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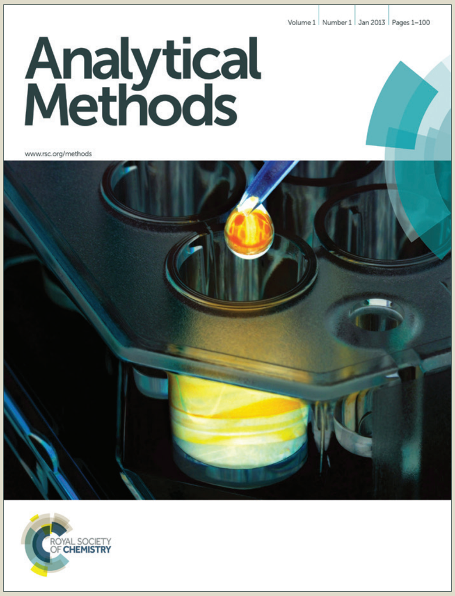

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A Simple and Rapid Method for the Determination of Mercury in Gas Condensates by Inductively Coupled Plasma - Mass Spectrometry

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ABSTRACT: A method for the accurate determination of mercury content in gas condensates is of significance in the application of condensates. In this paper, a simple and rapid method for the determination of mercury in gas condensates using inductively coupled plasma - mass spectrometry was established. The effects of experimental conditions including extraction reagent, sample mass, extraction time in water bath, and membrane filtration treatment were investigated. A sample mass of 1.00 g, 10 mL of aqua regia as pretreatment reagent, and boiling water bath time of 60 min were selected as the optimized pretreatment conditions. After hydrophilic membrane filtering, the obtained solution was diluted 10 times using 3 % (*v/v*) nitric acid and the inductively coupled plasma - mass spectrometry determination was conducted. The method detection limit was 0.4 ng/g, and the relative standard deviation range was from 2.8 % to 5.4 % for the samples of different natures. Both standard addition recovery experiments and comparison results with microwave-assisted digestion method indicated that the proposed method was reliable for

the determination of mercury in the gas condensates.

1. Introduction

With the development of the petrochemical industry, gas condensate, a quality material for fine chemical products, has increasingly been paid great attention. However, mercury (Hg) contained in the gas condensate (generally 10-3000 μg/L)[1] can not only generate amalgam with other metals corroding equipment, but also cause catalyst poisoning in the process of refining.[2] Moreover, the Hg in the gas condensate can affect subsequent product quality, threaten the operator's health, and lead to environmental pollution.[3,4] So investigating the methods for accurate determination of the Hg content in gas condensates is of significance in the condensate application process.

At present, there are few research reports on the methods for the determination of Hg in gas condensates.[5-7] However, there are multiple reports on the methods for the determination of Hg in oils of a similar nature to gas condensates, and different sample pretreatment methods and different determination techniques can be used.[8-12]

The sample decomposition methods include thermal decomposition techniques[8] or wet-chemistry procedures[13,14]. Various wet-chemistry sample decomposition procedures that involve pressure-tight vessels,[9] microwave-assisted digestion,[13] and vessels sealed using a methane/oxygen gas torch (Carius tube)[14] have been used for the determination of Hg in crude oils and related products. The complexity of the matrices and the high volatility of Hg mean that the decomposition methods require careful adjustment of the experimental parameters so that the matrices are destroyed at elevated temperatures without the loss of volatile mercury species or contamination.[8,14] The sample dilution method is an extensively employed and easy approach for petroleum samples.[10] Olsen *et al*. reported an analysis method for naphtha and petroleum condensates, which were diluted with xylene and then determined by inductively coupled plasma - mass spectrometry (ICP-MS), however, the standard deviation of determination results for Hg was very high, probably because of the instability of this element in organic solvent and some memory effects.[15] So the selection of solvent is one of the most critical stages in the dilution procedure. An emulsification method was proposed as an alternative to sample dilution, [11] because the organic mass is reduced, the emulsification method benefits most determination methods. Jesus *et al*.[2] reported an emulsification method in which the microemulsions were prepared by mixing the naphtha and petroleum condensate samples with propan-1-ol and a small amount of water. The surfactant selection is the most important aspect in emulsification procedures. Changes in physical properties may affect the signal intensity, the analyte transport efficiency, and the stability of the emulsion.[10] No matter what technology (dilution method, emulsification method, or direct sample introduction technology) is used, the sample introduction system is more complex than that for an aqueous solution.[5-6] Photochemical vapor generation method[16] and liquid-liquid microextraction method[17] were also used in the determination of Hg in liquid samples, which have the potential advantages for the pretreatment of gas condensate.

Liang *et al*.[12] studied the determination of total mercury in gasoline and other petroleum products. In their method, organic mercury compounds and low-valence inorganic mercury compounds were simply oxidized, extracted into aqueous solution in the forms of mercuric ions, and then determined by the cold-vapor technique. Uddin *et al*.[4] extracted Hg from crude oil using BrCl/HCl, and determined the aqueous-phase solution using atomic fluorescence spectrometry (AFS) with the detection limit (DL) of 0.38 μg/kg. When the element Hg in oils is determined, a suitable extraction method makes the sample pretreatment very simple and effective, and the obtained aqueous solution is suitable for instrumental determination.

Although AFS is widely used in Hg determination,[18-20] for ICP-MS, there are many technical advantages, including wide dynamic linear range, simple spectral line, little interference, rapid analysis speed, and low detection limit for Hg (< 0.01 μg/L), and ICP-MS has been applied in the determination of Hg in samples of different nature.[21-23] When ICP-MS is used for the determination of Hg, the major problem is the serious memory effect.[24] Using a dilute acid instead of deionized water for cleaning before sample introduction can effectively reduce the memory effect of Hg.[25-26]

In this work, an extraction mode with water bath heating was employed to optimize the extraction conditions for Hg in gas condensates (including extraction reagent, sample mass, extraction time, and membrane filtering treatment), and determined the obtained aqueous-phase extraction solution by ICP-MS, which is a simple and rapid method for the determination of Hg in gas condensates.

2. Experimental

2.1 Materials. The standard stock solution were ρ (Hg) = 1 g/L (1.5 mol/L HNO_3 and 0.01 mol/L K_2CrO_7 as medium) and ρ (Rh) = 1 g/L (2.0 mol/L HCl as medium), grade I standard solution, from the China National Standard Reference Center. All standard working solutions used in the experiments were prepared by diluting the standard stock solution step by step, using a solution medium of 3 % HNO_3. Nitric acid **(**HNO_3) and hydrochloric acid (HCl) were all guaranteed reagents (GR) from the Beijing Chemical Plant. The water was deionized (> 18 MΩ·cm). Micropore filter membranes (hydrophobic membrane and hydrophilic membrane) were 0.22 μm from the Membrana, Germany.

2.2 Apparatus. ICP-MS measurements were carried out using Element XSeries II (ThermoFisher Scientific, USA, and the operating conditions used were given in Table 1) and ^{202}Hg (maximal abundance and without isobaric elements interferences) was selected as the investigating isotope.[5] A microwave oven Mars Xpress (CEM, USA) equipped with a rotor for forty PTFE vessels was used for digestion of gas condensate, and heating program was performed as described in the literature.[13] A high speed refrigerated centrifuge Himac CR22G (Hitachi, Japan) was also used in the experiments.

Table 1 Operating conditions of ICP-MS

Parameter	Value	Parameter	Value
Forward power/W	1400	Dwell time/ms	10
Nebuliser gas flow/(L/min)	0.89	Sweeps	50
Auxiliary gas flow/(L/min)	0.80	Channels	1
Cool gas flow/(L/min)	14.0	Resolution	125
Sampling depth/step	250	Sampler cone/mm	1.0
Acquisition mode	Peak jumping	Skimmer cone/mm	0.7

2.3 Sample preparation. 1.00 g of gas condensate sample was weighed and placed in a 25 mL graduated polyethylene test tube, and 10 mL of aqua regia was added accurately. The test tube was next placed in a boiling water bath for 60 min, and was shaken once every 20 min. Then the test tube was taken out, cooled to room temperature, and conducted separation for 4 min in the centrifuge at a rotation speed of 6000 rpm. After carefully removing the upper layer of the oil with a pipette gun, the volume was made up to 10 mL using deionized water and shaken sufficiently. The obtained solution was diluted 10 times using 3 % (*v/v*) HNO_3, and determined using the ICP-MS with ^{103}Rh (10 ng/mL) as internal standard. To avoid memory effect of Hg, 3 % (*v/v*) aqua regia (HCl/HNO_3, 3:1, *v/v*) and deionized water were used orderly for cleaning after each determination.

Calibration curve was constructed by analyzing a series of working standard solutions of mercury in 3 % (*v/v*) HNO_3 at concentrations of 0, 5, 10, 20, and 40 μg/L (^{103}Rh was also used as the internal standard).

3. Results and discussion

3.1 Effect of sample pretreatment reagent

The selection of sample pretreatment reagent is a key factor in the determination of total content of Hg in gas condensates. A large number of experiments had been carried out to study the extraction capability of different acids or mixed acids, including HNO_3,[25,27] HCl,[28] aqua regia,[27,29] mixture of HNO_3 and sulfuric acid (H_2SO_4)[30] for Hg in samples of different nature. The 30 % (*v/v*) HCl was performed as the optimized agent to extract Hg from inorganic fertilizer samples.[28] Park *et al.*[27] compared the Hg extraction effects of HCl, HNO_3, H_2SO_4, and aqua regia, and found that HNO_3 was most effective for the coal samples whereas aqua regia was for the soil samples. Many researches indicated that aqua regia was more sufficient than the other acids or the other mixed acids for the extraction of Hg from different samples.[26,29,31] On the basis of pre-experiments, aqua regia and Lefort aqua regia (HCl/HNO_3, 1:3, *v/v*) were selected as the sample pretreatment agent to study their extraction effects for Hg in gas condensate samples using the boiling water bath.

Four samples (#1-#4, from different regions) were weighed (1.00 g each) and tested in parallel. 10 mL of aqua regia and 10 mL of Lefort aqua regia were added, respectively. The samples were placed in a boiling water bath for 60 min, and then the operations described in Section 2.3 were carried out. The determination results are shown in Fig. 1. For samples #1, #3, and #4 with low Hg content, the extraction effects of aqua regia and Lefort aqua regia were similar, but for sample #2 with a high Hg content, the Hg concentration in solution after extraction by aqua regia was about 16 % higher than that after extraction by Lefort aqua regia. Although aqua regia and Lefort aqua regia can both oxidize low-valence inorganic mercury and organic mercury, and then extract mercuric ions into aqueous-phase solution, the results indicate that the extraction capability of aqua regia is higher than that of Lefort aqua regia for Hg in gas condensates. Therefore, in this experiment aqua regia was selected as the extraction agent.

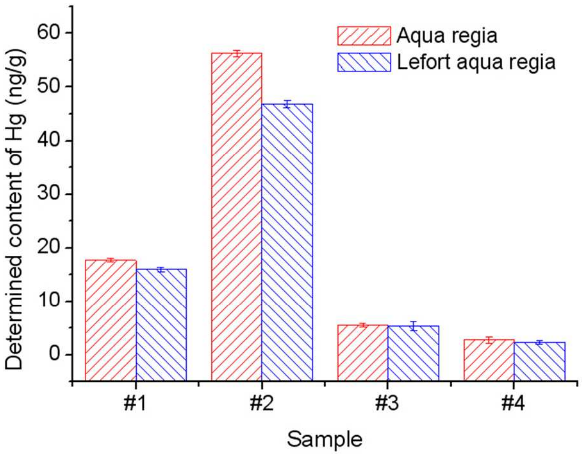

Fig. 1 Effect of sample pretreatment reagent on mercury extraction

3.2 Effect of sample mass

Sample #1 was used to study the effect of sample mass on determination results. The selected sample masses were 0.50 g, 1.00 g, and 2.00 g, respectively. Water bath time was 60 min for all experiments. The results are shown in Fig. 2. When the sample masses were 0.50 g and 1.00 g, the determined values of Hg had a good linear relationship with the sample masses, therefore, the final determined contents (determined content = determined value/sample mass) of Hg were consistent; when the sample mass was increased to 2.00 g, the determined content of the sample was obviously decreased. With the increase in sample mass, the oil-layer thickness increased, and as a result, the extraction efficiency was reduced. To improve the precision of results and to reduce the detection limit, the sample mass should be increased while ensuring sufficient extraction, thus, the sample mass was selected as 1.00 g.

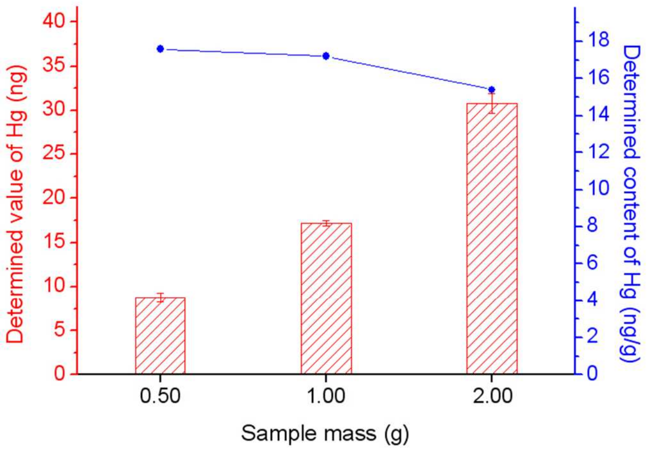

Fig. 2 Effect of sample mass on mercury extraction

3.3 Effect of extraction time

To study the effect of extraction time in the water bath on the determination results, sample #1 was also used for the experiment. With sample mass as 1.00 g, the selected extraction times in the water bath were 20-120 min. It can be seen from the results (Fig. 3) that when the extraction time increased from 20 min to 60 min, the determined contents of Hg increased; when the extraction time exceeded 60 min, the determined contents were presented fluctuant results. With the extraction time increases, the extraction will be more sufficient, but the volatilization loss of the extraction reagent will increase simultaneously, which may sometimes lead to a larger determination error. During the extraction, when the water bath time was shorter than 60 min, the volatilization loss of the reagent was less than 1 mL; while when the water bath time was 120 min, the volatilization loss of the reagent was more than 2 mL. Thus, the final extraction time was selected as 60 min.

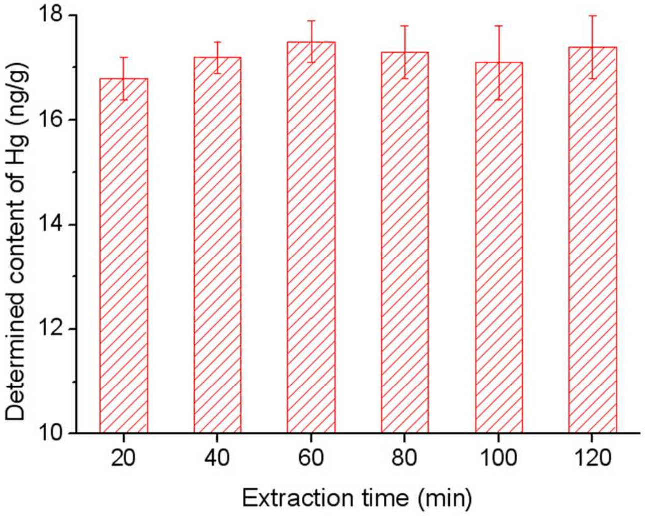

Fig. 3 Effect of extraction time on mercury extraction

3.4 Effect of treatment by hydrophobic membrane

As the original samples of gas condensate may contain an oil phase, an aqueous phase, and a solid-particle phase (in some samples, sediments were observed in clear bottles), which are complex multiphase systems. To ensure the homogeneity of samples used in the experiment, hydrophobic membrane had been used to filter the original samples to study the effect of experimental conditions given in both Sections 3.2 and 3.3. Eight samples (#1-#8) taken from different regions were compared with hydrophobic membrane filtration and hand shaking without filtration to investigate the effect of hydrophobic membrane filtration on Hg determination.

Table 2 shows that gas condensates from different regions were extremely different in nature, and hydrophobic membrane filtration had completely different effect on the Hg determination results. The Hg content in sample #2 changed the most, decreasing by more than 93 %; the Hg content in sample #7 was the highest and that in sample #6 was relatively lower, but the Hg content of sample #7 and #6 almost did not change after hydrophobic membrane filtration; and the Hg contents in other samples slightly decreased after the hydrophobic membrane filtration. The results indicate that Hg in the gas condensate sample is not homogeneously distributed in the oil phase, but distributed in the oil, aqueous, and solid-particle phases in different proportions according to the sample nature.

Table 2 Comparison results of hand-shaking and hydrophobic membrane filtration

w_B/(ng/g)

Sample	Hand-shaking	Hydrophobic membrane filtration	Sample	Hand-shaking	Hydrophobic membrane filtration
#1	17.7±0.2	17.2±0.5	#5	5.2±0.8	4.7±0.3
#2	56.2±2.1	3.7±0.1	#6	4.5±0.8	5.1±0.1
#3	5.1±0.3	4.3±0.3	#7	2458±33	2444±29
#4	3.5±0.4	1.2±0.2	#8	16.3±0.5	11.0±1.0

3.5 Method precision

Using the optimized conditions, twelve experiments in parallel were conducted for sample #1, and the relative standard deviation (RSD) of the determination results was calculated. A little residual oil remained dispersed on the surface of the aqueous solution after careful removal of the oil layer with a pipette gun, and thus perhaps might affect the determination results. As hydrophilic membrane can absorb oil in aqueous solution, two treatment methods of the solution were designed: (1) the oil layer removed by pipette gun carefully, and (2) after removal of the oil layer, the solution filtered by hydrophilic membrane. After the solution was subjected to hydrophilic membrane filtration, the RSD decreased from 5.6 % (only by pipette gun, mean value of Hg = 17.2 ng/g) to 2.8 % (filtered by hydrophilic membrane, mean value of Hg = 17.0 ng/g). The precision of the determination results became better, and the accuracy was not affected. When the aqueous solution contains oil phase, the temperature of plasma may be disturbed by the presence of organic substance, as a result, the RSD of determination results without filtration is larger than that treated by filtration. Therefore, it was selected to treat the extraction solution by hydrophilic membrane filtration after the oil layer removed with a pipette gun.

To make the results being more representative, an additional three samples (#6, #9, and #10) with large differences in Hg content were selected to verify the method precision. The RSDs of the determination values were 4.9 % (#6, mean value of Hg = 5.6 ng/g), 4.3 % (#9, mean value of Hg = 2055 ng/g), and 5.4 % (#10, mean value of Hg = 7.6 ng/g), respectively.

3.6 Method accuracy

Standard addition recovery method was performed to verify the accuracy of the method. Although the added mercury standard solution was aqueous, the partition coefficient of Hg between oil phase and aqueous phase could be verified. Three samples (#6-#8) of different nature and large difference in Hg content were selected for the recovery rate of the method using the optimized extraction conditions. The quantity of added standard substance matched the content of Hg in the samples. The added standard solutions and determined results are presented in Table 3. The recovery rates of these three samples ranged from 90.2 % to 98.8 %.

Table 3 Experiment results of the method recovery rate

	Sample	Determined value/ng*	Mass of standard addition/ng**	Mass of recovery/ng	Recovery rate/%
#6	Sample	5.5±0.3			
	Sample+standard	54.9±2.0	50 (100 μg/L×0.5 mL)	49.4	98.8
#7	Sample	2465±52			
	Sample+standard	3386±64	1000 (1000 μg/L×1 mL)	921	92.1
#8	Sample	11.0±0.4			
	Sample+standard	56.1±2.5	50 (100 μg/L×0.5 mL)	45.1	90.2

* ‘Determined value of sample’ is the mean value of two parallel experiments; ‘Determined value of sample+standard’ is the mean value of three parallel experiments.

** In brackets is ‘concentration of standard solution (μg/L)×addition volume(mL)’.

Moreover, to validate the proposed method with other methods used in oils of a similar nature to gas condensates, a comparison of results with microwave-assisted digestion was conducted for samples #11-#15. Munoz *et al*.[13] developed a method for the digestion of crude oil and diesel fuel by microwave-assisted digestion, in which the used sample mass was 0.1 g. In microwave-assisted digestion, pressure and safety considerations severely limit the sample mass (in general, sample masses lower than 0.5 g are used).[32] For the comparison experiment of microwave-assisted digestion, the sample mass of 0.1 g, 0.2 g and 0.5 g were selected, and other pretreatment procedures were conducted as described in literature[13]. When the sample mass was 0.5 g, there was obviously residual oil on the wall of the vessel, correspondingly, when the sample mass was 0.1 g or 0.2 g, a clear solution could be obtained. As the precision of 0.2 g was better than that of 0.1 g, the sample mass of 0.2 g in microwave-assisted digestion was finally selected. The results of comparison between the method proposed in this paper and microwave-assisted digestion method are shown in Table 4. Good agreements were obtained when the Hg contents were relatively high (> ~ 80 ng/g). But when the Hg contents were lower than ~ 30 ng/g, the accuracy result could not be obtained by microwave-assisted digestion. The proposed method can employ a larger sample mass than microwave-assisted digestion method, which results to lower detection limit and better precision.

Table 4 Comparison between this method and microwave-assisted digestion

	This method		Microwave-assisted digestion	
	Determined content/(ng/g)*	RSD/%	Determined content/(ng/g)*	RSD/%
#11	9.6±0.7	7.3	N.D.	
#12	30.7±1.2	3.9	N.D.	
#13	97.4±4.9	5.0	83.5±10.7	12.8
#14	255±11	4.3	261±26	10.0
#15	913±15	1.6	863±41	4.8

* ‘Determined value of sample’ is the mean value of five parallel experiments.

3.7 Method detection limit

The method detection limit was calculated for three times the standard deviation (σ) of twelve process blanks, which were performed independently as described in Section 2.3 only without samples, thus, the dilution factor was considered into the detection limit. The determined results were (ng/g): 1.8, 2.1, 1.9, 2.0, 1.8, 2.2, 2.0, 2.1, 2.0, 1.8, 1.9 and 2.1. As a result, the standard deviation was 0.13 ng/g, and the detection limit of Hg was 0.4 ng/g.

4. Conclusion

A simple and rapid method for the determination of Hg in gas condensates using ICP-MS was established. Aqua regia was employed to extract Hg in gas condensate in a boiling water bath, which could avoid both the possible mercury loss in the complete decomposition methods and the special requirements for the ICP-MS sample introduction system in the dilution methods or in the emulsification methods. In addition, the proposed method had such advantages as simple operation, time saving, and suitable for the determination of a large number of samples. Through the optimization of the experimental conditions, the standard addition recovery rate of samples achieved 90.2 % - 98.8 %, and the comparison results indicated that the proposed method not only had a good agreement with microwave-assisted digestion method in high Hg content, but also had analytical advantages in low Hg content.

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