Low-Temperature Electrothermal Vaporization Coupled With ICP-MS for Speciation of Inorganic Chromium Using Diethyldithiocarbamate as an Extractant and Chemical Modifier

Shizhong Chen* and Dengbo Lu

College of Chemical and Environmental Engineering, Wuhan Polytechnic University
Wuhan 430023, P.R. China

INTRODUCTION

In recent years, environmental pollution from trace metals, especially heavy metals, has received considerable attention. Chromium is a ubiquitous element originating from natural sources and human activities. Chromium speciation is of great interest because its toxicity depends on its oxidation state (1,2) and exists mainly as Cr(III) and Cr(VI). Cr(III) is considered essential to mammals for maintenance of the glucose, protein, and lipid metabolism, whereas Cr(VI) can have acute and chronic toxic effects on biological systems, even at relatively low levels (3-6). This is mainly attributed to the ability of Cr(VI) to penetrate the biological cell membrane, thus increasing the intracellular chromium concentration (7). It has, therefore, become increasingly important to monitor the concentration of individual chromium species.

Solvent extraction is one of the classical and well-rounded methods of separation and preconcentration. It is simple, selective, rapid, and gives high recovery. Compared with other solvent extraction methods, a chelating extraction system has the advantage of high efficiency and a large coefficient of separation, while forming very stable chelates. Among chelating reagents, ammonium pyrrolidine dithiocarbamate (APDC), 1-(2-pyridylazo)-2-naphthol (PAN), diphenylcarbazide (DPC), and

ABSTRACT

A novel method was developed for the speciation of inorganic chromium by low-temperature electrothermal vaporization inductively coupled plasma mass spectrometry (LETV-ICP-MS) using diethyldithiocarbamate (DDTC) as an extractant and a chemical modifier. The main factors affecting the formation of the Cr(VI)-DDTC chelate and its vaporization behavior were investigated in detail.

In this work, DDTC was used not only as an extractant for the separation of Cr(III) and Cr(VI), but also as a chemical modifier for ETV-ICP-MS determination of Cr(VI). Using the optimized conditions, the detection limit of Cr(VI) was 0.045 ng mL⁻¹ and the relative standard deviation (RSD) for 1.0 ng mL⁻¹ Cr(VI) was 4.6% (n=9, v=10 μ L). The linear range of the calibration curve spanned three orders of magnitude. The proposed method was applied to the determination of Cr(III) and Cr(VI) in water samples with recoveries of 94.3–103%.

8-hydroxyquinolinate (HOx) have been used for the analysis of elements and their speciation (8-11).

Electrothermal vaporization (ETV), used as an effective tool for sample introduction into the ICP-MS, has consistently received considerable attention because of high sample introduction efficiency, small sample requirements, low absolute detection limits, and its ability to analyze both liquid and solid samples (12-14). However, the

refractory elements, such as Cr, Al, V, Ti and Zr, are difficult to vaporize either in simple substances or oxide forms due to their high boiling points. For this reason, the sensitivities of these elements in conventional ETV are generally low, and severe memory effects are encountered. In order to solve these problems, the utilization of a chemical modifier for changing the chemical form of a refractory element to a more volatile species is an alternative way to improve the sample introduction efficiency by ETV.

Recently, a significant development was achieved in the exploration and application of organic chelating reagents as chemical modifiers in ETV (15-19). The organic chelating reagent as a chemical modifier may offer the following advantages: (a) the vaporization temperature is much lower than in conventional ETV and prolongs the vaporizer lifetime, (b) refractory elements are introduced into the ICP as volatile chelates from the vaporizer, (c) the application range can be broadened, and (d) the analytical performance can be improved by combining this technique with chemical separation/preconcentration. Thus, further research and exploration of new chelating reagents as chemical modifiers for ETV-ICP-MS can be promising.

Diethyldithiocarbamate (DDTC) is an excellent chelating reagent. It is known to selectively form chelates with Cr(VI), which can be extracted with an organic solvent (20). In addition, DDTC can react

*Corresponding author
E-mail: chensbizhong62@163.com

with metal ions to form stable chelates, some of which have abnormally high volatility (21). These characteristics have attracted special interest with regard to extraction separation and vapor phase introduction of the sample in analytical chemistry (22).

However, the application of DDTC in ETV for elemental speciation by ICP-MS has received little attention so far. The aim of this work was to develop a new method by combining extraction separation with LT-ETV-ICP-MS for chromium speciation analysis. Here, DDTC is utilized as both a chelating reagent for the effective extraction of Cr(VI) and as a chemical modifier for LT-ETV-ICP-MS determination. The formation conditions of the chelate and the factors affecting vaporization and transportation were also investigated in detail. The proposed method was applied to the determination of Cr(III) and Cr(VI) in water samples with satisfactory results.

EXPERIMENTAL

Instrumentation

An X-7 ICP-MS system (Thermo Elemental Corporation, USA), equipped with a modified commercially available WF-4C graphite furnace (Beijing Analysis Instrument Factory, Beijing, P.R. China) as an electrothermal vaporizer, was used for the determination of the analytes. The optimum operating conditions of the ETV-ICP-MS are summarized in Table I. The pH values of the solutions were measured with a pH meter (Thermo Orion Corporation, USA) supplied with a combined electrode.

Reagents

A stock standard solution (1.0 mg mL⁻¹) of Cr(III) was obtained from the National Analysis Center of Iron & Steel (Beijing, P.R. China). Cr(VI) was prepared by dis-

solving K₂Cr₂O₇ (Tianjin Reagent Factory, Tianjin, P.R. China) in water. A 0.10 mol L⁻¹ DDTC solution was prepared by dissolving 1.713 g DDTC (Shanghai Reagent Factory, Shanghai, P.R. China) in 100 mL CHCl₃ (Shanghai Reagent Factory, Shanghai, P.R. China).

Working solutions were prepared daily by appropriate dilution of the stock solutions. All other reagents used were ultrapure or at least of analytical grade. High purity deionized water (18.2 MΩ), obtained from a Milli-Q™ A10 system (Millipore Corporation, USA), was used throughout this work.

Procedure

Liquid-liquid extractions were carried out by shaking equal volumes of the aqueous and organic

TABLE I
LT-ETV-ICP-MS
Operating Conditions

ICP-MS	
Plasma power	1300 W
Plasma argon flow rate	14.3 L min ⁻¹
Auxiliary argon flow rate	0.77 L min ⁻¹
Nebulizer argon flow rate	0.96 L min ⁻¹
Sampler orifice (Ni)	1.1 mm
Skimmer orifice (Ni)	0.7 mm
Acquisition mode	Peak-jumping
Number of sweeps	100
Dwell time	10 ms
Acquisition time	40 s
Number of measurements per peak	3
Isotopes	⁵² Cr
ETV	
Sample volume	10 μL
Carrier gas flow rate	0.43 L min ⁻¹
Drying step	100 °C, ramp 10 s, hold 10 s
Vaporization step	1000 °C, hold 4 s

phase for a required time at 25 °C. In most cases, distribution equilibrium was attained within less than 30 minutes. For speciation studies, two aliquots of the sample solutions were adjusted to pH 5.0: one was directly extracted using a DDTC-CHCl₃ solution, while the other was extracted using a DDTC-CHCl₃ solution after oxidation with 20% (m/v) H₂O₂. The former was used for the determination of Cr(VI), and the latter for the determination of total Cr. Cr(III) was obtained by subtracting Cr(VI) from total Cr. After phase separation, 10 μL of the organic phase was pipetted into the graphite tube with a microsyringe. The sample inlet hole was sealed with a graphite rod before the graphite furnace heating cycle was started. The gaseous chelate produced from the ETV was carried into the ICP by argon carrier gas for the analysis.

RESULTS AND DISCUSSION

Separation of Cr(VI) and Cr(III) With DDTC

The experimental results showed that DDTC can effectively extract Cr(VI) at pH 4.0–6.0, while Cr(III) remains in the aqueous phase. In this work, a pH value of 5.0 was used for the DDTC extraction and separation of Cr(VI) from Cr(III). Figure 1 shows the signal profiles of Cr(III) and Cr(VI) after extraction with equal volumes of DDTC-CHCl₃ solution. It can be seen that a strong signal was recorded (B) in the organic phase after DDTC-CHCl₃ extraction of Cr(VI). However, the signal of Cr(III) can hardly be detected in the organic phase (A) after DDTC-CHCl₃ extraction of the same amount of Cr(III). In order to verify this result, Figure 1 shows the signal profile (C) obtained after DDTC-CHCl₃ extraction of 5.0 ng mL⁻¹ Cr(VI) mixed with 5.0 ng mL⁻¹ Cr(III). It is obvious that the intensity and shape of the signal from

(C) are the same as those for DDTC- CHCl_3 extraction of an equal concentration of Cr(VI) alone (B). This shows that Cr(VI) was effectively separated from Cr(III) with DDTC- CHCl_3 .

Effect of DDTC Concentration

The effect of DDTC concentration on the signal intensity of the analyte was studied. The results in Figure 2 indicate that the signal intensities of the analyte (5.0 ng mL^{-1} Cr(VI)) strongly depend on DDTC concentration. The signal intensi-

ties of the analyte increased remarkably with an increase in DDTC concentration, and the maximum signal intensity was obtained when the DDTC concentration was more than 0.06 mol L^{-1} . This concentration of Cr(VI) is much higher than that obtained by graphite furnace. The reasonable mechanism for the experimental fact may be that, on one hand, a large amount of extra DDTC favors the formation of the Cr(VI)-DDTC complex while, on the other hand, the vapor produced from the extra DDTC in the rapid

vaporization process suppresses the thermal decomposition of the Cr(VI)-DDTC chelates. Thus, a concentration of 0.08 mol L^{-1} DDTC- CHCl_3 solution was used in this work.

Volatile Behavior of Cr(VI)-DDTC Chelate

It was found that DDTC can react with some metal ions to form volatile chelates with good thermal stability (20,21). This demonstrates that low-temperature electrothermal vaporization of Cr(VI) is possible using DDTC as a chemical modifier. Figure 3 shows the typical signal profiles of Cr(VI) obtained by LT-ETV-ICP-MS with DDTC. As can be seen, a sharp, intense, and symmetrical signal profile of Cr(VI) was recorded at the comparatively low temperature of 1000°C with DDTC due to the formation of the volatile Cr(VI)-DDTC complex (B). However, no signal was observed for the same concentration of Cr(VI) in an aqueous standard solution at the same vaporization temperature (C). The signals of the relative blank solutions were not determined in this experiment (A). The results show that the analyte was introduced into the ICP as a gaseous DDTC chelate.

Fig. 1. Signal profiles of Cr(VI) and Cr(III) with DDTC- CHCl_3 extraction. (A): 5.0 ng mL^{-1} Cr(III) with DDTC- CHCl_3 ; (B): 5.0 ng mL^{-1} Cr(VI) with DDTC- CHCl_3 ; (C): 5.0 ng mL^{-1} Cr(III) and 5.0 ng mL^{-1} Cr(VI) with DDTC- CHCl_3 .

Fig. 2. Effect of DDTC concentration on signal intensity.

Fig. 3. Typical signal profiles for Cr(VI) vaporized at 1000°C . (A): Only 0.08 mol L^{-1} DDTC; (B): 5.0 ng mL^{-1} Cr(VI) with DDTC; (C): only 5.0 ng mL^{-1} Cr(VI).

Selection of Drying Conditions

In the present work, a drying temperature of 100 °C was used to remove the water and the organic solvent from the graphite tube. At the selected drying temperature, the effect of drying time on the vaporization behavior of the analyte was investigated. The experimental results showed that drying time had no significant influence on the signal intensity of the analyte and was constant after a drying time of more than 5 seconds. As a result, a drying temperature of 100 °C for 10 seconds was chosen in the following experiments.

Optimization of Vaporization Conditions

The effect of vaporization temperature on the signal intensity of the analyte is shown in Figure 4. It can be seen that at 300 °C, a weak signal was detected, showing that Cr(VI)-DDTC chelate was formed and vaporized into the ICP. As the temperature increased, the signal intensity enhanced markedly. At 900 °C, the analytical signal intensity reached its maximum and remained constant at a higher temperature.

The effect of vaporization time on the vaporization behavior of the DDTC-Cr(VI) chelate was also

investigated. The experimental results showed that maximum signal intensity of the analyte was obtained when the vaporization time was set at greater than 3 seconds. This means that vaporization of the analyte can be completed within a short time. Based on the above results, a vaporization temperature of 1000 °C and a vaporization time of 4 seconds was utilized in the present work.

Effect of Coexisting Ions

The effect of common metal ions, such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Zn²⁺, Al³⁺, Fe³⁺, PO₄³⁻, SiO₃²⁻, and SO₄²⁻, in environmental water samples in the determination of Cr(VI) was examined by LT-ETV-ICP-MS. The tolerance amounts of coexisting ions, which give less than 10% error for the determination of 5.0 ng mL⁻¹ Cr(VI), were evaluated. The experimental results (see Table II) show that the selected ions did not interfere in the determination of Cr(VI) in the range of their amounts tested.

Proof of Vaporization and Transportation of Cr(VI)-DDTC Chelate

With DDTC as the chemical modifier, as described above, the vaporization character of Cr(VI) was greatly improved. However,

did the system really work as expected? In other words, was the Cr(VI)-DDTC chelate vaporized and transported from the ETV into the ICP? To answer these questions, the following experiments were carried out. A 50 µg mL⁻¹ Cr(VI) solution was added to an equal volume of 0.10 mol L⁻¹ DDTC solution. At the optimum experimental conditions, the ETV was run, as usual, ten times with 50 µL of the resulting organic phase as sample. The resulting sample vapor was collected in CHCl₃ for analysis by ultraviolet-visible spectrophotometry (UV-VIS). The obtained absorption spectrum of the collected solution was very similar to that of the Cr(VI)-DDTC chelates in CHCl₃. The above experimental results indicated that the DDTC-Cr(VI) chelate could indeed be vaporized and transported from the ETV into the ICP.

Precision and Detection Limit

The detection limit (DL), the lowest concentration level that can be determined to be statistically different from a blank, is defined as three times the within-batch standard deviation of a signal blank determination, corresponding to the 99% confidence level. The detection limit for Cr(VI) in the presence of DDTC was determined as 0.045 ng mL⁻¹. The precision, expressed as the relative standard deviation obtained for nine repli-

Fig. 4. Influence of vaporization temperature on signal intensity with DDTC.

TABLE II
Effect of Coexisting Ions on the Determination

Coexisting Ion	Concentration Ratio ^a
Na ⁺ , K ⁺	5000 ^b
Ca ²⁺ , Mg ²⁺	2000 ^b
Cu ²⁺ , Zn ²⁺	500 ^b
Fe ³⁺ , Al ³⁺	200 ^b
PO ₄ ³⁻ , SiO ₃ ²⁻ , SO ₄ ²⁻	2000 ^b

^a Concentration ratio: Foreign ion / Cr(VI)

^b Maximum concentrations tested.

cate determinations at 1.0 ng mL⁻¹ Cr(VI), was 4.6% (v=10 µL). The linear dynamic range of the calibration curve covered three orders of magnitude.

Sample Analysis

The proposed method was applied to the determination of Cr(VI) and Cr(III) in environmental water samples. The results obtained are presented in Table III, with recoveries of 94.3–103%. Before the analysis, water samples, including wastewater, pool water, and lake water, were filtered through a 0.25 µm membrane filter and stored for future use. The blank was prepared exactly as the samples, except no analytes were added.

CONCLUSION

In this work, a new method was developed for the analysis of Cr(III) and Cr(VI) by low temperature electrothermal vaporization inductively coupled plasma mass spectrometry (LT-ETV-ICP-MS), using diethyldithiocarbamate (DDTC) as an extractant and chemical modifier. The experimental results showed that the Cr(VI)-DDTC chelate was quantitatively vaporized into the ICP at the relatively low temperature of 1000 °C. DDTC as a chelating reagent can effectively separate Cr(VI) and Cr(III). On the other hand, DDTC as a chemical

modifier not only effectively prohibits the formation of refractory carbides and eliminates memory effects, but also greatly promotes the vaporization efficiency and improves the analytical sensitivity due to the formation of a thermal stable and volatile Cr(III)-DDTC complex. Therefore, it is likely to become an effective method for the determination of ultra-trace elements and their speciation in real samples.

ACKNOWLEDGMENTS

This work was supported by the Provincial Science Foundation of Hubei, P.R. China.

Received September 30, 2011.

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TABLE III
Analytical Results and Recoveries of Cr(III) and Cr(VI) in Water Samples

Sample	Added (ng mL ⁻¹)		Found ^a (ng mL ⁻¹)		Total	Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III) ^b	Cr(VI)		Cr(III)	Cr(VI)
Pool Water	0	0	2.19±0.15	0.84±0.07	-	-	-
	1.0	1.0	3.13±0.21	1.82±0.14	4.95±0.35	94.3	98.2
	2.0	2.0	4.10±0.29	2.77±0.19	6.87±0.52	95.7	96.5
Lake Water	0	0	0.94±0.08	0.51±0.04	1.45±0.11	-	-
	1.0	1.0	1.90±0.15	1.52±0.11	3.42±0.25	95.6	101
	2.0	2.0	2.89±0.18	2.41±0.17	5.30±0.38	97.3	95.2
Wastewater	0	0	4.23±0.28	5.74±0.43	9.97±0.58	-	-
	5.0	5.0	8.97±0.52	10.6±0.65	19.6±1.32	94.8	98.0
	10	10	13.7±0.64	16.0±1.10	29.7±1.62	95.1	103

^a Mean value ± standard deviation, n=5.

^b Calculated value.