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Volatilization of Cr, Co, Mn and Ni as their pyrrolidinecarbodithioate chelates from electrothermal vaporizer for sample introduction in inductively coupled plasma optical emission spectrometry

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Abstract

Based on gaseous compound introduction as pyrrolidinecarbodithioate chelates of Cr, Co, Mn and Ni by electrothermal vaporization (ETV) in inductively coupled plasma optical emission spectrometry (ICP-OES), a novel method for the determination of trace Cr, Co, Mn and Ni was developed. It was found that in the presence of ammonium pyrrolidinecarbodithioate (APDC) the trace amounts of analytes were vaporized at a low temperature of 1500 °C. The main factors affecting the formation and vaporization of analytes chelates were investigated in detail. Thermal gravimetric analysis of Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates and UV–vis analysis of the sample vapor collected in $CHCl_3$ after vaporization of their chelates indicated that the analytes were vaporized and transported into ICP as their chelates. Under the optimized conditions, the limits of detection (LOD) (3σ) and the relative standard deviations (R.S.D.) of Cr, Co, Mn and Ni were 0.36, 0.19, 0.073 and 0.32 ng, and 3.9, 4.9, 3.8 and 3.3% ($c = 0.5\ \mu g\ ml^{-1}$, $n = 7$), respectively. By combination with a solvent extraction step, the proposed method had been successfully applied to analysis of Cr, Co, Mn and Ni in the artificial seawater. To evaluate the accuracy of the developed method, two certified reference materials (human hair GBW 09101 and poplar leaves GBW 07604) were also analyzed, and the determined values obtained were in good agreement with the certified values.

Keywords: Ammonium pyrrolidinecarbodithioate; Chemical modifier; ETV–ICP-OES; Cr, Co, Mn and Ni; Biological samples

1. Introduction

In recent years, electrothermal vaporization (ETV) as a means of sample introduction technique had been widely studied and applied in atomic spectrometry/mass spectrometry [1–4]. The main advantages of ETV over conventional solution nebulization were the improvement of sensitivity as well as the ability to analyze microliter volumes/micrograms of wide variety of sample types including highly acidic and saline solution and solids. However, this approach inherits the disadvantages of electrothermal vaporization with respect to the formation of refractory carbides by elements in group IVB to VIB, which leads to a decrease or even complete suppression of analyte from one determination to the next, thus causing memory effects, moreover, the high temperature (ca. 2500 °C) used in ETV method causes problems such as the vaporizing behavior of trace analyte varied with the sample matrix, which is one of the possible error sources in analytical results [5]. In order to solve these problems, the use of chemical modification via the addition of chemical modifier changing the chemical form of refractory elements to a more volatile species has been proven to be one of the most effective methods. Examples are the successful application of halogenating agents [6,7] especially polytetrafluoroethylene (PTFE) [8,9].

Black and Browner [10] described a method for ICP-OES determination of trace metals by the formation of the metallic β-diketonates with ligands such as trifluoroacetylacetonate and hexafluoracetylacetone through heating the chelate reaction vessel. Their experimental results indicated that this technique could offer high sample introduction

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efficiency and a much lower detection limits. However, it was time consuming. Tao and Kumamaru [11–13] reported the vaporization of refractory elements, such as Cr, V and Al as their 8-hydroxyquinolinates for gaseous compound introduction by ETV, and vaporization temperatures were not more than 1000 °C. The proposed method was successfully applied to analyze trace metals in some standard materials. Recently, other chelate reagents including 1-phenyl-3-methyl-4-benzoyl-pyrazolone (PMBP) [14], 1-(2-pyridylazo)-2-naphthol (PAN) [15], acetylacetone (AcAc) [16], benzoylacetone (BZA) [17] and diethyldithiocarbamate (DDTC) [18] have also been used as chemical modifiers to the determination of rare earth elements, transition elements and platinum group elements for gaseous compound introduction by ETV–ICP-OES/MS. All these facts demonstrated that organic chelating reagents are the another kind of effective chemical modifiers in the ETV–ICP-OES/MS, and it has some characteristics such as: (1) refractory elements can be vaporized at lower temperatures which is beneficial to prolong the lifetime of evaporator; (2) organic chelating reagents can be used both as chemical modifiers and as extracting reagents, and therefore, the application range can be broaden and the determination sensitivity can be further improved.

Ammonium pyrrolidinecarbodithioate (APDC) is well known as an excellent chelating reagent for the separation/preconcentration several trace metal ion in analytical chemistry [19–21]. In the present paper, APDC was attempted to be used as a new chemical modifier in ETV–ICP-OES for low temperature vaporization of Cr, Co, Mn and Ni as well as an extracting reagent for the separation/preconcentration of Cr, Co, Mn and Ni. The factors affecting the formation of the chelates and their vaporization behaviors were investigated in detail. It was found that Cr, Co, Mn and Ni could be vaporized at a temperature as low as 1500 °C in the presence of APDC. The proposed method was applied to the determination of trace Cr, Co, Mn and Ni in seawaters and certified reference materials with satisfactory results.

2. Experimental

2.1. Apparatus

The graphite furnace ETV sample introduction device used in this work and its combination with ICP-OES were identical with that reported previously [8]. An ICP spectrometric system (Beijing Broadcast instrument Factory, Beijing, China) with 2-kW plasma generator was used with a conventional silica plasma torch. A WF-1B type heated device with a matching graphite furnace (Beijing Second Optics, Beijing, China) was used for the sample introducing; pyrolytic graphite-coated tubes were used throughout. The radiation from the plasma was focused as a 1:1 image on the entrance slit of a WDG 500-1A type monochromator (Beijing Second Optics) having a reciprocal linear dispersion of 1.6 nm mm^{-1}. The transient emission signals from plasma were detected with a R456 type photomultiplier tube (Hamamatsu, Japan) fitted with a laboratory-built direct current amplifier, and recorded by a U-135C recorder (Shimadzu, Kyoto, Japan). The ICP-OES instrument was initially optimized using conventional pneumatic nebulization, then converted to operate with the ETV. The used instrument operating conditions and wavelength are given in Table 1.

Table 1
ETV–ICP-OES operating conditions for determination of Cr, Co, Mn and Ni

Wavelength (nm)	Cr 283.56; Co 343.90; Mn 257.61; Ni 352.45
Incident power (kW)	1.0
Carrier gas (l min^{-1})	0.6
Coolant gas (l min^{-1})	16
Plasma gas (l min^{-1})	0.8
Observation height (mm)	12
Entrance slit-width (μm)	25
Exit slit-width (μm)	25
Drying temperature (°C)	80 Ramp 10 s, hold 10 s
Pyrolysis temperature (°C)	200 Ramp 10 s, hold 10 s
Vaporization temperature (°C)	1500 Ramp 0 s, hold 4 s
Cleaning temperature (°C)	2500 Ramp 0 s, hold 5 s
Sample volume (μl)	20

Thermal analyses of the metal chelates were done under nitrogen with a NETZSCH STA 449C Thermal Analysis System (German). Sample masses of 5–10 mg were run at a heating rate of 20 °C min^{-1} from ambient to 500 °C.

2.2. Standard solution and reagents

The stock standard solutions of Cr, Co, Mn and Ni (1 mg ml^{-1}) were prepared by dissolving 0.1000 g of pure metal (Shanghai Reagent, Shanghai, China) in 2% (v/v) HNO_3, and diluting to 100 ml volume with doubly deionized water. The standard working solutions were prepared daily by stepwise dilution of standard stock solutions with 2% (v/v) HNO_3. 0.25 and 2.0% (m/v) of APDC solution was prepared by dissolving 0.25 and 2.0 g of APDC (Shanghai Reagent Factory, Shanghai, China) in 100 ml deionized water solution. The pH values were adjusted by drop-wise addition of 0.1 mol l^{-1} ammonia or HCl solutions before use. Doubly deionized water was used throughout. All other reagents used were of analytical reagent grade.

The certified reference materials used in this work are human hair GBW 09101 and poplar leaves GBW 07604 (both obtained from National Institute of Standards and Technology, Beijing, China).

The Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates were prepared by the general procedure [22]. The isolated complexes were purified by recrystallization from chloroform.

2.3. Sample preparation

2.3.1. Artificial seawater

Artificial seawater (250 ml) was prepared by dissolving 0.3675 g of $CaCl_2{\cdot}2H_2O$, 3.275 g of $MgSO_4{\cdot}7H_2O$ and 6.975 g of NaCl in doubly deionized water [23].

2.3.2. Certified reference material

0.5000 g of sample was weighed and transferred into a 100 ml PTFE beaker. Then 10 ml of HNO_3:H_2O_2 (2:1,v/v) was added to the beaker, and digested for about 1 h until the sample was completely decomposed, the resulting solution was heated to near dryness, then the residue was dissolved in 5 ml of 2% (v/v) HNO_3.

2.3.3. Sample extraction

The above sample solution was adjusted to pH 4.0 by drop wise adding appropriate amounts of 0.1 mol l^{-1} HCl or ammonia before 2.0 ml 2% (m/v) of APDC was added. The mixed solution was shaked for about 5.0 min. After 1.0 ml of chloroform was added, the solution was shaked for 10 min, and then transferred to a separatory funnel to remove the aqueous phase. The organic phase containing the Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates was pipetted into graphite furnace for ETV–ICP-OES determination.

For determination of the blank values, three blank samples were prepared in the same way as the samples. The contents of analyte in samples were obtained by subtracting blank values from the determined values.

2.4. Analytical procedure

In a 5-ml volumetric flask, a mixed solution of 0.5 μg ml^{-1} Cr, Co, Mn and Ni, 0.05% (m/v) APDC was prepared. After the plasma had stabilized, 20 μl of the resulting solution was pipetted into the graphite furnace with a microsyringe. The sample inlet hole was sealed with a graphite cylinder before the graphite furnace heating cycle was started. The gaseous analyte by ETV was carried into the ICP by the argon carrier gas. The signal intensity of Cr, Co, Mn and Ni was recorded, and the peak heights were measured for quantification.

3. Results and discussion

3.1. Vaporization behaviors of Cr, Co, Mn and Ni

The effect of APDC as chemical modifier on the signal profiles of elements of interest in ETV–ICP-OES was observed. Fig. 1(a and b) are the signal profiles of Cr, Co, Mn and Ni in the presence and absence of APDC, respectively. As found in Fig. 1(b), without APDC, no emission signal could be observed for Cr, Co, Mn and Ni at the vaporization temperature of 1500 °C, and the weaker and wider emission signals of Cr, Co, Mn and Ni were detected at the temperature of 2500 °C. On the contrary, with the use of APDC as chemical modifier, more intense and sharper emission signal profiles for Cr, Co, Mn and Ni were observed at lower vaporization temperature of 1500 °C, and no obvious memory signal was found at the temperature of 2500 °C (Fig. 1(a)), which means that Cr, Co, Mn and Ni could be evaporated at 1500 °C completely. This signal enhancement and the vaporization temperature decrease of Cr, Co, Mn and Ni in presence of APDC were attributed to the formation of volatile Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC complexes, which improved the vaporization behaviors of analytes and increased the transport efficiency of analytes from the graphite furnace to the plasma. Many factors could affect the vaporization behaviors of Cr, Co, Mn and Ni, which should be explored in the following studies.

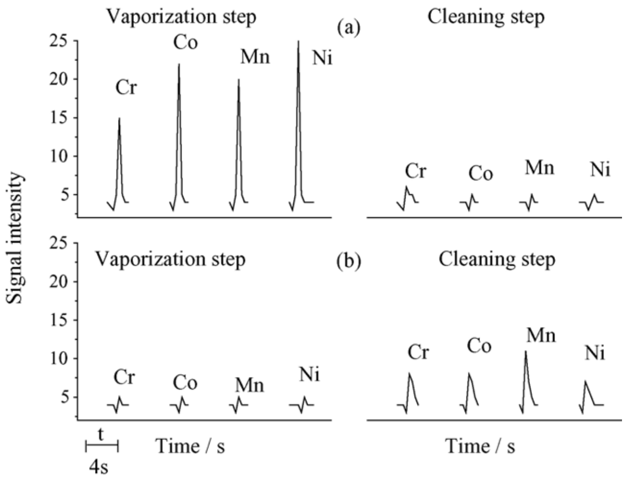


Fig. 1. Signal profiles of Cr, Co, Mn and Ni: (a) with APDC as chemical modifier; (b) without APDC as chemical modifier. Cr, Co, Mn and Ni, 10 ng; APDC, 0.05% (m/v); sample volume 20 μl.

3.2. The effect of pyrolysis temperature and time on the signal intensity

The effect of pyrolysis temperature on the signal intensity of Cr, Co, Mn and Ni in the presence of APDC was evaluated at pyrolysis temperature varying between 100 and 400 °C. It was found that a loss of the signal of analytes occurs after 250 °C for all elements, this loss was presumably owing to vaporization of the volatile organic compounds of Cr, Co, Mn and Ni. In this work, a pyrolysis temperature of 200 °C was selected.

Under the selected pyrolysis temperature, the effect of pyrolysis time on the signal intensity of Cr, Co, Mn and Ni was studied. The loss of the signal of analytes occurs after 40 s. Therefore, a pyrolysis time of 20 s was selected in this study.

3.3. The effect of the vaporization temperature and time on the signal intensity

The vaporization temperature must be optimized in order to obtain the maximum analytical signals. Fig. 2 shows the

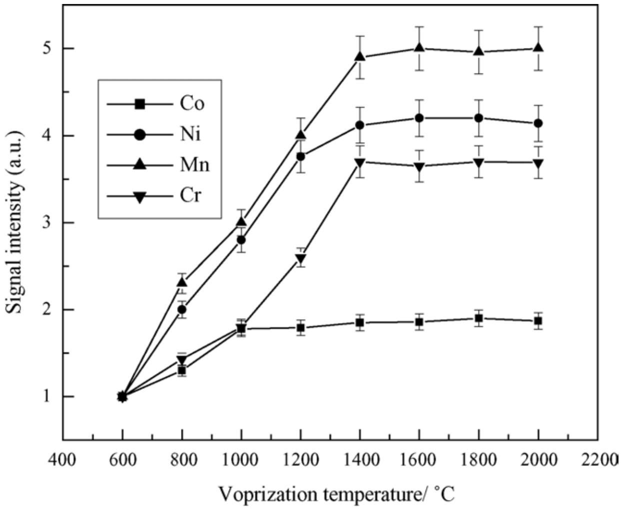


Fig. 2. Effect of the vaporization temperature on the signal intensity of Cr, Co, Mn and Ni. Cr, Co, Mn and Ni, 10 ng; APDC, 0.05% (m/v); sample volume 20 μl.

effect of the vaporization temperature on the signal intensity of Cr, Co, Mn and Ni. It was found that the signals of the elements studied increased gradually with the increase of vaporization temperature and the maximum emission signals of the analytes were obtained at 1400 °C for Cr, Mn and Ni, 1000 °C for Co, and this maximum signal was kept constant with the further increase of vaporization temperature to 2000 °C. In this work, a temperature of 1500 °C was selected as the appropriate vaporization temperature for Cr, Co, Mn and Ni. By applying the established heating program, the effect of vaporization time on the analytical signal of analytes was studied. It was found that the signal increased with the increase of vaporization time, and the maximum signal intensity was achieved after the vaporization time approached to 2 s, and it remained constant up to 6 s. Thus, a vaporization time of 4 s was chosen in further experiments.

3.4. The influence of pH and medium on the signal intensity

It is well known, the pH of the reaction solution was one of the important factors affecting the formation of complexes. The effect of pH on the signal intensity of the elements of interest was evaluated at pH values varying between 2 and 8, and the results indicated that no obvious effect of pH on the signal intensity of Cr, Co, Mn and Ni was observed in the tested pH range, which might be attributed to that the Cr, Co, Mn and Ni can react with APDC and stabilize at pH range of 2–8. Considering that APDC is unstable in the acid medium, and metal ions are easily hydrolyzed in alkali medium, a pH 4.0 was selected for further study.

The signal intensity of Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC in both $CHCl_3$ phase (after extraction) and aqueous phase (after back extraction with 2.0 mol l^{-1} HNO_3) was comparatively studied, and no obvious difference in signal intensity was observed. This means that the direct analysis of organic phase is feasible and no back extraction is required.

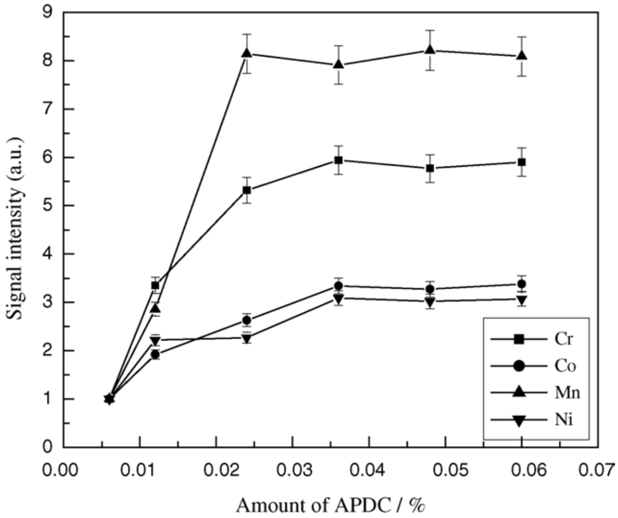


Fig. 3. Effect of APDC concentration on the signal intensity of Cr, Co, Mn and Ni. Cr, Co, Mn and Ni, 10 ng; sample volume 20 μl.

3.5. Effect of APDC concentration

As described previously, the emission signal intensity of Cr, Co, Mn and Ni was enhanced remarkably in the presence of APDC. The reasons for this are that APDC can react with Cr, Co, Mn and Ni to form the Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates. These chelates are volatile and thermal stable, and could be vaporized and transported from the furnace to the plasma very easily. Therefore, the transportation efficiency of analytes increased greatly. However, a notable fact is that the concentration of APDC will influence on the formation of metal chelates along with its vaporization and transportation in ETV–ICP-OES. Fig. 3 is the dependence of analytical signal intensity of Cr, Co, Mn

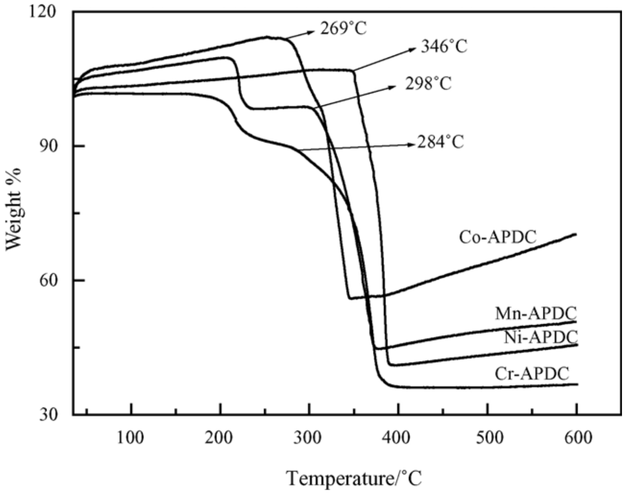
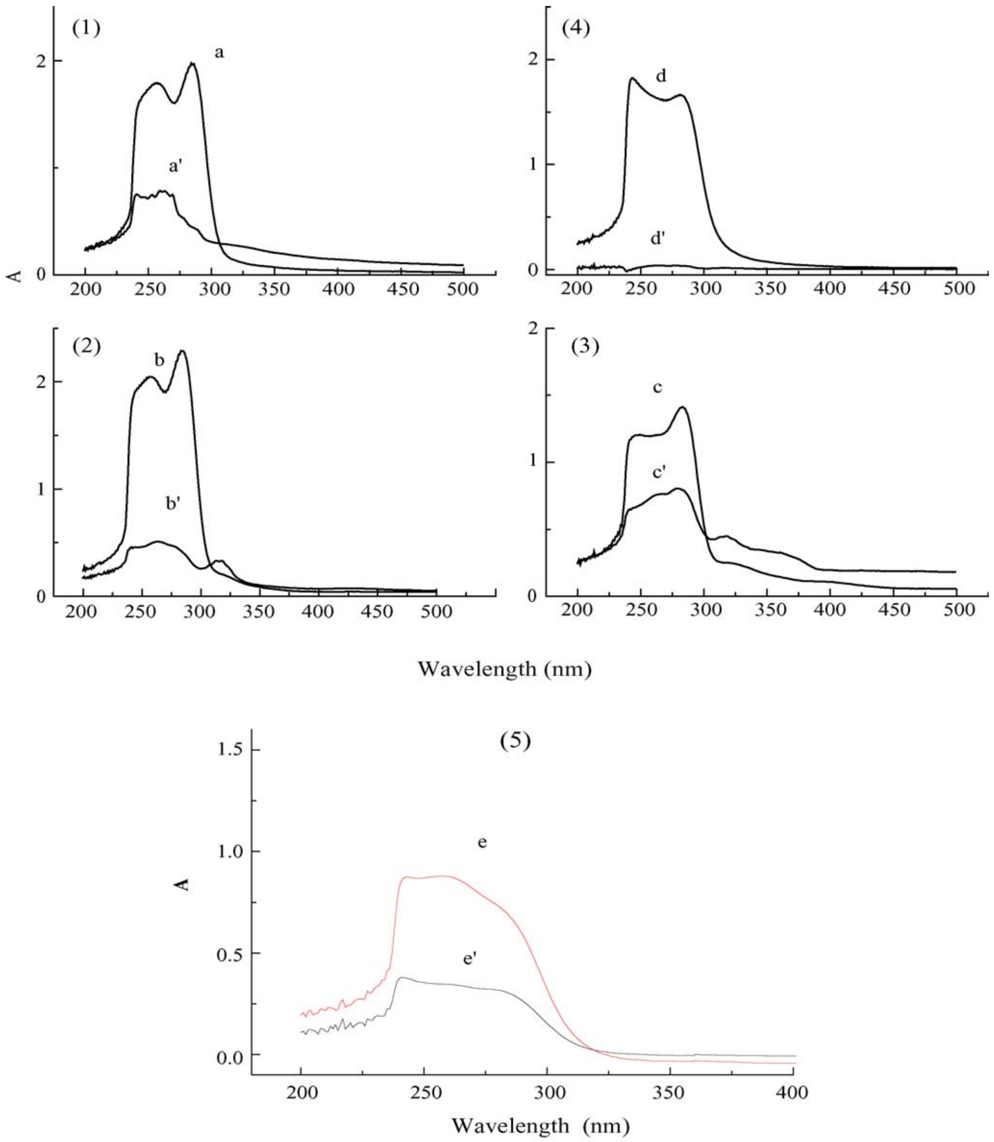


Fig. 4. Thermal gravimetric (TG) analysis of Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates.

and Ni on the APDC concentration. As could be seen, the signal intensity of the analytes increased with the increase of APDC concentration from 0.005% (m/v) to 0.035% (m/v) and then levels off up to the concentration of 0.06% (m/v). In this study, APDC concentration of 0.05% (m/v) was chosen.

3.6. Proof of the vaporization and transportation of metal–APDC chelates

For verification of the above conclusion, both thermal gravimetric (TG) analyses of the metal chelates and UV–vis analysis of sample vapor collected in $CHCl_3$ were carried out. Fig. 4 is the thermal gravimetric curves for Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates. As could be seen, one-step weight losses in the temperature range of 269–400 °C were observed for Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates. These results clearly indicated that the Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates have good properties of volatility and thermal stability, and Cr, Co, Mn and Ni was probably vaporized and transported from the furnace to the plasma at low vaporization temperature as their APDC chelates. For UV–vis analysis of sample vapor collected in $CHCl_3$, the following experiment was designed. A 0.1 mg ml^{-1} Cr, Co, Mn and Ni solution was added into an equal volume of 2% (m/v) APDC solution. At the optimum experimental conditions, ETV heating programs was run ten times with 40 μl of the resulting solution injection. The produced sample vapor was collected in $CHCl_3$ and analysed by UV–vis spectrophotometry. The experimental results are shown in Fig. 5. It can be



e standard solution, e' absorption solution

Fig. 5. UV spectra of Cr–APDC, Co–APDC, Ni–APDC and Mn–APDC chelates in $CHCl_3$. (1) Ni–APDC; (2) Cr–APDC; (3) Co–APDC; (4) APDC; (5) Mn–APDC; a–e: standard solution; a′–c′, e′; sample vapor collected in $CHCl_3$; d′ sample vapor collected in H_2O.

seen that the obtained absorption spectrum of the collected solution was very similar to that of standard metal–APDC chelates in $CHCl_3$. The above experimental results indicated that Cr, Co, Mn and Ni was indeed vaporized and transported as its APDC chelates from graphite furnace to the plasma.

3.7. Interferences

The influence of the common metal ions such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}/Fe^{3+}, Cu^{2+} and Zn^{2+} in the biological and environmental samples on the determination of Cr, Co, Mn and Ni was investigated. The solutions of 10 ml 0.1 μg ml^{-1} Cr, Co, Mn and Ni containing the corresponding interfering ions were prepared and extracted according to the sample extraction procedure. The experimental data showed that the developed method was not affected by the potential interferences from the major matrix elements such as alkali and alkaline earth elements because these elements do not form stable complexes with APDC. The interferences was possible in the presence of a excess of Al^{3+}, Zn^{2+}, Fe^{2+}/Fe^{3+}, Cu^{2+} and Pb^{2+} since these elements can react with APDC to form their corresponding stable chelates under the operation conditions used. The amounts of tested element which could be tolerated without interference occurring are as follows (μg ml^{-1}): K^+, Na^+(5000); Ca^{2+}, Mg^{2+}(2500); Al^{3+}, Zn^{2+}(3); Fe^{2+}/Fe^{3+}, Cu^{2+} and Pb^{2+}(2) (results within 10% error).

3.8. Analytical performance

With the use of established experimental parameters as shown in Table 1, the analytical performance of the method was evaluated. The limits of detection were calculated as three times the standard deviation of the reagent blank signal ($n = 7$), in accordance with IUPAC recommendations. The limits of detection (LODs) and the relative standard deviations (R.S.D.) of Cr, Co, Mn and Ni were 0.36, 0.19, 0.073 and 0.32 ng, and 3.9, 4.9, 3.8 and 3.3% ($c = 0.5$ μg ml^{-1}, $n = 7$), respectively. The above LODs values are comparable with that of 0.009–1.03 ng for Cr, 0.012–0.45 ng for Co, 0.0003–0.16 ng for Mn and 0.027–4.85 ng for Ni which given in reference [24].

3.9. Sample analysis

3.9.1. Artificial seawater

Artificial seawater was analyzed to check the accuracy of the proposed method, and the results are given in Table 2. As could be seen, the recoveries for the spiked samples were in the acceptable range (96.4–104.8%).

Table 2
Analytical results for Cr, Co, Mn and Ni in artificial seawater samples ($n = 3$)

Element	Added (ng ml^{-1})	Found [a] (ng ml^{-1})	Recovery (%)
Cr	0	–	–
	25	24.3 ± 1.4	97.2
	50	48.9 ± 2.9	97.8
Co	0	–	–
	25	26.2 ± 2.1	104.8
	50	49.6 ± 3.3	99.2
Mn	0	–	–
	25	24.1 ± 1.9	96.4
	50	51.3 ± 2.4	102.6
Ni	0	–	–
	25	25.6 ± 1.8	102.4
	50	50.7 ± 2.3	101.4

[a] Values expressed as mean ± s ($n = 3$).

3.9.2. Certified reference material

To further verify the accuracy of the method, the developed method was applied to the determination of Cr, Co, Mn and Ni in certified reference materials of human hair GBW 09101 and poplar leaves GBW 07604, and the analytical results are given in Table 3. As could be seen, the determined values obtained by the proposed method coincided very well with the certified values.

Table 3
Analytical results for Cr, Co, Mn and Ni in two certified reference materials (GBW09101 human hair and GBW07604 poplar leaves)

Sample	Element	Measured value [a] (μg g^{-1})	Certified value (μg g^{-1})
GBW09101	Cr	4.56 ± 0.35	4.77 ± 0.38
	Mn	2.91 ± 0.09	2.94 ± 0.20
	Ni	3.66 ± 0.13	3.7 ± 0.40
GBW07604	Cr	0.51 ± 0.09	0.55 ± 0.07
	Co	0.45 ± 0.05	0.42 ± 0.03
	Ni	1.81 ± 0.34	1.9 ± 0.30

[a] Values expressed as mean ± s ($n = 3$).

4. Conclusions

The application of APDC as chemical modifier in ETV–ICP-OES for the determination of trace amounts of Cr, Co, Mn and Ni had been described. Thermal gravimetric analysis of Cr–APDC, Co–APDC, Mn–APDC and Ni–APDC chelates and UV–vis analysis of the sample vapor collected in $CHCl_3$ after vaporization of their chelates indicated that the analytes were vaporized and transported into ICP as their chelates. The proposed method is applicable to the analysis trace elements in samples with complicated matrix by combined with chemical separation/ preconcentration.

Acknowledgement

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