APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 29–36 (1995)

Determination of Mercury Species in Gas Condensates by On-line Coupled High-performance Liquid Chromatography and Cold-vapor Atomic Absorption Spectrometry*

C. Schickling and J. A. C. Broekaert†
University of Dortmund, Department of Chemistry, Otto Hahn Str. 6, D-44221 Dortmund, Germany

A method for the speciation of mercury in gas condensates is reported. Mercury(II) chloride ($HgCl_2$), methylmercury chloride (MeHgCl), phenylmercury acetate (PhHgAc) and diphenylmercury (Ph_2Hg) are separated by reversed-phase high-performance liquid chromatography (HPLC) using gradient elution. Prior to the determination, the organic ligands and the matrix were destroyed by oxidation with $K_2Cr_2O_7$. Mercury is detected with cold-vapor atomic absorption spectrometry (CVAA), where the mercury compounds are reduced to metallic mercury by a treatment with $NaBH_4$. In a continuous-flow system the concentrations of the reagents used are optimized using a modified simplex algorithm. Detection limits for mercury are at the 10 ng ml^{-1} level. Analysis of multi-compound mixtures indicates that chemical reactions between $HgCl_2$ and Ph_2Hg and between MeHgCl and Ph_2Hg take place. The method developed was applied to the speciation of mercury in gas condensates and did not require use of any solvent extraction or chemical derivatization steps. In the gas condensates, mercury(II) compounds were found to be present at the 100 ng ml^{-1} level.

Keywords: cold vapour atomic absorption spectrometry; high-performance liquid chromatography; mercury speciation; gas condensates

INTRODUCTION

Oil products, as a result of their geogenesis and their processing for energy production and in the chemical industry, contribute a considerable source of heavy metals for different compartments of the environment. The concentration of mercury in crude oils varies in the range of 0.01–3 μg ml^{-1}, depending on the geological origin.[1] After crude oil distillation, more than 50% of mercury is found in the gas fraction (b.p. 36–170 °C).[2] Whereas in natural gases mercury occurs mostly in the metallic form, gas condensates may contain a wide variety of mercury compounds ranging from the elemental and inorganic to organometallic species.[2] The determination of mercury in its different compounds, referred to as 'speciation', for the case of gas condensates is interesting not only because of ecotoxicological aspects but also because of increasing problems in the processing of gas condensates containing mercury. Indeed, catalytic processes such as hydrogenation can suffer seriously from catalyst poisoning by mercury, which may thus lead to reduced lifetimes for the catalyst. It has also been reported that mercury impurities in gas condensates led to corrosion in steam-cracker cold boxes.[2] Therefore, knowledge of the mercury species present in the nanogram range in gas condensates is very important with a view to their removal.

In recent years, many methods have been developed for the speciation of mercury. Among these methods two basic categories can be distinguished: in the first, a distinction is made between inorganic and organic mercury on the basis of special separation techniques. For instance, a separate determination of elemental mercury and Me_2Hg can be carried out by using the different adsorption behaviour on gold or Carbotrap.[3] In the case of solid samples one can isolate well-defined groups of mercury compounds by an extraction with selective solvents.[4] Thus one can isolate the water-soluble fraction of mercury in soil by leaching under standard conditions. Furthermore, inorganic mercury compounds can be distinguished from organic mer-

* Dedicated to Prof. Dr. F. Huber on the occasion of his 65th birthday.

† Author to whom correspondence should be sent.

CCC 0268–2605/95/010029–08

Received 4 March 1994
Accepted 25 June 1994

cury compounds by using reducing reagents such as tin(II) chloride ($SnCl_2$).[5-7]

Analytical techniques which allow a species-specific determination of mercury are becoming increasingly important. This is due to the fact that the toxicity of mercury compounds depends on the species present. The presently available techniques are based on the combination of a separation method such as gas chromatography (GC)[8-15] and HPLC[16-27] with different detection methods. The main detectors used in GC for the determination of mercury are the electron capture detector (ECD),[28] optical emission spectrometry (OES)[12-15] and atomic absorption spectrometry (AA).[9-11]

The main problem in GC-based methods is the need to have volatile and thermally stable mercury compounds.[29] Despite the use of complex sample pretreatment procedures for a series of mercury compounds, this problem cannot be completely solved. Therefore, the separation of a great variety of mercury compounds by HPLC has found more and more application, as shown by combinations with microwave-induced plasma[25] and inductively coupled plasma[26] OES, atomic fluorescence spectrometry[24] and AA.[20-22] Especially in the latter case, low detection limits (1 ng) could be obtained by using an interface enabling mercury cold-vapour generation.

In this work, a coupling of HPLC and cold-vapour atomic absorption spectrometry (CVAA) has been developed and optimized for the speciation of mercury in gas condensates as organic matrix. The method is a further development of the one described by Gaston Wu,[23] who determined mercury species in water samples down to 0.8 ng ml^{-1}. The method developed combines the high separation efficiency of the HPLC and the high power of detection of CVAA. It will be shown that the organic matrix can be separated from the mercury species in the gas condensates by using gradient elution HPLC.

REAGENTS

All mercury solutions were freshly prepared every week and they were stored in quartz vessels at 4 °C. Stock solutions of $HgCl_2$ (purity: Specpure powder; cat. no. 87239; Alpha, Karlsruhe, Germany) and MeHgCl (purity >95%; cat. no. 37123; Alpha) were prepared by dissolving the compounds in a mixture of acetonitrile (cat. no. 15500; Merck, Darmstadt, Germany) and water, 35:65 (v/v). The standard solutions were prepared by diluting the stock solutions with the mixture of acetonitrile and water. For quantitative determinations in the gas condensates, a standard addition with a solution of $HgCl_2$ was applied. It was prepared in ethanol and diluted with cyclohexane (cat. no 9666; Merck). A stock solution of PhHgAc (purity >95%; cat. no. 37125; Alpha) was prepared by dissolving the compound in ethanol and standard solutions were obtained by dissolving the stock solution in a mixture of acetonitrile and water (35:65). A stock solution of Ph_2Hg (purity >95%; cat. no. 37119; Alpha) was prepared by dissolving the compound in cyclohexane and a subsequent dilution with ethanol (cat. no. 12727; Merck) (1:100). The standard solutions were prepared by diluting the stock solution in a mixture of acetonitrile and water (35:65). All the other chemicals used were analytical grade. The $NaBH_4$ solution (obtained from $NaBH_4$; cat. no. 71320; Fluka, Neu-Ulm, Germany) was freshly prepared every day. The $K_2Cr_2O_7$ solution (prepared from $K_2Cr_2O_7$; cat. no. 1470; Grüssing, Filsum, Germany) was renewed weekly. The gas condensates analysed were stored in brown glass bottles at 4 °C and injected without any sample pretreatment.

APPARATUS

A coupling of HPLC and CVAA was used for the speciation of mercury. A scheme of the set-up is given in Fig. 1. The optimized operating conditions are listed in Table 1 and details of the instrumentation are described below.

HPLC system

The HPLC system used included two HPLC pumps (Model BT 8100; Biotronic, Maintal, Germany) equipped with a Rheodyne injector (Model 7125) and a 250 mm × 4 mm column (packed with RP-18 LiChrospher® material, 5 μm; Merck, Germany). It served to separate the analytes before the detection of mercury by CVAA. Mixtures of acetonitrile/water (35:65–100:0) and of acetonitrile/aqueous potassium bromide (KBr) solution (0.1 M) (35:65–100:0) were used as mobile phase. The flow rate of the mobile phase was 1 ml min^{-1}.

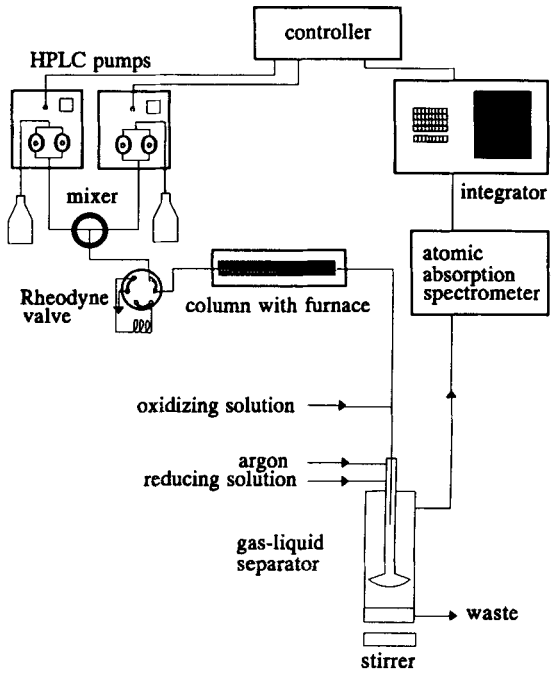

Figure 1 HPLC–CVAA system for the speciation of mercury.

Atomic absorption spectrometer

A Perkin–Elmer model 2380 atomic absorption spectrometer (Überlingen, Germany) with a continuum source background correction was used for the detection of mercury. The mercury hollow cathode lamp was operated at 5 mA in all measurements. The mercury I 253.7 nm line was used as analytical wavelength and a spectral slit width of 0.7 nm was selected. A laboratory-made quartz cell (10 cm × 1 cm i.d.) was used as absorption volume. The chromatograms were recorded with a Chromatopac integrator (Model C-R6A; Shimadzu, Duisburg, Germany) connected to the analogue output of the AA spectrometer.

Gas–liquid separator

The gas–liquid separator was made of quartz (Herasil; Heraeus, Hanau, Germany) and was similar to the one described by Gaston Wu.[23] The outer vessel of the separator has a diameter of 35 nm and a height of 160 mm. The inner tube for the mixing of the analyte solution has a diameter of 8 mm and a length of 100 mm. The oxidizing solution is introduced first into this tube, and subsequently the reducing solution. A peristaltic pump (Ismatec, IPS-IG no. 12-0447, Zürich, Switzerland) was used. The reagent solution tubes (0.5 m i.d.), the T-pieces and the fittings to the gas–liquid separator were made of PTFE (Latek, Eppelheim, Germany). The metallic mercury generated in this system was swept into the quartz absorption cell of the AA spectrometer by an argon carrier gas flow, which was found to be optimum at 10 lh^{-1} (see Table 1). The mercury entered the cell through a polyethylene (PE) tube (0.5 cm i.d.).

RESULTS AND DISCUSSION

Optimization of the CVAA

For the determination of mercury in an organic medium the most important parameters to be optimized are the concentrations of the $NaBH_4$ reducing solution, of the $K_2Cr_2O_7$ oxidizing solution and of HNO_3 in the oxidizing solution. In this work a so-called 'modified' simplex method[30,31] was applied with this aim. As target function, the area of the AA signal for mercury was selected. The optimization was carried out for the case of $HgCl_2$, so as to find out the ideal dilution circumstances and to avoid unnecessary handling of the much more toxic organomercury compounds. In control experiments, it was found that the same optimum conditions would apply to the determi-

Table 1 Optimized parameters for the determination of mercury by CVAA

Parameter	Introduction mode	Flow rate (ml min^{-1})	Concentration (%, w/v)
$K_2Cr_2O_7$	Continuous	1.2	0.8
$NaBH_4$	Continuous	1.8	0.6
HNO_3	—	—	3
Acetonitrile/water (35:65)	Continuous	1.0	—
Samples	Pulsed	1.0	—
Carrier gas	Continuous	167	—

nation of the mercury compounds MeHgCl, PhHgAc and Ph_2Hg. The results of the optimization are given in Table 1.

It was found that a concentration of 20% HNO_3, which was reported to be optimum in the literature,[23] led to irreproducible absorbance signals. A 3% (w/w) acid concentration in the oxidizing solution was found to be optimum.

The signals for organic mercury compounds were lower than those for $HgCl_2$, viz. only 83% for PhHgAc, 80% for MeHgCl and 75% for Ph_2Hg. An increase of the length of the reaction tube used for the oxidation step from 10 cm to 250 cm led to peak broadening and to a deterioration of the signal-to-noise ratio. In order to increase the recoveries for the organic mercury compounds, the use of oxidants other than $K_2Cr_2O_7$ was investigated. With neither $KMnO_4$ nor $K_2S_2O_8$, however, could improvements with respect to the results of an oxidation with $K_2Cr_2O_7$ be obtained.

Separation of mercury species

For the separation of the four mercury species investigated ($HgCl_2$, MeHgCl, PhHgAc and Ph_2Hg) by reversed-phase HPLC, different mixtures of acetonitrile/water were applied. In the isocratic mode $HgCl_2$ and MeHgCl were eluted with a mixture of acetonitrile and water (35:65) after 3.06 min and 3.85 min, respectively. This means that these two mercury compounds pass along with the solvent front (3.00 min). Under similar conditions, PhHgAc and Ph_2Hg had retention times of 17.75 min and even of 45 min, respectively. This might relate to a lower polarity as compared with $HgCl_2$ and MeHgCl. This shows that, as a result of the different chemical characters of mercury compounds, gradient elution is required. For the polar compounds ($HgCl_2$ and MeHgCl) it was found that the interaction with the stationary phase could be increased by using an aqueous solution of 0.1 M potassium bromide (KBr). Indeed, according to the literature KBr would counteract the ionic character of the mercury analyte[23] and we found that the addition of KBr leads to an increase of the retention times and of the peak heights and areas along with its concentration (Fig. 2).

With solutions containing only one component it was found that the retention times were 4.42 min for $HgCl_2$, 7.96 min for MeHgCl, 10.42 min for PhHgAc and 11.69 min for Ph_2Hg. In Fig. 3 the chromatogram is shown for a mixture

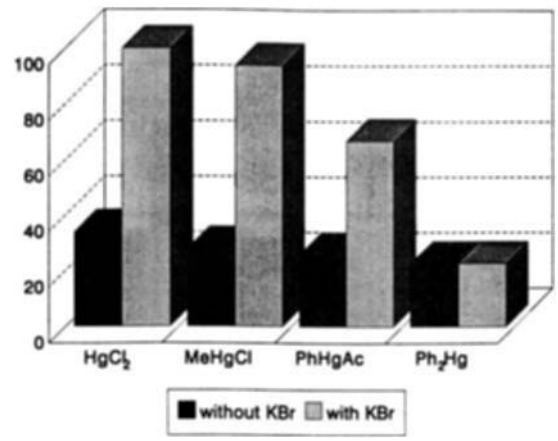

Figure 2 Influence of the use of KBr on the signals obtained for $HgCl_2$, MeHgCl, PhHgAc and Ph_2Hg standards (each compound: 100 ng Hg ml^{-1}) by HPLC–CVAA.

of the four mercury compounds at the 100 ng ml^{-1} level. In all experiments with a mixture of the four compounds at equal concentrations we never found equal intensities, but we did observe a decreased $HgCl_2$ peak and an increased PhHgCl peak compared with the one-component solutions, whereas a Ph_2Hg peak failed to appear. Both facts suggest the need for further investigations.

Investigations of two-component mixtures

The reactions which led to the effect described above with mixtures of the four organomercury species studied were examined by experiments with solutions containing two compounds. Neither for the mixture of $HgCl_2$ and MeHgCl nor for the mixture of PhHgAc and Ph_2Hg could mutual influences of the mercury compounds be observed. This contrasts with the results for a mixture of $HgCl_2$ and Ph_2Hg. The latter effect could be explained by assuming the existence of a transphenylation, which is known from the literature (Eqn [1]):[32]

$$HgCl_2 + Ph_2Hg \rightarrow 2\ PhHgCl \qquad [1]$$

To verify this hypothesis, freshly prepared solutions of $HgCl_2$ and Ph_2Hg (each 100 ng Hg ml^{-1}) were mixed and subjected to HPLC–CVAA immediately after mixing as well as 200 min later. The conversion of $HgCl_2$ and Ph_2Hg to PhHgCl took place immediately. Measurements were also

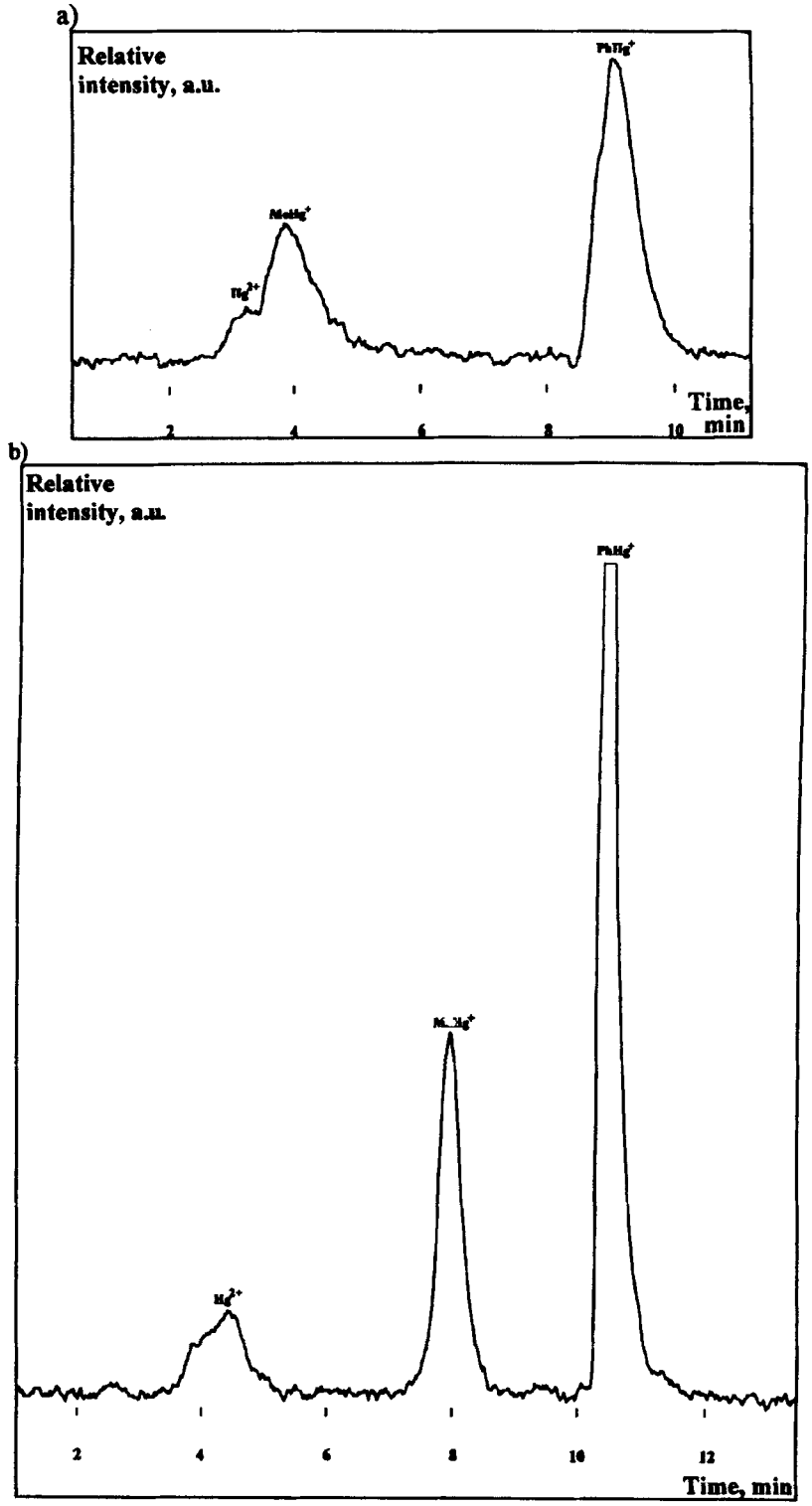

Figure 3 Chromatograms for a mixture of four mercury compounds: $HgCl_2$, MeHgCl, PhHgAc, Ph_2Hg (each compound: 100 ng Hg ml^{-1}): (a) without KBr; (b) with KBr — a peak for Ph_2Hg as a result of reaction (1) does not appear.

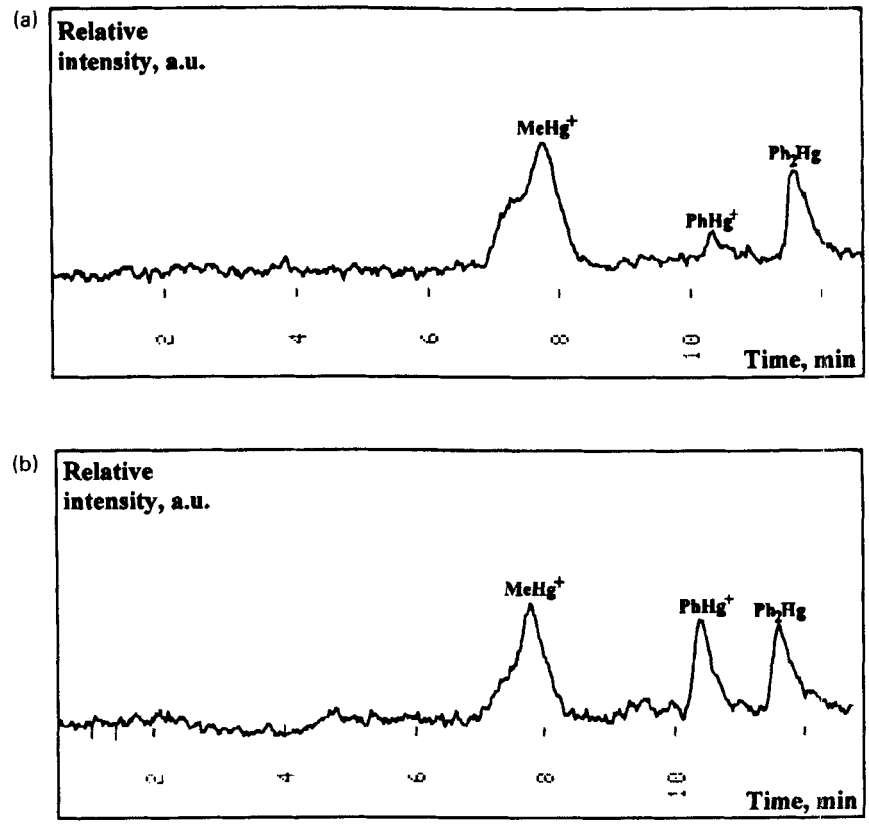

Figure 4 Chromatograms for a mixture of MeHgCl and Ph_2Hg standards (each compound: 100 ng Hg ml^{-1}, with KBr), (a) 0 min and (b) 200 min after mixing.

performed with a mixture of MeHgCl and Ph_2Hg. Immediately after mixing the two standard solutions we found a small peak at a retention time of 10.4 min in addition to the peaks of MeHgCl and Ph_2Hg (Fig. 4). This peak has the same retention time as PhHgCl and, in the first 200 min after mixing, this peak was found to increase. Therefore, it can be concluded from the chromatogram in Fig. 3 that both the depression of the $HgCl_2$ peak and the absence of a Ph_2Hg peak should be attributed to the reaction [1]. The quantitative consequence of the reaction of MeHgCl with Ph_2Hg (Fig. 4) could not easily be predicted.

The mutual interferences of the mercury compounds $HgCl_2$, MeHgCl and Ph_2Hg show that in the analysis of real samples, even with standard addition, serious errors in calibration may occur. Therefore, it is advisable to apply calibration with monoelement solutions to avoid at least errors stemming from conversion reactions. For the case in which the analyte compound determined reacts with other compounds of the element in the sample, the only remaining possibility is to calibrate off-line after the separation.

Analytical applications

Under optimized conditions the detection limits for the four mercury compounds were determined with solutions containing one component. The detection limits, defined as three times the standard deviations, were 9 ng Hg ml^{-1} ($HgCl_2$), 9 ng Hg ml^{-1} (MeHgCl), 8 ng Hg ml^{-1} (PhHgAc) and 14 ng Hg ml^{-1} (Ph_2Hg), respectively. Accordingly, they were ten times better than the lowest values reported by Gaston Wu[23] for cases in which he did not apply a preconcentration on a precolumn. The calibration curves for the mercury species were linear over more than one order of magnitude and in this range the correlation coefficients obtained were better than 0.995.

The optimized method was finally used for the speciation of mercury in two different gas condensates. In the chromatograms obtained for the real samples (Fig. 5) nearly the same peaks were

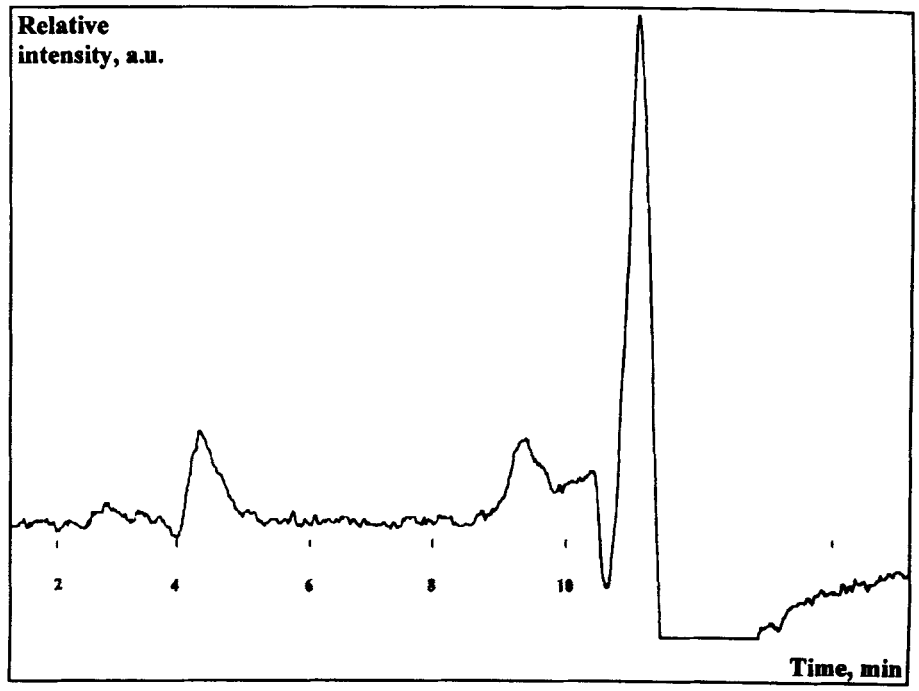

Figure 5 Chromatogram for a gas condensate obtained by HPLC–CVAA.

found. The peak after *ca* 4 min according to the data of Fig. 3(b) is caused by Hg^{2+}. The drastic change of the baseline and the peaks after 9 min resulted from the organic matrix. Both the occurrence of peaks at *ca* 9 and 11 min as well as the decrease of the background after 10 min may be attributed to the deuterium-background correction. This overcompensation could also be observed when injecting a mixture of benzene, toluene, cyclohexane and xylene — the four major compounds of the gas condensates. An identification of the mercury compounds in the gas condensates could be performed by a standard addition. From these measurements under optimized conditions the presence of $MeHg^+$ could be excluded. As possible interferences with the peaks from the organic matrix could occur in the case of gradient elution, the presence of $PhHg^+$ and of elemental mercury had to be investigated in isocratic conditions with a 35:65 mixture of acetonitrile/aqueous solution of KBr (0.1 M), and either $PhHg^+$ or elemental mercury could be excluded. Even under isocratic conditions a separation of the signal for Ph_2Hg and the organic matrix would not be possible and accordingly Ph_2Hg cannot be detected.

For the quantitative determination of Hg^{2+} in the two gas condensates, a calibration with $HgCl_2$ standard solutions and a calibration by standard addition with $HgCl_2$ were applied (Table 2). When injecting the gas condensates, serious instabilities of the working pressure in the HPLC column could be observed (190–220 bar). These resulted in standard deviations of the order of 10% as a result of which only a semiquantitative determination of mercury in the gas condensates remained possible. In addition, the total mercury concentration in the gas condensates was determined. Therefore, we applied a digestion of the samples with aqua regia, a preconcentration of mercury on a gold net and a determination of mercury by CVAA. With this independent method the results for mercury obtained by a coupling of HPLC and CVAA could be confirmed to a first approximation.

Table 2 Determination of mercury in gas condensates

	Concentration (ng ml^{-1})	
	(1)	(2)
Total mercury	95 ± 12[a]	101 ± 10
Hg^{2+} with synthetic standard	81 ± 9	112 ± 10
Hg^{2+} with standard addition	122 ± 12	147 ± 12

[a] Figures following ± are the standard deviations resulting from three measurements.

CONCLUSIONS

It has been shown that HPLC coupled to CVAA can be successfully applied for the direct determination of mercury in complex samples such as gas condensates. The method described is simple and offers several advantages over alternative methods: indeed, no sample pretreatment has to be performed, whereas other methods often need an acid digestion and solvent extraction. This favours both the accuracy and the sample throughput. Further, it has been shown that interferences may arise from the chemical composition of the matrix and therefore a calibration by standard addition is recommended.

It has been shown that in multicomponent standards mutual interactions of the mercury compounds may occur. This indicates that precautions must be taken in the calibration procedure. At this state-of-the-art, the method can be used for qualitative and semiquantitative determinations of mercury species in real samples. However, possible interferences as well as errors arising from sample conditioning require additional investigations. In this respect the availability of a 'blank' gas condensate with respect to the relevant mercury species would be very helpful. Further, work on certification and the use of suitable standard reference materials in the determination of organomercury species in gas condensates is of prime importance.

Acknowledgements The authors gratefully acknowledge financial support by the Fonds der Chemischen Industrie.

REFERENCES

1. S. Mitra, Mercury in the ecosystem. Trans. Tech. Publications Ltd, Aedermannsdorf, Switzerland (1986).
2. P. Sarrazin, C. J. Cameron, Y. Barthel and M. E. Morrison, *Oil Gas J.* **25**, 86 (1993).
3. R.-D. Wilken, R.-D. Behling and G. Petersen, Quecksilber und Quecksilberspezies in der Atmosphäre, in *GKSS Jahresbericht*, pp. 38–52 (1991).
4. R. C. Campos and A. J. Curtius, *J. Anal. At. Spectrom.* **8**, 247 (1993).
5. M. Hempel, H. Hintelmann and R.-D. Wilken, *Analyst (London)* **117**, 669 (1992).
6. R.-D. Wilken, metallorganyle als Beispiel von Speziation: Plädoyer für eine Anorganische Spurenstoff-Analytik, in *DFG-Berichtsband zum Expertengespräch 'Bewertung und Kriterien der Güte von Oberflächen-, Grund- und Trinkwasser'*.
7. R.-D. Wilken, Analysis of mercury-species in sediments, in *Metal Speciation in the Environment, edited by* J. A. C. Broekaert, F. Adams and S. Gücer, NATO ASI Series, Vol. 23, pp. 339–59. Springer Verlag, Berlin (1990).
8. S. Rapsomanikis, *Anal. Chim. Acta* **248**, 563 (1991).
9. J. Gui-Bin, N. Zhe-Ming, W. Shun-Rong and H. Hing-Bin, *Fresenius J. Anal. Chem.* **334**, 27 (1989).
10. H. Paudyn and J. C. Van Loon, *Fresenius J. Anal. Chem.* **325**, 369 (1985).
11. J. W. Robinson and J. C. Wu, *Spectrosc. Lett.* **18**, 47 (1985).
12. K. Chiba, K. Yoshida, K. Tanabe, H. Haraguchi and K. Fuwa, *Anal. Chem.* **55**, 450 (1983).
13. W. E. L. Grossman, J. Eng and Y. C. Tong, *Anal. Chim. Acta* **60**, 447 (1972).
14. Y. Talmi, *Anal. Chim. Acta* **74**, 107 (1975).
15. K. B. Ohlsen, D. S. Sklarew and J. C. Evans, *Spectrochim. Acta* **40B**: 357 (1985).
16. W. Langseth, *Anal. Chim. Acta* **185**, 249 (1986).
17. Y. Xing-Dong, L. Jin-Chun, J. Cheng and Y. Zeng, *Anal. Sci.* **8**, 255 (1992).
18. Y.-C. Wang and C.-W. Whang, *J. Chromatogr.* **628**, 133 (1993).
19. O. Evans and G. D. McKee, *Analyst (London)* **113**, 243 (1988).
20. F. E. Brinckman, W. R. Blair, K. L. Jewett and W. P. Iverson, *J. Chromatogr. Sci.* **15**, 493 (1977).
21. J. W. Robinson and E. D. Boothe, *Spectrosc. Lett.* **17**, 673 (1984).
22. W. Holak, *Analyst (London)* **107**, 1457 (1982).
23. J. C. Gaston Wu, *Spectrosc. Lett.* **24**, 681 (1991).
24. H. Hintelmann and R.-D. Wilken, *Appl. Organomet. Chem.* **7**, 173 (1993).
25. D. Kollotzek, D. Oechsle, G. Kaiser, P. Tschöpel and G. Tölg, *Fresenius' J. Anal. Chem.* **318**, 485 (1984).
26. I. S. Krull, D. S. Busnee, R. D. Schleicher and S. B. Smith, *Analyst (London)* **111**, 345 (1986).
27. F. Palmisano, P. G. Zambonin and N. Cardellicchio, *Fresenius' J. Anal. Chem.* **346**, 648 (1993).
28. G. Westöö, *Acta Chem. Scand.* **20**, 2131 (1966).
29. J. E. O'Reilly, *J. Chromatogr.* **238**, 433 (1982).
30. S. N. Deming and S. L. Morgan, *Anal. Chem.* **45**, 278A (1973).
31. C. K. Bayne and I. B. Rubin, *Practical Experimental Optimization Methods for Chemistry*, pp. 129–44. Verlag Chemie, Weinheim (1986).
32. A. F. Hollemann and N. Wiberg, *Lehrbuch der anorganischen Chemie*, 100th edn. Walter de Gruyter, Berlin (1985).