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Direct analysis of mercury in Traditional Chinese Medicines using thermolysis coupled with on-line atomic absorption spectrometry

Ru-Jin Huang [a], Zhi-Xia Zhuang [a,*], Yi Tai [a], Rong-Fu Huang [a], Xiao-Ru Wang [a,b], Frank S.C. Lee [b]

[a] *Department of Chemistry and The Key Laboratory of Analytical Sciences of the Ministry of Education, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*
[b] *QingDao Key Laboratory of Analytical Technology Development and Standardization of Chinese Medicines, First Institute Oceanography, S.O.A., Qingdao 266061, China*

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Abstract

The purpose of this study is to develop and apply a mercury analyzer system capable of quantitative analysis of mercury in Traditional Chinese Medicines (TCM) drugs in the concentrations range from ng g^{-1} to mg g^{-1}. No sample pre-treatment was needed and this greatly simplifies the analytical procedure and minimizes potential sources of contamination. The precisions of analyzing solid mercury standard sample and real TCM materials were 2.1% and 2.5–8.2%, respectively; and the recovery based on the analysis of standard reference materials ranged from 95.2% to 105%. The performance of the method has been compared with inductively coupled plasma-mass spectrometry (ICP-MS) technique and excellent agreements were observed between the two methods. The method has been applied to the investigation of Hg content in several TCM drugs containing or not containing cinnabar. Mercury concentration in the same TCM products differs widely with different manufacturers, suggesting that external contamination and the Hg presence in raw herbal materials are the main sources of Hg. In addition, comparison of mercury thermal releasing profiles between TCM drug and cinnabar suggests that mercury conversion from cinnabar to biological matrices-bound Hg could occur because of the aid of other ingredients in the formulated drug.

Keywords: Mercury; Cinnabar; Traditional Chinese Medicines; Thermolysis; Atomic absorption spectrometry

1. Introduction

Recently, Traditional Chinese Medicines (TCMs) as natural medicinal materials have been receiving increasing attention because of their outstanding therapeutic effects. One of the major problems in TCMs usage is the issue of safety related to the presence in some products of high concentrations of toxic metals. Several severe cases associated with heavy metal poisoning by Hg, As, Pb, Cd, etc., have been reported [1,2]. These fatalities have destroyed severely the overall image of TCM materials.

Mercury is a well-known neurotoxin and its toxic properties have been extensively documented. But some mercury chemical forms such as cinnabar (red HgS), mercurous chloride (Hg_2Cl_2), etc., are still often used in TCMs as part of the active ingredients in formulation with proven efficacy. Prescriptions containing cinnabar account for 9.8% (i.e., 45 drugs containing cinnabar) of the total TCM concoction drugs collected in Pharmacopoeia of China (2000) [3]. As a common contaminant in TCMs, mercury exists in TCM material in different chemical forms, which differ dramatically in their biological interaction and toxicity. For instance, of the various species of mercury, organic mercury is in general far more toxic than inorganic forms and the ability of $HgCl_2$ in biological accumulation is stronger than that of HgS [2,4]. It is therefore important

* Corresponding author. Tel.: +86 592 2184510; fax: +86 592 2186401.
E-mail address: zxzhuang@xmu.edu.cn (Z.-X. Zhuang).

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to speciate mercury in TCM material for safety and quality assessment.

Several techniques are currently available in the determination of mercury and these include cold vapor atomic absorption/fluorescence spectrometry (CV-AAS/AFS), gas and liquid chromatography (GC/LC) and inductively coupled plasma with either atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS), etc. [5–12]. These methods are often used for solution analysis. Frequently, however, the analysis for solid matrices is required. Thus, the conversion of solid matrix into aqueous form is necessary in order to utilize the above methods. As is often the case, the samples need to be digested in hot, concentrated acid, sometimes under elevated pressure using sealed or open vessels. This sample pre-treatment step is time-consuming, and quite often also the major source of contamination. Potential losses of the volatile mercury species in the sample may also occur. Furthermore, still some difficulties exist in the analysis of mercury in some TCM drugs because of its extremely low concentrations following the interferences caused by the complex sample matrices and the wide change in matrix composition from sample to sample [1]. These problems, hence, mark the quantitative analysis and speciation of mercury in TCMs a challenging task. Thus, an ideal and effective analytical method is prone to properties of high sensitivity and specificity, prominent background correction and wide sample adaptability because it helps to reduce the risk of false negatives in trace contaminant analysis.

The thermolysis atomic absorption method provides an attractive alternative in mercury analysis [13–16], which eliminates tedious sample digestion or derivatization steps commonly used in conventional methods because of its direct solid sampling without pre-treatment. The method is rapid, typically requiring only 4 min to complete a total mercury analysis. Moreover, the method provides high sensitivity, low detection limit and outstanding background correction capability utilizing Zeeman-effect. In this study, our objective is to develop and apply this technique to investigate the content of mercury and the preliminary species in several TCM drug products for quality assessment and regulatory purposes.

2. Materials and methods

2.1. Apparatus

The system used was a Lumex RA–915$^+$ multifunctional mercury analyzer with Model 91C thermolysis unit from Lumex Ltd., Russia (Fig. 1). The system consists of a first atomizer section, where at a temperature near 750 °C, the mercury compounds in samples are decomposed into volatile Hg species in molecular or elemental forms. Carried by the air flow, these species are directed to the second atomizer section, where at a temperature near 800 °C, complete atomization of mercury compounds occurs, aided possibly by the catalytic action of the sample organic matrix. Then the mercury–air mixture flows further into AA detector.

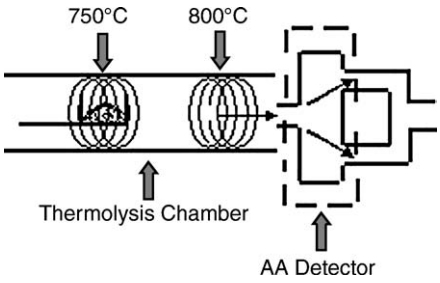

Fig. 1. Scheme of Hg-thermolysis coupled with on-line AAS.

2.2. Materials and reagents

A range of TCM drugs with or without the presence of cinnabar as an active ingredient has been analyzed. Each drug was purchased from an open market and the related information is as follows: TWBXW I and LWDHW I-2 were manufactured by Foci pharmaceutical factory, Lanzhou; TWBXW II, DQLS and LWDHW II-2 were manufactured by Dinglu pharmaceutical factory, Xiamen; AGNHW, NHQXW and LWDHW II-3 were manufactured by Tongrentang pharmaceutical factory, Beijin; LWDHW I-1 was manufactured by Wanxi pharmaceutical factory, Henan; LWDHW I-3 was manufactured by Huiren pharmaceutical factory, Jiangxi and LWDHW I-1 was manufactured by Lingfeng pharmaceutical factory, Guangxi, (TWBXW: Tianwang Buxin Wan, AGNHW: Angong Niuhuang Wan, NHQXW: Niuhuang Qingxin Wan, DQLS: Daqili San, LWDHW: Liuwei Dihuang Wan; I: Concentrated Pill (Nongsuo Wan), II: Diluted Pill (Shuimi Wan)). In addition, licorice samples, each grew in different soil, were supplied by Elion Resources Group Co. and alisma orientalis samples were from Jianou, Fujian.

In order to obtain representative samples for all the subsequent measurements, the samples were freeze dried and then ground, homogenized and sieved ($d \leq 175\,\mu m$) before analyses. Samples with excessive concentrations of Hg were diluted with spectral-grade graphite. Five different types certificated reference materials, i.e. apple leaves (NIST-1515), sand (CRM7183-95), peach leaves (GBW08501), rice (GBW08508) and human hair (GBW09101), were analyzed by RA-915$^+$ mercury analyzer for calibration and analytical performance studies.

2.3. Hg determination by Hg analyzer and ICP-MS

The total mercury in samples was analyzed by placing the solid samples (5–25 mg) directly into the thermolysis chamber of the Hg analyzer. In the analyzer, the fully atomized elementary Hg vapor thermally released from molecular Hg species in the sample at high temperatures was directed into the AA detector. An inter-method comparison was made between this and the ICP-MS technique. For ICP-MS

Table 1
Instrumental conditions and data acquisition parameters of ICP-MS

Condition	Value
RF power	1350 W
Sampling depth	6.8 mm
Plasma gas	16.0 L min^{-1}
Auxiliary gas	1.00 L min^{-1}
Carrier gas	1.07 L min^{-1}
Diameter of sampler	1.0 mm
Diameter of skimmer	0.8 mm
Sample uptake rate	1.0 mL min^{-1}
Acquisition mode	Quantity
Points/mass	3
Scan mode	Jump
Dwell time	30 ms
No. of replicates	3
Integration times	0.1000 s

analysis, the samples were first digested by a full power (1200 W) MK-III optical fibre pressure controlled microwave decomposition system (Shinco, Shanghai, China). About 100 mg sample or reference material was weighed accurately into the PTFE container. Pre-digestion was performed by first adding 5 mL of ultra pure HNO_3 to the sample. The mixture was allowed to stand overnight. On the next day, the pre-digested samples were further digested in a microwave oven. The pressure of the oven was 15 MPa and the digestion time was 5 min. After cooling to ambient temperature, 1 mL of analytical pure H_2O_2 was added to the sample, which was then digested again at the pressure of 10 MPa for another 3 min to ensure complete dissolution. Finally, the samples were transferred into a 25 mL calibrated flask and made up to the volume with de-ionized water (Milli-Q purification system, Millipore Corp., Bedford, MA, resistivity of 18 $M\Omega\,cm^{-1}$) for ICP-MS analyses on a HP4500 instrument (Agilent, USA). The optimized operating conditions are given in Table 1. ^{115}Indium was used as an internal standard to correct for matrix effects.

3. Results and discussion

3.1. Optimization of conditions in Hg analyzer

The operation of the Hg analyzer involves a two-step mechanism. The first step is the temperature dependent thermal evaporation or decomposition of Hg species in the sample into volatile Hg. This is followed by the transfer of the volatile mercury into the analysis chamber by the carried gas flow. Inside the chamber, the volatile Hg is further converted into atomic mercury (Hg^0) to facilitate AA detection. In the first step, catalysts are usually used to aid to the effective decomposition of the bound Hg species. The mercury atoms produced in the process are likely to originate from a combination of sources including direct thermal evaporation of metallic Hg, thermal decomposition of Hg-compounds and thermolytic reduction of bound Hg species in the samples. Since a wide concentration range of Hg is anticipated in the investigated samples, i.e., from ng g^{-1} to mg g^{-1}, the analyzer is equipped with both short (optical absorption length 72 mm) and long (optical absorption length about 10 m in the multiple reflection cell) measuring cells to accommodate high and low level mercury samples, respectively. The detection limit of the system (long cell) is 3.9 ng g^{-1} (3σ) assuming that all Hg in the sample is released as a single peak. The application of direct Zeeman-effect based on high-frequency modulation of light polarization in the instrument provides highly selective mercury detection, allowing direct determination of mercury in the samples with simultaneous control for non-selective absorption in the dynamic regimes.

Two different types of certificated reference materials, i.e., apple leaves (NIST-1515) and sand (CRM7183-95), were used for calibrating the long and the short measuring cells, respectively. Correlation coefficients (r) of the calibration lines were 0.994 for the long measuring cell ($n = 6$), and 0.997 for the short cell ($n = 6$). Spectral-grade graphite as a diluter was used in samples with excessive concentrations of Hg. The total mercury in the sample was determined by measuring the integrated area under the Hg releasing profile upon heating. For samples with multiple peaks in their Hg thermal profiles, the total Hg was determined by summing of all individual peaks.

3.2. Analytical performance

The analytical performance of the method was evaluated by examining the precision (R.S.D.), recovery and accuracy of Hg measurements. The R.S.D. of the method obtained from six replicate determinations of a standard reference material (peach leaves) was 2.1%. But the R.S.D.s obtained for the real TCM drugs were 2.5–8.2%, which were slightly higher than the peach leaves due to the highly heterogeneous nature of the TCM materials. The accuracy of the method was established by analyzing three different types of certificated reference materials, namely, peach leaves (GBW08501), Rice (GBW08508) and human hair (GBW09101). The measured Hg data for these samples as listed in Table 2 are in close agreements with their respective certified values, with their differences ranged from 2.2% to 3.7%. Meanwhile, the recovery of the method ranged between 95.2% and 105%, as listed in Table 3, indicates the absence of any significant losses of volatile mercury species or matrix interference.

The accuracy and precision of the method were compared with those from ICP-MS analysis. Differences observed

Table 2
Accuracy of the method: results from the analysis of CRMs

Certificated reference materials	Certified value (ng g^{-1})	Found value (ng g^{-1})[a]	Differences (%)
Peach leaves (GBW08501)	46 ± 6	47 ± 2	2.2
Rice (GBW08508)	38 ± 6	39 ± 1	2.6
Human hair (GBW09101)	2160 ± 210	2082 ± 84	3.7

[a] Mean ± S.D. ($n = 3$).

Table 3
Recovery of the method[a]

Sample	Concentration ($ng\,g^{-1}$)	Added ($ng\,g^{-1}$)	Found ($ng\,g^{-1}$)	Recovery (%)
LWDHW	32.8	46	77.9	98.1
LWDHW	32.8	23	54.7	95.2
NHQXW	114	92	206	100
Licorice	16.8	34.5	52.9	105

[a] Mean of three replicates.

between the two methods are shown in Table 4. In each case, excellent agreements were observed between the two methods with the differences ranged from 0.6% to 7.2%. For the two analytical methods, statistical analysis of variance and the student's *t* tests suggest that at 95% confidence, the measured mercury concentrations are not significantly different from each other. It also should be noted that for peach leaves the result obtained by thermolysis-AAS agreed well with the certified value with only 2.2% difference; but the data obtained by ICP-MS was 9.3% higher than the certified value. It is likely that mercury contamination occurred in the sample per-treatment step prior to ICP-MS analysis.

3.3. Total Hg in TCMs

The total mercury in two sets of selected TCM drugs were determined by thermolysis-AA. The samples were analyzed direct without pre-treatment. The first set includes five different drugs produced from different manufacturing sources. Each drug contains cinnabar as part of the active ingredients, and the Hg concentrations determined for each sample are listed and compared in Table 5. The second set of samples consists of TCM herbs as well as drug products, which do not contain cinnabar as part of the formulation. The Hg determination results for these samples are listed in Table 6. The total Hg concentrations in these two sets of samples vary widely from $ng\,g^{-1}$ to $mg\,g^{-1}$. The Hg-thermolysis analyzer, however, is able to perform analysis of samples with this wide concentration range of Hg with high precision because of its equipment with two measuring cells. The precision (2.5–8.2% R.S.D.), as is slightly higher than the peach leaves, is considered very satisfactory in view of the highly complex matrices and the wide distribution of mercury compound types in these samples.

Table 4
Inter-method comparison between thermolysis-AA and ICP-MS

	Peach leaves	LWDHW	TWBXW
Mercury concentration ($ng\,g^{-1}$)			
Certified value	46 ± 6		
By thermolysis-AAS[a]	47 ± 2	166 ± 3	9.38 ± 0.23[b]
By ICP-MS[a]	50.5 ± 1	167 ± 4	9.82 ± 0.41[b]
Differences between thermolysis-AAS and ICP-MS (%)	7.2	0.6	4.6
Differences between certified and ICP-MS data (%)	9.3		

[a] Mean ± S.D. ($n = 3$).
[b] $mg\,g^{-1}$.

Table 5
The Hg contents in several TCM drugs containing cinnabar

TCMs	Number of replicates	Mean mercury concentration ($mg\,g^{-1}$)	S.D. ($mg\,g^{-1}$)	R.S.D. (%)
TWBXW-I	5	15.0	0.4	2.6
TWBXW-II	6	9.38	0.23	2.5
AGNHW	4	29.2	1.8	6.3
NHQXW	6	115[a]	5[a]	4.1
DQLS	3	76.1[a]	2.7[a]	3.5

[a] $ng\,g^{-1}$.

The results presented in Table 6 indicate that the Hg levels in different herbal medicines, such as licorice and alisma orientalis, are quite different. The licorice and alisma orientalis samples investigated here were grown in different soils, resulted in different Hg concentrations because of different pollution levels. Factors affecting mercury uptake in plant include soil organic content, carbon exchange capacity, oxide and carbonate contents, redox potential, speciation and total content of mercury [17–19]. With increasing levels of mercury pollution, the amounts in plants increase correspondingly. Besides, from the data listed in Table 6, it also can be seen that mercury concentrations are considerably different (about two to four times) in cortex and xylem of the same licorice sample. This could be related to the metal transport mechanism in plant body where the metals moves initially from the bulk soils to the root cortex, and as the time proceeds, a small amount of mercury then transfers into xylem [20].

Since the raw materials in TCMs show natural variations in composition, the final products also vary, sometimes greatly, even under standardized manufacturing process. The Hg concentrations in the five selected TCM drugs contain-

Table 6
The Hg Concentrations in several TCM drugs uncontaining cinnabar

TCMs	Number of replicates	Mean mercury concentration ($ng\,g^{-1}$)	S.D. ($ng\,g^{-1}$)	R.S.D. (%)
LWDHW I-1	6	59.5	3.3	5.6
LWDHW I-2	5	166	5	2.7
LWDHW I-3	5	23036	783	3.4
LWDHW II-1	5	34.4	1.5	4.2
LWDHW II-2	4	23.2	0.8	3.6
LWDHW II-3	4	32.8	1.3	3.8
Cortex of licorice #1	6	29.2	0.9	3.0
Xylem of licorice #1	6	7.72	0.57	7.4
Cortex of licorice #2	6	15.0	0.7	4.5
Xylem of licorice #2	6	9.37	0.74	7.9
Cortex of licorice #3	6	13.1	0.5	3.9
Xylem of licorice #3	6	4.77	0.33	6.8
Cortex of licorice #4	6	16.8	0.9	5.1
Xylem of licorice #4	6	8.16	0.62	7.6
Alisma orientalis #1	5	7.59	0.59	7.9
Alisma orientalis #2	5	4.84	0.39	8.2
Alisma orientalis #3	5	5.11	0.41	8.0

ing cinnabar vary widely from sub-μg g^{-1} to mg g^{-1}. On the other hand, the external contamination either in processing or at the raw herbal sources should not be neglected. A comparison of mercury content in a series of LWDHW drugs, which do not contain cinnabar, shows that Hg concentrations in the same drug vary widely with their source of manufacturing and the difference even reaches one thousand times. Meanwhile, the Hg concentration in concentrated pill is in general much higher than that in diluted one, indicating that Hg was also concentrated during the process of drug concentration.

A previous study in our lab had indicated that the toxicity of cinnabar as a TCM drug is slight, but its toxic effects towards kidney and liver should not be ignored if the medicine is taken continuously for a prolonged time period [4]. But the Hg contents in some TCM drugs containing cinnabar are alarmingly high. For instance, according to the instructions on the packet of TWBXW-I and TWBXW-II (9 g and 12 g per day for adult, respectively), 135 mg and 113 mg of Hg per day, respectively, could be ingested by patient. Some TCM drugs which do not contain cinnabar, such as LWDHW, is also contaminated by the concomitant occurrence of mercurial ions in the drug, and the toxicity of mercury ions is known to be more serious than that of cinnabar. Hence, strict quality control to minimize the contents of cinnabar and contaminant mercury in TCM drugs is a top priority item requiring immediate action.

3.4. Thermal Hg releasing profiles of TCM samples

It is known that the inorganic mercury compounds have higher dissociation energy than organic ones [15,16]. Hence, the thermal releasing rate of organic-bound Hg-compounds is much faster than the inorganic ones. This can be seen from Fig. 2, in which the thermal releasing profiles (720 °C) of a synthetic mercury standard mixture spiked with graphite particles are shown. The standard mixture consists of Hg-cysteine and red HgS, representing

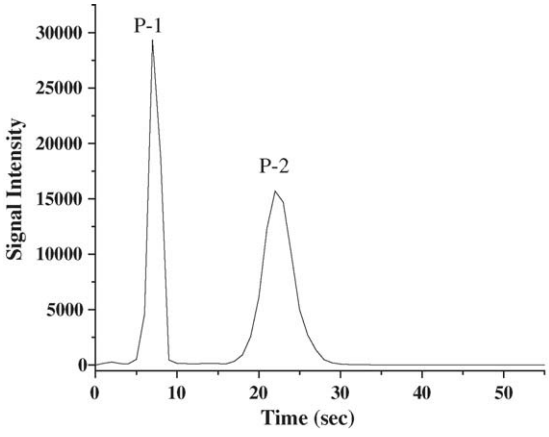

Fig. 2. Hg thermal releasing profiles from synthetic Hg standard mixture spiked with graphite particles at 720 °C. P-1: 35 ng g^{-1} Hg-cysteine; P-2: 50 ng g^{-1} red HgS.

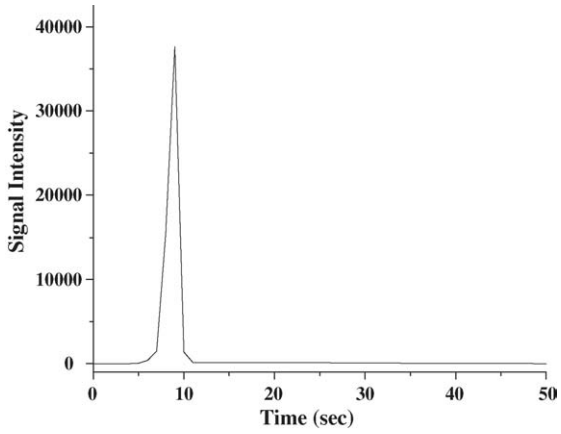

Fig. 3. Hg thermal releasing profiles from 46 ng g^{-1} peach leaves at 720 °C.

respectively organic-bound and inorganic mercury species. In the thermal releasing profiles obtained, Hg-cysteine (Peak-1) was released quickly, followed by HgS (Peak-2). Thus, it is possible that one could characterize different types of mercury species based on their different rate of release as is observed in the thermogram given in Fig. 2.

The thermogram of peach leaves as shown in Fig. 3 consists of a single sharp peak, which came out quickly, representing Hg released from matrices-bound Hg species. Nevertheless, for real TCM materials containing cinnabar, the thermal releasing profiles are more complicated than that of the peach leaves. Two well known TCM materials, i.e. TWBXW and AGNHW, are investigated in this study. Double peaks rather than a single one were observed at 720 °C. It can be seen from the thermogram of TWBXW (Fig. 4) that a very sharp peak came out quickly upon heating (the width was about 4 s), followed by the main peak after about 8 s. The width of the main peak was about 20 s at the base. The slight tailing of the second peak reflects the compositional complexity of the material. The reproducibility was considered very satisfactory with 2.6% R.S.D. ($n = 5$) on total peak areas. Similar results as presented in Fig. 5 were also obtained

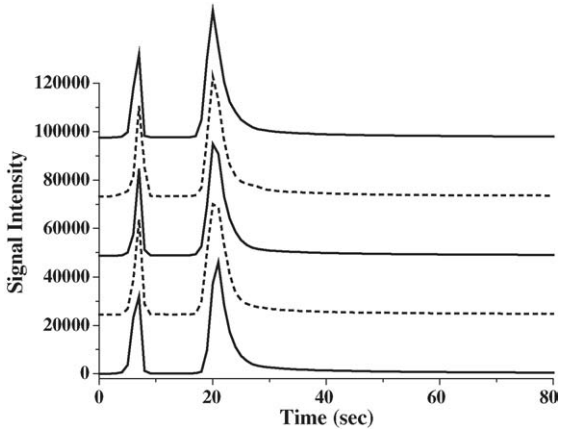

Fig. 4. Hg thermal releasing profile from 15.0 mg g^{-1} TWBXW at 720 °C, sampling: 5 mg (graphite diluted), R.S.D. = 2.6% ($n = 5$).

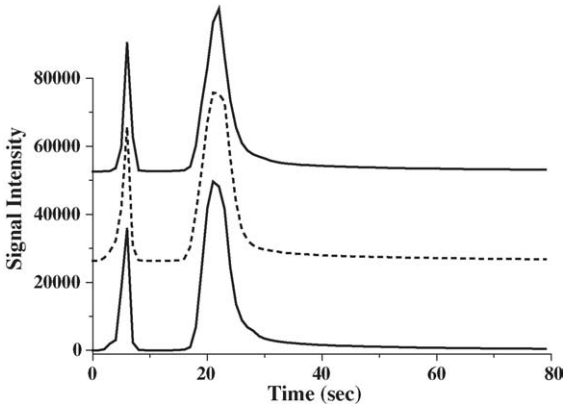

Fig. 5. Hg thermal releasing profile from 29.2 mg g^{-1} AGNHW at 720 °C, sampling: 2.5 mg (graphite diluted), R.S.D. = 4.9% (n = 3).

by thermal releasing Hg in AGNHW at the same analytical conditions as described above. The reproducibility was also fine with 4.9% R.S.D. (n = 3) on total peak areas.

It is rationalized that the double peaks observed in the thermgrams correspond to the different types of Hg-compounds in the TCM materials. The first peak probably originated from elemental Hg (Hg^0) and reducible Hg species as bound with the sample matrices, e.g. biological matrices-bound Hg. The second peak, however, represented possibly mercury released from inorganic Hg, mainly from cinnabar. The intensities of the first peak in TWBXW drug accounted for 18.1% of the total observed mercury signal intensities. And the percentage value was 14.8% for AGNHW drug. Nevertheless, for cinnabar, the proportion dropped to 10.4%. Comparison between cinnabar and TWBXW drug are shown in Fig. 6. It is speculated that the presence of other ingredients in the formulation of TWBXW and AGNHW could have aided to the mercury species conversion from inorganic forms to the organic matrices-bound ones. A previous study in our lab had also indicated the aid of biological matrices of TWBXW in the species transform from cinnabar to dissolvable mercury [21]. It also should be noticed that the Hg intensity proportion of the first peak for TWBXW is higher than that of the AGNHW drug. The major ingredients in TWBXW include tuckahoe, angelica, salvia, rehmanniae, figwort; but the major ingredients in AGNHW are bezoar, muskiness, Chinese goldthread, tulip and gardenia. It is therefore suggested that each ingredient in formulation could have different aid to the conversion between mercury compounds. The exact cause of the aid is in progress in our laboratory.

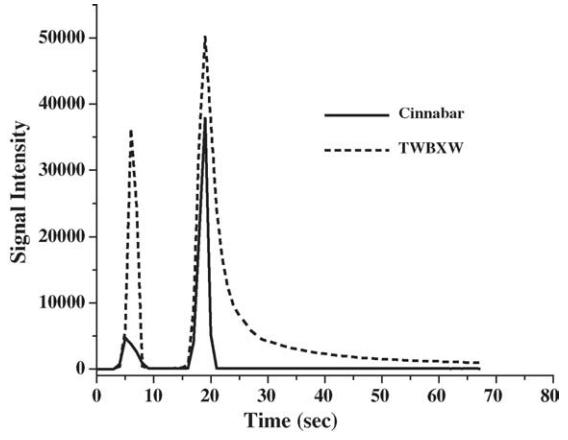

Fig. 6. Hg thermal releasing profile: TWBXW vs. Cinnabar. Sampling: 15.0 mg g^{-1} TWBXW, 5 mg (graphite diluted); 860 mg g^{-1} Cinnabar, 3 mg (graphite diluted).

4. Conclusions

The thermolysis-AA method established in this work is considered practical and reliable for the direct determination Hg in TCMs in the concentration range of ng g^{-1} to mg g^{-1}. It provides direct solid analysis, and is therefore fast and less prone to procedural contamination, a common problem in conventional methods. The method has been validated by the analysis of standard reference materials, recovery study, and inter-method comparison with ICP-MS. The Hg contents in different TCM drugs with widely different mercury concentrations have been analyzed by the technique. The mercury contents of the same drug but from different manufacturers differ widely, suggesting their origination from external contaminations either at the raw herbal sources or in the manufacturing process. In addition, comparison of mercury thermal releasing profiles between TCM drug and cinnabar suggests that mercury conversion from cinnabar to biological matrices-bound Hg could occur because of the aid of other ingredients in the formulated drug.

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References

[1] X.R. Wang, Z.X. Zhuang, D.H. Sun, J.X. Hong, X.H. Wu, F.S.C. Lee, Atom. Spectrosc. 20 (1999) 86.
[2] K.A. Graeme, C.V. Pollack, J. Emerg. Med. 16 (1998) 45.
[3] C.F. Zhou, Y.H. Lin, Chin. J. Chin. Mater. Med. 28 (2003) 1096.
[4] Z.Y. Huang, J.C. Shen, Z.Y. Huang, X.R. Wang, F.S.C. Lee, Appl. Organomet. Chem. 18 (2004) 255.
[5] F. Barbosa, C.D. Palmer, F.J. Krug, P.J. Parsons, J. Anal. Atom. Spectrom. 19 (2004) 1000.
[6] S.Q. Tao, S.F. Gong, L. Xu, J.C. Fanguy, Analyst 129 (2004) 342.
[7] M. Logar, M. Horvat, H. Akagi, B. Pihlar, Anal. Bioanal. Chem. 374 (2002) 1015.
[8] L.P. Yu, X.P. Yan, Atom. Spectrosc. 25 (2004) 145.
[9] G. Centineo, E.B. Gonzalez, A. Sanz-Medel, J. Chromatogr. A 1034 (2004) 191.
[10] I. Ipolyi, P. Massanisso, S. Sposato, P. Fodor, R. Morabito, Anal. Chim. Acta 505 (2004) 145.

[11] J. Qvarnstrom, W. Frech, J. Anal. Atom. Spectrom. 17 (2002) 1486.
[12] Z.Y. Huang, J.C. Shen, Z.X. Zhuang, X.R. Wang, F.S.C. Lee, Anal. Bioanal. Chem. 379 (2004) 427.
[13] G.E.M. Hall, P. Pelchat, Analyst 122 (1997) 921.
[14] H. Biester, G. Nehrke, Fresenius J. Anal. Chem. 3598 (1997) 446.
[15] S. Scholupov, S. Pogarev, V. Ryzhov, N. Mashyanov, A. Stroganov, Fuel Process. Technol. 85 (2004) 473.
[16] B. Chen, X.R. Wang, F.S.C. Lee, Anal. Chim. Acta 447 (2001) 161.
[17] U.H. Cho, J.O. Park, J. Plant Biol. 42 (1999) 41.
[18] A. Crowder, Environ. Pollut. 71 (1991) 171.
[19] M. Patra, A. Sharma, Bot. Rev. 66 (2000) 379.
[20] M. Patra, N. Bhowmik, B. Bandopadhyay, A. Sharma, Environ. Exp. Bot. 52 (2004) 199.
[21] X.H. Wu, D.H. Sun, Z.X. Zhuang, X.R. Wang, H.F. Gong, J.X. Hong, F.S.C. Lee, Anal. Chim. Acta 453 (2002) 311.