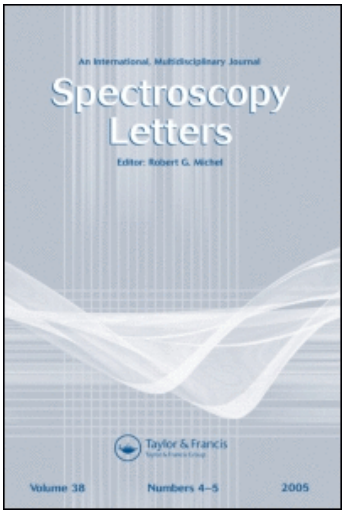

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Flow Injection Kinetic Spectrophotometric Determination of Cerium Based on the Decolorization Reaction Between Arsenazo III and Cerium (IV)

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Flow Injection Kinetic Spectrophotometric Determination of Cerium Based on the Decolorization Reaction Between Arsenazo III and Cerium (IV)

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ABSTRACT Trace amounts of cerium were analyzed by flow injection kinetic spectrophotometry, based on the decolorization reaction between arsenazo III and Ce(IV) in sulfuric acid medium at room temperature. The absorbance difference (ΔA) of decolorization was linear with the concentration of Ce(IV). The flow injection technique was used to precisely control the timing. Under the optimum conditions, the determination of Ce(IV) in the range 0.0–8.0 $\mu g\,mL^{-1}$ with a correlation coefficient (r) of 0.9982, the regression equation was $\Delta A = 0.0014 + 0.0406c$ ($\mu g\ mL^{-1}$). The detection limit (3σ) of 0.2 $\mu g\,mL^{-1}$ was achieved at a sampling frequency of 60 h^{-1}. The proposed method was applied to the analyses of Ce in soil successfully.

KEYWORDS Arsenazo III, Ce(IV), flow injection, kinetic spectrophotometry

INTRODUCTION

As one of the rare earth elements (REEs), cerium is the most widely distributed. Cerium is used in agriculture, forestry, and animal husbandry, and attention is now being paid to the study of cerium in the environment.[1] The increasing industrial use of cerium together with reports on cerium toxicity make it essential to have analytical procedures suitable for monitoring cerium in the environment. This necessiates the development of convenient and reliable analytical methods for the determination of cerium. Analytical techniques, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES),[2] e-electrothermal vaporization (ETAA) after HPLC separation,[3,4] stripping voltammetry,[5,6] spectrofluorometry,[7,8] chemilumine-scence,[9] and ICP-MS,[10] have been reported for the determination of cerium. But most of these techniques require costly and specialized instrumentation, which may not be available in many laboratories.[1] Hence, the current authors planned to develop reasonably sensitive and economically viable techniques.

Kinetic spectrophotometry is an attractive alternative for the analysis of trace amounts of Ce(IV).[11–13] However, manual procedures for kinetic

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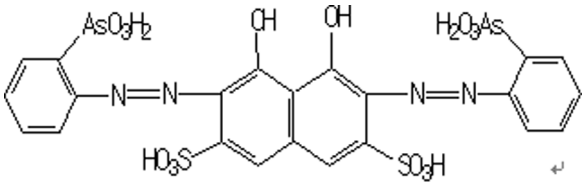

FIGURE 1 The structure of arsenazo III.

measurements are tedious and time-consuming. It is difficult to precisely and reproducibly control the time of mixing of reagent and sample, and the precision is poor. In addition, fairly long reaction time is often required for these reported systems in order to achieve satisfactory sensitivity.[12] Attempts have been made to enhance the reaction rate by increasing reaction temperature.[11–14] Kinetic spectrophotometry could be improved by selecting the fast-lower-temperature reaction coupled with flow injection analysis (FIA) technique. FIA offers better precision and particularly higher automation and sampling throughput, which enhance its potential usefulness in routine analysis.[15,16]

Arsenazo III is a bis-azo derivative of chromotropic acid used extensively for spectrophotometric analysis (Fig. 1). In the current paper, we propose flow injection kinetic spectrophotometry for the determination Ce(IV), which is based on arsenazo III (AAIII) oxidized by Ce(IV) with obvious decolorization in a sulfuric acid medium. This reaction continues quickly at room temperature. The decolorization of AAIII (ΔA) is a function of the concentration of Ce(IV). The flow injection technique was used to reproducibly and precisely control the reaction time of the reagents and samples. The proposed method was simple, economical, rapid, and successfully applied to analysis of Ce(IV) in soil samples.

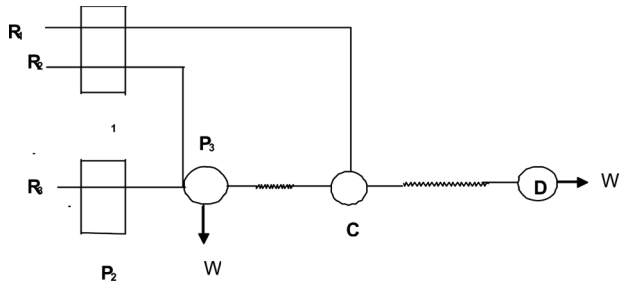

FIGURE 2 Reaction flow diagram. P_1, auxiliary pump 1; P_2, main pump 2; P_3, injection valve; C, confluence; Rc, reactor; D, detector; W, waste; R_1, Ce(IV); R_2, H_2SO_4; R_3, AAIII.

MATERIALS AND METHODS

Instrumentation

A model UV-2501 spectrophotometer (Shimadzu, Kyoto, Japan) was used.

The flow assembly (Fig. 2) was provided with an injection valve, two peristaltic pumps, and a spectrophotometer (CMFIA-1, Shandong, China). The reaction coils were made of PTFE tubing (the diameter of the flow tubing was 0.8 mm).

Reagents

Unless otherwise stated, all chemicals were of analytical reagent grade. Distilled water was used throughout.

A standard cerium (IV) of 100.0 μg mL^{-1} was prepared by dissolving 0.2386 g ammonium cerous sulfate in 7 mL of sulfuric acid (1:1) and diluted with distilled water to 100 mL.

AAIII solution (6.4×10^{-4} mol L^{-1}) was prepared by dissolving 0.1250 g of the reagent in 250 mL of distilled water. Sulfuric acid solution: H_2SO_4:H_2O 1:1 (v/v).

Procedure

Determination of Absorbance

The FIA procedures are schematically shown in Fig. 2. The injected AAIII solution (R_3) (controlled by pump P_2) merged in sequence with sulfuric acid (R_2) and cerium (IV) (R_1) solution (controlled by pump P_1). A stopped flow was used. The FIA parameters are listed in Table 1.

The absorbance was detected at 533 nm. The blank was obtained by repeating the experimental process with only distilled water without cerium (IV).

TABLE. 1 Flow Injection Parameters List.

Variable	Optimum value
Reactor length (m)	3.0
Flow rate (mL min^{-1})	6.7
Loading time (s)	6.0
Stopping time (s)	25.0
Regenerating time (s)	30.0

Samples Preparation

Soil sample preparation: The 2.000 g of dry and thin soil sample was placed in a 100 mL beaker, 50 mL of aqua regia added, soaked for 24 h in draught cupboard, and the solution for 3–4 h on digested a hot plate at low temperature. The contents were heated to dryness. Then, 10 mL of $HClO_4$ was added, and the contents heated to dryness at 90°C. The residue was dissolved with 20 mL sulfuric acid(1:1), After filtrating and then pH mol·L^{-1} adjusted to 6.0 with 1 mol·L^{-1} NaOH, the solution was transferred to a 50-mL volumetric flask and diluted to the mark with distilled water, which was ready for analysis.

RESULTS AND DISCUSSION

Absorption Spectra

In the current paper, the analysis of trace amounts of cerium was based on the oxidation reaction between Ce(IV) and AAIII in sulfuric acid medium. The absorption spectra against distilled water are shown in Fig. 3. It was observed that (1) the spectrum of free arsenazo III consists of a broad band with maximum absorbance at 533 nm (curve 1); (2) the absorption spectrum of AAIII was the same in water and sulfuric acid; (3) the absorbance of AAIII exhibited obvious decolorization after the Ce(IV) was added. The reason for the discoloration may be that a redox reaction between AAIII and Ce(IV) takes place. The –N=N– in AAIII (Fig. 1) probably breaks due to the oxidation of Ce(IV). In the experiment, $\lambda_{max} = 533$ nm was chosen.

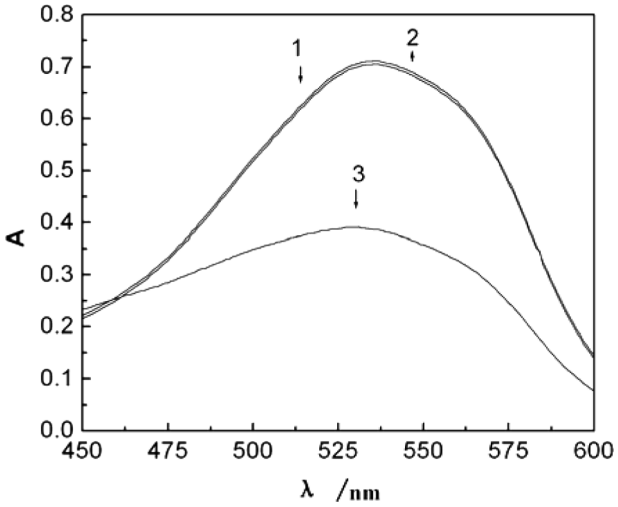

FIGURE 3 Absorption curves ($c_{Ce(IV)}$: 8.0 μg mL^{-1}): 1,- AAIII; 2, H_2SO_4 + AAIII; 3, H_2SO_4 + AAIII + Ce(IV).

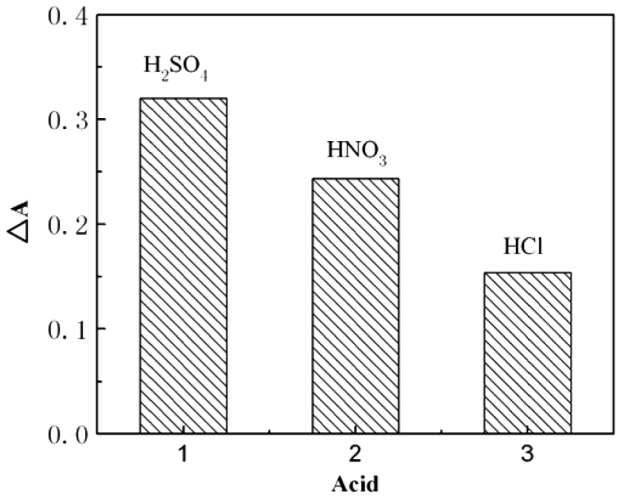

FIGURE 4 Effects of different acid on ΔA ($c_{Ce(IV)}$: 8.0 μg mL^{-1}; C_{acid}: 1.26 mol/L).

Effects of Different Acid

The decolorization reaction was influenced by acid medium. In the experiment, the effects of several equimolar acids (H_2SO_4, HNO_3, HCl) on ΔA were tested, and the results are shown in Fig. 4. ΔA reached a maximum in the case of sulfuric acid medium. Therefore, sulfuric acid was chosen for further work.

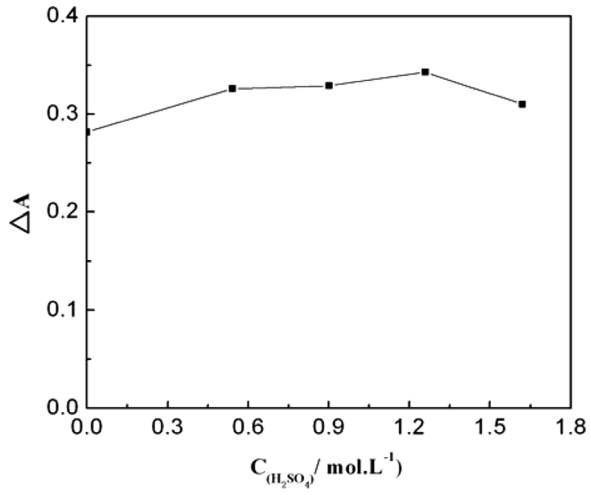

FIGURE 5 Effect of sulfuric acid concentration on ΔA ($c_{Ce(IV)}$: 8.0 μg mL^{-1}).

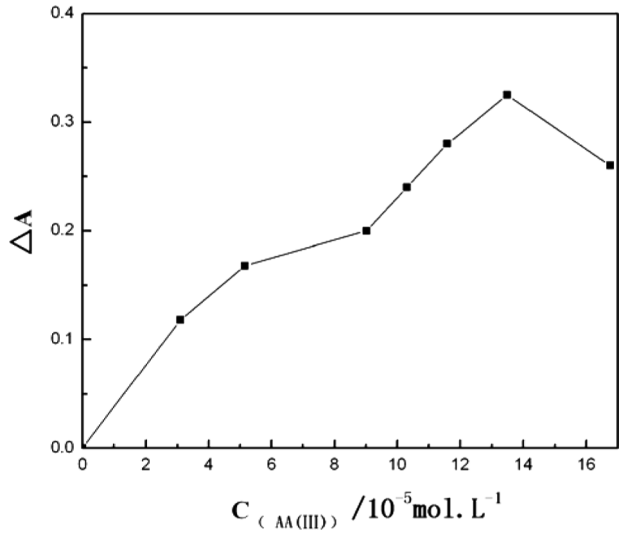

FIGURE 6 Effect of AAIII concentration on ΔA ($c_{Ce(IV)}$: 8.0 μg mL^{-1}).

Effect of Sulfuric Acid Concentration

The effect of sulfuric acid concentration on ΔA is shown in Fig. 5. The ΔA was maximum at 1.26 mol L^{-1}. The concentration 1.26 mol L^{-1} of sulfuric acid was selected as optimum.

Effect of AAIII Concentration

The effect of AAIII concentration in the range 0.0 to 16.8×10^{-5} mol L^{-1} on ΔA was tested (Fig. 6). ΔA was increased with the concentration of AAIII. The maximum ΔA was at 13.5×10^{-5} mol L^{-1}. Thus, 13.5×10^{-5} mol L^{-1} AAIII was optimum.

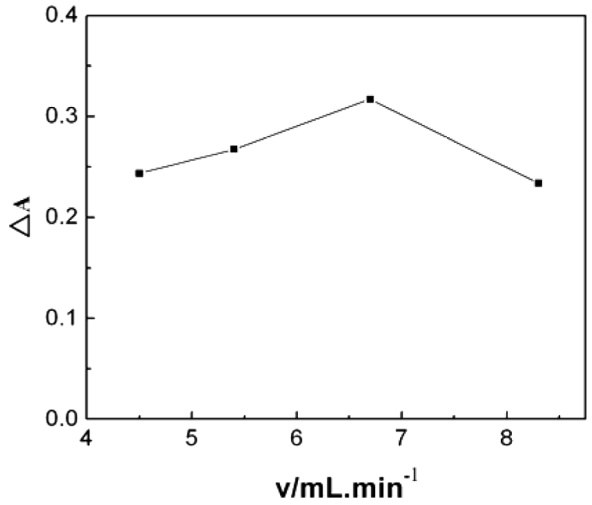

FIGURE 7 Effect of the flow rate on ΔA ($c_{Ce(IV)}$: 8.0 μg mL^{-1}).

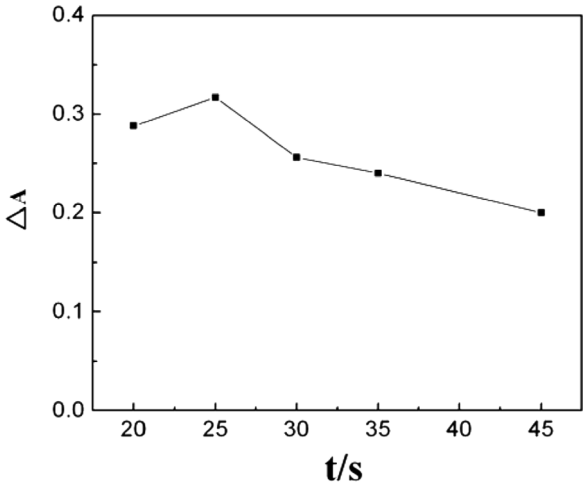

FIGURE 8 Effect of the stopping time on ΔA ($c_{Ce(IV)}$: 8.0 μg mL^{-1}).

FIA Variables

As known, the solution flow rate and residence time in the FIA system would influence the ΔA. Therefore, after optimizing the chemical variables, the effect of flow rate and residence time on ΔA was examined (Figs. 7 and 8). As seen from Figs. 7 and 8, the maximum flow rate was 6.7 mL·min^{-1} and the maximum residence time was 25 s.

The parameters of the FIA system are shown in Table 1.

Analytical Parameters

Under the optimum experimental conditions, there was a linear relationship between ΔA and

TABLE. 2 Tolerance Limits of Interfering Ions

Tested ions	Tolerance limit (w/w)
Na^+	>500
NH_4^+	455
NO_3^-	31.5
PO_4^{3-}	24.5
Al^{3+}	20
Cu^{2+}	13
K^+	9
Mg^{2+}, Co^{2+}	7.5
Zn^{2+}	5
Mo(VI), Pb^{2+}, Cl^-	4.5
Ni^{2+}	1.9
Ca^{2+}	1.5
V^{5+}	1
Bi^{3+}	0.75
Mn^{2+}, Sn^{2+}	0.25
Cr^{3+}	0.1

TABLE 3 Determination Results and Percent Recoveries of the Method

Sample	Added ($\mu g\ g^{-1}$)	Found ($\mu g\ g^{-1}$)	Recovery (%)
	0	21.9 ± 0.1	
soil	4.8	27.0 ± 0.1	106.3
	16.0	038.6 ± 0.1	104.5

concentration of Ce(IV) in the range 0.0–8.0 $\mu g\,mL^{-1}$. The regression equation was $\Delta A = 0.0406c + 0.0014$ ($r = 0.9982$). The detection limit (3, σ) of 0.2 $\mu g\,mL^{-1}$ was achieved at a sampling frequency of 60 h^{-1}.

Effect of Interfering Ions

The interference of different foreign substrates were discussed when Ce(IV) was 8.0 $\mu g\,mL^{-1}$. With a relative error of less than $\pm 5\%$, the tolerance-limits for various foreign ions are listed in Table 2.

Sample Analysis

The proposed method was applied to the analysis of Ce(IV) in soil. The standard addition method was used and analytical results and recovery are presented in Table 3.

CONCLUSIONS

The proposed flow injection kinetic spectrophotometry was used for determination of Ce(IV), based on the decolorization reaction between AAIII and Ce(IV) in a sulfuric acid medium at room temperature. The absorbance difference (ΔA) of decolorization was linear with Ce(IV) concentration. The proposed method was validated by the analysis of standard rare earth oxides and applied to the analysis of soil with satisfactory results.

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