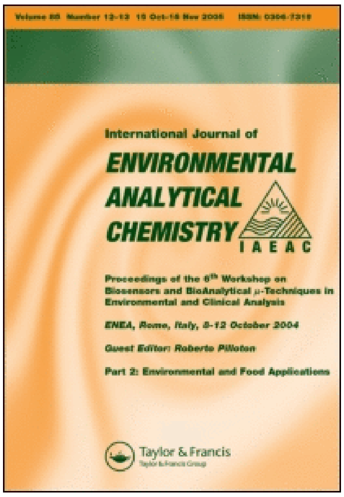

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Cloud point extraction combined with graphite furnace atomic absorption spectrometry for the determination of chromium species and their distribution in cigarette and cigarette ash

Xiashi Zhu[a]; Bin Hu[a]; Zucheng Jiang[a]
[a] Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China

To cite this Article Zhu, Xiashi , Hu, Bin and Jiang, Zucheng(2004) 'Cloud point extraction combined with graphite furnace atomic absorption spectrometry for the determination of chromium species and their distribution in cigarette and cigarette ash', International Journal of Environmental Analytical Chemistry, 84: 12, 927 — 934

To link to this Article: DOI: 10.1080/03067310410001730628

URL: http://dx.doi.org/10.1080/03067310410001730628

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 12, pp. 927–934, 15 October 2004

Taylor & Francis
Taylor & Francis Group

CLOUD POINT EXTRACTION COMBINED WITH GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY FOR THE DETERMINATION OF CHROMIUM SPECIES AND THEIR DISTRIBUTION IN CIGARETTE AND CIGARETTE ASH

XIASHI ZHU, BIN HU and ZUCHENG JIANG*

Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China

(Received 24 November 2003; In final form 15 March 2004)

In this article, the contents and distribution of total chromium, Cr(III) and Cr(VI) in various cigarettes and cigarette ashes were determined by using a cloud point extraction (CPE) separation/preconcentration combined with graphite furnace atomic absorption spectrometric (GFAAS) detection. Different extraction reagents, such as tetramethylammonium hydroxide (TMAH), Na_2HPO_4, Na_2CO_3/NaOH, NaOH and H_2O, were tested for the extraction of Cr species, and the extraction efficiency was estimated. The experimental results showed that TMAH was the most efficient extraction reagent for the analyte in cigarette samples. By using the established method, the total chromium, Cr(III) and Cr(VI) in various cigarettes and cigarette ashes were determined and their distribution was studied. It was found that Cr(III) is a main species in cigarettes, but that it can be partly oxidized to Cr(VI) during smoking.

Keywords: Chromium speciation; Cigarette; GFAAS; CPE

INTRODUCTION

Smoking has become a social and medical problem in relation to people's health. It has been reported that tobacco normally contains metal elements, such as Cr, Cd, Mn, Cu, Pt and Hg. Thus, the study of the harmful effects of toxic metal elements in cigarettes has received increasing attention [1].

Various methods have been employed to determine trace elements in cigarettes and cigarette smoke. The heavy metal elements in cigarette and cigarette smoke were determined using neutron activation analysis (NAA)[2,3]. Ye *et al.* [4] used flow injection–catalytic spectrophotometry for the determination of Hg(II) in cigarettes. Cd in cigarettes was determined by using differential stripping voltammetry [5]. Torrence *et al.* [6] used slurry sampling/GFAAS or ICP-MS for the determination of trace amounts of As, Cd and Pb in cigarette smoke. It should be stressed that the toxicity

---

*Corresponding author. Fax: +86-27-87647617. E-mail: zcjiang@whu.edu.cn

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310410001730628

of a given element is dependent not only on its total amount but also to a larger extent on its species and concentration in the sample.

It is well known that there are two principal chemical species of inorganic chromium in environmental samples. Among the chromium oxidation states, Cr(III) is one of the essential trace elements for the human body, because its β-globin complexes are indispensable to the maintenance of regular metabolism. In contrast, Cr(VI) is toxic to humans, and was found to be carcinogenic [7]. Therefore, the determination of total chromium concentration in a given sample cannot be used to estimate its environmental impact, and chromium speciation is more important than the determination of total chromium.

In order to determine trace concentrations of chromium species, a chemical separation/preconcentration step is required prior to speciation. For this purpose, a number of methods have been reported, which are usually based on solvent extraction, ion-exchange, solid-phase extraction, high-performance liquid chromatography and capillary electrophoresis. Recently, cloud point extraction (CPE) has been used for the separation and preconcentration of trace metal ions after the formation of a suitable hydrophobic complex, and offers an advantage in simplicity, high efficiency and lower toxicity. Atomic spectrometry or atomic mass spectrometry is usually selected as the detection method. It should be pointed out that sample treatment is a vital step in speciation analysis. The principal requirements include a negligible impact of the pretreatment procedure on the original distribution of chemical species. In view of the complexity of biological and environmental samples, the digestion or extraction methods can be divided into four kinds: (1) dilute acid digestion, followed by solvent extraction; (2) alkali extraction, including inorganic and organic alkali; (3) enzyme extraction; (4) organic complexant or solvent extraction. For biological samples, tetramethylammonium hydroxide (TMAH), or a TMAH–NaOH mixture is an ideal extractant. Martins *et al.* [8] reported a method for the determination of trace elements (Cr, Cd, Ni, Pb, Cu, Ag) in biological samples after extraction with TMAH and Pozebon *et al.* [9] used TMAH as extractant for ETV-ICP-MS determination of volatile metal elements in biological samples. Other extractants, such as NaOH–Na_2CO_3 solution [10], phosphate-buffered saline (PBS) [11] and NaOH solution [12], were also employed for the pretreatment of biological samples.

In our previous research [13], we reported a CPE method for the separation/preconcentration of Cr(III) and Cr(VI) in water samples after formation of a Cr(III) complex with 8-hydroxyguionline (8-Ox). Cr(III) in a surfactant-rich phase and total chromium were then determined by ETAAS. The purpose of this study is to combine CPE with ETAAS for the speciation of chromium at trace levels in cigarettes samples, and explore the most efficient extractants for chromium and its species. Finally, the proposed method was used for the investigation of chromium species and distribution in cigarettes and cigarette ash.

EXPERIMENTAL

Reagent and Apparatus

Stock standard solution of $1.0\,\mathrm{mg\,mL^{-1}}$ Cr(III) was prepared from analytical-reagent grade Cr powder (Japan) by adding HCl (1 : 1) and doubly distilled water.

TABLE I Operating conditions for ETAAS

Parameters	
Element	Cr
Wavelength (nm)	357.9
Slit (nm)	1.3
HCL current (mA)	7.5
Graphite furnace	
Dry temp. (°C)	120 (ramp 15 s, hold 15 s)
Ashing temp. (°C)	1000 (ramp 10 s , hold 10 s)
Atomization temp. (°C)	2700 (ramp 0 s , hold 6 s)
Cleaning temp. (°C)	2800 (ramp 2 s, hold 3 s)
Flow rate (Ar) (mL min^{-1})	200

Stock standard solution of 1.0 mg mL^{-1} Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ in doubly distilled water. Triton X-100 solution of 10.0 g L^{-1} was prepared from the commercially available product. 8-Hydroxyquinoline solution of 0.1 mol L^{-1} (8-Ox) was prepared from reagent grade 8-hydroxyquinoline (A.R., Shanghai Reagent Factory, Shanghai, China) by dissolving 1.450 g in 100 mL of alcohol (A.R.). 0.1 mol L^{-1} NH_3–NH_4Cl buffer solution, 10% tetramethylammonium hydroxide solution and 0.1 mol L^{-1} Na_2HPO_4 solution were prepared by dissolving appropriate amounts of the reagents in water. Na_2CO_3–NaOH solution was prepared by dissolving 3.0 g Na_2CO_3 in 100 mL of 0.5 mol L^{-1} NaOH. All other reagents used in this work were of the highest available purity free from chromium traces.

A Hitachi 180-50 atomic absorption spectrometer with a deuterium background correction and a GA-3 graphite atomizer system was employed. A 056 HITACHI pen-recorder was used for absorbance and signal profiles. All parameters of the graphite furnace were set using a microcomputer. This microcomputer processed the heating program. The operating conditions for GFAAS are given in Table I.

To verify the analysis results obtained by the proposed method, the cigarette and cigarette ash samples were digested for pneumatic nebulization-ICP-MS measurements. For this purpose, a quadrupole(Q) ICP-MS (Model Agilent 7500a, Hewlett-Packard, Yokogawa Analytical Systems, Tokyo, Japan) with a Babington nebulizer was used and its operation parameters are given in Table II.

For cleaning, all labware was kept in a detergent solution for at least 12 h, and was then rinsed several times with doubly distilled water.

Sample Pretreatment

The wrapping paper of the cigarette and the filter tip were removed from the cigarettes. The remaining cigarette tobacco was crushed with a grinder and then sieved (180 mesh). The sieved sample was dried for 12 h at 85°C to remove the absorbed moisture. Cigarette ash samples were collected quantitatively after burning cigarettes.

Sample Preparation

Acid Digestion

Acid digestion was used for the analysis of total chromium. 1.000 g of cigarette sample was accurately weighed and put into a conical flask (50 mL). 40 mL of HNO_3 was added

TABLE II Operating parameters for Agilent 7500a ICP-MS

Plasma		Ion lenses	
Incident power (W)	1300	Extract 1	−143.5
RF matching (V)	1.6	Extract 2 (V)	−67
Carrier gas (Ar) flow rate ($\mathrm{L\,min^{-1}}$)	1.16	Einzel 1,3 (V)	−94
External gas (Ar) flow rate ($\mathrm{L\,min^{-1}}$)	15	Einzel 2 (V)	0
Sampling depth (mm)	7	Plate bias (V)	0
Sample uptake rate ($\mathrm{mL\,min^{-1}}$)	0.4	Omega bias (V)	−27
Q-pole		Omega (+) (V)	2.7
AMU gain	126	Omega (−) (V)	−0.1
AMU offset	126	QP focus	7.3
Axis gain	0.9998		
Axis offset	0.02	Integration time (s)	0.1
QP bias (V)	1.2	Nebulizer	Babington
Detector		Torch	Fassel (quartz)
Discriminator (mV)	8.7		
Analog (V)	1460	Sampler	Ni, 1.0 mm diameter orifice
Pulse HV (V)	900	Skimmer	Ni, 0.4 mm diameter orifice

and kept overnight for decomposition. After that, 10 mL $HClO_4$ was added, and the flask was mildly heated on a hot plate to near dryness. The residue was dissolved and diluted into a 25-mL volumetric flask with deionized water for later use.

Solvent Leaching

1.000 g of each cigarette sample was accurately weighed and put into a conical flask (50 mL); 20 mL of corresponding extractants were added and kept overnight. After that, the flasks were slowly heated on the hot plate for 1 h at 60–70°C. After filtration, the final solutions were diluted to 25 mL.

Analytical Procedure

Determination of Total Cr

10 μL of the solution was injected on the wall of the pyrolytic graphite-coated graphite tube using a microsyringe. Under the optimum conditions, the absorption signal of the analyte was recorded, and the peak heights were measured for quantification [13].

Determination of Cr(III)

0.5 mL solution containing Cr(III) was accurately transferred to a 10-mL centrifuge tube followed by sequential addition of 1.0 mL of 10.0 $\mathrm{g\,L^{-1}}$ Triton X-100, 1.0 mL of 0.1 $\mathrm{mol\,L^{-1}}$ 8-Ox and 5.0 mL of NH_3–NH_4Cl buffer solution and dilution to 10 mL with deionized water. After ultrasonic dispersion for 1 min it was centrifugally separated at 4000 rpm. The aqueous phase was removed, and the rich micellar phase was dissolved with 0.2 mL of 0.1 $\mathrm{mol\,L^{-1}}$ HNO_3. 10 μL of solution was injected into the graphite tube and the absorbance was determined under optimized conditions.

Determination of Cr(VI)

The content of Cr(VI) was obtained by subtracting the Cr(III) amount from the total Cr.

All of the experimental data are against the corresponding reagent blanks.

RESULTS AND DISCUSSION

Determination of Total Chromium in Cigarettes and Their Ashes

The concentrations of total chromium in cigarettes and corresponding ashes were determined after acid decomposition of the sample, and the results are summarized in Table III. It can be seen that the concentrations of total chromium in three different brands of cigarette are at the microgram per gram level. As expected, the total chromium concentration in cigarette ashes is much higher than that in the corresponding cigarettes owing to the elimination of the volatile matrix, mainly the organic substance.

Table IV lists the analytical results of total chromium amount in one sample of cigarette and its ash. As can be seen, the total chromium amount in different brands of cigarette and the corresponding ash is different. Table IV also shows that for any one cigarette, the total chromium amount in the ash is lower than that in the corresponding cigarette, regardless of the cigarette brand. In other words, about 30–50% of total Cr in the original cigarette was volatilized during smoking.

Extraction Efficiency of Different Extractants

Different reagents, including TMAH, Na_2HPO_4, Na_2CO_3/NaOH, NaOH and H_2O were tested for the extraction of total chromium from cigarettes and corresponding ash samples, and their extraction efficiency was evaluated. Table V and Fig. 1 indicate the extraction efficiency of the tested extractants. It can be seen that TMAH is the most efficient extractant for chromium from both cigarettes and their ashes. For cigarettes, the chromium content in a TMAH extraction solution is close to the content in its acid digested solutions (Fig. 1). The extraction efficiency of the tested extractants for the extraction of chromium from the cigarette sample are in the

TABLE III Analytical results for total Cr concentration in cigarettes and their ashes with sample digested by acid decomposition

Sample No.	*Cigarette* ($\mu g\,g^{-1}$)	*Cigarette ash* ($\mu g\,g^{-1}$)
1	4.61 ± 0.10	14.41 ± 0.50
2	4.09 ± 0.30	43.00 ± 0.50
3	2.90 ± 0.30	8.93 ± 0.40

TABLE IV The total Cr amount in one sample of cigarette and its corresponding ash for three different brands of cigarette after acid digestion

Sample No.	*Cigarette* (µg/sample)	*Cigarette ash* (µg/sample)	$Cr_{Cigarette\ ash}/Cr_{Cigarette}$
1	3.23 ± 0.10	1.63 ± 0.10	0.50
2	2.86 ± 0.30	1.72 ± 0.10	0.60
3	2.03 ± 0.30	0.57 ± 0.05	0.28

TABLE V The total Cr amount in one sample of cigarette and its corresponding ash for three different brands of cigarette after extraction with different extractants

Sample No.	*Extractant*	*Cigarette* (μg/sample)	*Cigarette ash* (μg/sample)
1	TMAH	3.33 ± 0.21	0.10 ± 0.02
	Na_2HPO_4	2.36 ± 0.10	0.12 ± 0.02
	$Na_2CO_3/NaOH$	2.07 ± 0.17	0.07 ± 0.02
	NaOH	1.64 ± 0.20	0.06 ± 0.01
	H_2O	0.25 ± 0.05	0.01 ± 0.002
2	TMAH	2.77 ± 0.25	0.27 ± 0.05
	Na_2HPO_4	2.45 ± 0.23	0.27 ± 0.05
	$Na_2CO_3/NaOH$	2.13 ± 0.20	0.30 ± 0.06
	NaOH	1.04 ± 0.15	0.15 ± 0.03
	H_2O	0.22 ± 0.08	0.09 ± 0.02
3	TMAH	1.95 ± 0.28	0.35 ± 0.03
	Na_2HPO_4	1.38 ± 0.21	0.30 ± 0.04
	$Na_2CO_3/NaOH$	0.65 ± 0.10	0.51 ± 0.06
	NaOH	0.50 ± 0.10	0.37 ± 0.04
	H_2O	0.22 ± 0.07	0.16 ± 0.02

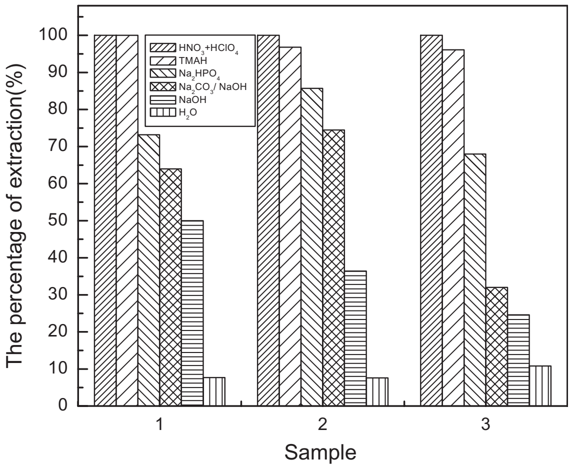

FIGURE 1 Efficiency of different extractants for Cr from cigarettes.

order: TMAH > Na_2HPO_4 > $Na_2CO_3/NaOH$ > NaOH > H_2O. The chromium content in the water extract is very small, and only about 10% of Cr in cigarette sample can be extracted. For cigarette ashes, although the order of the extraction efficiency is similar to that for cigarettes, the amounts of total chromium extracted are much lower than those obtained after acid digestion. The possible reason is that the chromium in cigarette ash has been converted into a refractory compound at the high temperature reached during cigarette smoking and this refractory compound of Cr cannot be extracted by the extraction reagents used.

The Cr Species and Their Distribution

Cloud point extraction–graphite furnace atomic absorption spectrometry was applied to the separation and determination of the Cr(III) content in cigarettes and their ashes. The total Cr in a cigarette and its ash can be directly determined by

TABLE VI The extracted amount of Cr(III) and Cr(VI) in one sample of cigarette and its corresponding ash for three different brands of cigarette after extraction with different extractants

Sample No.	*Sample preparation*	*Cigarette*		*Cigarette ash*	
		Cr (III) (μg/sample)	*Cr (VI)* (μg/sample)	*Cr (III)* (μg/sample)	*Cr (VI)* (μg/sample)
1	TMAH	3.12 ± 0.20	0.11	0.05 ± 0.01	0.05
	Na_2HPO_4	2.20 ± 0.17	0.16	0.04 ± 0.01	0.08
	Na_2CO_3/NaOH	2.00 ± 0.20	0.07	0.04 ± 0.01	0.03
	NaOH	1.63 ± 0.20	0.01	0.04 ± 0.01	0.02
	H_2O	0.20 ± 0.05	0.05	0.005 ± 0.001	0.005
2	TMAH	2.45 ± 0.20	0.32	0.19±0.05	0.08
	Na_2HPO_4	2.30 ± 0.22	0.15	0.20 ± 0.05	0.07
	Na_2CO_3/NaOH	2.12 ± 0.21	0.01	0.20 ± 0.05	0.10
	NaOH	0.70 ± 0.12	0.34	0.07 ± 0.01	0.08
	H_2O	0.10 ± 0.03	0.12	0.03 ± 0.005	0.06
3	TMAH	1.90 ± 0.18	0.05	0.22 ± 0.05	0.13
	Na_2HPO_4	1.30 ± 0.15	0.08	0.20 ± 0.05	0.10
	Na_2CO_3/NaOH	0.63 ± 0.10	0.02	0.18 ± 0.04	0.33
	NaOH	0.35 ± 0.07	0.15	0.10 ± 0.01	0.27
	H_2O	0.10 ± 0.03	0.12	0.07 ± 0.005	0.09

GFAAS after the samples have been digested with mixed acids, and the Cr(VI) content can then be calculated by subtraction of Cr(III) from the total chromium. Table VI lists the analytical results for Cr species and their distribution in cigarettes and cigarette ash. Based on the experimental results, the following conclusions can be drawn: (1) In the extraction solution of cigarettes, Cr(III) is the main species, and accounts for 90% of total chromium; and Cr(VI) is only 10%. (2) Compared with the species distribution of chromium in cigarettes, the proportion of Cr(III) in the extracted solution of cigarette ash was significantly lower. The probable reason is that Cr(III), on the one hand, could be oxidized Cr(VI) during smoking. On the other hand, Cr(III) exists in the form of Cr_2O_3, which cannot be extracted completely. For example, in the TMAH extraction solution the ratio of Cr(III)/Cr(VI) greatly decreased from 28 : 1 in a cigarette to 1 : 1 in cigarette ash. (3) The extraction efficiency of both Cr(III) and Cr(VI) from cigarette ash is obviously lower than that from the cigarette. The reason is that during smoking volatilization of Cr may occur at high temperature, and Cr in cigarette ash is difficult to extract as stated above. (4) The ratio of Cr(III)/Cr(VI) in cigarette ash extraction solution is lower than that in cigarette extraction solution, regardless of the extractants used.

Detection Limit, Precision and Calibration

According to the IUPAC definition, the detection limit of the proposed method for Cr(III) with an enrichment factor of 50 is $0.022\,\mu g\,L^{-1}$ and the relative standard deviation (RSD) was 1.1% ($c = 2.0\,\mu g\,L^{-1}$, $n = 6$). The calibration curve ranged from 0.5 to $10.0\,\mu g\,L^{-1}$.

Verification of Analytical Results and the Recovery of Cr(III)

In order to verify the accuracy of the method, ICP-MS was used to analyze the total Cr in a cigarette and its ash. Table VII shows the GFAAS and ICP-MS analytical results

TABLE VII Comparison of the analytical results of total Cr in one sample of cigarette and its ash samples with sample digestion by mixed acids

Sample No.	*GFAAS* (μg)		*ICP-MS* (μg)	
	Cigarette	*Ash*	*Cigarette*	*Ash*
1	3.23 ± 0.10	1.62 ± 0.10	3.61 ± 0.12	1.66 ± 0.10
2	2.86 ± 0.30	1.72 ± 0.10	2.80 ± 0.20	1.80 ± 0.11
3	2.03 ± 0.30	0.67 ± 0.05	2.10 ± 0.18	0.77 ± 0.05

for total Cr in one piece of cigarette and its ash after the samples were digested by mixed acid decomposition. The results show that the analytical values obtained by both methods are in good agreement. The recovery of Cr(III) for the spiked cigarette and its ash samples was between 100 and 103%.

CONCLUSION

CPE, as an easy, safe and efficient method for separation and preconcentration of the Cr(III)–Ox complex, was combined with GFAAS for speciation analysis of chromium, and the information on total Cr, Cr(III) and Cr(VI), together with their distribution in cigarettes and cigarette ash, were studied. Different extractants were tested for the analytes from the samples and TMHA is found to be a very effective extraction reagent for chromium species in cigarettes and their ashes. It was also found that Cr(III) is the main species in cigarette samples. The relative content of Cr(VI) in cigarette ash was increased, the possible reason being that Cr(III) was oxidized to Cr(VI) at the high temperature during smoking.

References

[1] Zhiguo Zhu, Guixian Wang and Jinhua Cheng, *Spectrosc. Spectral Anal. (Chinese)*, **19**, 210–211 (1999).
[2] A. Nada, M. Abdel-Wahab, A. Sroor, A.S. Abdel-Haleem and M.F. Abdel-Sabour, *Appl. Radiat. Isot.*, **51**, 131–136 (1999).
[3] S. Landsberger and D. Wu, *Sci. Environ.*, **323**, 173–174 (1995).
[4] Cunling Ye, Jing Fan, Suling Feng and Xiaoyi Huang, *Chinese J. Anal. Chem.*, **28**, 1155–1157 (2000).
[5] Zen Yang, Liping Zhang, Guozhong Yang and Cuiying Yang, *Chinese J. Health Lab. Technol.*, **11**, 177–179 (2001).
[6] K.M. Torrence, R.L.M. Daniel, D.A. Self and M.J. Chang, *Anal. Bioanal. Chem.*, **372**, 723–731 (2002).
[7] Chen Hangting, Cao Shuqin and Zeng Xianjin, *Chinese J. Anal. Chem.*, **29**, 592–600 (2001).
[8] P. Martins, D. Pozebon, V.L. Dressler and G.A. Kemieciki, *Anal. Chim. Acta*, **470**, 195–204 (2002).
[9] D. Pozebon, V.L. Dressler and A.J. Curtius, *Talanta*, **51**, 903–911 (2000).
[10] M.J. Marqués, A. Salvador, A. Morales-Rubio and M. de la Guardia, *Fresenius' J. Anal. Chem.*, **367**, 601–613 (2000).
[11] H. Rüdel and K. Terytze, *Chemosphere*, **39**, 697–708 (1999).
[12] S. Simon, M. Bueno, G. Lespes, M. Mench and M. Potin-Gautier, *Talanta*, **57**, 31–43 (2002).
[13] Zhu Xiashi, Jiang Zucheng, Hu Bin and Minfang Li, *Chinese J. Anal. Chem.*, **31**, 1312 (2003).