FUNCTIONAL SPECIATION OF NON-VOLATILE, SOLUBLE FORMS OF MERCURY IN HYDROCARBON LIQUIDS (LIGHT DISTILLATES)

Mercury in the Oil and Gas Industry

Mercury is a naturally occuring contaminant found in almost all oil and gas reservoirs. Typically, the mercury is present primarily in an elemental (metallic) form (Hg^0), but will often react to form other species during production and processing.

The production of oil and gas yields a complex, multiphase fluid which, during the production process, may be subjected to variations in temperature, pressure, phase, pH and redox potential. Although the full reaction mechanisms of mercury throughout this production process are not fully understood, it is known that mercury species partition into different phases of the produced fluids as conditions change. For example, whilst elemental mercury (Hg^0) has a relatively high boiling point (357°C), due to its high vapour pressure, it demonstrates characteristics associated with volatile compounds, with some partitioning into the gas phase during gas and oil separation.

The liquid (condensate or oil) phase may contain a complex mixture of mercury species (1), including Hg^0, insoluble mercury species (predominantly HgS), soluble ionic mercury (Hg^{2+}) and some non-ionic / organic mercury compounds e.g. dimethyl mercury ($(CH_3)_2Hg$) and mercury thiolates (RS Hg–SR). In the gas fraction, typically only Hg^0 will be present [2, 3].

Mercury concentrations in the oil range from < 0.1 µg/kg up to 20 mg/kg [4] whilst in the gas phase, concentrations from < 0.01 µg/m^3 up to 5000 µg/m^3 have been reported (5).

Processing of gas and hydrocarbon liquids that are rich in mercury can be problematic and needs to be monitored and managed on an ongoing basis. The three main issues of concern resulting from the presence of mercury are:

- **Corrosion**: primarily liquid metal embrittlement of aluminum components
- **Catalytic poisoning**: an issue for downstream refining processes
- **Environmental issues**: includes worker exposure and release to the environment

Mercury forms amalgams with other metals, particularly aluminium, and has the potential to cause corrosion of welds, cryogenic components, aluminium based heat exchangers, compressor seals/stems/seats and pump shafts made from copper alloys. There have been some widely publicised incidents where mercury corrosion of aluminium heat exchangers has caused catastrophic failures leading to plant shutdowns and, in one unfortunate case, resulted in several fatalities (6).

Why is Mercury Speciation Required in Liquid Hydrocarbons?

As a consequence of the issues arising from the presence of mercury, even at parts per billion (µg/kg) concentrations, it may be necessary to incorporate a mercury removal system into the production/process design. There are several options for removal of mercury from liquid hydrocarbons but, most commonly, mercury removal beds (MRBs) are employed. MRBs are generally filled with media that removes, by chemical reaction, Hg^0 only; however, a significant proportion of any particulate forms of mercury may be removed physically. As other forms of soluble mercury will almost certainly be present, speciation is necessary in order to estimate the expected efficiency and appropriateness of a standard MRB, prior to installation.

Molecular Speciation Techniques

Due to the losses of mercury that occur over time when hydrocarbon samples are stored, even in inert coated sampling bottles (7), and the relatively quick transformation of mercury from one species to another in liquid hydrocarbons (8), it is desirable to perform speciation analysis on site immediately after sampling. This excludes the use of molecular speciation techniques such as GC-ICP-MS (9) and SEC-ICP-HR-MS (10) since portable instruments are not available.

The international standard test method UOP 938-10 describes a procedure for the functional speciation of soluble mercury in hydrocarbon liquids. The precise application of this method on site or in an offshore environment is difficult as there are often unyielding time constraints that necessitate adaptations. Modifications are also necessary to accommodate direct analysis of samples with very high mercury concentrations and the use of combustion/AAS analysers supplied by alternative manufacturers; however, the method provides a base from which on-site mercury speciation methodology can be developed.

UOP 938-10 utilises the chemical and physical properties of soluble mercury species in particulate-free samples to categorise them into (i) total soluble (ii) elemental (iii) non-ionic organic and (iv) ionic species. The initial filtering of the sample provides a route for the quantification of insoluble mercury species. However, UOP 938-10 provides no information on the extraction efficiency of individual ionic species and very little documentation can be found in the literature to support the assumption that the extraction employed will yield a complete separation and consistently accurate quantification of the non-ionic organic and ionic species.

Clearly, a more comprehensive understanding of the efficiency of extraction of the commonly found ionic mercury species would provide the necessary information for assessing how much of each compound is included in each of the two categories and assessing the suitability of the mercury removal technologies available without having to instigate a live trial. It would also help identify where the mercury species may be expected to partition within the hydrocarbon processing system.

Aims of the Study

The aims of this initial study conducted by Qa^3 were to (i) evaluate the use of a fine sintered frit during the purge stage and the effect on the recovery of Hg^0 (ii) identify the most efficient aqueous solution for extraction of soluble ionic species (iii) quantify the extraction efficiency of various inorganic and organic ionic mercury species and (iv) evaluate the impact that the partitioning behaviour of the species under study may have on the accuracy of quantification of the non-ionic organic and ionic species.

Experimental

Purge and Trap (Figure 1)

Synthetic deoxygenated condensates were spiked in turn with a known concentration of (i) Hg^0 (ii) $(CH_3)_2Hg$ and (iii) mercuric chloride ($HgCl_2$). An aliquot of the spiked condensate was decanted into a Drechsel bottle, held at 0°C and purged with nitrogen at a flow rate of 500 mL/min for a period of 30 minutes using a fine sintered frit to provide a greater contact area between purge gas and sample.

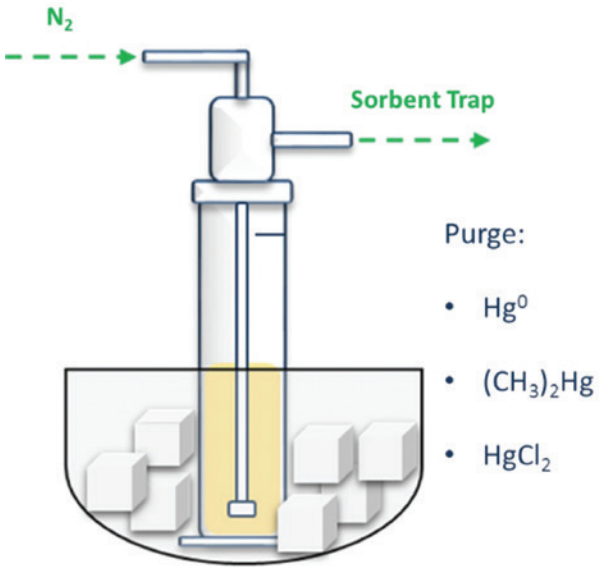

Figure 1: Schematic of purge and trap apparatus

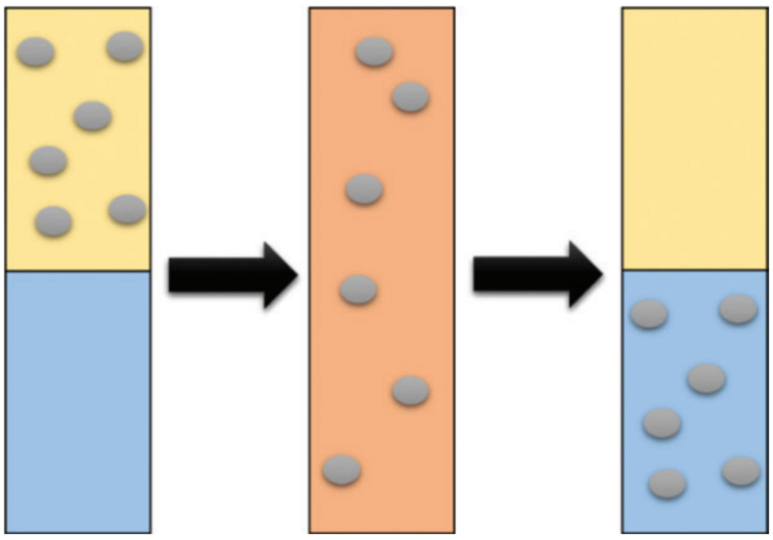

Figure 2: Schematic of aqueous extraction.

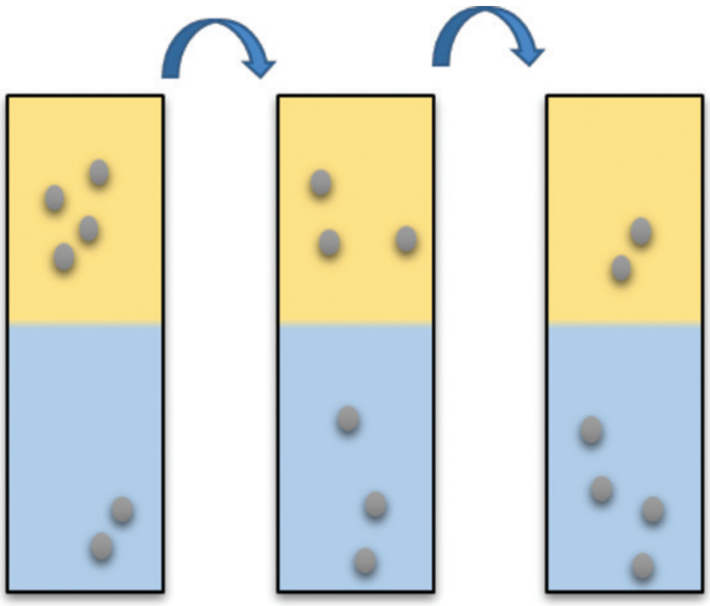

Figure 3: Schematic of serial aqueous extraction.

The exit gas was captured onto a solid phase sorbent trap which was then analysed by combustion/Atomic Absorption Spectrometry (AAS) using a Milestones DMA-1 Mercury Analyser in accordance with ASTM D5954-98 (14) (modified).

Liquid-Liquid Extractions

Samples of synthetic deoxygenated condensate (5 mL) were spiked in turn with known concentrations (50 - 350 µg/kg) of a number of inorganic and organic (salts) mercury compounds. Five aqueous solutions, L-cysteine (1% m/v), sodium chloride (saturated), sodium chloride (100 mg/L), nitric acid (1% v/v) and deionised water were used in a 1:1 ratio with the condensate to extract the respective compounds.

The first series of extractions involved mixing the solution vigorously for five minutes and allowing the mixture to separate over 25 minutes (Figure 2). An aliquot of both phases was then taken and the mercury quantified by combustion/AAS in accordance with ASTM D7623 10 (15) (modified) using a Milestone DMA-1 Direct Mercury Analyser. The mixture was then agitated for an additional ten minutes and allowed to separate for a further 80 minutes (120 minutes total contact time) before allowing the two phases to separate and redetermining the mercury in both.

A second series of extractions was conducted adopting a serial extraction (Figure 3). The spiked condensate was extracted with the aqueous solutions under test at a 1:1 ratio, mixing vigorously for three minutes and allowing to separate for seven minutes before quantifying the mercury in both phases. The organic phase was then removed and decanted into a fresh aliquot of aqueous solution and the extraction and analysis repeated twice.

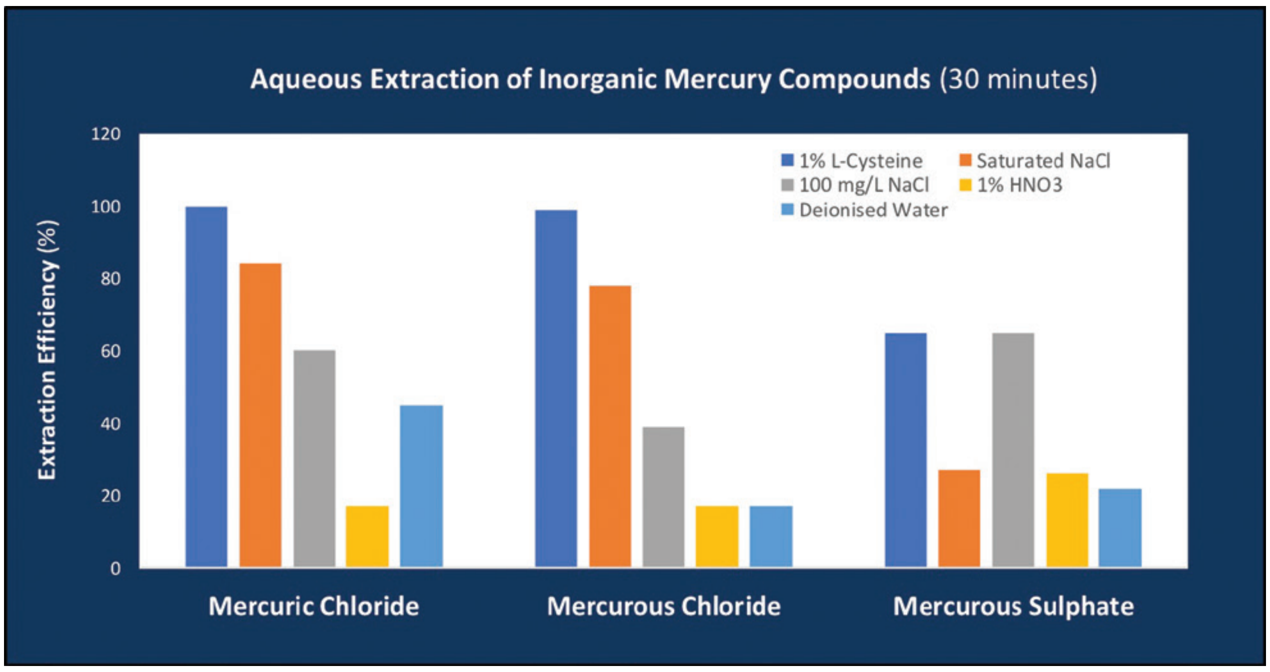

Figure 4: Bar chart showing the extraction of inorganic mercury salts from condensate into various aqueous solutions.

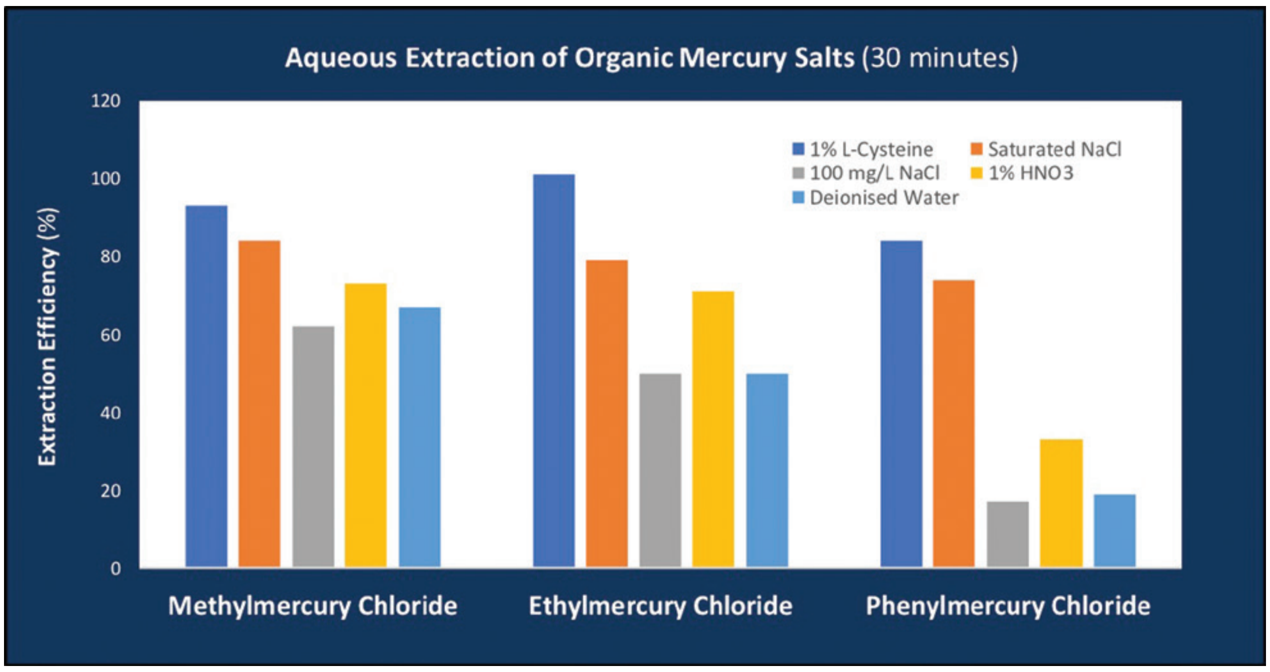

Figure 5: Bar chart showing the extraction of organic mercury salts from condensate into various aqueous solutions.

Summary of Results

Purge and Trap

After purging for 30 minutes with nitrogen at 500 mL/min, 100% of the Hg^0 was recovered, effectively reducing the time required for purging by 90 minutes (75%). Under the same conditions 9% of the $(CH_3)_2Hg$ was also removed, which is not unexpected as UOP 938-10 states that during the two-hour purge 'up to 30% of the dimethyl mercury may be removed during purging'. The application of a fine sintered frit appears to facilitate the use of a larger flow rate to remove the Hg^0 more quickly. The decrease in purge time reduces the potential for desorption of $(CH_3)_2Hg$; however, by adjusting the flow rate of the purge gas and the volume of liquid hydrocarbon taken, it may be possible to optimise the purge conditions to achieve 100% recovery of Hg^0 with no loss of $(CH_3)_2Hg$. This would provide not only a quicker method but also one that quantifies both elemental mercury and non-ionic organic mercury potentially more accurately than UOP 938-10. As a pseudo control, the removal of $HgCl_2$ under the same purge conditions was also quantified and, as expected, found to be < 1%.

Liquid-Liquid Extractions

The 30-minute extractions showed that for all inorganic (Figure 4) and organic (Figure 5) ionic mercury compounds tested, L cysteine (1% v/v) was the most efficient extractant. The 100 mg/L NaCl advocated by UOP 938-10 exhibited poor extraction efficiency for all compounds with only mercurous sulphate (Hg_2SO_4) having an affinity comparable with that exhibited for L-cysteine.

The data shows that there are solubility / partitioning inadequacies with many soluble ionic mercury species when 100 mg/L NaCl is used under the modified extraction conditions and elevated mercury concentrations employed in this study. The data indicated that if a NaCl solution is to be used then saturated NaCl should be adopted as this exhibited superior extraction efficiency for all mercury species tested except Hg_2SO_4.

Extending the total contact time to 120 minutes did not significantly improve the extraction efficiency of any extractant for any species under test. Indeed, for 100 mg/L NaCl, a significant decrease in extraction efficiency was observed for $HgCl_2$, Hg_2Cl_2 and C_2H_5HgCl which is most likely due to the extracted species migrating to the liquid-liquid interface on extended standing.

Adopting a serial extraction resulted in a significant improvement in removal efficiency for most compounds when 100 mg/L NaCl was employed; however, for all compounds tested the performance of L-cysteine remained markedly superior (Table 1). The extraction of mercurous sulphate into 100 mg/L NaCl was found to be lower than that observed when a single/ longer extraction was employed. For the serial extractions, the agitation, separation and contact time for each extraction was reduced, although the effective total volume of aqueous extractant and total agitation and contact time was increased. This suggests that for some compounds, in particular mercurous sulphate, the rate of partitioning into the aqueous phase is slow and is largely dependent on the total contact time and the time allowed for separation.

Aqueous Solution	L-Cysteine			Saturated NaCl			NaCl (100 mg/L)		
No of Extractions	1	2	3	1	2	3	1	2	3
Inorganic Species									
Mercuric Chloride	100	100	100	98	98	98	81	88	90
Mercurous Chloride	89	99	100	77	90	93	47	67	69
Mercurous Sulphate	59	68	69	28	43	46	19	30	37
Organic Species									
Methylmercury Chloride	90	97	98	92	96	97	75	90	92
Ethylmercury Chloride	93	97	98	70	79	81	43	68	80
Phenylmercury Chloride	85	91	95	68	72	73	22	39	44

Table 1: Recoveries of a selection of inorganic and organic mercury standards with serial extraction using L-cysteine, saturated NaCl and the UOP-938 stipulated solution of 100 mg/L NaCl.

In Conclusion

The use of a fine sintered frit during the purge stage reduces significantly the time needed to remove all elemental mercury. It also decreases the proportion of any $(CH_3)_2Hg$ present that would be desorbed and thus improves the accuracy of quantification of both the elemental and non-ionic organic mercury species in a condensate sample.

The study to date has shown that L-cysteine (1% v/v) exhibits far greater efficacy than NaCl (100 mg/L) for extraction of soluble ionic mercury species from condensate. Indeed, even with mercury concentrations that exceeded the UOP 938-10 limit (in some cases) and with an extraction/contact time of just 10 minutes (from the first serial extraction), the L-cysteine extraction efficiency for all inorganic and organic ionic mercury species tested, except Hg_2SO_4, exceeded 85%. Where time permits, employing an optimised serial extraction with L-cysteine is likely to be the best approach for on-site mercury speciation.

The relatively poor extraction efficiency of 100 mg/L NaCl excludes it from being the aqueous solution of choice for Qa³ on-site applications. It must also surely cast some doubt upon the efficiency of UOP 938-10, certainly in samples where Hg_2SO_4 and C_2H_5HgCl are present.

If accurate, on-site speciation and quantification of mercury species in the oil and gas industry is to be achieved so that fully effective mercury removal systems are employed and mercury partitioning within the hydrocarbon processing system is fully understood, then a robust method is required. Thus, further studies involving the optimisation of the parameters during the purge stage and extraction of a mixture of standards and additional compounds, including organo sulphides and organo thiolates (mercaptides) and extraction from other matrices including naphtha and crude oils must be undertaken.

References

(1) Wilhelm, S.M., Liang, L and Kirchgessner, D. (2006). Energy Fuels 20, pp 180-186

(2) Spiric, Z. and Mashyanov, N.R. (2000). Fresenius J Anal Chem, 366 pp 429-432.

(3) Lang, D., Gardner, M., and Holmes, J. (2012). http://www.mercurynetwork.org.uk/wp-content/uploads/2009/09/IKIMP-Oil-and-Gas-2012-Final-Report.pdf

(4) Wilhelm, S.M., Liang, L., Cussen, D. and Kirchgessner, D. A (2007). Environ Sci Technol, 41 (13), pp 4509-4514.

(5) Carnell, P.J.H., Row V.A. and McKenna, R. (2007). http://www.ivt.ntnu.no/ept/fag/tep4215/innhold/LNG%20Conferences/2007/fscommand/PO_08_Row_s.pdf

(6) Harfoushian J. (2013). SPE, 166220.

(7) Kirby M. and Baker S. (2017). Poster presented at: 13th International Conference on Mercury as a Global Pollutant, July 16 – 21 2017, Providence, Rhode Island, USA.

(8) Rahman, G.M.M., Fahrenholz T.M., Kingston H.M.S, Pamuku M., Hwang J.D. and Young L.A (2010). Spectroscopy, 25(1) pp 36 – 45.

(9) Bouyssiere, B., Baco, F., Savary, L and Lobiński, R. (2002). Journal of Chromatography A, 976 pp 431–439.

(10) Gaulier, F., Gibert, A., Walls, D., Langford, M., Baker, S., Baudot, A., Porcheron, F. and Lienemann, C-P. (2015). Fuel Processing Technology, 131 pp 254–261.

Author Details

Stuart Baker, Matthew Kirby, Matthew Bower, David Walls and Mark Andrew, Qa³ Ltd • Unit 3, The Calvert Centre, Woodmancott, Winchester, Hampshire, SO21 3BN, UK

Tel: + 44 (0) 1256 397390 • Email: enquiries@qa3.co.uk • **Web: www.qa3.co.uk**