

Ion Exchange Separation of Minor Elements from Iron for the Analysis of S/G Sludge

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1. Introduction

The chemical data of minor elements in steam generator sludge could give information about the contamination sources such as a system corrosion, an intrusion of chemicals, etc. The major component of sludge is iron. Iron of a high concentration in a measuring solution worsens the determination limit of the minor elements in a spectroscopic atom analysis. Moreover, iron has so many absorption or emission bands in a wide wavelength range that it has a spectroscopic interference on the atomic spectroscopy of various minor elements such as B, Pb, etc. Thus, the quantitative separation of minor elements from the iron matrix is essential for their determination. Gas sublimation, co-precipitation, solvent extraction and ion exchange are used for this separation[1]. Ion exchange chromatography is applied to the separation of specific minor elements[2]. Ion exchange method has an advantage from the point of experimental space, waste production, and number of elements when applied to radioactive samples. This presentation describes the results of a separation of some minor elements(Al, B, Ba, Ca, Cd, Co, Cr, Cu, Gd, Mg, Mn, Mo, Nd, Ni, P, Pb, Si, Sn, Sr, Ti, V, Yb, Zn and Zr) from synthetic iron samples by anionic and cationic exchange methods for the purpose of analyzing them in the S/G sludge from a power plant.

2. Experiments

Minor elements were determined by ICP-AES(JY50P, Jobin Yvon) and Fe(III) by an absorption spectroscopy of the sulfosalicylate complex(Lambda 4B, Perkin Elmer). Fe(III) solution was prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ by dissolving it in HCl. Single-element solution standards for the plasma emission spectroscopy were used for the minor elements. Washed anionic(AG 1X8, 200-400 mesh, Bio-Rad, 1.2 meq./ml resin bed) and cationic(Dowex 50WX8, 100-200 mesh, Sigma, 2.0 meq./ml resin bed) exchange resins of 6.5 ml were packed in polyethylene columns(ID=12.5 mm). These amounts are equivalent to 220 and 250 mg of Fe(III) as FeCl_5^{2-} and Fe^{3+} ions, respectively. The synthetic working solutions were prepared to contain 100 mg of Fe and/or 150 μg of every minor element in the HCl solutions.

For the separation by an anionic exchange, the synthetic working solutions of various compositions of HCl with ethanol, NH_4Cl or ethylenediamine were loaded. The relative Fe(III) adsorption abilities for each loading condition were estimated by a visual

comparison of the widths of the dark colored Fe(III) adsorption bands. The loaded Fe(III) was washed out by various HCl-HBr mixed solutions, and the minor elements remaining in the column were eluted by 1 M HNO_3 . For the separation by a cationic exchange, the synthetic working solutions of 0.7 M HCl were loaded. Fe(III) was washed out with 3 M H_3PO_4 , and the H_3PO_4 was washed out with 0.1 M HCl. The elements remaining in the column were eluted with 6 M HCl. Several constant volumes of a solution were consecutively added to the columns to decide the optimum volume of the washing and elution.

3. Result and discussion

3.1. Separation by an anionic exchange

The adsorption ability of Fe(III) was influenced by the loading condition. It was almost constant at $[\text{HCl}] > 6$ M, while most of the Fe(III) was passed out of the column at < 1.6 M. It increased with an increasing of the ethanol concentration and it was almost constant at more than a 0.3 volume ratio at 3.8 M HCl. At 5.5 M HCl, by increasing NH_4Cl to 1.5 M it did not influence the adsorption ability while by increasing ethylenediamine to 1.1 M it decreased it. The sample loading conditions of 6 M HCl, 3.8 M HCl-EtOH(0.3 v/v), 6 M HCl-1.3 M NH_4Cl and 6 M HCl-0.5 M ethylenediamine showed similar results about the Fe(III) adsorption abilities and minor elements recoveries. Thus, 6 M HCl was chosen as a loading condition.

The volume of HCl-HBr for a complete washing out of Fe(III) increased as the concentration of HCl or HBr increased. After the washing out of Fe(III) with 0.1 M HCl-1.0 M HBr, Cu and Mo which are expected to remain in a column were not found in the 1 M HNO_3 eluate, and Zn was recovered at less than the added amount. This indicates that even the transition elements which easily form anionic species with Br^- had been completely or partially washed out together with Fe(III).

The determined recoveries of the minor elements with and without Fe(III) is presented in table 1. The elements which do not easily form an anionic complex with Cl⁻ such as Al, B, Ba, Cr, Gd, Mg, Nd, Ni, P, Sr, Ti, V and Yb were almost quantitatively recovered at the Fe(III) loading step. However, the elements which form anionic species such as Cd, Co, Cu, Mo, Pb, Sn and Zn were not quantitatively recovered. Only zinc was quantitatively recovered at the elution after the washing out of Fe(III), suggesting that the elution process is not economically advantageous for expanding the number

of determinable minor elements. The recoveries of Cd, Co, Cr, Mn, Ni, P and Zn were higher than what was added when Fe(III) was present in the synthetic samples, indicating that they existed in the Fe(III) chemical as impurities. And, the recoveries of Ca and Si were higher than what was added regardless of the Fe(III) presence, indicating that they existed in other chemicals and can be corrected by a blank analysis.

Table 1. Determined recoveries of minor elements with and without Fe(III). Mean of 3 measurements. $2\sigma < 5\%$.

	Anionic exchange				Cationic exchange			
	Loading		Elution		Loading		Elution	
	W	WO	W	WO	W	WO	W	WO
Al	1.03	0.99	0.00	0.00	0.05	0.05	0.80	0.73*
B	0.95	0.95	0.00	0.00	0.95	0.94	0.00	0.00
Ba	0.98	1.00	0.00	0.00	0.00	0.03	0.41	0.47
Ca	1.20	1.24	0.13	0.13	0.00	0.00	0.96	0.81*
Cd	0.00	0.00	1.93	0.97	0.89	0.85	0.10	0.14
Co	0.81	0.58	0.00	0.00	0.00	0.00	1.02	0.97
Cr	1.08	1.00	0.00	0.00	0.09	0.03	0.98	0.85*
Cu	0.01	0.00	0.01	0.23	0.00	0.00	1.07	0.98
Gd	0.99	1.01	0.00	0.00	0.01	0.01	0.82	0.72*
Mg	0.94	0.97	0.03	0.03	0.00	0.00	1.01	0.97
Mn	3.09	1.01	0.00	0.00	0.00	0.00	3.10	0.97
Mo	0.00	0.00	0.01	0.03	0.72	0.88	0.00	0.00
Nd	0.97	1.00	0.00	0.00	0.00	0.01	0.76	0.67*
Ni	1.05	0.99	0.00	0.00	0.00	0.00	1.10	0.99
P	0.97	0.91	0.01	0.05	0.48	0.80	0.82	-
Pb	0.72	0.73	0.07	0.06	0.00	0.00	1.02	1.00
Si	1.54	1.64	0.00	0.00	0.95	0.93	0.00	0.00
Sn	0.41	0.39	0.64	0.51	0.54	0.51	0.37	0.32*
Sr	1.06	1.10	0.00	0.00	0.00	0.00	0.99	0.87*
Ti	0.98	1.01	0.00	0.00	0.10	0.08	0.00	0.00
V	0.99	1.01	0.00	0.00	0.01	0.01	0.00	0.02
Yb	0.99	1.02	0.00	0.00	0.00	0.00	0.97	0.83*
Zn	0.01	0.00	1.22	0.96	0.00	0.00	1.16	1.02
Zr	0.98	1.01	0.00	0.00	0.12	0.14	0.03	0.18

W : with Fe(III), WO : without Fe(III), * : $2\sigma < 20\%$

3.2. Separation by a cationic exchange

Metal ions including transition elements can be adsorbed onto cation exchange resin at a low HCl concentration. All the tested metal ions except B, Cd, Mo, P, Si, Sn, Ti and Zr were quantitatively adsorbed, and were not found in the solution passed through the column at the Fe(III) loading step. The ions not quantitatively adsorbed might exist as anionic or neutral species. Fe(III) and some minor ions classified as a hard acid can be eluted by a hard base such as phosphate, while the transition elements classified as a soft acid could remain in the column. Fe(III) was completely washed out by 3 M H_3PO_4 . After the washing out of Fe(III), the column was eluted by 6 M HCl. The heavier the alkaline earth metal ions were, the larger the volume required for the elution. Ba required more than 25 ml for a complete elution. The elution curve of Co, Ni, Cu and Zn, which were not recovered at the anionic exchange, are shown as an example in figure 1. They were eluted by less than 10 ml. Ln(III) such as Gd and Nd remained in the column after an elution by 3 M H_3PO_4 , and was eluted by 6M HCl at more than 25 ml, while Yb was completely eluted within 20 ml. Pb, Al, Cr and Mn were eluted by less than 10 ml. Sn and Cd

showed two elution peaks, indicating that they existed with two oxidation states.

The determined recovery of minor the elements with and without Fe(III) is presented in table 1. Only B, Cd and Si were recovered at Fe(III) the loading step. Ca, Co, Cr, Cu, Mg, Ni, Pb, Sr, Yb and Zn were quantitatively recovered by an elution with 6 M HCl after a washing out of the Fe(III). Ba, Gd and Nd were not quantitatively eluted because of shortage in elution volume.

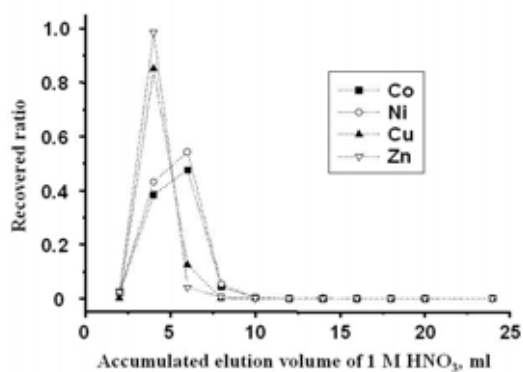


Figure 1. Elution curves of transition elements on cation exchange resin by 1 M HNO_3 after washing out of Fe(III) with 3 M H_3PO_4 .

4. Summary

Some minor elements(Al, B, Ba, Ca, Cd, Co, Cr, Cu, Gd, Mg, Mn, Mo, Nd, Ni, P, Pb, Si, Sn, Sr, Ti, V, Yb, Zn and Zr) in iron compounds such as the S/G sludge of a power plant were separated from iron by anionic and cationic exchange methods. If a ICP-AES or AAS determination follows this method, minor elements of more than 2 or 20 ppm of Fe can be determined with an error less than 20% except Sn and Mo. Alkaline elements were excluded from this study since they can be easily recovered from an anionic exchange. Application to real sludge samples is ongoing.

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