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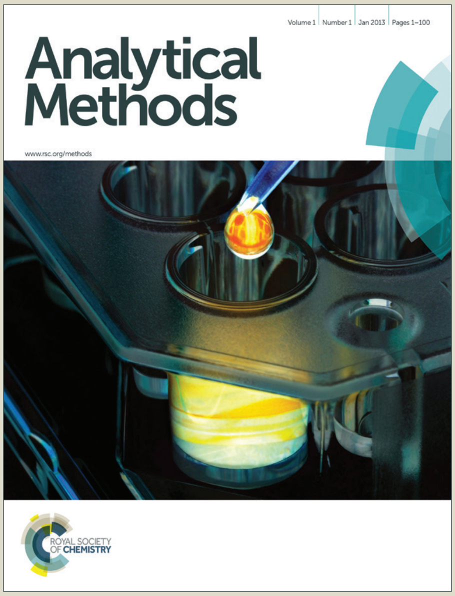

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Abstract：

An inductively coupled plasma atomic emission spectrometry (ICP-AES) method was established for the determination of trace cadmium in steel. The steel sample was dissolved with hydrochloric acid，then the sample solution was passed through a mini-column packed with anion exchange resin DOWEX 1×8-200. Cadmium was selectively adsorbed on the column, while iron was passed through. The analyte Cd was then eluted with 1.6 mol L^{-1} nitric acid and collected in a volumetric flask, thus Cd was enriched and effectively separated from matrix iron. Separation conditions were optimized via experimental determination of distribution coefficient for Cd and Fe, respectively. Detection limit of Cd was 0.12 μg g^{-1}. Recovery was in the range of 90% to 98%. The relative standard deviation was ranged in 5.8%-7.3 % (n=7). The proposed method has been applied to the determination of trace cadmium in the steel industry.

Determination for trace cadmium in steel by inductively coupled plasma atomic emission spectrometry after removal of iron matrix with an adsorption column

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1. Introduction

Cadmium, as a component of pigments or alloys，is widely used as a protective coating in industry.[1] Cadmium is also a carcinogenic element that harms to mammalian organs such as kidney, liver, lung, pancreas, testis, and placenta, and has a biological half-life of over 20 yr.[2,3] Cadmium in the steel possibly results in healthy problem if it exposes in acidic environment. The problem of determination of cadmium in steel is that all the main analytical lines are suffered the spectral interferences from iron matrix.[4,5] In this case, a separation measure of removing the interference matrix is normally used to improve the accuracy and precision of the analysis.

Several methods for determination of cadmium after removal of iron have been reported. Matsumiya[6] separated Cd from Fe by adding polyoxyethylene-4-isononylphenoxy ether (PONPE, nonionic surfactant) to the iron sample and using lithium chloride as the aggregate reagent. The iron matrix was collected into the condensed surfactant phase, while the trace metals (e.g. Ti, Cr, Mn, Co, including Cd) remained in the aqueous phase and then concentrated onto the imino-diacetic acid-type chelating resin. The trace metals were desorbed with dilute nitric acid and determined by inductively coupled plasma-mass spectrometry (ICP-MS) or graphite-furnace atomic absorption spectrometry (GFAAS). The surfactant (PONPE) coated XAD-4 was otherwise packed into a polypropylene column (7 mm i.d. × 50 mm high) to remove the iron matrix.[7] The system offered a selective and almost quantitative method for removal of iron matrix, allowing the determination of trace impurities in large amount of iron.

Fujimoto determined the trace amounts of mercury, lead and cadmium in steel by ICP-MS after cation–exchange chromatographic separation.[8] The sample was decomposed with nitric acid, and the analytes were separated from the iron matrix on the cation exchange resin column in medium of 1 mol L^{-1} hydrofluoric acid solution. The elements adsorbed on the resin were then eluted by 8 mol L^{-1} hydrochloric acid and determined by ICP-MS.

Tokahoglu[9] reported a method for the determination of trace metals including Cd, Bi and Pb in high-purity aluminum, zinc and commercial steel by flame or graphite furnace atomic absorption spectrometry. The analytes were pre-concentrated as iodo complexes and adsorbed on a XAD-1180 resin cartridge.

A method of using anion exchange resin DOWEX 1×8-200 for separation and determination of trace rare earth elements (REEs) in steels has been reported in our earlier research[10]. In the present paper, we report using this resin for the separation of cadmium from iron matrix under similar conditions. Cadmium was subsequently determined by ICP-AES. The resin column was designed as 0.5 cm *i.d.* and 25 cm in length, and a glass tube size in 2.0 cm *i.d.* and 6 cm high was set on its top for connection. The method has been used to the routine analysis of determination of trace cadmium in steels.

2. Experimental

2.1 Apparatus

Inductively Coupled Plasma Atomic Emission Spectrometer used in this paper was Thermo Fisher iCAP 6300 Model (Thermo Fisher Co., USA). The operating parameters were listed as follows:

RF Power: 1.15 kW; Frequency 27.12 MHz; Plasma gas flow: 15 L min^{-1}; Auxiliary gas flow: 0.5 L min^{-1}; Nebulizer gas flow: 0.8 L min^{-1}.

Analytical lines(nm) :Cd 228.802{447}, Fe 238.204{142} ; internal standard line(nm) :Y 224.306{450}.

2.2 Materials and reagents

All reagents used in this work were of analytical grade. Deionized water (18 MΩ cm) was produced from a Milli-Q Plus system (Millipore, Milford. MA, USA). Standard solutions were purchased from the National Analysis Center for Iron and Steel (Beijing, China).

Anion-exchange resin DOWEX 1×8-200 was purchased from Dow Chemical Company, USA. The resin was ground and sifted in size of 100~200 mesh. A glass tube for packing the sieved resins was designed as 0.5 cm in *i.d.* and 25 cm in length, a sleeve sized 2.0 cm *i.d.* and 6 cm height was set on the top for connection. The height of the resin bed was 5.0 cm. The flow-rate in resin column was controlled by a stopcock at the bottom. A polyester fiber layer was placed at the terminal of the column for retaining the resin.

2.3 Analytical procedures

A 1.000±0.002 g test portion of steel granules was weighed into a 250 mL glass beaker. 10 mL of hydrochloric acid (6.0 mol L^{-1}) was added and heated gently. Nitric acid was added in drops, until boiling. After the sample was dissolved completely, the solution was evaporated to near dryness. The residue was re-dissolved with 1.0 mol L^{-1} hydrochloric acid, and transferred into a 100 mL volumetric flask, made up to the volume with 1.0 mol L^{-1} hydrochloric acid. An aliquot of 10.0 mL solution was loaded onto the DOWEX 1×8-200 resin packed column and passed through it at a flow-rate of 1.0 mL min^{-1}. Cadmium ion was adsorbed on the resin while iron was passed out of the column. The column was then rinsed with 15 mL of 1.0 mol L^{-1} hydrochloric acid for removing all the iron out of the column. Cadmium ion was then eluted with 10 mL of 1.6 mol L^{-1} nitric acid, and the effluent was collected in a 10mL volumetric flask for ICP-AES analysis. Regeneration of the resin after the effluent collection procedure was completed, the resin column was regenerated by rinsing with 20 mL of water then 20 mL of 1.0 mol L^{-1} hydrochloric acid.

The distribution coefficients (K_d) between the aqueous phase and the resin at different concentrations of hydrochloric acid，for cadmium and iron，were individually determined. 1.00 mL of standard cadmium solution (1000 μg mL^{-1}), 1.00 mL of standard iron solution (1000 μg mL^{-1}), 1.00 mL of internal standard solution (50 μg mL^{-1}) and 47 mL of various concentrations of acid containing 0.50 g resin were added into series of 100 mL Erlenmeyer flasks respectively. The solutions were stirred for 30 min before determination. Concentration of cadmium and iron in aqueous phase was determined by ICP-AES. The distribution coefficients were calculated as the ratio of the element quantity on resin to that in the aqueous phase, according to the following equation,[11] the result was given in Table 1.

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \cdot \frac{V}{G} \qquad (1)$$

Where C_0 refers to the original concentration before equilibration with the resin (μg mL^{-1});

C_{eq} refers to the determined concentration after equilibration with the resin (μg mL^{-1});

V refers to the volume of solution (mL);

G refers to the mass of resin (g).

The equation means that the larger K_d value, the less element amount in aqueous phase, or in other words, the larger adsorbed amount on resin column.

Adsorption behavior of iron and cadmium on the column was also experimentally investigated via a recovery test of standard additions. A solution of 10 mL of 1.0 mol L^{-1} hydrochloric acid spiked with 1000 μg iron and 100.0 μg cadmium, was prepared. The solution was loaded onto the column and then rinsed with 10 mL of hydrochloric acid. The effluent was stepwise collected as every 1 mL fractions. Cadmium was eluted with 1.6 mol L^{-1} nitric acid and also stepwise collected as every 1 mL fractions. The collected fractions were individually diluted to 10 mL and determined by ICP-AES. Results were showed in Table 2 and Fig 1, Fig 2.

3. Results and discussions

3.1 Optimization of acidity for separation of Cd and Fe

Ideally，the acidity should ensure that all the cadmium is effectively adsorbed in the column and at the same time no iron is retained. In this paper, medium acidity was optimized via experimental study of the distribution coefficient K_d for cadmium and iron, respectively. The results in Table 1 showed that value K_d for cadmium is increased with the increase of HCl concentration up to the climax at 2.0 mol L^{-1}, then the value is decreased with the increase of HCl concentration. Value K_d for cadmium is larger than 10^3 in the HCl concentration range of 0.5-4.0 mol L^{-1}, indicating that in this acidity range, cadmium could be adsorbed strongly on the resin.

Table 1 Distribution coefficients for Cd and Fe on DOWEX 1×8-200 resin at various concentrations of HCl

element	HCl con. (mol L^{-1})	K_d	element	HCl con. (mol L^{-1})	K_d
Cd	0.1	517	Fe	0.1	1.8
	0.5	1539		0.5	4.2
	1.0	2281		1.0	8.9
	2.0	2678		2.0	24
	3.0	2122		3.0	100
	4.0	1415		4.0	302

On the other hand, the value K_d for iron is less than 10 in the HCl concentration range of 0.1-1.0 mol L^{-1}, indicating that only micro amount of iron could be retained on the resin. The value K_d for iron is beyond 10 in case the hydrochloric acid concentration is larger than 2.0 mol L^{-1}, indicating that only a little amount of iron can be retained on the resin.

The significant difference in K_d ensures the effective separation of cadmium from matrix iron. Hence, 1.0 mol L^{-1} hydrochloric acid was chosen as the acidity for the separation in this study. After sample loading, cadmium was strongly adsorbed on the anion exchange resin column, while only negligible amount of iron might be adsorbed. A rinse procedure using 1.0 mol L^{-1} hydrochloric acid as an eluant was followed to wash out all the remaining iron， while cadmium was still adsorbed on the column.

Cd(II) forms complex anion $CdCl_4^{2-}$ with Cl^-. Handbook of Analytical Chemistry[12] gives log K_D values 3.5 (in 2.0 mol L^{-1} HCl) and 2.1 (in 0.1 mol L^{-1} HCl) for $CdCl_4^{2-}$, our experimental results well agree with these values.

3.2 Adsorption behavior of cadmium and iron on the column during loading and rinsing

The adsorption behavior of cadmium and iron on the column in the media of 1.0 mol L^{-1} and 2.0 mol L^{-1} hydrochloric acid was experimentally observed, the results were listed in Table 2. The results indicated that both in the medium of 1.0 mol L^{-1} and 2.0 mol L^{-1} of hydrochloric acid, cadmium was strongly adsorbed on the resin. No cadmium was determined in effluent in case the sample solution was in HCl medium. Though, cadmium could be eluted rapidly with 1.6 mol L^{-1} nitric acid and the amount reached maximum in the third fraction of effluent. Iron started to detect from the first fraction up to the last fraction， illustrating iron has not been adsorbed on the resin column in 1.0 mol L^{-1} hydrochloric acid medium. A little amount of iron in the second and third collection of effluent was detected in case the medium is 2.0 mol L^{-1} hydrochloric acid, illustrating iron was slightly adsorbed in this case. Fig.1 and Fig.2 also showed that 1.0 mol L^{-1} HCl was preferable to 2.0 mol L^{-1} HCl, for the separation of cadmium from iron.

Table 2 Elution curve, illustrating adsorption behavior of Cd and Fe on the resin column in different HCl concentrations, during loading , rinsing and eluting procedures

Fraction collected (mL)		Cd (μg)	Fe (μg)	Fraction collected (mL)		Cd (μg)	Fe (μg)
Sample in 1.0 mol L^{-1} HCl medium	0-1	0	6.8	Sample in 2.0 mol L^{-1} HCl medium	0-1	0	3.8
	1-2	0	79.7		1-2	0	50.3
	2-3	0	100.2		2-3	0	69.1
	3-4	0	98.8		3-4	0	80.7
	4-5	0	99.8		4-5	0	90.8
	5-6	0	102.2		5-6	0	92.1
	6-7	0	97		6-7	0	95.2
	7-8	0	92.5		7-8	0	101.3
	8-9	0	92.7		8-9	0	101.8
	9-10	0	91.9		9-10	0	100.5
Rinse with 1.0 mol L^{-1} HCl	0-1	0	78.7	Rinse with 2.0 mol L^{-1} HCl	0-1	0	82.4
	1-2	0	20.1		1-2	0	20.8
	2-3	0	8.6		2-3	0	13.4
	3-4	0	5.6		3-4	0	11.4
	4-5	0	4.3		4-5	0	9.8
	5-6	0	3.3		5-6	0	8.2
	6-7	0	2.7		6-7	0	7.3
	7-8	0	2.4		7-8	0	5.8
	8-9	0	2.2		8-9	0	4.9
	9-10	0	2.4		9-10	0	3.5
Elute with 1.6 mol L^{-1} HNO_3	0-1	0	1.4	Elute with 1.6 mol L^{-1} HNO_3	0-1	0	5.2
	1-2	0.28	1.4		1-2	0.89	19.4
	2-3	66.54	1.6		2-3	66.77	14.3
	3-4	21.3	1		3-4	17.21	8.7
	4-5	7.66	0.3		4-5	6.78	4.1
	5-6	3.52	0.2		5-6	3.78	3.3
	6-7	1.66	0.1		6-7	1.83	3.1
	7-8	0.45	0.1		7-8	0.56	2.3
	8-9	0.11	0		8-9	0.34	1.6
	9-10	0	0		9-10	0	0.8

It could be concluded that the analytes of interest were successfully separated from the bulk iron matrix after the loading and rinsing procedures, because of their different apparent distribution behavior on the resin.

3.3 Elution of cadmium

Cadmium can be eluted with nitric acid. Concentration of the nitric acid was optimized based on the distribution coefficient of cadmium at different concentrations of nitric acid. In case nitric acid concentration was lower than 3.2 mol L^{-1}, the value K_d of cadmium was reduced down to below 10, indicating that cadmium could no longer be actually retained on the resin. 1.6 mol L^{-1} nitric acid medium was chosen as the elution solution. The elution curve (Fig. 1) showed that 10 mL of 1.6 mol L^{-1} nitric acid was adequate to the elution of adsorbed cadmium.

3.4 Use of the internal standard

ICP spectrometric determination results may be affected by solution acidity in the nebulization course. Internal standard method is able to efficiently improve the determination accuracy. 1.0 µg mL^{-1} yttrium was used as a representative element for testing acidity effect. Table 3 showed that the nebulization efficiency was decreased with the acidity increase. About 10 percent reduction in line intensity occurs in case the hydrochloric acid concentration is increased to 4.0 mol L^{-1} or the nitric acid concentration is increased to 4.8 mol L^{-1}. Yttrium was selected as the ideal internal standard in the present work, because it was not adsorbed on the resin during the different concentrations of hydrochloric acid and nitric acid.

Table 3 Determined result of 1.00 mg L^{-1} yttrium in different acidities of HCl or HNO_3

HCl (mol L^{-1})	Y(224.306nm) (mg L^{-1})	HNO_3 (mol L^{-1})	Y(224.306nm) (mg L^{-1})
0.1	1.00	0.16	0.99
0.5	0.99	0.64	0.98
1.0	0.98	1.6	0.96
2.0	0.95	3.2	0.93
3.0	0.93	4.8	0.91
4.0	0.92	---	---

3.5 Theoretical explanation of the mechanism

The mechanism of separation of Cd from Fe can thus be theoretically explained. In medium of 1.0 mol L^{-1} HCl, anion $CdCl_4^{2-}$ reacted with the exchangeable anion radical Cl of the resin and be adsorbed, while anion $FeCl_4^-$ or $FeCl_6^{3-}$ has not be efficiently formed and cannot exchange with the anion radical because of its too low distribution coefficient. In rinse course, nitric acid radical replaced chlorine anion, $CdCl_4^{2-}$ was dissociated, resin radical released Cd(II) and Cd in effluent can be determined by ICP spectrometry.

3.6 Application to the analysis of actual samples

The detection limit of the proposed method, corresponding to the three times of standard deviation of blank was 0.12 μg g^{-1}. The method has been applied to the determination of cadmium in steel samples. Analysis results of some steel samples were shown in Table 4. Recoveries were in the range 90% ~ 98% in case 0.2 and 0.5 μg of the cadmium were spiked in the steel sample solution. The relative standard deviation for Cd determination (n=7 samplings) for two samples was in the ranged of 5.8% -7.3%.

Table 4 Analytical results for steel with recovery and precision tests

sample No.	determined [a](μg)	RSD (%)	Spiked (μg)	Total determined(μg)	Recovered(μg)	Recovery (%)
CS120924	0.12±0.007	5.8	0.20	0.31	0.19	95
			0.50	0.59	0.47	94
CS120926	0.11±0.008	7.3	0.20	0.29	0.18	90
			0.50	0.60	0.49	98

[a] 0.1g steel sample was analyzed. Values were calculated based on seven parallel analysis.

4. Conclusions

After the steel was dissolved with hydrochloric acid, the analyte cadmium and the matrix iron can be successfully separated on the mini-column packed with anion-exchange resin DOWEX 1×8-200 in medium of 1.0 mol L^{-1} hydrochloric acid. Based on the quite different apparent distribution coefficient between anion exchangeable radical Cl^{-} of the resin and $CdCl_4^{2-}$， or $FeCl_4^{-}$， in 1.0 mol L^{-1} hydrochloric acid, an effective separation of cadmium from matrix iron can be carried out. Cadmium can be eluted with 1.6 mol L^{-1} nitric acid, Cd in effluent can thus be determined by ICP-AES without spectral interferences from iron. The established method provides a convenient and practical way to determine cadmium in the samples containing large amount of iron.

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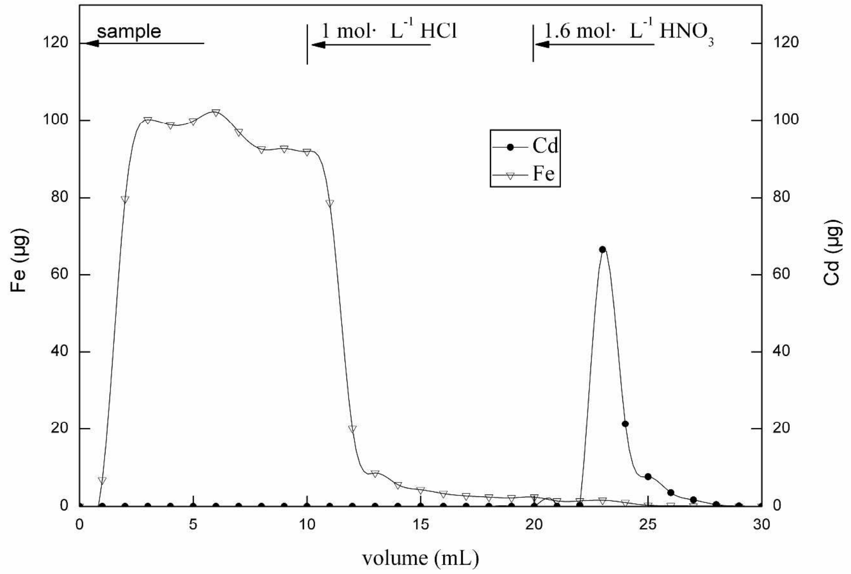
Fig.1 Elution curve of cadmium and iron during loading, rinsing and eluting. The ordinate is analyte concentration in each 1-mL fraction, during loading and rinsing in medium of 1.0 mol L^{-1} hydrochloric acid; eluting with 1.6 mol L^{-1} nitric acid

Fig.2 Elution curve of cadmium and iron during loading, rinsing and eluting. The ordinate is analyte concentration in each 1-mL fraction during loading and rinsing in medium of 2.0 mol L^{-1} hydrochloric acid; eluting with 1.6 mol L^{-1} nitric acid



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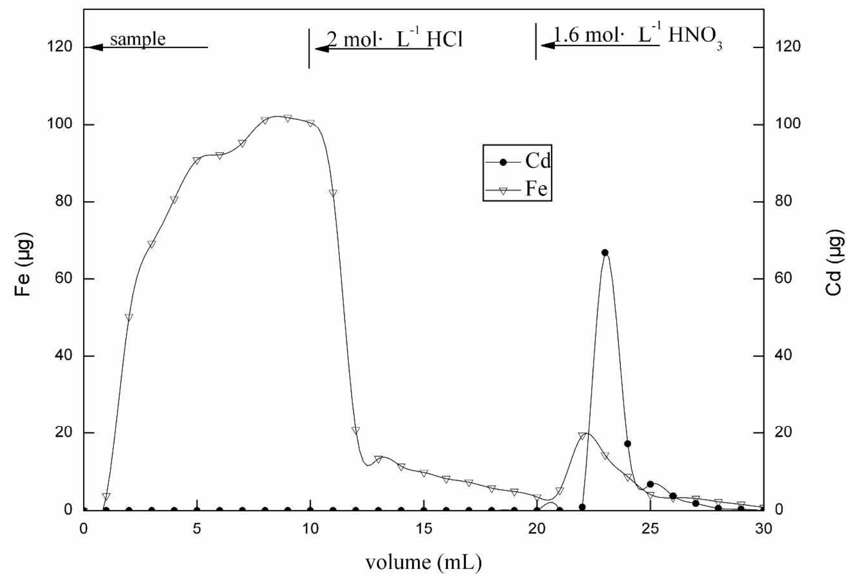

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