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Determination of Aluminum Fractionation in Soil Extracts by Using Eriochrome Cyanine R Modified Anion-Exchange Resin as Solid Phase Extraction Cartridge Coupled with ICP-AES

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Abstract: By using Eriochrome Cyanine R modified anion-exchange resin as solid phase extraction cartridge coupled with ICP-AES, a novel method for the determination of Al fractionation in soil extracts has been developed. The proposed method possesses the following distinct advantages: (1) Good selectivity. The Eriochrome Cyanine R modified resin shows good recognizing ability for Al fractions. The total monomeric Al_a can be adsorbed on the modified resin in the pH range of $6 \sim 10$ by column procedure, and the organic monomeric Al_o can be determined by batch procedure rapidly while no adsorption of inorganic monomeric Al_i was found in 30 min at least. Thus Al_i can be obtained by subtraction between Al_a and Al_o. Major matrix's interference (Fe, Mn and organic substances) in soil extracts can be avoided. (2) Simple manipulation. The modified resin is very easy to prepare just simply by impregnating the resin with a solution containing Eriochrome Cyanine R. This method has been applied to the determination of five fractions of Al in soil extracts with the experimental results being in agreement with those obtained by Driscoll's method. In addition, Calcon, 8-hydroxyquinoline-5-sulfonic acid, Tiron, Solochrome Violet RS, Pyrocatechol Violet, Xylenol orange, Ferron and Alizarin Red S are also modified to anion-exchange resin as solid-phase extractants. Their conditions to pre-concentrate

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and determine Al fractionation are investigated, and the adsorptive characteristics of various chelating reagents have been discussed and compared.

Keywords: Aluminum fractionation; Eriochrome cyanine R; Modified anion-exchange resin; Soil extracts; Solid phase extraction

INTRODUCTION

During the last two decades, acid atmospheric deposition associated with human's activities has continuously entered into the environment, which results in the growing concerns of soluble aluminum (Al) in soils waters and ground waters (1–6). The Al's bioavailability and toxicity are greatly dependent on its speciation rather than on the total concentration alone (7–11). In complex environmental matrices such as soil solutions, inorganic and organic ligands compete with OH^- for the formation of Al complexes (8). It is clear that the fractionation of inorganic monomeric Al_i (major in the forms of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)^{2+}$, Al-F and $Al\text{-}SO_4$ complexes in aqueous media) is a key determinant of bioavailability and toxicity, whereas the organic monomeric Al_o is non-toxic. Therefore, it is of necessity to develop effective analytical methods for the determination of Al speciation in soil water and surface water.

However, up to now, there are still some problems existing for the directly accurate determination of Al speciation in complex environmental samples (10). Mostly, operational defined fractionation of Al rather than speciation is determined in routine analysis since the true speciation is difficult to detect by the present analytical methodologies. There are several reviews on analytical methods for Al fractionation (8,12,13) in the literature. The most widely used method is Driscoll's procedure (14), in which five Al fractions (inorganic monomeric Al_i, organic monomeric Al_o, total reactive Al_T, total monomeric Al_a, and acid soluble Al_s) can be distinguished based on an 8-hydroxyquinoline extraction-colorimetric method in combination with a strong acid cation-exchange resin separation. Recently, Tangen et al employed commercially available solid-phase extraction (SPE) cartridges for the fractionation of Al and Fe in soil water (15). This technique is friendly to environment and portable use in site, since SPE merits the metal ions fractionation (16–21) due to its simple and rapid manipulation and avoiding the use of toxic organic solvent as extracting reagent. Macrospores anion-exchange resin (22) and chelating resin have also been used for the determination of total Al (23). In addition, some resins modified with various reagents, such as 8-hydroxyquinoline (24), Chrome azurol S (25), Chromotrope 2B (26) and Tiron (27), were used for this purpose. However, in the above studies, only strong acid cation-exchange chelating resins were used for Al determination, and the applications of ion exchange resin to the fractionation of Al are rare. Therefore, it is necessary to develop new SPE procedure based on chelating resins for getting much more information on Al fractionation. Based on the differences of kinetics for different Al species reacting with some chemical reagents, e.g., Ferron (28,29) and Pyrocatechol Violet (PCV) (30), it is of possibility to pre-concentrate and separate Al fractionation using chelating resin modified with different chemical reagents.

This work is the continued fraction of our research project concerning the use of solid phase extraction procedure for Al fractionation. Three Al fractions were distinguished using Calcon modified anion-exchange resin as SPE cartridge coupled with ICP-AES in our previous report (31). In this work, we extended the analytical uses of modified anion-exchange resin by loading various dyes including Eriochrome Cyanine R (ECR), 8-hydroxyquinoline-5-sulfonic acid (HQS), Tiron, Solochrome Violet RS (SVRS), PCV, Xylenol orange (XO), Ferron, and Alizarin Red S (ARS). ECR was taken as a typical study chelating reagent and was systematically investigated for the determination of five Al fractions in real soil extracts coupled with ICP-AES. The adsorptive characteristics of different chelating reagents were also evaluated and compared in order to elucidate the general rule for selecting SPE sorbents.

EXPERIMENTAL

Apparatus

An ICP-AES (Atomscan16, Thermo Jarrell Ash Co., USA) was used for all experiments. The instrumental operating conditions are shown in Table 1.

Table 1. ICP-AES operating conditions

Items	Parameters
Wavelength, nm	396.15
Power output, W	1150
Carrier gas (Ar), L min^{-1}	1
Intermediate gas (Ar), L min^{-1}	1
Coolant gas (Ar), L min^{-1}	14
Observation height, mm	15
Entrance slit, μm	10
Exit slit width, μm	10
Integration time, s	3

For measurement, ICP-AES instrument was calibrated according to manufacturer's recommended procedure using calibration standard or blank for a minimum of 15 s after reaching the plasma before beginning signal integration. A rinse with calibration blank for at least 60 s was used between each standard in order to eliminate any carryover from the previous standard. A HL-1 peristaltic pump (Shanghai Huxi Instrumentation Factory, Shanghai, China) was used for pumping the sample through the SPE micro-column. Homemade polypropylene micro-column (60 mm × 2.5 mm i.d.) was used. A spectrophotometer (UV-260, Shimadzu Corporation, Japan) was used for PCV photometry. A pH meter (pHS-3C, Shanghai Rex Instrumentation Factory, China) was used to measure the pH values. An orbital shaker was used to agitate the sample during the batch uptake experiments (HY-4, Shanghai Medical Instrument Factory, China).

Reagents

All chemicals were of analytical-reagent grade or better and purchased from Chemical Reagents Corporation of Shanghai (Shanghai, China) unless otherwise stated. All the water used was doubly distilled water. All laboratory glassware and plastic ware were immersed in 10% nitric acid for at least 24 h and rinsed with water before use.

An Al stock solution ($500\,\mu g\,mL^{-1}$) was prepared by dissolving 0.2500 g high purity Al powder in 10 mL of concentrated HCl and heated until completely dissolved. Then the solution was cooled and transferred to a 500 mL of calibrated flask, diluted to the mark with distilled water, and then mixed well. Working standard solutions were prepared by appropriated dilution of the stock solution with water each day. Al-citrate was made by mixing 50 mL of standard Al solution ($40\,\mu g\,mL^{-1}$) with an appropriate amount of sodium citrate solution (3:1 ligand to Al ratio) followed by the pH adjustment to pH 6 and dilution to 100 mL (32).

PCV solution (0.038%, w/v) was prepared by dissolving a certain amount of PCV in about 50 mL of water. The solution was transferred to a 200 mL brown flask and diluted to the mark with water.

The strong base anion-exchange resin (201 × 8 type, 100 $\sim$ 120 mesh, styrene-divinylbenzene copolymers containing quaternary ammonium) and the strong acid cation-exchange resin (001 × 7 type, 100 $\sim$ 120 mesh, styrene-divinylbenzene copolymers containing sulfo-group) were purchased from Shanghai Yaolong Chemical Factory (Shanghai, China). An appropriate amount of resin was immersed in $0.1\,mol\,L^{-1}$ NaOH for 10 h, and then in $1\,mol\,L^{-1}$ HCl for subsequent 10 h. The treated resin was washed with water and dried at 60 °C, then stored in desiccators before use.

Ammonium acetate buffer solution ($0.1\,\text{mol}\,L^{-1}$) was prepared by adding an appropriate amount of acetic acid to ammonium acetate solution to result in solution of pH 4–6. Hexamethylenetetramine buffer solution was prepared by dissolving 150 g in 500 mL of doubly distilled water and adjusted to the desired pH ($6 \sim 8$) with $6\,\text{mol}\,L^{-1}$ HCl and $6\,\text{mol}\,L^{-1} NH_3 \cdot H_2O$. Ammonium chloride buffer solutions ($0.1\,\text{mol}\,L^{-1}$) were prepared by adding an appropriate amount of ammonia to ammonium chloride solution to result in solution of pH 8–10.

Preparation of Modified Resins and Micro-column

A total of 3 g of the treated 201 × 8 type anion-exchange resin was added to the solution containing 100 mL of 0.5% (W/V) of ECR, and settled for 12 h. The mixture was filtered and washed with $3\,\text{mol}\,L^{-1}$HCl and $1\,\text{mol}\,L^{-1}$NaOH respectively, then conditioned to near neutrality with 10 mL doubly distilled water, and finally dried at 60 °C, and stored in a desiccators before use. In this work, 0.20 g of ECR modified resins was packed in a micro-column (2.5 × 60 mm). The Calcon, HQS, Tiron, SVRS, PCV, XO, Ferron and ARS modified resins were made in a similar procedure as described above.

Preparation of Samples

Soil extracts were prepared as the following procedure according to our previous work (4,5). The soil samples were collected from different areas of China: Fuan, Sanming, Shanwu of Fujian Province, Ninhai of Zhejian Province, and Yichang of Hubei Province. All the samples were taken at a depth of 0–20 cm. The samples were air-dried, and sieved through 2 mm sieve, then milled in an agate pot to the fine powder, which was used for the extraction. A 10.0 g of sample powder was shaken with 100 mL of water for 16 h in an oscillator, centrifuged (10,000 rpm, 20 min) and decanted, and filtered through 0.45 μm filter. This procedure will guarantee that no particle was retained on the column. The filtrate was stored in a 100 mL of polypropylene bottle just before analysis (33).

Procedures

Batch Method for Al_o

Sorption rate: Al-citrate was selected to investigate the interaction of the organic monomeric Al with the chelating resin. Several aliquots of 0.1 g of resin and 10 mL 27 μg mL^{-1} Al-citrate solution (pH 5.0) were mixed into a polycarbonate bottles, then shaken for different time. The concentration of Al in the supernatant solution was detected by ICP-AES. Adsorptive capacity Q (mg g^{-1}) and loading half time $t_{1/2}$ (min) were calculated based on the above results.

Determination: A 25 ml of sample solution containing the analytes and 0.1 g of modified resin were taken in a polycarbonate bottle, shaken vigorously in an oscillator for 5 min. After filtration, the modified resin was washed with 3 mL buffer solution, and eluted with 2.5 mL of 1 mol L^{-1} HCl. The effluent was collected for the determination of Al by ICP-AES.

Continuous Column Method for Al_a

Column method: A micro-column was linked to peristaltic pump. The general procedure was similar to our previous work (4,5). Firstly, 0.5 mL 0.5 mol L^{-1} of NaOH, 0.5 mL 0.5 mol L^{-1} of HCl, and 5 mL doubly-distilled water were successively passed through the micro-column at 1 mL min^{-1}. Secondly, 3 mL of buffer solution with the same pH as sample solution, and 25 mL of sample solution containing Al_i (Al^{3+} solution) or Al_o (Al-citrate), with the pH adjusted to a range of $4 \sim 12$ by 6 mol L^{-1} HCl or 6 mol L^{-1} $NH_3{\cdot}H_2O$, was passed through the micro-column in sequence at a flow rate of 1 mL min^{-1}. Finally, the adsorbed Al was eluted with 2.5 mL of 1 mol L^{-1} HCl and determined by ICP-AES. After each experiment, the column was rinsed with a very large volume of the water and stored for the next use.

Breakthrough curve: A series of standard solution of 10 μg mL^{-1} Al_i was passed through the micro-column packed with 0.20 g of modified resin, and then the Al in the effluent was determined by ICP-AES.

Recommended Procedures for Determining Five Al Fractions

Al_o was analyzed by batch method and Al_a was obtained by column method with 25 mL of the sample solution respectively. Total reactive Al (Al_T) was determined directly by ICP-AES. Al_i was calculated as the difference between the concentration of Al_a and Al_o. The acid-soluble Al (Al_s) was calculated by the difference between Al_T and Al_a. The flow diagram for determining Al fractionation is given in Fig. 1.

Verification of the Proposed Method

Driscoll's method (30): For Al_T, up to 3.5 mL of sample solution was adjusted to pH 1.0 with 50 μL of concentrated HCl, and determined by PCV method (see below) 10 min later. For Al_o, a certain amount of

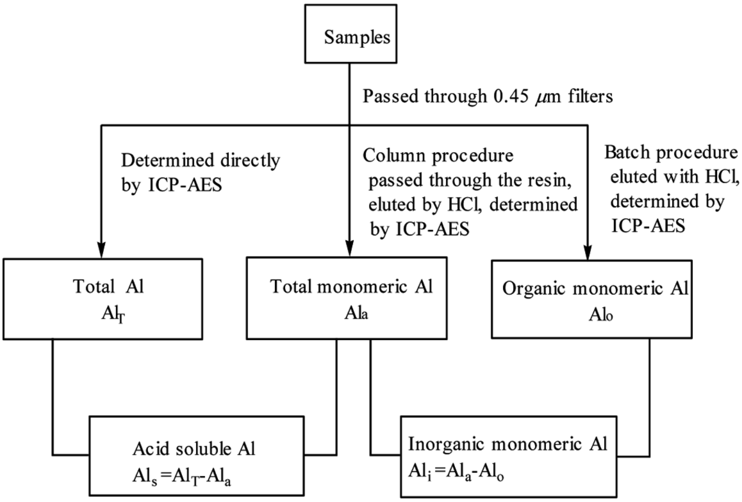

Figure 1. The flow diagram for the determination of five kinds of Al fractionation.

sample solution was passed through the 001 × 7 strong acid cation-exchange resin (which is similar to Amberlite IR-120 P cation-exchange resin). The extract from 10 mL to 13.5 mL was detected by PCV method (see below). For Al_a, a certain amount of sample solution was mixed with 50 μL of concentrated HCl and hexamethylenetetramine buffer solution, and then detected by PCV method (see below). The acid-soluble Al_s was calculated by the difference between Al_T and Al_a. The inorganic monomeric Al_i was obtained by the difference between Al_a and Al_o.

PCV method: To a 3.5 mL volume of sample solution, whether the standard or the blank, 0.1 mL of the iron-masking reagent (0.1% 1,10-phnanthroline and 10% hydroxylamine hydrochloride), 0.2 mL of the 0.038% (m/v) PCV solution and then 1.0 mL of the buffer solution (30% hexamethylenetetramine and 1.65% ammonia solution) were added and mixed together (pH 6.2). The solution was diluted to a constant volume. 10 min later, the Al concentration was measured by spectrophotometry at 580 nm. The linear range was found to be between 5 and 400 $\mu g\,L^{-1}$.

RESULTS AND DISCUSSION

Batch Method

Batch adsorption acidity: The effect of pH on the adsorption behaviors of Al_i (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2{}^+$) and Al_o (Al-citrate) was investigated. As can be seen in Fig. 2, organic monomeric Al (Al_o) at pH 7 ~ 10

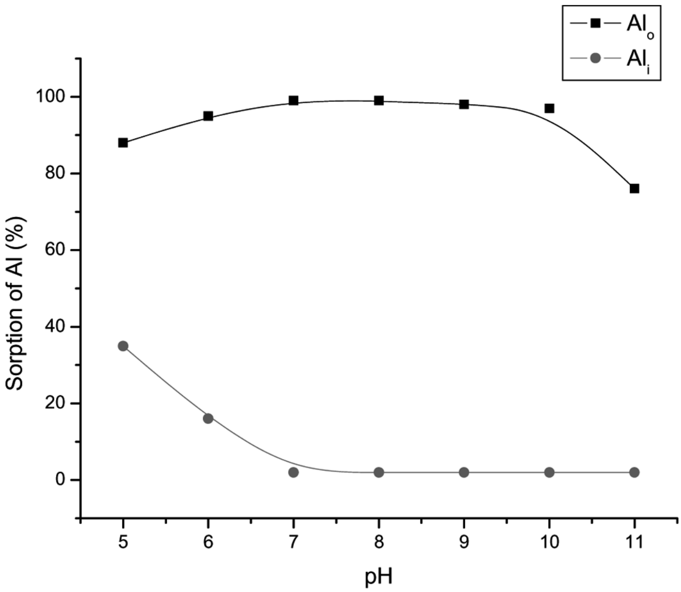

Figure 2. The effect of pH on the sorption of Al_i and Al_o (Al_o, 20 μg mL^{-1}; Al_i, 20 μg mL^{-1}; resin, 0.1 g; t, 5 min).

can be quantitatively adsorbed by the ECR modified resin while Al_i was not adsorbed by the modified resin within 30 min. Thus, the pH 8.5 (5 mL^{-1} of pH 8.5 ammonium chloride buffer solutions was used) and 5 min of contact time were selected for all further batch procedures.

Sorption rate of organic monomeric Al: Fig. 3 shows the results of kinetics sorption of Al_o on ECR modified resins. The sorption capacity Q (mg g^{-1}) and loading half time $t_{1/2}$ (min) (the time needed to reach sorption at 50% of the total loading capacity) were calculated based on the above results (24). The Q and $t_{1/2}$ were 2.5 mg g^{-1} resin and 0.6 min for ECR modified resin, respectively. It is confirmed that the equilibrium was achieved in 4 min. The reasonably rapid kinetics of the resin-metal interaction at the optimum pH reflects the good accessibility of the chelating sites of the resin to Al_o.

Column Method

Effect of pH on adsorption: The result of the effect of pH on the sorption of total monomeric Al ($Al_a = Al_i + Al_o$) on ECR modified resin is shown in Fig. 4. As can be seen, the retention of Al_a on the resin was quantitative (>95%) at the pH range of 6–10. Hence, in all further studies, 3 mL of ammonium acetate buffer solution at pH 6 are used.

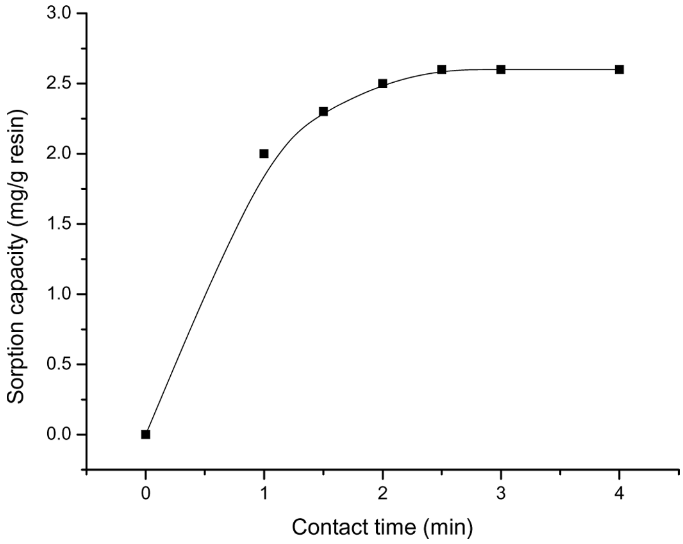

Figure 3. Kinetics of sorption of Al_o on ECR modified resins (Al, 10 ml of 27 μg mL^{-1}; resin, 0.1 g; pH, 8.5).

Effects of eluent agent concentration and volume: The adsorption of the retained Al_i on the ECR modified resin was studied at various concentrations of HCl. The quantitative recoveries were obtained with 2.5 mL 0.5 ~ 3 mol L^{-1} of HCl solution as eluent. In this study, 2.5 mL 1 mol L^{-1} of HCl was used. The interferences of Fe^{3+}, Cu^{2+} and Mn^{2+} can be avoided in the determination of Al by ICP-AES, since they are not retained on ECR modified resin.

Effect of flow rates: The degree of Al_i sorption on ECR modified resin was studied at various flow rates of the solution. It was found that the sorption of Al on the ECR modified resin bed was greater than 95% between the flow rate of 0.5 and 3 mL min^{-1}. Flow rates less than 0.5 mL min^{-1} were not selected in order to avoid longer analysis times. However, there was a decrease in the percentage sorption at a flow rate greater than 3.0 ml min^{-1}. Therefore, 1.0 mL min^{-1} flow rate was chosen throughout the experiments.

Breakthrough curve: The breakthrough volume and the sorption capacity by column method are two important parameters in this work. The result was given in Fig. 5, which indicates that the Al_i in the effluent has not been detected until the volume of the standard Al is up to 30 mL. The maximum sorption capacity ($C/C_o = 0.5$) by the column method was found to be 2.5 mg g^{-1} of resin, which is suitable for the preconcentration of the total monomeric Al.

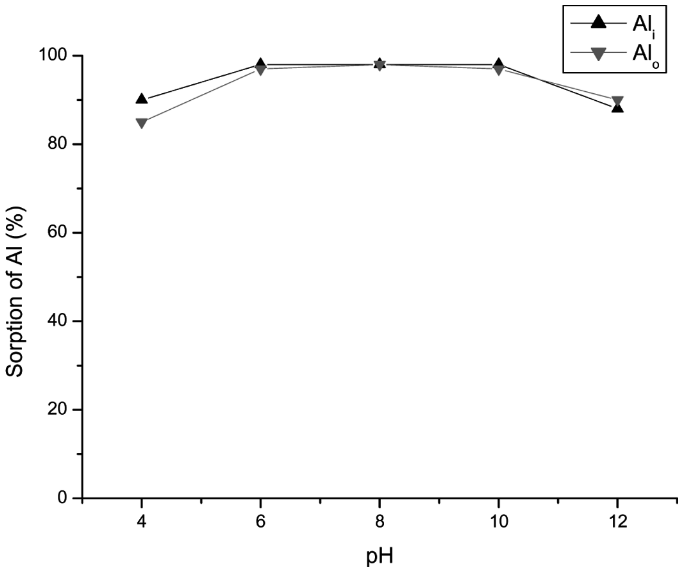

Figure 4. Effects of pH on the sorption of Al$_i$ and Al$_o$ on ECR modified resins (Al$_o$, 10 μg mL^{-1}; Al$_i$,10 μg mL^{-1}; resin, 0.20 g; flow rate, 1.0 mL min^{-1}; elute volume, 2.5 mL).

Interference Effects

In order to assess the potential analytical applications of the recommended procedure, the effect of some foreign ions was investigated at a fixed amount of total monomeric Al (10 μg). The results indicate that Al recoveries were not affected (recovery of Al $\geq$ 95%) in the presence of 1000 μg each of K^+, Na^+; 100 μg each of Ca^{2+}, Mg^{2+}; 30 μg of Fe^{3+}; 20 μg each of Mn^{2+}, Cu^{2+}; and 200 μg of F^-, respectively. The proposed modified resin possesses the property of chelating resin, which was bonded together with Al species by coordinating reaction, so that the resin had a better selectivity than that of cation-exchange resin. From the results obtained, it can be concluded that the presence of major cations and anions has no obvious influence on Al determination.

Limits of Pre-concentration, Pre-concentration Factor, and Detection Limit

The limits of pre-concentration and pre-concentration factor were investigated by using the column procedure. 2 μg of standard Al diluted to 100 mL, 200 ml, 300 mL, 500 ml, 800 mL was passed through

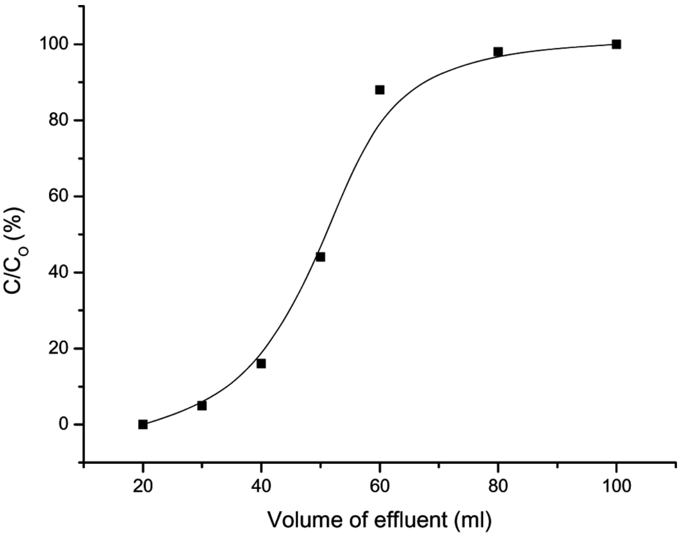

Figure 5. Breakthrough curve for Al (Al, 10 μg mL^{-1}; ECR modified resin, 0.2 g; flow rate, 1 mL min^{-1}; pH 6.0).

micro-column by using continuous column procedure. The results showed that the limit of pre-concentration was 4 μg L^{-1} when the quantitative recovery was considered up to 95%. The maximum pre-concentration factor was 200 for analyte ions when final volume was 2.5 mL. The detection limit for Al^{3+} based on three times the standard deviations of the blank ($n = 21$) on a sample volume 25 mL was 0.6 ng mL^{-1}.

Practical Applications for Soil Extracts

In order to establish the validity of the proposed procedure, the proposed method has been applied to the analysis of five kinds of Al fractions in soil extracts. The results are shown in Table 2. It can be seen that the results by this approach have given a good accordance with those of Driscoll's method except for sample 5. The reason for this is probably that the pH of sample 5 (Fujian Shanwu) is lower than other samples, so the coordination between Al^{3+} and organic ligand is weak. For PCV method, cation exchange resin can grabble part of Al^{3+} from the fractions of Al_o, thus make the found value of Al_o obtained by PCV method much lower than that obtained by the proposed procedure. The results obtained show the applicability of the method for trace Al fractionation determination with improvement in the detection limit

Table 2. Determination results of soil extracts by the proposed method and classical PCV spectrometry method (n = 3, ± S.D.)

Samples	Solution pH	This method ($mg \cdot L^{-1}$)					PCV spectrometry ($mg\,L^{-1}$)				
		Al_T	Al_a	Al_o	Al_s	Al_i	Al_T	Al_a	Al_0	Al_s	Al_i
1. Fujian Fuan soil extracts	6.7	0.32 ± 0.02	0.11 ± 0.01	0.06 ± 0.01	0.21 ± 0.02	0.05 ± 0.01	0.33 ± 0.02	0.12 ± 0.01	0.08 ± 0.01	0.21 ± 0.01	0.04 ± 0.01
2. Zhejian Ninhai soil extracts	6.9	0.72 ± 0.05	0.23 ± 0.01	0.07 ± 0.01	0.49 ± 0.02	0.16 ± 0.02	0.69 ± 0.04	0.19 ± 0.01	0.06 ± 0.01	0.50 ± 0.03	0.13 ± 0.01
3. Hubei Yichang soil extracts	6.1	0.65 ± 0.04	0.52 ± 0.02	0.10 ± 0.01	0.13 ± 0.01	0.42 ± 0.02	0.63 ± 0.04	0.51 ± 0.02	0.12 ± 0.01	0.12 ± 0.01	0.39 ± 0.01
4. Fujian Sanming soil extracts	6.8	0.43 ± 0.02	0.29 ± 0.01	0.15 ± 0.01	0.14 ± 0.01	0.14 ± 0.01	0.41 ± 0.02	0.30 ± 0.02	0.17 ± 0.01	0.11 ± 0.01	0.13 ± 0.01
5. Fujian Shanwu soil extracts	5.3	2.49 ± 0.15	1.38 ± 0.07	1.26 ± 0.04	1.11 ± 0.06	0.12 ± 0.01	2.51 ± 0.13	1.32 ± 0.08	0.34 ± 0.01	1.19 ± 0.09	0.98 ± 0.05

and very low interferences from either organic compounds or inorganic ion species.

Characteristic Comparison Among Various Modified Resins as Solid-phase Extractants to Determine Al Fractionation

Other modified resins loaded with some other reagents, Calcon, HQS, Tiron, SVRS, PCV, XO, Ferron and ARS, which contain sulfonic group and react selectively with Al^{3+} species, were prepared in a similar way as ECR resin. The properties of these prepared resins were also studied in column and batch experiments respectively. A comparison of adsorptive characteristics between different chelating reagents was made as can be seen in Table 3. In addition, according to our experiment, a chelating resin (Chelex-100) and a strong acid cation exchange resin (001 × 7 type) can also be used for Al fractionations in a narrow pH range (pH 5–6.5 and pH 4–6.5, respectively), which require the adjustment of sample pH before analysis. Based on the above experimental results, we can reach the following points of view:

(1) The sorption capacity and reaction rate play key roles in the separation and pre-concentration of Al fractionation. Generally, with an exception of PCV, the larger the stability constant of Al-reagent

Table 3. Comparison of adsorptive characteristics between different chelating reagents

	Modified reagents							
	ECR	Calcon	HQS	Tiron	SVRS	PCV	ARS	XO
PH range	5–10	4–10	4–6.5	5–6.5	5–10	5–10	4–10	4–10
Sorption capacity ($mg\ g^{-1}$ resin, column method)	2.5	4.5	4.6	5.6	2.9	1.0	1.7	0.8
Loading half time $t_{1/2}$ (min, batch method)	0.6	0.4	0.5	0.4	0.4	1.5	1.0	1.6
Column reuse (times)	20	30	15	30	20	20	15	10
Average recovery (%)	97	99	98	99	98	97	95	96
Sorption rate	fast	fast	fast	fast	middle	slow	slow	slow
Ability to quantitative retention of Al_a	yes	yes	yes	yes	yes	no	no	no
Ability to quantitative retention of Al_o	yes	yes	no	no	no	no	no	No

*For various chelating reagents, the following parameters are the same: flow rate = 0.5–3.5 $mL\ min^{-1}$, eluant concentration = 1 $mol\ L^{-1}$, and elution volume = 2.5 mL.

complex, the more stability of the modified resin, and the higher sorption capacity is gained. PCV, however, was examined to offer a poor sorption capacity, though it possesses nearly the same log K as Tiron does. It can be explained by the larger steric hindrance of PCV, which hindered the loading amount of PCV on the precursor resin, and a lower sorption capacity occurs as a result.

(2) Some reagents, although they react readily with monomeric inorganic or polymeric Al, can't be firmly loaded on the anion-exchange resin, so they are not suited for preparing modified resins. A case in point is Ferron, which is a common reagent widely used to separate inorganic or polymeric Al from other species. Compared with HQS, however, Ferron contains one extra iodine ion, which reduces the electrostatic attraction between sulfonic group and anion resin. Ferron combines with the resin so un-tightly that it can be easily eluted by diluted HCl or NaOH solution. To prepare high performance modified resins, Tiron, HQS, Calcon and ECR are appropriate chelating reagents as shown in Table 2. Further tests show that total monomeric Al is remained on the column packed with Calcon and ECR resins, while monomeric organic Al is adsorbed only in the batch procedure, then the two different species are identified successfully based on the experiment.

(3) Several advantages are observed when modified resins are employed to enrich Al. (i) the modified resins have the nature of SPE. It's likely to perform on-line pre-concentration, matrix separation and automatic detection; (ii) compared with conventional strong or weak acid resin, the proposed modified resins have certain priorities: higher selectivity, a wider pH range for quantitative adsorption of total monomeric Al. Most reagents, which complexed selectively with different Al species, are easily available. Therefore, corresponding modified resins may be prepared for various purposes; (iii) according to the special reaction between Al and modified resins, different Al species are separated and identified. The experimental results offer meaningful data for further study, and provide a basis for preparing new SPE as well.

CONCLUSIONS

A novel method for the determination of five Al fractionations in soil extracts has been developed by using ECR modified anion-exchange resin as solid phase extraction cartridge coupled with ICP-AES, with the distinct advantages of high sensitivity, good selectivity and simple manipulation. The adsorptive characteristics of other chelating reagents including ECR, HQS, Tiron, SVRS, PCV, XO, Ferron and ARS were evaluated and compared. The proposed method is expected to be applied to other elements (speciation) analysis, and then enlarge the study and application range of chelating reagent modified anion-exchange resins.

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