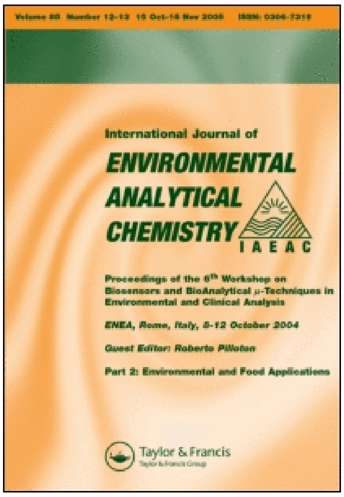

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Trace Copper, Lead, Cadmium, and Iron in Environmental and Biological Samples by Flame Atomic Absorption Spectrometry Coupled to Flow Injection On-Line Coprecipitation Preconcentration Using DDTC-Nickel as Coprecipitate Carrier

Jinsong Liu[ab]; Hengwu Chen[a]; Xueqin Mao[a]; Xin Jin[b]
[a] Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou, P. R. China [b] Zhejiang Environment Monitoring Center, Hangzhou, P. R. China

To cite this Article Liu, Jinsong , Chen, Hengwu , Mao, Xueqin and Jin, Xin(2000) 'Determination of Trace Copper, Lead, Cadmium, and Iron in Environmental and Biological Samples by Flame Atomic Absorption Spectrometry Coupled to Flow Injection On-Line Coprecipitation Preconcentration Using DDTC-Nickel as Coprecipitate Carrier', International Journal of Environmental Analytical Chemistry, 76: 4, 267 — 282

To link to this Article: DOI: 10.1080/03067310008034135

URL: http://dx.doi.org/10.1080/03067310008034135

Intern. J. Environ. Anal. Chem., Vol. 76(4), pp. 267-282
Reprints available directly from the publisher
Photocopying permitted by license only

DETERMINATION OF TRACE COPPER, LEAD, CADMIUM, AND IRON IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES BY FLAME ATOMIC ABSORPTION SPECTROMETRY COUPLED TO FLOW INJECTION ON-LINE COPRECIPITATION PRECONCENTRATION USING DDTC-NICKEL AS COPRECIPITATE CARRIER

JINSONG LIU[ab]*, HENGWU CHEN[a], XUEQIN MAO[a] and XIN JIN[b]

[a]Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou, P. R. China, 310028 and [b]Zhejiang Environment Monitoring Center, Hangzhou, P. R. China, 310012

(Received 17 June 1999; In final form 7 September 1999)

A flow injection on-line coprecipitation system with diethyldithiocarbamate (DDTC) nickel (II) being used as a carrier was coupled to the flame atomic absorption spectrometry (FAAS) for the determination of trace copper, lead, cadmium and iron in environmental and biological samples. Metal ions were on-line coprecipitated with DDTC-Ni (II) in 0.3 $mol \cdot l^{-1}$ nitric acid, and the precipitate was collected in a knotted reactor. The precipitate was then dissolved by isobutyl methyl ketone (IBMK), and the concentrated zone was transported directly into the nebulizer-burner system of a FAAS. Enhancement factors of 60, 58, 65, and 59 were obtained for copper, lead, cadmium and iron, respectively, at the sampling frequency of 60 h^{-1}. The detection limits (3σ) were 0.5 $\mu g \cdot l^{-1}$ for copper, 2.7 $\mu g \cdot l^{-1}$ for lead, 0.2 $\mu g \cdot l^{-1}$ for cadmium, and 2.5 $\mu g \cdot l^{-1}$for iron respectively, and a relative standard deviations (n=10) were 3.0% for 40 $\mu g \cdot l^{-1}$ copper, 2.0% for 80 $\mu g \cdot l^{-1}$lead, 3.5% for 10 $\mu g \cdot l^{-1}$ cadmium, and 2.8% for 60 $\mu g \cdot l^{-1}$ iron. The developed method was applied to determination of the metals in waters and environmental reference material of soil, and biological reference materials of mussle and human hair. Satisfactory results were obtained.

Keywords: Flow injection preconcentration; on-line coprecipitation; flame atomic absorption spectrometry; copper; lead; cadmium; iron; soil; water; biological samples

---

* : Corresponding author. Present address: Zhejiang Environment Monitoring Center, No. 19, Jiaosan Road, Hangzhou, P. R. China, 310012. Fax: +86–571–8837535; E-mail: myming@telekbird.com.cn

INTRODUCTION

Heavy metals such as cadmium, lead, and copper are among the most concern elements in environmental analysis due to their potential toxic to plants and/or animals[1]. The potential toxicity of heavy metals in environment depends on their concentration in the soil, water and living things. Iron is not so harmful to living things as cadmium or lead, however, the concentration of iron in water must be less than 0.1 $mg{\cdot}l^{-1}$ when the water is used in the dyeing or textile industry. Thus, it is essential to grasp the accurate concentration of these metals in environment.

One of the most widely used methods to monitor the heavy metals is atomic absorption spectrometry (AAS). The use of graphite furnace AAS improves the sensitivity, but the analysis is suffer severe matrix interference and produce low sample throughput rate than the use of the flame AAS technique. Unfortunately, The concentration of copper, iron, cadmium and lead in environmental and biological samples are usually below the detection limits of FAAS whether samples are directly used for analysis (as for waters) or after they have been brought into solution by acid digestion (as for soil and human hair). Some preconcentration and/or separation method about these heavy metals such as chelating ion exchange [2–5], extraction [6,7], or coprecipitation [8] have frequently been recommended for their determination.

In the past two decades, flow injection (FI) on-line preconcentration using various separation and concentration methods has been successfully coupled to FAAS, thereby leading to an improvement in the detection limits by 1–2 orders of magnitude[9]. Such coupled techniques provide adequate sensitivity for determination of trace metals but require lower instrument cost and yield higher sample throughput rate (ca 30–60/h). Thus, they could be used as alternatives to GFAAS for the determination of metals in environmental and biological samples. Among the most attractive FI on-line preconcentration approaches, FI on-line coprecipitation preconcentration without filtration, which was first reported by Fang et al[10], has the merits of simple instrumentation and operation. high tolerance level towards foreign ions, and moderate enhancement factors. Thus following the first paper that employed hexamethyleneammonium-hexamethelenedithiocarbamate (HMA-HMDTC) to chelate Fe^{2+} as a carrier for coprecipitation-peconentration and FAAS determination of lead, several FI on-line coprecipitation system such as HMA-HMDTC-Fe^{2+} for cadmium, nickel and cobalt[11], and for cadmium and nickel[12], pyrrolidinedithiocarbamate (PDDC)-Fe^{2+} for cadmium, nickel, cobalt[13] and for molybdenum[14]; diethyldithiocarbamate (DDTC)-Fe^{2+} for silver[15], DDTC-Zn^{2+} for lead[16], DDTC-Cu^{2+} for lead, cadmium and nickel[17] and for silver[18] have been on-line coupled to FAAS[11,13–18] and GFAAS[12]. Features of the various on-line coprecipitation systems have been summarized in a recent review on FI on-line separation and preconcentration by precipitation or coprecipitation[19]. Hitherto, to our best knowledge, no on-line coprecipitation system, with which trace copper and iron together with cadmium and lead can be preconcentrated, has been developed.

Recently, Atsuya et al reported that trace amount of copper, lead and other transition metals could be efficiently concentrated in a wide acidity range by manual batch-wise coprecipitation using APDC-Ni^{2+} as carrier[20]. Based on this work, we employed nickel (II) and DDTC, a relatively cheap and water soluble chelating reagent, to develop a new on-line copricipitation system for FI preconcentration and FAAS determination of copper, iron, cadmium and lead in environmental and biological samples. This paper reported the main results of the work.

EXPERIMENTAL

Instrumentation and reagents

A Shimadzu Model AA-6501F atomic absorption spectrometer equipped with a deuterium-arc background corrector was used to measure the absorption signal. Copper, cadmium, lead and iron hollow cathode lamps were operated at 6, 6, 14, and 10 mA, respectively. The resonance line and bandpass were 324.8 nm and 0.5 nm for copper, 228.8 nm and 0.2 nm for cadmium, 217.0 nm and 0.2 nm for lead, and 248.3 nm and 0.2 nm for iron, respectively. A slightly leaner flame than the manufacturer recommended was used to allow introduction of organic eluent.

A model LZ-2000 computerized FI processor, composed of two variable-speed peristaltic pumps and an eight-channel valve (Zhaofa Institute for Lab. Automation, Shenyang, China), was used for setting up the manifold illustrated in Fig. 1.

Knotted reactor (KR) was made with 0.5 mm i.d. PTFE tubing as described in [10]. PTFE tubing with 0.5 mm i.d. was used for all connections and PVC pump tubing was used to propel the sample, reagent, and water. The organic solvent (IBMK) was driven by the introduction of a water stream into a displacement bottle.

A 3.0% DDTC solution was prepared by dissolving 3.0 g sodium diethyldithiocarbamate (No. 3 Chemical Co., Shanghai, China) in a pH 9.2 buffer solution (0.04 $mol \cdot l^{-1}$ ammonia-0.02 $mol \cdot l^{-1}$ acetic acid) and filtered before use.

A 1000 mg·l^{-1} nickel solution was prepared by dissolving 1.24 g $Ni(NO_3)_2·6H_2O$ in 250 ml water with 5 ml 0.5 mol·l^{-1} nitric acid.

Individual copper, cadmium, lead, and iron standard solutions (500 mg·l^{-1}) were provided by China Environmental Monitoring Center.

Environmental reference materials of soil ESS-1, ESS-4 were obtained from China Environmental Monitoring Center (Beijing, China), and that of soil GSS-1 was obtained from Institute of Geophysical and Geochemical Exploration, Ministry of Geology and Resources (Langfang, China). Biological reference materials of mussel (GBW-08571) was obtained from National No.2 Marine Institute (Hangzhou, China), and that of human hair (GBW-09107) was from Shanghai Institute of Atomic Nucleus, Academia Sinica (Shanghai, China).

All reagents were of analytical reagent grade or better, and dually-deionized water was used throughout the work.

Sample preparation

Standard series for calibration contained 100 mg·l^{-1} Ni^{2+} and 0.3 mol·l^{-1} HNO_3.

Water samples were acidified to pH 2 with diluted nitric acid immediately after collection. A portion of 80 ml water sample was pipetted into 100 ml volumetric flask, 10 ml of 1000 mg·l^{-1} Ni^{2+} and 6 ml 5 mol·l^{-1} HNO_3 were added, then it was diluted to volume with water.

Environmental and biological standard reference materials: certain amount of environmental or biological reference materials was accurately weighted into a PTFE crucible, 10 ml concentrated nitric acid was added. The sample was gently heated on a sand bath for about 30 min. After cooling, 5 ml concentrate fluorhydric acid was added and the sample was heated on the sand bath for about 10 min (for biological sample, this step was omitted). After cooling, 3 ml concentrate perchloric acid were added. It was heated again till disappearance of the dense white fumes. After cooling, 6 ml 5 mol·l^{-1} nitric acid and 20 ml water were added into the crucible to dissolve the residues. The solution was transferred into a 100 ml volumetric flask. 10 ml 1000 mg·l^{-1} Ni^{2+} solution was added, and diluted to mark with water.

Procedure

FI manifold and operation sequences with optimized parameters for on-line coprecipitation are illustrated in Figure1. In first step (Figure1a, the precipitation step), sample solution and DDTC solution were pumped by pump 1 and merged at a T connector located at 10 mm upstream of the KR. Yellow precipitate immediately formed inside the KR and collected in its inner wall. During this stage water was aspirated into the nebulizer to define the baseline. This step lasted for 40 s. With the injector being-switched to dissolution position (Figure1b), the dissolution step began. In this step, Pump 1 was stopped and pump 2 propelled the water into the displacement bottle to drive the IBMK into the KR. The precipitate adhering on the walls of the KR was flushed and dissolved by IBMK, and the concentrate zone of the analyted was directly transported into the nebulizer. This step lasted for 20 s. Then the valve was switched back to the coprecipitation position for next cycle.

Three replicates were made for each test solution, and the peak heights were used for quantification.

RESULTS AND DISCUSSION

Elimination of peak split

In preliminary studies of the present work using the FI manifold illustrated in Figure1, split peaks were observed for all of four analytes. Peak split not only decreased the peak heights on which the readouts were made but also deteriorated the precision. Using Cu^{2+} as a model analyte, the shoulder appeared in the front of the main peak was identified being produced by the analyte rather than by the change of flame conditions resulted from organic solvent entering the flame, because the shoulder was not corrected by background correction but disappeared in blank test. It was also noticed that the shorter the connection tubing (indicated by XY in Figure 1) between the valve and the "T" connector, the lower the shoulder. This observation implied that the shoulder most possibly be caused by the small bolus of the acidic sample solution which was stored in the tubing XY at the end of the precipitation stage. Thus, after valve was switched to the dissolution position (Figure1b) the bolus was pushed by IBMK into the knotted reactor without any DDTC solution being merged (note: pump 1 was stopped during the dissolution stage). If the dispersion which occurred in the boundary between the bolus and the forgoing DDTC-merged sample zone could be neglected, precipitate would not be formed in the bolus. Moving downstream the knotted reactor, this bolus of acidic sample solution might wash away some fine precipitate particles that was not so strongly adhered on the wall of the knotted reactor, and partially dissolve it. When reached the atomizer the bolus might contain analyte species (both in ionic form and in fine particle form) concentrate enough to produce an absorption signal in the front of the main peak that was

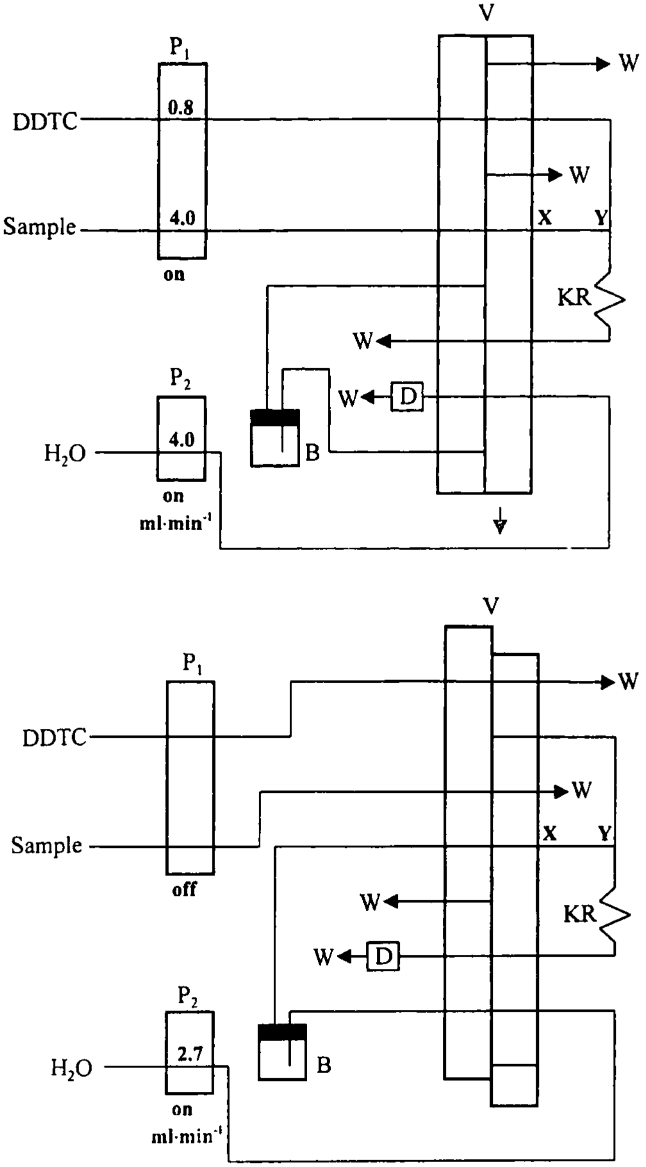

FIGURE 1 Flow injection manifold for on-line coprecipitation preconcentration. V, injection valve; P_1 and P_2, peristaltic pumps; B, displacement bottle; KR, 0.5 mm i.d. and 150 cm knotted reactor; W, waste; D, flame atomic absorption spectrometer; XY, connecting tubing between valve and KR (see text). (a), precipitation step; (b), dissolution step. Experimental conditions: Ni^{2+} concentration, 100 mg·l^{-1}; sample acidity, 0.3 mol·l^{-1} nitric acid; sample flow rate, 4.0 ml·min^{-1}; DDTC concentration, 3.0%; DDTC flow rate, 0.8 ml·min^{-1}; IBMK flow rate, 2.7 ml·min^{-1}; loading time, 40 s

produced by the concentrated analyte in the following IBMK zone. When tubing XY was cut as short as possible, the bolus of acidic sample solution became so short that the dispersion between the bolus and forgoing DDTC-merged sample zone became significant. Hence DDTC entered the bolus and precipitation-coprecipitation occurred in the bolus, leading to the precipitate particles of analyte being carried onto the wall of knotted reactor by large amount of DDTC-Ni^{2+} precipitate, and adhered herein. Under this instance, the shoulder became lower. Based on the assumption, elimination of peak split might be possible if the DDTC concentration would be increased to such a extent that the DDTC entered the bolus (due to dispersion) might lead to complete precipitation and coprecipitation for both the coprecipitant of nickel ion and the analyte of copper ion. Test verified the expectation: when DDTC concentration increased from 0.5 % to 2.5 %, split peaks were no longer observed. The same observation was obtained for other three analytes. Therefore, shortest tubing XY (about 3.0 cm) and moderate DDTC concentration (3 %) were the quartette for sensitive and reproducible determinations.

Optimization of chemical parameters

Ni^{2+} concentration

The Figure 2 illustrates the influence of the Ni^{2+} concentration on the copper, cadmium, lead and iron signals. As can be seen, about half of the maximum signals of the four analytes could be obtained in the absence of nickel, most possibly resulted from the adsorptive effect of the PTFE tubing towards water-insoluble analyte-chelates. With increase of the Ni^{2+} concentration, the absorption signals increased sharply, and reached maximum in the range of 50–125 $mg \cdot l^{-1}$. Excess 125 $mg \cdot l^{-1}$ (150 $mg \cdot l^{-1}$for copper), the signals declined. Thus, 100 $mg \cdot l^{-1}$ Ni^{2+} was selected for application to the various samples.

DDTC concentration

Test revealed that the signals remained constant after the DDTC concentration excess 2.5% (Figure 3). As above test mentioned, higher DDTC concentration was also beneficial to diminish the peak-split and improve precision. Thus, a 3.0% DDTC solution was used.

Sample acidity

As shown in Figure 4, the signals sharply increased with the increase of the nitric acid concentration from 0 to 0.1 $mol \cdot l^{-1}$, then they kept constant up to 1.5 $mol \cdot l^{-1}$, the highest tested acid concentration. Compared with the on-line

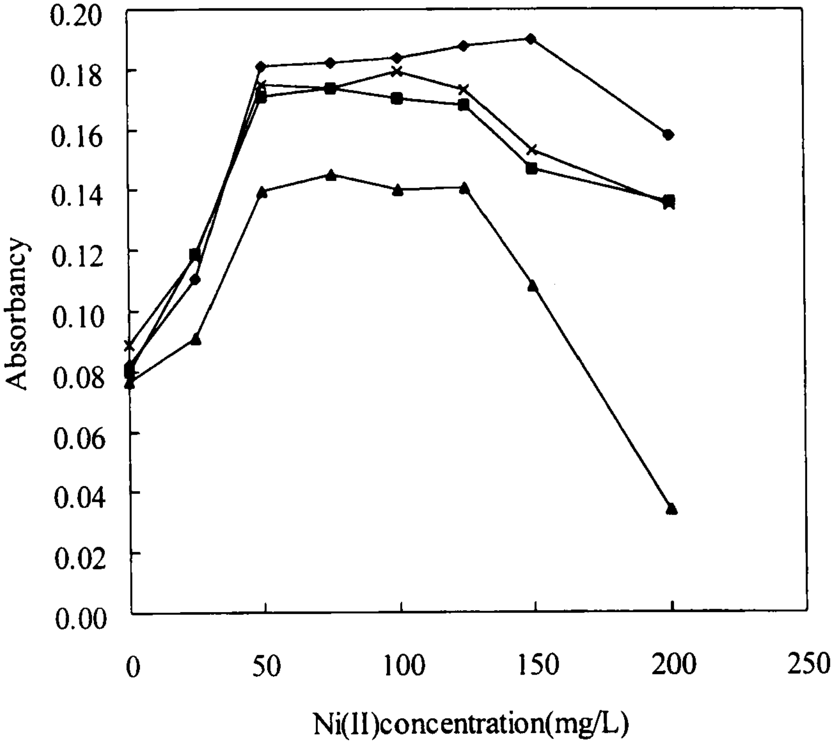

FIGURE 2 Effect of Ni^{2+} concentration on signals of 40 μg·l^{-1} copper (◆), 10 μg·l^{-1} cadmium (■), 100 μg·l^{-1} lead (x) and 60 μg·l^{-1} iron (▲). Experiment conditions as in Figure1 except the Ni^{2+} concentration

coprecipitation systems where the ferrous chelates of various dithiocarbamates were employed as coprecipitate carrier[10–15], the present system could work at much higher acidity and suffer less interference from the change of the sample acidity. Thus, strict control of acidity with buffer[10] is not required. For practical applications, a 0.3 mol·l^{-1} nitric acid was made in both standard solutions and sample solutions.

Optimization of physical parameters

The tubing length of KR

As can be seen in Figure 5, the analyte signals increased with the increase of tubing length up to 150 cm and leveled off till the length reached 250 cm, after which the signals declined again. As the 150 cm KR produced a maximum absorbance signals for all of the four analytes, it was used for further studies.

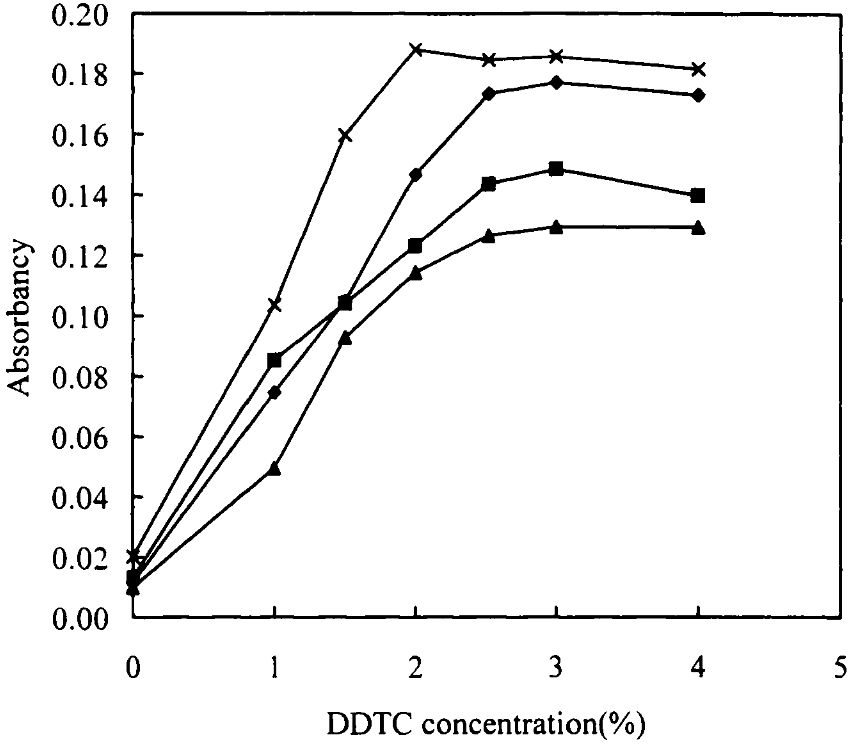

FIGURE 3 Effect of DDTC concentration on the signals. Experiment conditions as in Figure 1 except the DDTC concentration. Symbols for analytes and concentrations of analytes are the same as Figure 2

Influences of sample flow rate and loading time

As a time-based sampling mode[9] was used in the present FI system, the loaded sample volume was dependent on both the sample flow-rate and the loading time. When a 150 cm KR and a sampling time of 40 s were selected, the AAS signals of 40 μg·l^{-1} Cu^{2+}, 10 μg·l^{-1} Cd^{2+}, 60 μg·l^{-1} Fe^{3+}, and 100 μg·l^{-1} Pb^{2+} linearly increased with the increase of the sample flow rate from 1 to 5 ml·min^{-1}. Above the up limit a slightly negative deviation from linearity was observed for all four elements, which might be attributed to either insufficient reaction time for chelating and precipitation or the breakthrough of the precipitates, or both of them. While 4.0 ml·min^{-1} sample flow rate was selected, the peak heights of the analytes linearly increased with the increase of the loading time from 10 s to 60 s. With a safety margin being taken into consideration, a loading period of 40 s and sampling flow rate of 4 ml·min^{-1} were used.

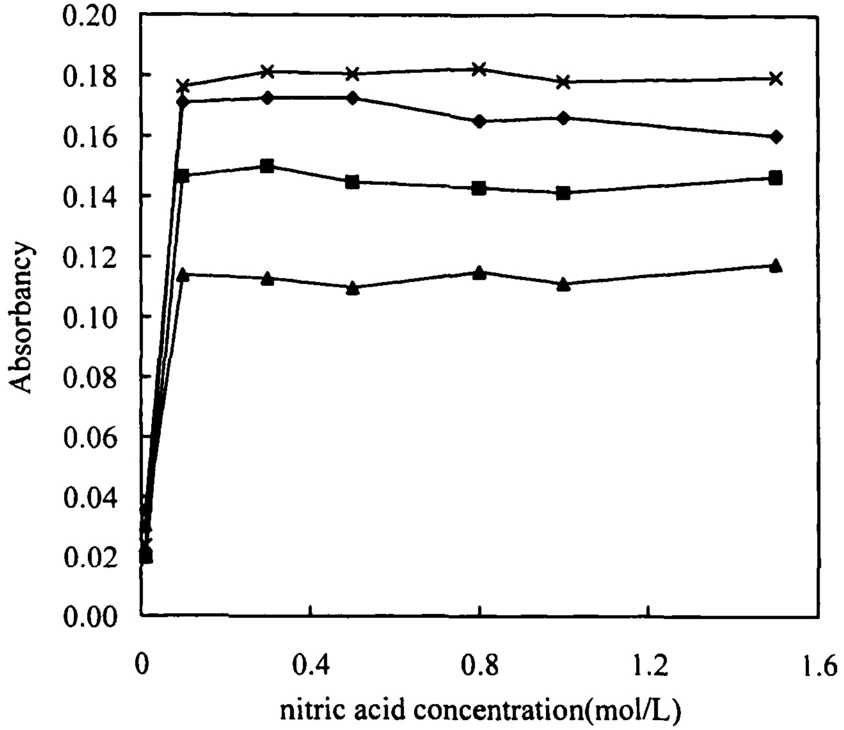

FIGURE 4 Effect of sample acidity on the signals. Experiment conditions as in Figure 1 except sample acidity. Symbols for analytes and concentrations of analytes are the same as Figure 2

Influence of IBMK flow rate

The effect of IBMK flow rate on the signals was shown in Figure 6. Maximum copper and iron signals were obtained in the flow rate range of 2.3–3.2 ml·min^{-1}, while those of cadmium and lead in the rate of 1.8–3.2 ml·min^{-1}. Poor signals observed at lower flow rates might be due to flow starvation in nebulizing system (the free uptaking rate of the nebulizer was 5.1 ml·min^{-1}), and those at higher flow rates might be ascribed to insufficient dissolution of the precipitate. In this work, an IBMK flow rate of 2.7 ml·min^{-1} was selected.

Preformance of the on-line coprecipitation preconcentration system

Characteristic performance data obtained under the optimized conditions described as in caption of Figure 1 and summarized in Table I.

TABLE I Characteristic performances for the on-line coprecipitation preconcentration flame AAS system for the determination of copper, cadmium, lead and iron

	copper	*lead*	*cadmium*	*iron*
Enhancement factor	60	58	65	59
Detection limit (3σ, $\mu g \cdot l^{-1}$)	0.5	2.7	0.2	2.5
RSD(%, n=10)	3.0(40 $\mu g \cdot l^{-1}$)	2.0(80 $\mu g \cdot l^{-1}$)	3.5(10 $\mu g \cdot l^{-1}$)	2.8(60 $\mu g \cdot l^{-1}$)
Regression equation[a]	A=0.0092+4.18C	A=0.010+1.67C	A=0.007+17.05C	A=0.0324+1.62C
Linearity range($mg \cdot l^{-1}$)	0–0.08	0.005–0.2	0–0.04	0–0.15
Correlation coefficient	0.9992	0.9997	0.9992	0.9992
Sample frequency (h^{-1})	60	60	60	60

a. A: absorbancy; C: concentration in $mg \cdot l^{-1}$

TABLE II The results of interference studies (analyte concentration: 40 $\mu g \cdot l^{-1}$ for copper, 100 $\mu g \cdot l^{-1}$ for lead, 10 $\mu g \cdot l^{-1}$ for cadmium and 60 $\mu g \cdot l^{-1}$ for iron)

Ions	*Conc. ($mg \cdot l^{-1}$)*	*Recovery (%)*			
		copper	*lead*	*cadmium*	*Iron*
Ca^{2+}	1000	110	109	110	105
Cd^{2+}	10	101	103	–	98
	20	100	95	–	104
Cu^{2+}	10	–	109	109	105
	50	–	125	106	107
Fe^{3+}	10	101	99	93	–
	50	91	106	106	–
Mg^{2+}	50	110	109	110	105
Mn^{2+}	10	101	110	95	105
	50	107	109	105	104
Pb^{2+}	10	101	–	92	97
	20	100	–	89	104
Zn^{2+}	10	101	94	92	104
	50	94	100	96	107
Ni^{2+}	50	108	96	98	100

Using copper and iron as model analytes, the phase transfer factors[9] of the DDTC-Ni^{2+} on-line coprecipitation system were evaluated as did in reference [11]. Experiment revealed that the percentages of the analytes collected by the KR were 67% for copper and 53% for iron, which were close to those obtained by DDTC-Fe^{2+} system[11].

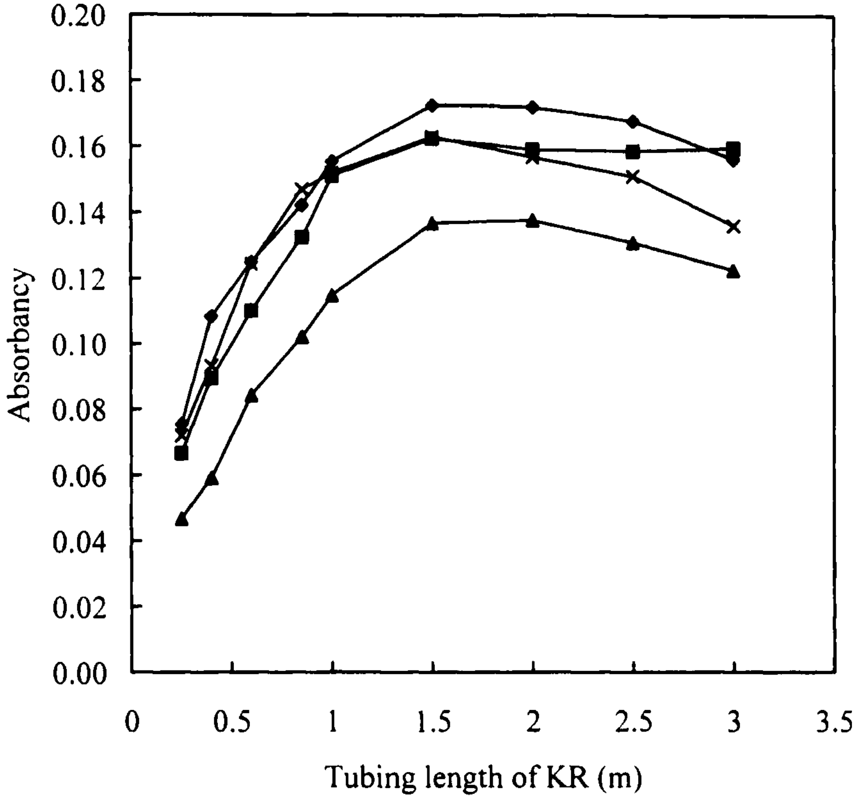

FIGURE 5 Effect of KR length on the signals. Experiment conditions as in Figure 1 except KR length. Symbols for analytes and concentrations of analytes are the same as Figure 2

Interference studies

The results of interference studies are shown in Table II. The interference-free levels of the present system towards such common ions as Cu^{2+}, Fe^{3+}, and Mn^{2+} were above 50 $mg \cdot l^{-1}$, which were not only better than that observed in on-line adsorption preconcentration of cadmium[21] and lead[22] using DDTC as a chelating reagent but also better than that obtained in on-line coprecipitation preconcentration of Pb^{2+} where DDTC-Zn^{2+} [16] were used as carrier.

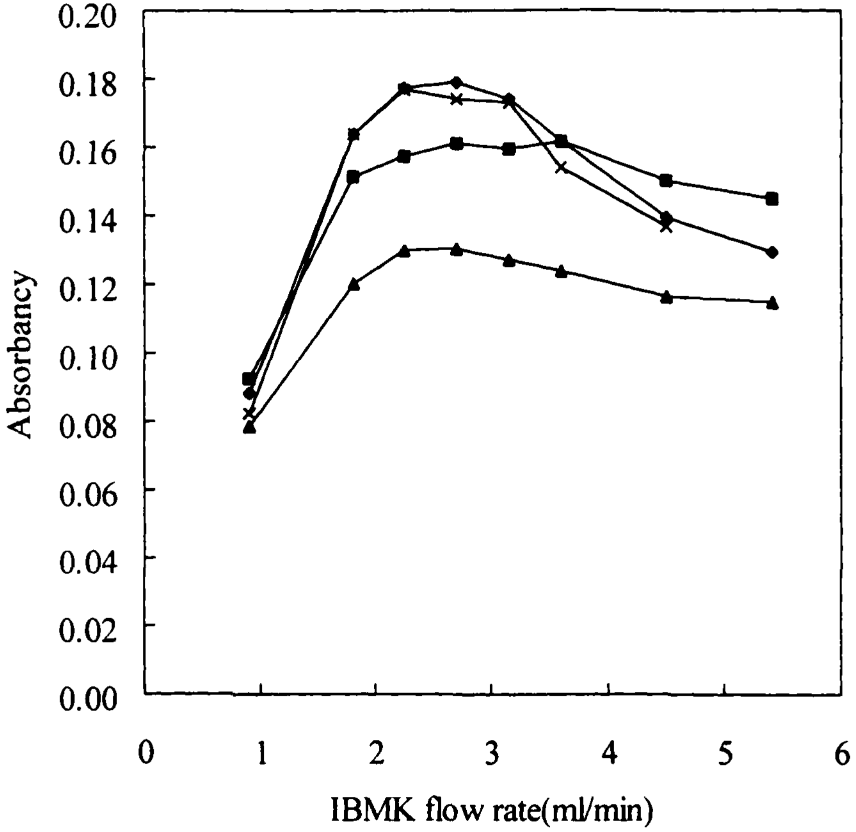

FIGURE 6 Effect of IBMK flow rate on the signals. Experiment conditions as in Figure 1 except IBMK flow rate. Symbols for analytes and concentrations of analytes are the same as Figure 2

The higher tolerance of interference allows the present system to be used for analysis of not only unpolluted water samples, but also such complicated sample as industrial waste waters, soil and sediment, and various biological samples.

Applications

The proposed method has been applied to the determination of copper, cadmium, lead and iron in tap water, industrial waste water. The analytical results, together with the recoveries of the spiked analytes, are listed in Table III. The method was also validated by determination of copper, cadmium, and lead in environmental and biological standard samples. The analytical results obtained are in good agreement with the certified values (Table IV).

TABLE III Analytical results of water samples and the recoveries of spiked analytes

Sample	*Element*	*Added* ($\mu g \cdot l^{-1}$)	*Found* ($\mu g \cdot l^{-1}$)	*Recovery* (%)
Tap water	Cu	0	Not detected	–
		10	10.1	101
	Pb	0	7.5	–
		25	31.7	97
	Cd	0	Not detected	–
		5	5.17	103
	Fe	0	133	–
		10	142	90
Industrial waste water I	Cu	0	Not detected	–
		10	9.2	92
	Pb	0	16.9	–
		20	35.5	93
	Cd	0	1.5	–
		5	6.0	90
	Fe	0	84	–
		20	103	95
Industrial waste water II	Cu	0	12.9	–
		10	22	91
	Pb	0	14.0	–
		20	34.2	101
	Cd	0	Not detected	–
		5	5.3	106
	Fe	0	90.1	–
		20	110.1	100
Industrial waste water III	Cu	0	Not detected	–
		10	9.7	97
	Pb	0	12.9	–
		20	31.8	95
	Cd	0	1.86	–
		5	6.54	94
	Fe	0	Not detected	–
		20	20.0	100

TABLE IV Analytical results for determination of copper, cadmium and lead in standard reference materials ($\mu g \cdot g^{-1}$)

Standard reference materials	*Copper*		*Lead*		*Cadmium*	
	certified value	*Found*[a]	*Certified value*	*Found*[a]	*certified value*	*Found*[a]
Mussel, GBW-08571	7.7 ± 0.6	7.72, 7.80	1.96 ± 0.09	nd	4.5 ± 0.3	4.26, 4.3
Soil, ESS-4	26.3 ± 1.7	25.4, 26.4	22.6 ± 1.7	21.4, 24.4	0.083 ± 0.008	nd
Soil, ESS-1	20.9 ± 0.8	21.4, 20.1	23.6 ± 1.2	23.1, 24.3	0.083 ± 0.008	nd
Soil, GSS-1	21 ± 0.6	20.6, 20.9	98 ± 3	103, 101	4.3 ± 0.2	4.5, 4.4
Human hair, GBW- 09107	23.0 ± 1.4	21.8, 23.0	7.2 ± 0.7	8.3, 8.9	0.095 ± 0.012	nd

nd: not determined due to that the analyte contents are too low to be detected after they are brought into the test solution.

a. Expressed by individual values of two parallel prepared sample solutions.

CONCLUSION

The proposed flow-injection on-line coprecipitation system using DDTC-Ni^{2+} as carrier has proved to be a promising on-line preconcentration approach for trace amounts of copper, iron, cadmium and lead. When coupled to FAAS for determination of these elements in environmental and biological samples, it offers the advantages of simplicity, automation, good precision and sensitivity, and freedom from interference. Sequential determination of these elements can be done under a set of optimized experiment conditions identical for all of the four analytes, resulting in less labor and time consumption for sample preparation. Another prominent merit of the proposed system lies in its capability of working in a wide range of sample acidity. Thus, strict control of sample acidity is not required for analysis of acid-digested samples, such as soil and various biological materials.

It is known that nickel is an efficient and inexpensive matrix modifier used in GFAAS. From this point of view, it is worthwhile studying on the role of the nickel containing carrier on the matrix modification when the present on-line coprecipitation system is coupled to GFAAS for the determination of ultra-trace of metals.

References

1. Y.M. Luo and D.L.Rimmer, *Environ. Pollut.*, **88**, 79–83 (1995).
2. Z.L. Fang and B. Welz, *J. Anal. At. Spectrom.*, **4**, 543–546 (1989).
3. P. Hashemi and A. Olin, *Intern. J. Environ. Anal. Chem.*, **63**, 37–46 (1996).
4. O. Hernandez-Torres and J. J. Arias-Leon, *Intern. J. Environ. Anal. Chem.*, **54**, 15-26 (1993).
5. M. Soylak and L. Elci, *Intern. J. Environ. Anal. Chem.*, **66**, 51–59 (1997).
6. K. K. Namboothiri, N. Balasubramanian and T. V. Ramakriskna, *Talanta*, **8**, 945–949 (1991).
7. P. L. Malvankar and V. M. Shinde, *Analyst*, **116**, 1081-1084 (1991).
8. Ch. Frigge and E. Jackwerth, *Anal. Chim. Acta*, **242**, 99–105 (1991).
9. Z. L.Fang, Flow Injection Separation and Preconcentration, VCH, Weinheim, 1993.
10. Z.L.Fang, M.Sperling and B.Welz, *J. Anal. At. Spectrom.*, **6**, 301–306 (1991).
11. B.Welz, S. K.Xu and M.Sperling, *Appl. Spectrosc.*, **45**, 1433–1443 (1991).
12. Z. L. Fang and L. P. Dong, *J. Anal. At. Spectrom.*, **7**, 439–445 (1992).
13. L. P. Dong and Z. L. Fang, *Guangpuxue yu Guangpu Fenxi*, **14(1)**, 85–90 (1994).
14. H. W.Chen, S. K.Xu and Z. L.Fang, *J. Anal. At. Spectrom.*, **10**, 533–537 (1995).
15. S. Q.Pei and Z. L. Fang, *Anal. Chim. Acta*, **294**, 185-193 (1994).
16. J. C.Jin and H. W.Chen, *Fenxi Ceshi Xuebao*, **16(1)**, 22-26 (1997).
17. H. W.Chen, J. C.Jin and Y. F.Wang, *Anal. Chim. Acta*, **353**, 181-188 (1997).
18. X. Q.Mao, H. W.Chen and J. S.Liu, *Microchem. J.*, **59**, 383–391 (1998).
19. H. W. Chen and J. S. Liu, *Lihua Jianyan (Huaxue Fence)*, **35**, 42–45 (1999).
20. I.Atsuya, K.Itoh and K.Ariu, *Pure and Appl. Chem.*, **63**, 1221-1226 (1991).
21. Z. L. Fang, T. Z. Guo and B. Welz, *Talanta*, **38**, 613–619 (1991).
22. J. C. Jin, H. W. Chen and X. Y. Shen, *Fenxi Huaxue*, **24**, 957–960 (1996).