ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/245172237

Direct determination of mercury in white vinegar by matrix assisted photochemical vapor generation atomic fluorescence spectrometry detection

ARTICLE *in* SPECTROCHIMICA ACTA PART B ATOMIC SPECTROSCOPY · JULY 2010

Impact Factor: 3.18 · DOI: 10.1016/j.sab.2010.06.004

CITATIONS
22

READS
66

1 AUTHOR:

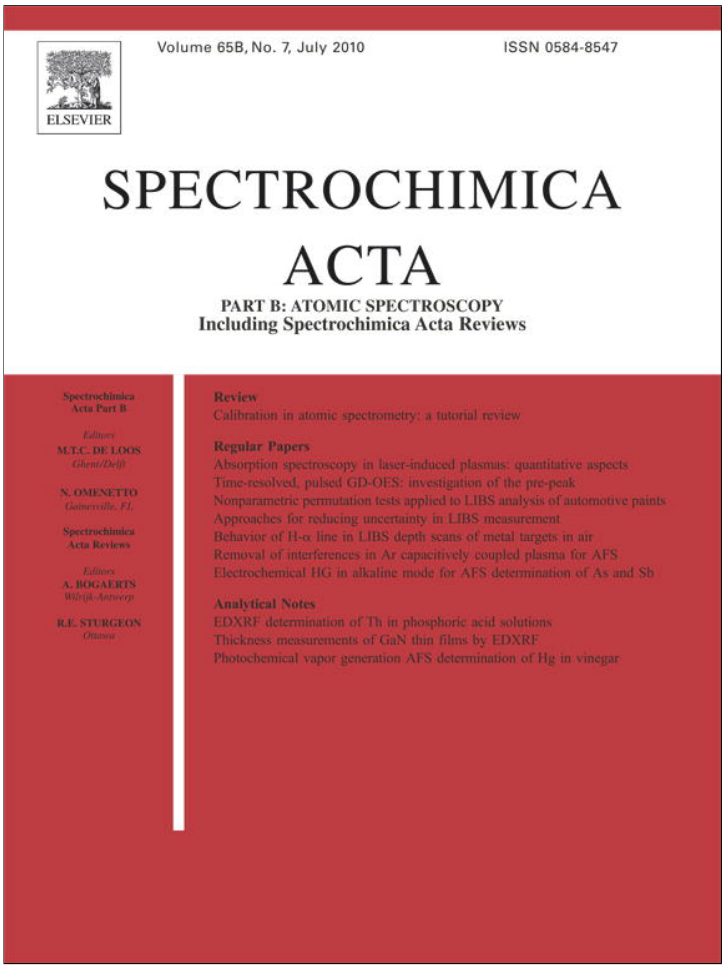
Qingyang Liu
Nanjing Forestry University
33 PUBLICATIONS **265** CITATIONS

SEE PROFILE

All in-text references underlined in blue are linked to publications on ResearchGate, letting you access and read them immediately.

Available from: Qingyang Liu
Retrieved on: 02 February 2016

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Author's personal copy

Spectrochimica Acta Part B 65 (2010) 587–590

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Analytical note

Direct determination of mercury in white vinegar by matrix assisted photochemical vapor generation atomic fluorescence spectrometry detection

Qingyang Liu *

Beijing Center for Physical and Chemical Analysis, Beijing 100089, China

ARTICLE INFO

Article history:
Received 16 April 2010
Accepted 9 June 2010
Available online 15 June 2010

Keywords:
Acetic acid
Photochemical vapor generation
Atomic fluorescence spectrometry
Mercury
White vinegar

ABSTRACT

This paper proposes the use of photochemical vapor generation with acetic acid as sample introduction for the direct determination of ultra-trace mercury in white vinegars by atomic fluorescence spectrometry. Under ultraviolet irradiation, the sample matrix (acetic acid) can reduce mercury ion to atomic mercury Hg^0, which is swept by argon gas into an atomic fluorescence spectrometer for subsequent analytical measurements. The effects of several factors such as the concentration of acetic acid, irradiation time, the flow rate of the carrier gas and matrix effects were discussed and optimized to give detection limits of 0.08 ng mL^{-1} for mercury. Using the experimental conditions established during the optimization (3% v/v acetic acid, 30 s irradiation time and 20 W mercury lamp), the precision levels, expressed as relative standard deviation, were 4.6% (one day) and 7.8% (inter-day) for mercury ($n=9$). Addition/recovery tests for evaluation of the accuracy were in the range of 92–98% for mercury. The method was also validated by analysis of vinegar samples without detectable amount of Hg spiked with aqueous standard reference materials (GBW(E) 080392 and GBW(E) 080393). The results were also compared with those obtained by acid digestion procedure and determination of mercury by ICP-MS. There was no significant difference between the results obtained by the two methods based on a *t*-test (at 95% confidence level).

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Vinegar is produced from a suitable raw material of agriculture origin by alcoholic and acetous fermentation. Traditionally, the main difference between Chinese vinegars and European vinegars is that Chinese vinegars are mainly produced from rice, sticky rice and wheat bran, while European vinegars are usually fermented from wine, cider, fruit juices, malted barley, honey and pure alcohol. Commercial vinegars are divided into five groups, namely, aromatic vinegar, mature vinegar, rice vinegar, white vinegar and fruit vinegar. The average acidity of aromatic, mature, rice and white vinegar were ranged from 3.0% to 6.0% v/v. The acidity of fruit vinegar was in the range of 2.0% to 3.0% v/v [1]. Heavy metal contamination could come into the vinegar through raw material. Due to its high demand in Asian, European, Western, and other traditional cuisines of the world, it has been considered necessary to investigate reliable analytical method to control food quality and safety [2]. Although several studies have been published on the determination of lead in vinegar, few studies are focused on the determination of mercury in vinegar [3, 4].

Mercury contamination is usually present at low levels in food samples, so that sensitive analytical techniques are required for its determination, such as inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GFAAS) and atomic fluorescence spectrometry (AFS) [5–7]. Sample pretreatment prior to the instrumental analysis is time-consuming. Therefore, the direct determination of toxic elements in liquid samples without any pretreatment step is important in atomic spectrometry [4]. Vinegar is a complex matrix that contains water, sugar, salt alcohol and glucose, and other organic substances [3]. Direct introduction of vinegar sample to ICP-MS could provoke plasma instability and accumulation of carbon deposits on the cones and lens. During the GFAAS analysis, incomplete pyrolysis of the organic matter produces fumes and accumulation of carbonaceous residue after several graphite tube firings, which affect the analysis [3].

Interest in, and the need for, direct determination of Hg in aqueous samples based on matrix assisted photochemical vapor generation have led to significant progress in the development of atomic fluorescence spectrometry [8]. Photochemical vapor generation is an emerging research field in atomic fluorescence spectrometry which may provide a powerful alternative to conventional chemical vapor generation owing to its simplicity, versatility and cost-effectiveness [9–11]. Guo and Sturgeon reported the photochemical vapor generation as alternative sample introduction technology coupled with AFS and ICP-MS for selenium determination [12]. Later, Zheng et al. [13] and Bendl et al. [14] have both successfully detected mercury following photochemical vapor generation in a UV/formic acid-AFS

* Corresponding author. Tel.: +86 010 68719783.
E-mail address: liuqingyang0807@yahoo.com.cn.

0584-8547/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2010.06.004

Author's personal copy

and UV/acetic acid-AAS system, respectively. More recently, these observations have been applied in mercury speciation analysis [15–19].

This study reports a sensitive and reliable method for direct determination of mercury in white vinegar samples by AFS based on matrix assisted photochemical vapor generation technology. Analysis of vinegar samples without detectable amount of Hg spiked with aqueous standard reference materials (GBW(E) 080392 and GBW(E) 080393) and acid digestion-ICP-MS method were carried out for validation of the method.

2. Experimental

2.1. Reagents and instrumentation

The mercury compounds (mercury chloride, monomethylmercury chloride and monoethylmercury chloride) were purchased from Merck (99%, Darmstadt, Germany). Working standard solutions of $HgCl_2$ were obtained by appropriate dilution of the stock standard solutions in 3% (v/v) acetic acid. Individual stock solutions of organo-mercury chloride were prepared by dissolving appropriate amounts of monomethylmercury chloride (MeHg) and monoethylmercury chloride (EtHg) in methanol, respectively. A Milli-Q (Dubuque, IA, USA) system which can supply 18.2 MΩ cm water was used to prepare the solution. All the reagents were purchased from Beijing Chemicals (Beijing, China). All solutions were stored at 4 °C in the refrigerator.

The analytical system comprises two main subsystems: a photochemical vapor generation and an AFS-9800 atomic fluorescence spectrometer (Beijing Haiguang Instrument Co., China) are used. The default intermittent reactor was replaced by a laboratory-constructed flow through photo reactor [17]. In order to assess the accuracy of the proposed method, an Agilent 7500ca ICP-MS was also used in this work as element mass detector. Mercury was detected at m/z 202. The optimized instrumental parameters for the AFS and ICP-MS determination of mercury are listed in Table 1.

2.2. Sample preparation and analytical procedures

White vinegar samples were purchased from local markets and used without any pretreatment. Spiked vinegar solutions were prepared by adding a certain amount of $HgCl_2$ standard solution. The standard solution with 3% v/v acetic acid was suck into the UV digestion reactor for 15 s, and then irradiated by UV for another 30 s. Then the solution was carried to the gas-liquid separator by argon gas, and mercury vapor was separated and introduced into the AFS spectrometer for detection. The signal intensity was integrated for 35 s and the instrument was stopped for 8 s to prepare for the next measurement. For ICP-MS determination, 2 mL portions of vinegar samples were added to a 25 mL Teflon container, and 1 mL concentrated HNO_3 and then 1 mL concentrated H_2O_2 were added. The container was then placed in a stainless steel bomb, then sealed with a screw closure, placed in an oven and heated at 180 °C for 1 h. The digested solution was diluted to 10 mL with de-ionized water for analysis. A blank sample was prepared at the same time. Two standard reference materials, GBW(E) 080392 (certified Hg concentration: 10 ± 0.1 μg L^{-1}) and GBW(E) 080393 (certified Hg concentration: 100 ± 1 μg L^{-1}) were also analyzed to assess the method accuracy. They were diluted (1 + 4, v/v) in blank white vinegar and then analyzed by photochemical vapor generation-AFS and acid digestion-ICP-MS method, respectively.

Table 1
The parameters of AFS and ICP-MS system.

Parameters	Optimized values
AFS	
Power of UV lamp	Mercury lamp, 20 W
Reaction coil	PTFE tube, 3 m × 0.5 mm i.d.
Lamp	Mercury hollow cathode lamp, 253.7 nm
PMT voltage	280 V
Lamp current	40 mA
Flow rate of carrier gas	300 mL min^{-1}
ICP-MS	
Forward power	1500 W
Flow rate of carrier gas	800 mL min^{-1}
Flow rate of makeup gas	300 mL min^{-1}
Sample uptake rate	1.5 mL min^{-1}
Flow rate of plasma gas	12 L min^{-1}
m/z	202
Integration time	1 s (3 times)

3. Results and discussion

3.1. Effects of irradiation time

In our system, only one UV lamp and peristaltic pump supplied by the manufacturer was utilized to realize the transformation of mercury species in the white vinegar. No other chemical reagent was needed. The PTFE tube enlaced outside the UV lamp was 3 m in length and 0.5 mm in inner diameter [17]. The efficiency of photochemical vapor generation is critical for atomic fluorescence detection. In this system, a solution containing 20 ng mL^{-1} mercury with 3% acetic acid matrix (v/v) was used to investigate the effects of irradiation time on the photochemical vapor generation. In the presence of 3% acetic acid (v/v), 30 s irradiation time was enough for the photo reduction of mercury, as shown in Fig. 1. With the increase of irradiation time, the signal intensity decreases slightly. Therefore, 30 s irradiation time was selected as the optimized condition.

3.2. Effects of acetic acid concentration

The UV generation efficiency was found to be dependent on the acetic acid concentration. As shown in Fig. 2, the intensity of fluorescence increased with the concentration of acetic acid and a plateau appeared when its concentration was around 3%. No notable negative effects were produced on the Hg signal intensity, when the concentration of acetic acid was further increased. The mechanism for photo reduction of Hg (II) by acetic acid is based on free CO radical generation. The CO arising from the photolysis of acetic acid provides

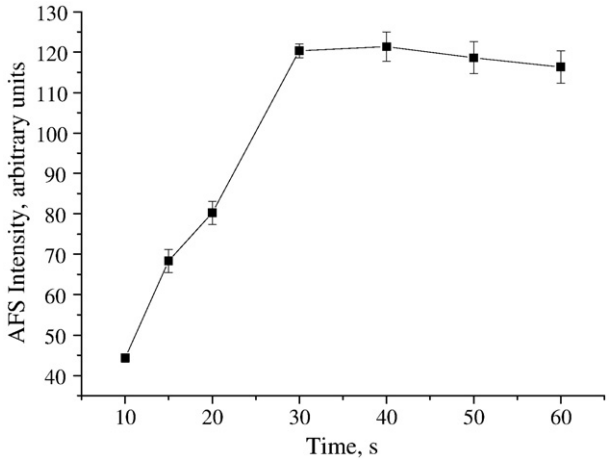


Fig. 1. Effects of irradiation time on mercury intensity (20 μg L^{-1}, 3% v/v acetic acid). Uncertainties, shown by the error bars, are expressed as the standard deviation for $n = 5$.

Author's personal copy

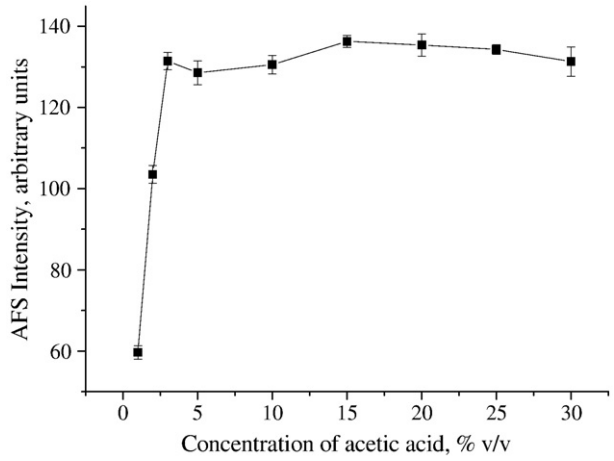


Fig. 2. Effects of acetic acid concentration on mercury intensity (20 μg L^{-1}, 30 s irradiation time). Uncertainties, shown by the error bars, are expressed as the standard deviation for $n = 5$.

the initial reagents that drive the overall process [11]. The amount of CO radicals increased with the concentration of acetic acid. Hence, the rate of reaction accelerated and resulted in the increase in the intensity. Finally, 3% acetic acid was chosen for use.

3.3. Effects of flow rate of carrier gas

Argon was used as carrier gas to bring mercury vapor from liquid phase to gas phase. The effect of argon flow rate on detection of mercury was studied from 200 mL min^{-1} to 900 mL min^{-1}. At 200 mL min^{-1}, the baseline was not stable. Better baseline could be obtained by increasing the argon gas flow. Increasing the flow rate of the carrier gas, the intensity of mercury decreased slightly, owing to dilution and shorter residence time of mercury vapor in the atomizer. An argon carrier gas flow rate of 300 mL min^{-1} was chosen as an optimized condition.

3.4. Matrix effects

Except for white vinegar, other types of vinegar all contain sugar [1]. The addition of sugar to the acetic acid solution was assessed to find its effect on the vapor generation efficiency. The tolerance limits of a foreign species as the concentration that cause a relative error greater than ±5% [1]. The results suggest negative interference from sugar, their effect on the analytical response could exceed ±10% at interference concentration of 1% v/v. Therefore, only white vinegar was selected in the real sample analysis.

The presence of organo-mercury species that could interference with the analysis of mercury in vinegar, due to their reactivity with acetic acid, may be of concern in the analysis of real samples [20]. In order to seek experimental evidence, the mercury speciation method established in our previous work was adopted to analysis the samples (Supporting Information) [17]. The sample solution was injected into the C18 column directly without any pretreatment. No organo-mercury compounds were found in real samples. As the concentration of organo-mercury compounds in natural liquids is normally at ng L^{-1} level [21, 22], these observations ensure there are no negative repercussions on the quality of the analytical results.

The major drawbacks of hydride generation are the interferences caused by the transition elements and notable metals, especially Fe, Co, Ni and Cu, because their metallic state and colloidal forms are formed in KBH_4 solution. In comparison with hydride generation, no significant interference was observed, even at concentration as high as 20 mg L^{-1} for Fe, 10 mg L^{-1} for Co and Cu, and 1 mg L^{-1} for Ni.

3.5. Analytical performance and potential applications

Analytical characteristics were established under optimal conditions for photochemical vapor generation. The equations for the calibration lines using peak area of the atomic fluorescence signal were as follows: $Y = 15.62C + 2.25$, $r^2 = 0.9995$, where Y is integrated absorbance and C is a Hg concentration (expressed as μg L^{-1}). The calibration curves were linear at least up to Hg concentration of 1 mg L^{-1}. Limits of detection (LODs) based on peak area measurement were 0.08 μg L^{-1}. These LODs compare well with those reported for the use of photochemical vapor generation in both batch and on-line systems (Table 3). The repeatability expressed as relative standard deviation for $n = 9$ measurements was 4.6% (one day) and 7.8% (inter-day) for mercury determination at the concentration of 5 μg L^{-1}, respectively.

Since there are no appropriate certified reference materials available in order to check the accuracy of the method, spike recovery experiments (vinegar samples spiked with mercury standard solution), acid digestion-ICP-MS method and analysis of blank white vinegar spiked with certified reference aqueous samples were also carried out in this work. The analytical results of the proposed method are in good agreement with acid digestion-ICP-MS method. The t-test was used to validate the significant differences between the certified value and determined value of GBW(E) 080392 and GBW(E) 080393, and also between the results obtained by AFS and ICP-MS, with no significant difference found at 95% confidence level. Furthermore, the proposed method was used to for the analysis the real samples collected in commercial markets. The recoveries are in the range of 92–98% (Table 2). It is appropriate to apply the method for the determination of mercury in commercial white vinegar, since the acetic acid concentration of commercial vinegar is almost 3%, which is in good agreement with the optimized condition.

Table 2
Analytical results of mercury in white vinegar (μg L^{-1}).

Sample	Acidity[a]	Method	Mercury concentration[b]	Spiked concentration	Recovery (%)[c]	Certified values
GEW(E)080392	3.0	AFS	9.6 ± 0.5			10 ± 0.1
		ICP-MS	9.2 ± 0.3			
GEW2(E)080393	3.0	AFS	93 ± 2.3			100 ± 1
		ICP-MS	91 ± 4.0			
White vinegar 1	3.5	AFS	n.d[d].	5	92	
		ICP-MS	n.d.	5	94	
White vinegar 2	3.95	AFS	n.d.	5	98	
		ICP-MS	n.d.	5	96	
White vinegar 3	4.0	AFS	1.8 ± 0.2	5	93	
		ICP-MS	2.0 ± 0.3	5	95	

[a] As acidity expressed in % acetic acid.
[b] Average ± 3 × standard deviation of 3 replicate.
[c] Spiked recovery: Vinegar samples spiked with mercury standard solution.
[d] n.d.: AFS after UV vapor generation <0.08 μg L^{-1}, ICP-MS, after acid digestion <0.06 μg L^{-1}).

Author's personal copy

Table 3
Comparisons of mercury determination by photochemical vapor generationatomic fluorescence spectrometry detection (μg L^{-1}).

Reductant	Pretreatment step	Sample	Detection limits	Reference
Acetic acid	Acid digestion	Dogfish liver	2.1	[14]
Formic acid	Direct introduction	Water sample	0.003	[13]
Mercaptoethanol	Acid digestion	Environmental samples/biological samples	0.06	[23]
Ethanol	Direct introduction	wine	0.07	[8]
Acetic acid	Direct introduction	vinegar	0.08	This work

4. Conclusions

In this work, the direct determination of the trace level of mercury in white vinegar by AFS based on matrix assisted photochemical vapor generation has been described. Under the optimized conditions applied in this study, reproducible and accurate analysis results for mercury in white vinegar were accomplished. Besides, the proposed method can serve as sample introduction method for screening of mercury contamination in vinegar samples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.sab.2010.06.004.

References

[1] Q.Y. Zhang, S.P. Zhang, C.S. Xie, Characterization of Chinese vinegars by electronic nose, Sensor Actuat. B 119 (2006) 538–546.
[2] M.J. Saiz-Abajo, J.M. Gonzalea-Saiz, C.H. Pizarro, Prediction of organic acids and other quality parameters of wine vinegar by near-infrared spectroscopy. A feasibility study, Food Chem. 99 (2006) 615–621.
[3] N. Kuria, H. Sharon, Determination of lead in vinegar by ICP-MS and GFAAS: evaluation of different sample preparation procedures, Talanta 64 (2004) 258–263.
[4] S.R. Oliveira, J.A. Gomes, Evaluation of Bi as internal standard to minimize matrix effects on the direct determination of Pb in vinegar by graphite furnace atomic absorption spectrometry using Ru permanent modifier with co-injection of Pd/Mg $(NO_3)_2$, Spectrochim. Acta Part B 62 (2007) 1046–1050.
[5] M. Resano, I. Gelaude, R. Dams, Solid sampling–electrothermal vaporization–inductively coupled plasma mass spectrometry for the direct determination of Hg in different materials using isotope dilution with a gaseous phase for calibration, Spectrochim. Acta Part B 31 (2005) 319–326.
[6] B. Izgi, C. Demi, S. Guçer, Application of factorial design for mercury determination by trapping and graphite furnace atomic absorption spectrometry, Spectrochim. Acta Part B 55 (2000) 971–977.
[7] J.L. Gomez-Ariza, F. Lorenzo, T. Garcia-Barrera, Guidelines for routine mercury speciation analysis in seafood by gas chromatography coupled to a home-modified AFS detector. Application to the Andalusian coast (south Spain), Chemosphere 61 (2005) 1401–1409.
[8] Y. Li, C.B. Zheng, X.D. Hou, Sample matrix-assisted photo-chemical vapour generation: a reagent free green analytical method for ultrasensitive detection of mercury in wine or liquor samples, J. Anal. At. Spectrom. 21 (2006) 82–85.
[9] R.E. Sturgeon, X. Guo, Z. Mester, Chemical vapor generation: are further advances yet possible ? Anal. Bioanal. Chem. 382 (2005) 881–883.
[10] Y.H. He, X.D. Hou, R.E. Sturgeon, Critical evaluation of the application of photochemical vapor generation in analytical atomic spectrometry, Anal. Bioanal. Chem. 388 (2007) 769–774.
[11] C.F. Han, C.B. Zheng, X.D. Hou, Photo-induced cold vapor generation with low molecular weight alcohol, aldehyde, or carboxylic acid for atomic fluorescence spectrometric determination of mercury, Anal. Bioanal. Chem. 388 (2007) 825–830.
[12] X.M. Guo, R.E. Sturgeon, UV vapor generation for determination of selenium by heated quartz tube atomic absorption spectrometry, Anal. Chem. 75 (2003) 2092–2099.
[13] C.B. Zheng, Y. Li, Y. He, X.D. Hou, Photo-induced chemical vapor generation with formic acid for ultrasensitive atomic fluorescence spectrometric determination of mercury: potential application to mercury speciation in water, J. Anal. At. Spectrom. 20 (2005) 746–750.
[14] R.F. Bendl, J.T. Madden, A.L. Regan, N. Fitzgerald, Mercury determination by cold vapor atomic absorption spectrometry utilizing UV photoreduction, Talanta 68 (2006) 1366–1370.
[15] Y.Y. Yin, J.F. Liu, G.B. Jiang, Simple interface of high-performance liquid chromatography–atomic fluorescence spectrometry hyphenated system for speciation of mercury based on photo-induced chemical vapor generation with formic acid in mobile phase as reaction reagent, J. Chromatogr. A 1181 (2008) 77–82.
[16] Y. Yin, J.F. Liu, B. He, G..B. Jiang, Photo-induced chemical vapour generation with formic acid: novel interface for high performance liquid chromatography-atomic fluorescence spectrometry hyphenated system and application in speciation of mercury, J. Anal. At. Spectrom. 22 (2007) 822–826.
[17] Q.Y. Liu, Determination of mercury and methylmercury in seafood by ion chromatography using photo-induced chemical vapor generation atomic fluorescence spectrometry, Microchem. J. 95 (2010) 255–258.
[18] Y.Y. Yin, J.F. Liu, G.B. Jiang, Photo-induced chemical vapour generation with formic acid: novel interface for high performance liquid chromatography-atomic fluorescence spectrometry hyphenated system and application in speciation of mercury, J. Anal. At. Spectrom. 22 (2007) 822–826.
[19] Y. Yin, J. Liang, L. Yang, Q.Q. Wang, Vapour generation at a UV/TiO_2 photocatalysis reaction device for determination and speciation of mercury by AFS and HPLC-AFS, J. Anal. At. Spectrom. 22 (2007) 1–5.
[20] Y.G. Yin, J.F. Liu, G.B. Jiang, Mercury speciation by a high performance liquid chromatography-atomic fluorescence spectrometry hyphenated system with photo-induced chemical vapor generation reagent in the mobile phase, Microchim. Acta 167 (2009) 289–295.
[21] Y.X. Mao, G.L. Liu, G. Meichel, Y. Cai, Simultaneous speciation of monomethylmercury and monoethylmercury by aqueous phenylation and purge-and-trap preconcentration followed by atomic spectrometry detection, Anal. Chem. 80 (2008) 7163–7168.
[22] E. Lanzillotta, C. Ceccarini, R. Ferrara, Photo-induced formation of dissolved gaseous mercury in coastal and offshore seawater of the Mediterranean basin, Sci. Total Environ. 300 (2002) 179–187.
[23] Y. Yin, J.H. Qiu, L.Q.Q. Wang, A new vapor generation system for mercury species based on the UV irradiation of mercaptoethanol used in the determination of total and methylmercury in environmental and biological samples by atomic fluorescence spectrometry, Anal. Bioanal. Chem. 388 (2007) 831–836.