Stabilization of organic and inorganic mercury in the graphite furnace with $(\text{NH}_4)_2\text{PdCl}_6$ – $(\text{NH}_4)_3\text{RhCl}_6$ as a mixed chemical modifier¹

Zhang De-Qiang^a, Ni Zhe-Ming^{a,*}, Sun Han-Wen^b

^aResearch Center for Eco-environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

^bDepartment of Chemistry, Hebei University, Baoding 071002, China

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Abstract

The thermal stabilization characteristics of mercury species (inorganic and organic) in the presence of different chemical modifiers, including PdCl_2 + ascorbic acid, $(\text{NH}_4)_2\text{PdCl}_6$ + citric acid, $(\text{NH}_4)_3\text{RhCl}_6$ + citric acid and a mixture of the last two salts, were investigated. The results indicate that PdCl_2 + ascorbic acid can stabilize mercury species up to a temperature of 500°C whereas, with the mixed $(\text{NH}_4)_2\text{PdCl}_6$ – $(\text{NH}_4)_3\text{RhCl}_6$ modifier, mercury can withstand a pyrolysis temperature as high as 920°C and can tolerate much higher concentration of interferents than with palladium or rhodium alone. The integrated absorbance for mercury was also much increased in the presence of the mixed modifier. The characteristic mass, which gives an integrated absorbance of 0.0044 s for mercury, is found to be 59 pg, and the absolute detection limit, based on the variability of the blank (3σ), is 38 pg. The proposed $(\text{NH}_4)_2\text{PdCl}_6$ – $(\text{NH}_4)_3\text{RhCl}_6$ mixed modifier has been applied to the determination of low levels of mercury in cosmetics with a recovery range of 97%–103%. © 1998 Elsevier Science B.V. All rights reserved

Keywords: Graphite furnace AAS; Mercury; $(\text{NH}_4)_2\text{PdCl}_6$ – $(\text{NH}_4)_3\text{RhCl}_6$; Chemical modifier; Mercury in cosmetics

1. Introduction

Low level mercury determinations have been achieved most commonly by cold vapour atomic absorption spectrometry (CV-AAS), especially when the mercury vapour is trapped on a gold-platinum gauze for amalgamation before measurement [1–4]. However, this technique is not without drawbacks when a reducing agent (SnCl_2 or NaBH_4) is added to generate the mercury vapour, as the hydride forming elements may affect the efficiency of mercury vapour production or collection of mercury on the gauze [5]. Further, the relatively large amount of

reducing agents used may introduce reagent blanks. The direct determination of mercury by graphite furnace atomic absorption spectrometry (GFAAS) seems to be simpler in manipulation. However, as a result of its high volatility, only a few papers appeared in the literature using this method. For the prevention of the volatilization loss of mercury prior to atomization in the furnace, several agents have been proposed, such as sulfide [6–8], permanganate [9] and hydrogen peroxide [10]. The maximum pyrolysis temperature was around 300°C, which was not high enough to remove the matrix in the sample without losing mercury. Additionally, the sensitivity of mercury obtained is not satisfactory for real sample analysis. Shan and Ni [11] first proposed the use of palladium for the stabilization of mercury to a temperature of

* Corresponding author. Fax: 011 86 10 255 5381.

¹ Dedicated to Professor C.L. Chakrabarti

500°C in an HGA-70 furnace. Since then, papers have been reported with the application of palladium as a chemical modifier for the stabilization of relatively volatile elements other than mercury [12]. Later, a mixture of palladium nitrate and magnesium nitrate was suggested [13]. However, with the use of the mixture it was found that the integrated absorbance for mercury remained constant at a pyrolysis temperature of 450°C. This was identical to the palladium nitrate alone, which implies that addition of magnesium nitrate is unnecessary.

Since rhodium has higher melting and boiling points (mp 1970°C, bp 3700°C) than those of palladium (mp 1550°C, bp 2900°C), it is expected that the former may have a higher thermal stabilizing effect on relatively volatile elements than the later, so that a substantial improvement in the pretreatment temperature can be observed with rhodium as a stabilizing agent. The Rh-plating of a graphite furnace was found to be effective in inhibiting the loss of volatile elements [14]. Rhodium, in the form of ammonium rhodium chloride, has been applied to the determination of arsenic [15] and selenium [16] in urine and biological samples. Comparison of the results obtained with $(\text{NH}_4)_2\text{PdCl}_6$ and $(\text{NH}_4)_3\text{RhCl}_6$ modifiers showed that the later can achieve better thermal stability: up to 1400°C for As and 1200°C for Se. It is possible that the rhodium salt will allow mercury to tolerate a higher pyrolysis temperature than the corresponding palladium salt.

The purpose of our present work is to compare palladium and rhodium modifiers in a graphite furnace AAS for the direct determination of mercury in real samples.

2. Experimental

2.1. Apparatus

All mercury determinations were performed using a Perkin–Elmer Model 1100B atomic absorption spectrometer equipped with an HGA-700 graphite furnace, complete with an AS-70 autosampler and personal computer for instrument control and data processing. The temperature of the furnace wall was checked with the melting points of platinum and silver wires (diameter of 0.2 mm). Mercury absorbance was measured

Table 1

Furnace program for the determination of mercury with platform using $(\text{NH}_4)_2\text{PdCl}_6$ – $(\text{NH}_4)_3\text{RhCl}_6$ mixed modifier

Step	Temperature (°C)	Ramp (s)	Hold (s)	Gas flow (ml min ⁻¹)
1	200	5	30	300
2	900	10	20	300
3	1800	1	5	0
4	2650	1	2	300

in the peak area mode under ‘gas stop’ condition. A mercury hollow cathode lamp (General Research Institute of Non-Ferrous Metals, Beijing, China) was operated as the line source at a lamp current of 1.0 mA. The 253.7 nm resonance line was selected with a spectral bandwidth of 0.7 nm. Perkin–Elmer standard graphite tubes (Part No. of 290-1633) with inserted platforms were used throughout the experiment. The recommended experimental conditions are reported in Table 1. A ramp atomization was used instead of maximum power heating in order to avoid the loss of mercury caused by rapid diffusion.

2.2. Reagents

A stock standard solution of inorganic mercury (containing 1000 $\mu\text{g ml}^{-1}$ Hg) was prepared by dissolving 135.4 mg of mercury chloride(II) (Beijing Chemical Factory, China) in deionized water and diluting to 100.00 ml with deionized water in a volumetric flask. Working standard solutions containing 400 $\mu\text{g ml}^{-1}$ of mercury were prepared through appropriate dilution of the stock solution just before use.

Methylmercury and ethylmercury stock solutions containing 1000 $\mu\text{g ml}^{-1}$ of mercury were prepared by dissolving 125.2 and 133.2 mg of methylmercury chloride and ethylmercury chloride (Merck–Schuchardt), respectively, in deionized water and diluting to 100.00 ml in volumetric flasks. The working solutions were obtained by diluting of the stock solutions daily with deionized water.

A phenylmercury standard solution containing 50 $\mu\text{g ml}^{-1}$ of mercury was obtained by dissolving 78.1 mg of phenylmercury chloride (Merck–Schuchardt) in deionized water and diluting to 1000.00 ml in a volumetric flask. The working solution was prepared by diluting the standard solution with deionized water just before use.

The PdCl_2 modifier solution was prepared by dissolving an appropriate amount of PdCl_2 in 10 ml of $0.1 \text{ mol l}^{-1} \text{ HNO}_3$ and diluting to 500.00 ml in a volumetric flask with deionized water. A 20 μl modifier solution containing 25 μg of Pd and 1.2 mg of ascorbic acid was injected into the furnace.

The $(\text{NH}_4)_2\text{PdCl}_6$ and $(\text{NH}_4)_3\text{RhCl}_6$ solutions containing 1000 $\mu\text{g ml}^{-1}$ of Pd or 500 $\mu\text{g ml}^{-1}$ of Rh were obtained by dissolving the salts in 10.00 ml deionized water in volumetric flasks each containing 0.60 g of citric acid. A volume of 20 μl of the modifier solution containing 20 μg of Pd or 10 μg of Rh with 1.2 mg of citric acid was injected into the furnace.

2.3. Sample pretreatment

Cosmetic samples were decomposed in Teflon pressure decomposition vessels. Samples of 2 g were weighed accurately into a 30 ml of Teflon container and mixed with 3 ml of concentrated HNO_3 and 0.5 ml of concentrated HClO_4 . The vessels were then covered with Teflon covers and put aside over night. The vessels were placed in stainless-steel bombs, which were sealed tightly with a screw closure to avoid gas leakage, and placed in an oven. The oven temperature was raised to 170°C over 0.5 h and kept at this temperature for 7 h. The bombs were taken out of the oven and cooled down to room temperature. The Teflon vessels were taken out of the stainless steel bombs and the Teflon covers were removed. The vessels were heated on a hot plate at a temperature of 100°C – 110°C and the solutions were evaporated to about half of their initial volume. After cooling to room temperature, the solutions were transferred to 10.00 ml volumetric flasks and diluted to the marks with 0.01 mol l^{-1} nitric acid.

2.4. Procedure

Four nanograms of mercury in the form of inorganic mercury (methylmercury, ethylmercury or phenylmercury) in a volume of 10 μl and a 20 μl of modifier solution containing PdCl_2 (20 μg of Pd) + ascorbic acid, $(\text{NH}_4)_2\text{PdCl}_6$ (20 μg of Pd) + citric acid, $(\text{NH}_4)_3\text{RhCl}_6$ (10 μg of Rh) + citric acid or $(\text{NH}_4)_2\text{PdCl}_6$ – $(\text{NH}_4)_3\text{RhCl}_6$ (20 μg of Pd + 5 μg of Rh) were introduced onto the graphite platform

using the AS-70 autosampler. The recommended furnace program is listed in Table 1.

3. Results and discussion

3.1. Thermal stabilization studies

3.1.1. PdCl_2 plus ascorbic acid

It was reported that palladium is an effective modifier in the reduced form as it catalyses the reduction of metal oxide by graphite, and that the reduced metals form solid solutions or intermetallic compounds with palladium, stabilizing the analytes to higher temperatures [17,18]. In our experiment, the palladium used was palladium chloride dissolved in dilute nitric acid. In order to enhance the reduction of palladium and to prevent the volatilization of analyte in the form of chloride at an early stage of the temperature program, ascorbic acid was added. With PdCl_2 + ascorbic acid as a mixed modifier, the maximum pyrolysis temperature of inorganic mercury on the platform is 500°C when 20 μg of Pd and 1.2 mg of ascorbic acid were added (Fig. 1). The results obtained were similar to that obtained previously [11]. The same modifier has been applied to stabilize methylmercury, ethylmercury and phenylmercury in the furnace and the results

Fig. 1. Pyrolysis and atomization temperatures of 4 ng of mercury in the form of inorganic mercury, ethylmercury and phenylmercury in the presence of: (●), PdCl_2 (20 μg of Pd) + ascorbic acid; (■), $(\text{NH}_4)_2\text{PdCl}_6$ (20 μg of Pd) + citric acid; (▲), $(\text{NH}_4)_3\text{RhCl}_6$ (10 μg of Rh) + citric acid; and (◆), $(\text{NH}_4)_2\text{PdCl}_6$ + $(\text{NH}_4)_3\text{RhCl}_6$ (20 μg of Pd + 5 μg of Rh) + citric acid as modifier.

Table 2

Maximum pyrolysis temperature, optimum atomization temperature and integrated absorbance for 4 ng of mercury (inorganic mercury (IM), methylmercury (MM), ethylmercury (EM) and phenylmercury (PM)) with different modifiers

Modifier	Maximum pyrolysis temperature (°C)				Optimum atomization temperature (°C)				Integrated absorbance (s)			
	IM	MM	EM	PM	IM	MM	EM	PM	IM	MM	EM	PM
PdCl ₂ ^a	500	500	500	500	2100	2000	2000	2100	0.154	0.149	0.157	0.153
(NH ₄) ₂ PdCl ₆ ^b	720	720	720	720	2000	1950	1900	2200	0.256	0.246	0.257	0.251
(NH ₄) ₃ RhCl ₆ ^c	920	870	920	920	2200	2200	2300	2200	0.183	0.177	0.179	0.180
(NH ₄) ₂ PdCl ₆ – (NH ₄) ₃ RhCl ₆ ^d	920	870	920	920	1800	1850	1900	1850	0.303	0.297	0.301	0.300

^a 25 µg.

^b 20 µg.

^c 10 µg.

^d 10 + 5 µg.

shown in Table 2 indicate that all three organic mercury species exhibit similar characteristics as inorganic mercury; no loss of signal occurs at 500°C when the amount of Pd added is increased to 25 µg for 4 ng of mercury in the form of organic mercury (Fig. 2).

3.1.2. (NH₄)₂PdCl₆ + citric acid

Our preliminary experiments showed that palladium, in the form such as (NH₄)₂PdCl₆, exhibited improved chemical modification over palladium in the form of palladium chloride or palladium nitrate.

Fig. 2. Pyrolysis and atomization temperatures of 4 ng of mercury in the form of methylmercury, ethylmercury and phenylmercury in the presence of: (●), PdCl₂ (25 µg of Pd) + ascorbic acid; (■), (NH₄)₂PdCl₆ (20 µg of Pd) + citric acid; (▲), (NH₄)₃RhCl₆ (10 µg of Rh) + citric acid; and (◆), (NH₄)₂PdCl₆ + (NH₄)₃RhCl₆ (20 µg of Pd + 5 µg of Rh) + citric acid as modifier.

The optimum pyrolysis temperature for inorganic mercury, methylmercury, ethylmercury and phenylmercury is found to be around 720°C (Figs 1 and 2). This implies that the stabilizing power of (NH₄)₂PdCl₆ + citric acid for mercury is significantly higher than the previously used palladium salt. Further, the sensitivities for the mercury species are apparently increased, as shown in Table 2, and the amount of palladium used can be more or less decreased. The reason for the advantages provided by (NH₄)₂PdCl₆ is not yet clear. It may be postulated that palladium forms a finely dispersed metal upon decomposition during the drying or pyrolysis cycles so that the metal is more evenly or homogeneously distributed on the surface of the graphite tube as compared with the palladium particles produced from PdCl₂ or Pd(NO₃)₂. Hence, there is more chance to react with mercury to form intermetallic compounds or solids solution, resulting in an increase in the maximum pyrolysis temperature for mercury, as

Fig. 3. Absorbance-time profiles for 4 ng of inorganic mercury with: (a) (NH₄)₂PdCl₆–(NH₄)₃RhCl₆ + citric acid; (b) (NH₄)₂PdCl₆ + citric acid; (c) PdCl₂ + ascorbic acid; and (d) (NH₄)₃RhCl₆ + citric acid.

well as an increase in the sensitivity of determination. The citric acid was added to avoid the loss of the analyte in the form of chloride during pre-atomization cycles. The organic compound also has the advantage of creating a favourable reducing atmosphere in the furnace. The decomposition products (active C, CO and H₂) enhance reduction of palladium and mercury and promote the formation of Pd–Hg intermetallic compounds. Since with (NH₄)₂PdCl₆ + citric acid both inorganic and organic mercury species can be stabilized to a temperature of 720°C, it is possible to determine total mercury in real samples.

3.1.3. (NH₄)₂PdCl₆ + (NH₄)₃RhCl₆

The pyrolysis curves obtained for both inorganic mercury and organic mercury with (NH₄)₃RhCl₆ + citric acid (Figs 1 and 2) indicate that mercury species can be stabilized to a temperature of 920°C. Even with the most easily volatile methylmercury (mp 170°C), a maximum pyrolysis temperature of 870°C can be achieved. To our knowledge, this is the highest pyrolysis temperature ever reported for mercury in

the literature. This is within our expectation since rhodium has higher melting and boiling points than palladium. However, with this modifier, the sensitivity for the determination of mercury is 30% lower compared with that obtained with the palladium salt. It is interesting to find that, with the use of a mixture of (NH₄)₂PdCl₆ and (NH₄)₃RhCl₆, not only can the maximum pyrolysis temperature of 920°C be achieved for mercury species (870°C for methylmercury), but the sensitivity can also be 20% better than that with palladium salt alone (Figs 1 and 2). The phenomena we observed for mercury are similar to those reported by Bulska et al. [19] in the determination of silicon with Pd–Rh. However, they used Pd(NO₃)₂ and RhCl₃ which we found to be unsatisfactory for mercury.

Fig. 3 shows the absorbance peak profiles of inorganic mercury in the presence of different modifiers. Obviously, the peak obtained with PdCl₂ + ascorbic acid has the lowest sensitivity, whereas (NH₄)₂PdCl₆ + (NH₄)₃RhCl₆ is the best. With (NH₄)₃RhCl₆ alone, the broadest peak is observed, while the peak becomes sharper with increasing atomization temperature from

Table 3
Interference of matrices on the absorbance signal for 4 ng of mercury

Interferent	Interferent mass (mg)	Relative absorbance (%)			
		PdCl ₂	(NH ₄) ₂ PdCl ₆	(NH ₄) ₃ RhCl ₆	(NH ₄) ₂ PdCl ₆ –(NH ₄) ₃ RhCl ₆
NaCl	0.2	106	101	102	100
	0.5	116	103	104	100
	1.0	126	106	106	100
	2.0	133	112	98	100
NaClO ₄	0.5	101	100	100	100
	1.0	101	101	100	100
	2.0	102	101	101	100
	3.0	102	101	101	100
Na ₂ SO ₄	0.1	96	99	99	100
	1.0	77	89	98	100
	2.0	63	85	97	99
Na ₂ PO ₄	0.5	103	101	101	100
	2.0	112	107	102	100
	3.0	120	111	103	100
Pb(II)	0.1	119	112	104	101
Ni(II)	0.1	120	110	104	100
Fe(III)	0.2	71	80	93	99
Cu(II)	0.1	133	120	107	101
Cr(VI)	0.1	112	104	102	100
Cd(II)	0.1	114	107	101	100
Co(II)	0.1	92	97	100	100

1900°C to 2200°C although the integrated absorbance remains nearly constant.

3.2. Interference study

Interferences from various cations and anions on the determination of mercury in the presence of different modifiers were examined and the results are summarized in Table 3. Among the matrices studied, NaClO_4 exerts only negligible effect with different modifiers, but NaCl and Na_3PO_4 have a pronounced positive influence when PdCl_2 + ascorbic acid are used. The effect can be minimized by adding $(\text{NH}_4)_2\text{PdCl}_6-(\text{NH}_4)_3\text{RhCl}_6$. The suppression effect caused by sodium sulfate can almost be completely overcome by the use of mixed modifier. Interferences which occurred with heavy metals using PdCl_2 + ascorbic acid and $(\text{NH}_4)_2\text{PdCl}_6$ + citric acid nearly disappear with the mixed modifier. In view of its strong ability to tolerate matrix interferences and the high sensitivity it can provide for mercury determination, the $(\text{NH}_4)_2\text{PdCl}_6-(\text{NH}_4)_3\text{RhCl}_6$ mixed modifier was preferred for real sample analysis.

3.3. Sample analysis

Since environmental mercury contamination can occur from different sources, including cosmetics, and it is known that some cosmetics contain mercury, there is a need for the determination of low levels of mercury in cosmetics. Samples were decomposed in a pressure bomb with acid (Section 2.3) and the digested solutions were analyzed for mercury using the $(\text{NH}_4)_2\text{PdCl}_6-(\text{NH}_4)_3\text{RhCl}_6$ mixed modifier. The

results are summarized in Table 4. In order to ascertain that mercury has not been lost during sample pretreatment, recovery studies were carried out. When 200–300 ng g^{-1} of mercury was added to the sample, the recoveries were in the range of 97%–103%.

4. Conclusion

The maximum pyrolysis temperature for mercury in the furnace can be raised to 920°C in the presence of a mixture of $(\text{NH}_4)_2\text{PdCl}_6$ + $(\text{NH}_4)_3\text{RhCl}_6$ + citric acid. This temperature is high enough to remove matrices in a sample without losing mercury and the sensitivity obtained is also better than that with palladium or rhodium salt alone. The exact mechanism of the reaction between mercury and the modifiers is not clear and needs further investigation.

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Table 4
Determination of mercury in cosmetic samples

Sample	Hg found ^a (ng/g)	Hg added (ng/g)	Recovery of added mercury (%)
1	247 ± 1.2	250	98
2	198 ± 1.5	200	97
3	326 ± 1.7	350	101
4	231 ± 2.1	250	103
5	282 ± 2.2	300	102

^a Mean value ± relative standard deviation of three replicate determinations

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