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ORIGINAL PAPER

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Determination of trace bismuth by flow injection-hydride generation collection-atomic absorption spectrometry

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Abstract Bismuth hydride gas was collected on-line and determined via a new flow injection-hydride generation collection-flame atomic absorption spectrometry system. The performance of the gas-liquid separator, hydride gas collection time, acidity of the sample solution, $NaBH_4$ concentration, and the effects of concomitant interferents were investigated to optimize the conditions of this new method. Interferences from concomitant elements were investigated, and recoveries of 94.7–105.3% for 10 ng mL^{-1} Bi were obtained after the addition of 0.2% ascorbic acid-thiourea masking reagents. The sensitivity of this new method was one order of magnitude higher than the continuous flow-hydride generation-flame atomic absorption method with a detection limit of 0.25 ng mL^{-1} and a precision of 2.3%. The method was evaluated by determining trace bismuth in standard biological reference material human hair GBW07601, and the results were consistent with the certified value. The proposed method was then employed to determine trace bismuth in ten colored gelatin samples; recoveries of 94.2–105.8% were obtained.

Keywords Hydride collection · Gas-liquid separator · Bismuth · Atomic absorption spectrometry

Introduction

Bismuth has been widely used in industry and medication in recent years. The effects of bismuth are influenced mainly by its concentration in materials [1, 2, 3]. The concentration of bismuth in colored gelatin films determines the quality of the film [4], which makes the determination of the trace amounts of bismuth necessary.

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Hydride generation-atomic spectrometry is a sensitive method to determine hydride-forming elements free from many interferences. Since the generation of hydride is by itself a process of separation and pre-concentration and is capable of being coupled with many detectors, it has been one of the most effective methods for the separation and pre-concentration of various hydride-forming elements for decades. [5, 6, 7, 8].

However, there are still several unsolved problems concerning this hydride generation method. Firstly, the further concentration of hydride gas is difficult. Secondly, all the metal hydrides are prone to be oxidized into metals that would be easily adsorbed in the flowing manifold causing serious memory effects and transportation problems. Thirdly, the generation of hydrides is not complete, and suffers interferences from matrix elements. In addition, it is very difficult for the generated hydrides to separate from solvents and volatile acids that are also source of interferences. To overcome these problems, cold-trap [9] and graphite furnace methods [10] were used to capture metal hydrides; all kinds of effective gas-liquid separators [11, 12, 13] were designed to obtain ideal analysis performance for this method. The interferents existing in the matrix were masked or removed by on-line redox [6, 14].

In this work, a flow injection-hydride generation collection-flame atomic absorption spectrometry (FI-HGC-FAAS) system was developed for the rapid pre-concentration and determination of bismuth. Hydride gas was collected on-line after flow injection sampling. The collected hydride gas was free from the dilution effects of carrier gas, which enabled higher sensitivity of the new system. Trace bismuth in a biological standard sample and gelatins were determined to evaluate the accuracy of the proposed method.

Experimental

Instrumentation

A diagram of the FI-HGC-FAAS system is shown in Fig. 1, which consisted of a Perkin-Elmer-3100 atomic absorption spectrometer

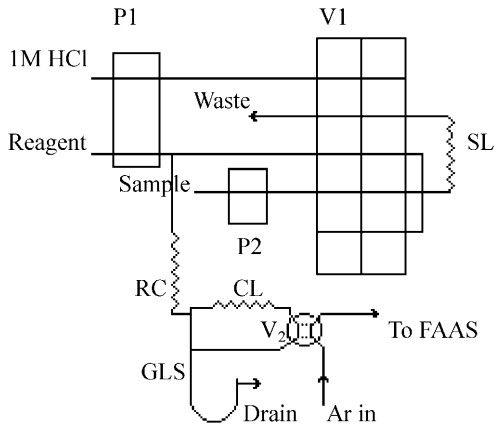

Fig. 1 Manifold for FI-HGC-FAAS diagram. *P1*,*P*2 peristaltic pumps, *V*1 sampling valve, *V*2 four-way valve, *SL* sampling loop, *KR* knotted reactor, *CL* collection loop, *GLS* gas-liquid separator, *C* 1 M HCl carrier. *R* $NaBH_4$+NaOH, *S* sample, *W* waste, *Ar* carrier gas

Table 1 Operating process for FI-HGC-FAAS system

Action	P1	P2	V1	V2	Time (s)
Sample intake	Off	On	A[a]	A	30
Hydride collection	On	Off	B[b]	A	40
Detection	Off	Off	B	B	60
Post-wash	On	Off	B	A	20

[a]Position A meant that V1 and V2 were at the status shown in Fig. 1.
[b]Position B referred to the contrary status of V1 or V2 to that shown in Fig. 1.

with acetylene-air flame, an acetylene flame-heated graphite furnace, two LP-2A speed-variable peristaltic pumps (P1, P2), a LZ-1020 type auto/manual multi-function valve (V_1), a lab-made four-way valve (V_2), and a gas-liquid separator (GLS). The graphite furnace was a round lab-made one for the atomization of the hydride. The three-dimensionally knotted reaction coil (RC) and 2.0 mL sample loop (SL) were all made from Teflon tube with an i.d. of 0.8 mm. The collection loops (CL) were made from different materials as stated later. Peak profiles were printed by a RW-11T electronic recorder (Tokyo, Japan). The operating process of the FI-HGC-FAAS system is shown in Table 1.

Comparative analyses were also carried out by using continuous flow-hydride generation-flame atomic absorption spectrometry (CFHG-FAAS) method and FAAS direct determination on the same Perkin-Elmer-3100 atomic absorption spectrometer.

Reagents and samples

Bi standard solutions were prepared by gradually diluting stock solution (Research Center of Standard Materials of China) containing 1000 μg mL^{-1} Bi with concentrated HCl and ultrapure water.

All the reagents used were of analytical-reagent grade, and water was ultrapure. Sodium borohydride (E. Merck, Darmstadt) was dissolved in ultrapure water with NaOH (0.1 g) to a concentration of 0.1–0.6%. This solution was always freshly prepared and kept in a refrigerator at 4 °C.

Ascorbic acid (2.0 g, Shanghai Chemical Reagent Co., Shanghai, China) and thiourea (2.0 g, Shanghai Chemical Reagent Station, Shanghai, China) were dissolved in ultrapure water (100 mL) to afford a 2.0% (*m*/*v*) solution of masking reagents, which was also kept in low temperature.

Biological reference material human hair GBW07601 and ten colored gelatin samples produced in China, Japan, and France were determined by the proposed method in this work to evaluate its accuracy and effectiveness.

Sample preparation

Human hair sample (0.25 g) was put in 50 mL beakers with HNO_3 (10 mL) and $HClO_4$ (0.5 mL) and then heated on an electric plate at 100 °C. After all the solids had dissolved entirely and the solution became brighter, the heating temperature was increased to 150 °C to let the solutions react with $HClO_4$ and residual $HClO_4$ was then vaporized until white smoke vanished from the beakers. Residual solids were dissolved in 1 M HCl to a total volume of 25 mL including the addition of 2.5 mL 2.0% mixed masking reagent of ascorbic acid and thiourea.

Colored gelatin samples were digested using the oxidization-hydrolyzation method [4]. One gram each of the samples was put into beakers and ultrapure water (20 mL) was added to swell the gelatin for 15 min. Then, concentrated HCl (1 mL) and concentrated HNO_3 (1 mL) were added and the beakers were then heated to 130 °C for two hours. After that, $HClO_4$ (0.5 mL) was added to guarantee complete digestion at 150 °C. Residual acids were vaporized while the residuals were treated as for the human hair sample.

Results and discussion

Effects of gas-liquid separator

Gas-liquid separator (GLS) was one of the most important components of the hydride-generation method [15]. The GLS configuration, volume, and the designation of the inlet and outlet modes were all important for the improvement of the analytical performance. As shown in Fig. 2, four lab-made gas-liquid separators GLS 1–GLS 4 were investigated for their effectiveness in the FI-HGC-FAAS method. The volumes of GLS 1 and GLS 2 were 3 mL, while the volumes of GLS 3 and GLS 4 were 5 mL. The configuration of GLS 2 was different from the other three separators. The configurations of GLS 1, GLS 3, and GLS 4 were similar, but their inlet and outlet modes for gas and liquid were all different.

Experiments were carried out separately by employing four gas-liquid separators GLS 1–GLS 4 under similar conditions. The FI-HGC-FAAS determining absorbance (*A*, *n*=3) of 10 ng mL^{-1} Bi standard solution after 40 s collection were: *A*(GLS 1)=0.087±0.003, *A*(GLS 2)=0.161±0.013, *A*(GLS 3)=0.190±0.006, and *A*(GLS 4)=0.108±0.004. GLS 3 is more sensitive in the determination of bismuth than the other three, because its longer argon inlet tube led to larger effective volume. The sensitivity obtained by GLS 2 was also good, but the stability was poor. GLS 3 was therefore selected for further experiments.

Optimization of the operating conditions

Following the procedure indicated in Table 1, the effect of the different parameters of the new system on the Bi signal was investigated in a univariant search. Maximum peak height at the 306.8 nm line of Bi was selected as the

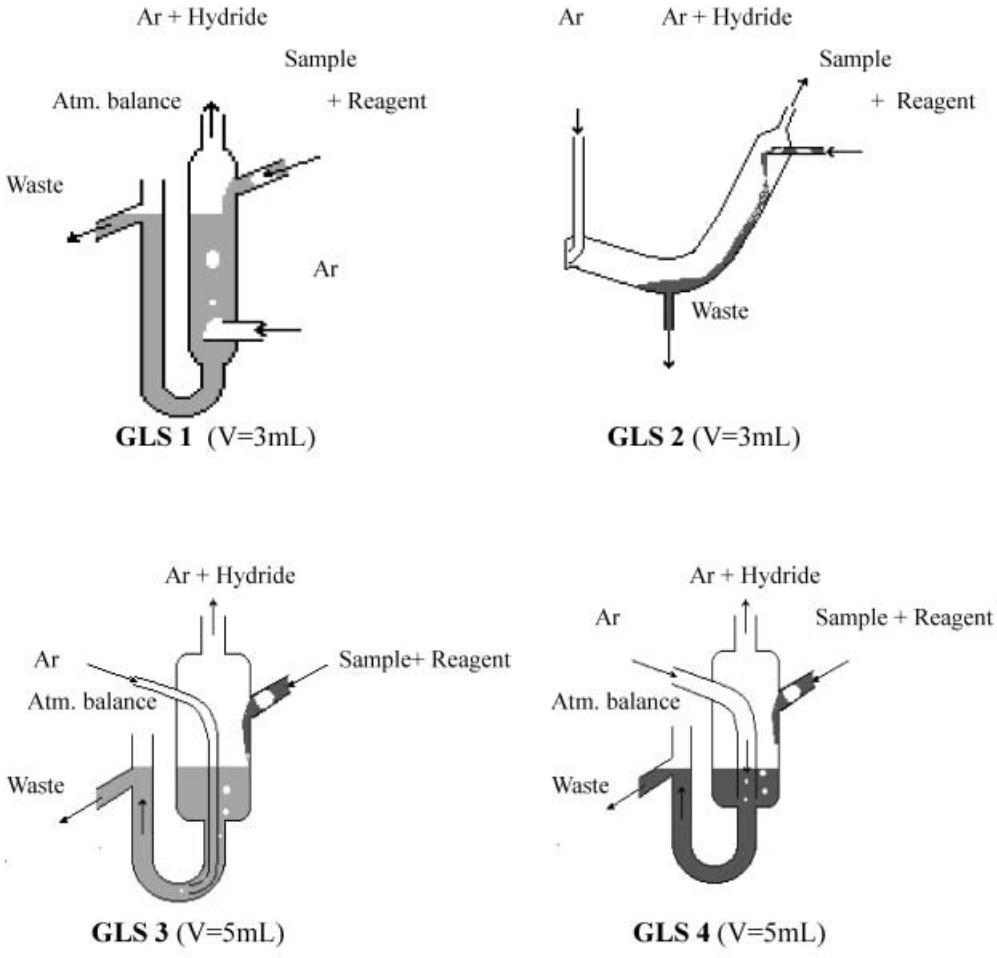

Fig. 2 Schematic diagrams of gas-liquid separators GLS 1–GLS 4

Table 2 Experimental conditions for Bi determination by FI-HGC-FAAS

Instrumental parameters	
Wavelength	306.8 nm
Lamp intensity	15 mA
Bandwidth	0.7 nm
Background correction	deuterium
Acetylene flow rate	1.5 mL min^{-1}
Argon flow rate	600 mL min^{-1}
Sample flow rate	4.0 mL min^{-1}
Flow parameters	
1 M HCl	1.5 mL min^{-1}
Reagent	1.5 mL min^{-1}
Sample	2.0 mL min^{-1}

optimization criterion. Optimum FAAS conditions and flow parameters in this experimental set-up were investigated, and the results are summarized in Table 2.

Optimization of chemical parameters

Sample acidity is a crucial parameter for hydride generation because of rapid hydrolysis of the $NaBH_4$ in even mild acidic conditions, and the competition between transition metal ions reacting with $NaBH_4$. The carrier and the sample were intentionally adjusted to be of the same acidity for fear of poor mixing when the sampling time was not long enough. As Fig. 3A shows, the signal was constant for an HCl concentration of 1.0–4.0 mol dm^{-1}. A sample acidity of 1.0 mol dm^{-1} HCl was therefore selected.

Experiments concerning the effect of $NaBH_4$ concentration on the Bi signal and blank value showed that the raw absorbance of Bi and the reagent blank absorbance increased when the concentration of $NaBH_4$ increased (Fig. 3B). But, the net absorbance of Bi did not increase after the concentration of $NaBH_4$ reached 0.5%. Therefore, 0.5% $NaBH_4$ +0.1% NaOH was selected.

Optimization of hydride gas on-line collection

It was reported that bismuth hydride (BiH_3) was not stable even when a cold-trap was used to concentrate it [16]. When bismuth hydride gas was directly collected on-line, the following factors must be considered: how long can this hydride gas keep stable during collection and transportation? How serious will the memory effect be? What will the concentrating efficiency be? Various collecting times and different type of collection loops were also investigated to get the optimum AAS signal of Bi according to the factors listed above.

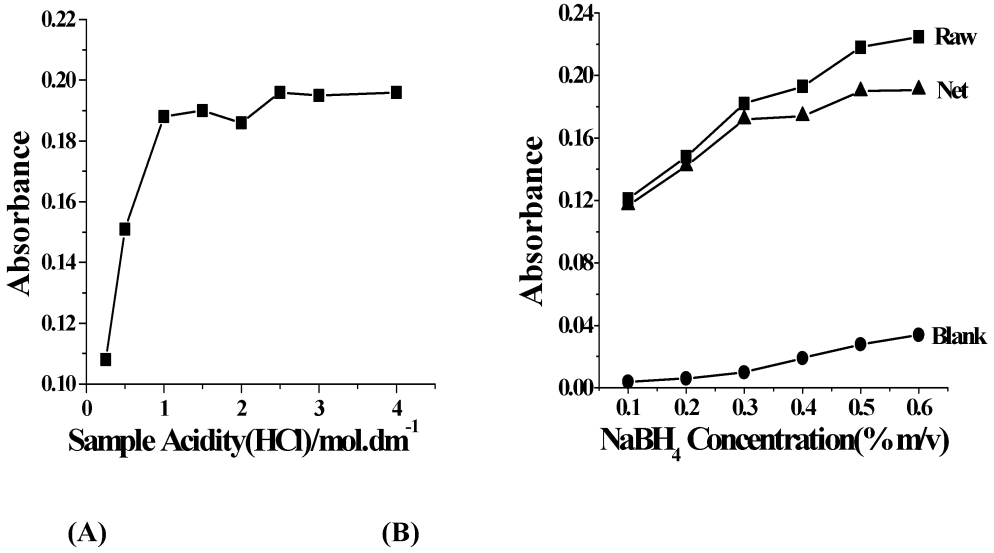

Fig. 3A,B Effects of sample acidity (**A**) and concentration of $NaBH_4$ (**B**). Conditions: A, 0.5% $NaBH_4$ and 10 ng mL^{-1} Bi; B, 1.0 M HCl and 10 ng mL^{-1} Bi

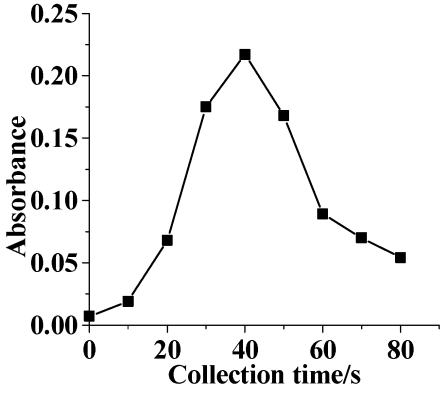

Fig. 4 Effects of hydride gas collection time on Bi AAS signal of 10 ng mL^{-1}

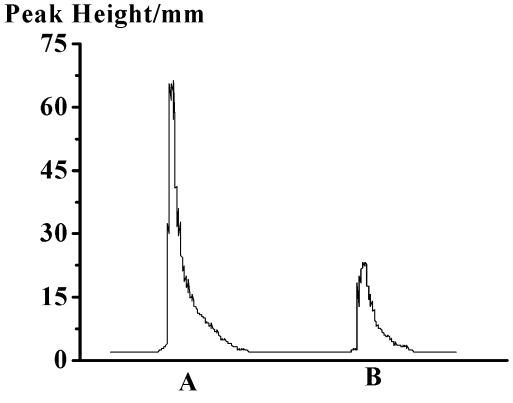

Fig. 5 Peak profiles for 10 ng mL^{-1} Bi at different collection times. A, 40 s collection; B, 20 s collection

Effects of collecting time on 10 ng mL^{-1} Bi AAS signal is shown in Fig. 4. Bismuth hydride gas was generated and collected and transported into the graphite furnace together with hydrogen gas. In this reductive environment of hydrogen, the bismuth hydride could be kept stable longer than being separated from hydrogen, as was the case in the cold-trap method [16]. But, a collection time longer than 40 s could also induce serious decomposition of the bismuth hydride, as was shown in Fig. 4. Therefore, 40 s collection time was selected, and the volume of the sample loop was reduced to 1.0 mL according to the flow rate of HCl carrier.

Profiles of Bi AAS absorbance peak at different collection times are shown in Fig. 5 to further demonstrate the effect of collection time. It was shown that either the absorbance peak height or the peak area obtained by 40 s hydride gas collection were larger than those obtained by 20 s collection by factors of 3.10 and 1.91, respectively. That was why peak height was chosen for quantitative purposes in the FI-HGC-FAAS method.

Different types of hydride gas collection loop were also investigated in the experiment. Loops made from Teflon and silastic tubes of the same 0.8 mm i.d., but different lengths between 50 cm and 200 cm were compared. Silastic collection loops were more efficient with fewer memory effects than Teflon loops. But, the Bi signal intensity only increased by 2.5% when the length of the collection loop increased from 50 cm to 200 cm. Knotted collection loops were also tested, but the three-dimensional structure created great resistant pressure in the loops that prevented them from efficiently collecting hydride gas, and the signal intensity of Bi reduced by a.u. 36% compared to silastic loops of the same length. Therefore, 100 cm long silastic collection loops were selected for further experiments.

Analytical performance characteristics

Under optimum conditions obtained above, the detection limit ($3\sigma_B$) obtained for Bi at 306.8 nm was 0.25 ng mL^{-1} in the peak height mode. The sensitivity of this new method was compared with FAAS direct determination of Bi and the CFHG-FAAS method on the same Perkin-

Elmer-3100 atomic absorption spectrometer. The detection limit of CFHG was 2.5 ng mL^{-1} while that of FAAS direct determination was 20 ng mL^{-1}; these were both much higher than the 0.25 ng mL^{-1} obtained by the FI-HGC-FAAS procedure.

The linear range of this new method was up to a Bi concentration of 100 ng mL^{-1}. The precision for ten replicate analyses of 10 ng mL^{-1} Bi was ±2.28%. The frequency of sampling was 24 h^{-1}.

Interference studies

The effect of various concomitant elements on the FI-HGC-FAAS procedure for Bi determination was investigated. Effects of ions added at 10 ng mL^{-1} Bi on the recovery experiments are listed in Table 3. It was found that only Cu^{2+} and Se^{2+} showed serious interferences on Bi determination. But, after thiourea was added to mask Cu^{2+}, and ascorbic acid was added to mask Se^{2+}, the recovery of Bi determination turned out to be excellent for quantitative analysis. A masking reagent of 0.25% *m*/*v* thiourea-ascorbic acid was prepared for real sample analysis.

Analysis of real samples

Once optimum conditions for the generation and collection of bismuth hydride gas had been established, the proposed FI-HGC-FAAS procedure was applied to determine trace levels of Bi in real samples.

Firstly, the accuracy of this method was checked by analyzing national certified reference human hair sample GBW07601 digestion solution. The certified value of Bi in the real sample was 0.34±0.02 μg mL^{-1}; therefore, the Bi concentration in the digested solution was 3.40±0.20 ng mL^{-1}.

Table 3 Interference studies on 10 ng mL^{-1} of Bi by FI-HGC-FAAS

Interferent	Ratio of interferent:Bi	Recovery (%)
Se[a]	100:1	111.6
Se[b]	100:1	98.6
Cd	1000:1	96.2
Fe	100:1	98.4
Cu[a]	100:1	80.4
Cu[b]	100:1	96.8
Mn	500:1	94.7
Pb	100:1	105.3
As	100:1	101.7
Zn	100:1	99.5
Sn	1000:1	95.1
Sb	100:1	97.8

[a]No mask reagent was added. [b]Mixing mask reagent of 0.25% (*m*/*v*) was added.

Table 4 Recovery experiments of Bi in ten gelatinsa

Sample Code	Obtained value (ng g^{-1})	Recovery (%)
No.1	28.76	98.0
No.2	31.51	105.8
No.3	29.25	94.2
No.4	40.66	104.2
No.5	64.95	100.6
No.6	38.83	101.1
No.7	42.10	97.3
No.8	64.42	105.3
No.9	60.14	103.8
No.10	70.38	103.6

[a]Spike of 20 ng mL^{-1} Bi.

The result of the FI-HGC-FAAS determination was 3.37±0.08 ng mL^{-1} (*n*=5), while that of the CFHG-FAAS determination was 3.47±0.23 ng mL^{-1} (*n*=5). The FI-HG-FAAS method was superior over the CFHG-FAAS method in accuracy or precision. Also, this bismuth concentration in the digested solution was out of the detection limit of the direct FAAS method.

Ten gelatin digestion solutions were analyzed by the FI-HGC-FAAS method, and recovery experiments were carried out after the spike of 20 ng mL^{-1} Bi. The results are summarized in Table 4. Bi concentration in the colored gelatin samples was 28.76–70.38 ng mL^{-1}. Recoveries of 94.2–105.8% showed that the proposed FI-HGC-FAAS method was capable of determining a wide concentration range of bismuth in real samples.

References

1. Dasilva JBB, Giacomelli MBO, Curtius AJ (1999) Analyst 124:1249
2. Moyano S, Gasquez JA, Olsina R, Marchevsky E, Martinez LD (1999) J Anal Atom Spectrom 14:259
3. Itoh S, Kaneco S, Ohta K, Mizuno T (1999) Anal Chim Acta 379:169
4. Chen SY, Zhang M (1995) Spectrosc Spectral Anal 15:85
5. Morrow A, Wiltshire G, Hursthouse A (1997) At Spectrosc 18: 23
6. Cabredo S, Galban J, Sanz J (1998) Talanta 46:631
7. Hall GEM, Pelchat JC (1997) J Anal Atom Spectrom 12:103
8. Delacampa MRF, Garcia ES, Temprano MCVHY, Fernandez BA, Gayon M, Sanzmedel A (1995) Spetrochim Acta 50B:377
9. Mortlock RA, Froelich PN (1996) Anal Chim Acta 332:277
10. Murphy J, Schlemmer G, Shuttler IL, Jones P, Hill SJ (1999) J Anal At Spectrom 14:1593
11. Rayman MP, Shakra FRA, Ward NI (1996) J Anal Atom Spectrom 11:61
12. Magnuson ML, Creed JT, Brockhoff CA (1996) J Anal At Spectrom 11:893
13. Xiao CL, Cullen WR, Reimer KJ (1994) Talanta 41:495
14. Bowman J, Fairman B, Catterick T (1997) J Anal At Spectrom 12:313
15. Fang ZL (1999) Flow injection analysis. Science Press, Beijing, p 201
16. Lee DS (1982) Anal Chem 54:1682