	21.7		
	8	23.8		
	9	22.6		
	10	24.7		
GC2	1	49.5	49.7 \pm 2.6	5
	2	53.2		
	3	51.0		
	4	46.7		
	5	46.0		
	6	48.3		
	7	47.0		
	8	50.1		
	9	52.0		
	10	52.8		
GC3	1	7.5	7.5 \pm 0.3	4
	2	7.6		
	3	8.0		
	4	7.6		
	5	7.2		
	6	7.2		
	7	6.8		
	8	7.6		
	9	7.2		
	10	7.7		
GC4	1	13.8	12.8 \pm 0.9	7
	2	14.0		
	3	13.2		
	4	11.9		
	5	12.0		
	6	12.1		
GC5	1	42.4	43.3 \pm 1.7	4
	2	45.2		
	3	45.6		
	4	42.4		
	5	42.8		
	6	43.6		
	7	40.8		

As a preliminary study to investigate whether a heavier fraction oil sample could also be analysed for mercury with this system, two commercial heavy gas oil samples, A and B, with boiling-points between 260 and 538 °C were also analysed. Prior to analysis the samples were diluted with toluene, 100-fold for sample A and 50-fold for sample B. Sample A was seen to be more dense and more viscous than sample B. The total mercury concentration for sample A was found to be $22.2 \pm 0.6 \mu\text{g ml}^{-1}$ with an RSD of 3% ($n = 4$) and sample B contained $2.3 \pm 0.1 \mu\text{g ml}^{-1}$ of mercury with an RSD of 3% ($n = 7$). The results indicate that a heavier oil fraction can also be analysed using this system, provided that the sample can be diluted with a suitable solvent to a suitable concentration range.

Conclusion

A simple and rapid procedure for the determination of total mercury in condensate has been developed despite the volatile and complex nature of natural gas condensate. Total mercury in liquid hydrocarbons, particularly condensate, can be determined by using a procedure of vaporisation and trapping of mercury species by an Amasil gold trap at an elevated temperature (200 °C). The overall recoveries of mercury species spiked into real condensate were good. The recoveries of several species, *i.e.*, DMM, DEM, DPM, MMC, EMC, PMC and MC, and a mixture of them were almost 100%. Other real gas condensates have also been analysed for total mercury and the results indicated the consistency of the procedure. The procedure offers rapid and consistent results without recourse to complicated methods, such as digestion of volatile matrices, or the use of chemical modifiers and reagents, which may introduce contamination. Only small amounts of sample (0.25 ml) are required and the simple instrumentation used is easy to set up and to operate.

The only requirement for this direct injection method is that the hydrocarbon or condensate completely vaporises at the trap temperature of 200 °C. The typical carbon number for gas condensates, C₁–C₁₅, results in an organic liquid composition that easily meets the above requirement. For heavier samples,

dilution to a desired concentration range with a suitable solvent is required to ensure complete vaporisation of the sample, as demonstrated by the analysis of Conostan and heavy gas oil.

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References

- 1 M. D. Bingham, *SPE Prod. Eng.*, 1990, 120.
- 2 G. G. Haselden, *Mech. Eng.*, 1981, **103**, 46.
- 3 W. W. Bodle, A. Attari and R. Serauskas, paper presented at the Institute of Gas Technology Sixth International Conference on Liquefied Natural Gas, Kyoto, Japan, April 7–14, 1980.
- 4 J. E. Leeper, *Energy Process. Can.*, 1981, 46.
- 5 *Arsenic and Mercury Removal in Natural Gas, Refining and Petrochemical Industries, IGP Techn. Bull.*, 1983, 1–10.
- 6 J. E. Leeper, *Hydrocarbon Process.*, 1980, **59**, 237.
- 7 W. Frech, D. C. Baxter, G. Dyvik and B. Dybdahl, *J. Anal. At. Spectrom.*, 1995, **10**, 769.
- 8 W. Frech, D. C. Baxter, B. Bakke, J. Snell and Y. Thomassen, *Anal. Commun.*, 1996, **33**, 7.
- 9 J. Snell, W. Frech and Y. Thomassen, *Analyst*, 1996, **121**, 1055.
- 10 J. Snell, J. Qian, M. Johansson, K. Smith and W. Frech, *Analyst*, 1998, **123**, 905.
- 11 C. Schickling and J. A. C. Broekaert, *Appl. Organomet. Chem.*, 1995, **9**, 29.
- 12 H. Hintelmann and R. D. Wilken, *Appl. Organomet. Chem.*, 1993, **7**, 173.
- 13 *Mercury in Naphtha, UOP Method 938-95*, UOP, Des Plaines, IL, 1995.
- 14 P. B. Stockwell and W. T. Corns, *Hydrocarbon Asia*, 1993, 36.
- 15 P. B. Stockwell and W. T. Corns, *Oil Gas Sci. Technol. Now*, 1994, Autumn, 58.
- 16 R. C. Weast, (ed.), *CRC Handbook of Chemistry and Physics, 51st edn.*, CRC Press, Cleveland, OH, 1971.

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