On-site Separation of Sb(III) and Sb(V) and Antimony Stable Isotope Analysis by a Sulfonated Silane Strong Cation Exchange Resin

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1 Supplementary method

1.1 Parameter control and material screening experiments in the separation of Sb(III) and Sb(V)

A working solution (1 mg L^{-1}) containing Sb(III) and Sb(V) at a 1:1 molar ratio was prepared by dissolving potassium antimony tartrate and potassium pyroantimonate and adjusting the pH to 7. Based on a single-variable experimental design, a series of optimization tests were carried out, including screening five ion-exchange resins, evaluating different activation reagents, controlling the elution rate (0.5, 1, 1.5, 3, 6, and 12 mL min^{-1}), adjusting the dosage of the Sb(V) rinsing solution (2, 4, 6, and 8 mL), and determining the optimal concentration of the Sb(III) eluent (0.1-10 mol L^{-1}).

1.2 Reusability Verification of SCX

The working solution prepared in Section 1.1 was subjected to the standard separation procedure (Fig. 2). After each separation cycle, the SCX column was reactivated and subsequently used to process a fresh aliquot of the working solution under identical operating conditions. This process was repeated, and the recoveries of Sb(III) and Sb(V) were quantified after each cycle while recording the cumulative number of SCX reuses. The reuse assessment was continued until a marked decline in the recovery of either Sb(III) or Sb(V) was detected.

1.3 Collection and on-site separation of groundwater samples

Xikuangshan in Hunan Province is the world's largest Sb mine and is widely referred to as the "capital of Sb." Groundwater samples were collected from Xikuangshan (n = 3, Table S1) as representative waters for separation of Sb(III) and Sb(V) and subsequent isotope analysis. The samples were filtered through mixed cellulose ester membranes (0.22 μm, Jinteng, China) immediately after collection. Sb(III) and Sb(V) were then separated on-site using the SCX column. The separated Sb(III) and Sb(V) fractions were stored in sealed containers at 4 °C and transported to the laboratory for determination of Sb concentrations and isotope compositions.

Table S1. Sampling sites

Sample name	sample location Longitude	Latitude
XKS1	111.491879	27.783146
XKS2	111.493395	27.768893
SKS3	111.502831	27.789889

Table S2. Concentrations of metal elements with levels below 1 mg L^{-1}

Sample name	Li (ug L^{-1})	Mn (ug L^{-1})	Fe (ug L^{-1})
XKS1	4.32	3.26	3.72
XKS2	51.2	29.6	37.6
XKS3	6.71	91.2	28.4

1.4 Spike recovery validation using field samples

Field-collected samples were filtered and then mixed with standard solutions at an equal volume ratio of 1:1. The total Sb concentration in the standard solution was 1 mg L^{-1}, with an Sb(III):Sb(V) ratio of 1:1. This standard solution is prepared by mixing an Sb(III) standard solution (solvent: 10% HCl, pH < 2) with an Sb(V) standard solution (solvent: ultrapure water, pH = 6.56 ± 0.17). After mixing, a 2 mL aliquot of the mixed sample was subjected to Sb(III) and Sb(V) separation following the procedure shown in Fig. 2. After separation, the concentrations of Sb(III) and Sb(V) were determined by AFS (Table S3). The spike recoveries were subsequently calculated using the following equation:

$$R_s = \left(C_{mix} \cdot V_1 - C \cdot V_2\right) / (C_s \cdot V_3) \tag{1}$$

Where R_s represents the recovery of Sb(III) or Sb(V); C_{mix} is the concentration of Sb(III) or Sb(V) in the mixed sample after separation; V_1 is the volume of the mixed sample (2 mL); C is the concentration of Sb(III) or Sb(V) in the field sample after separation (Table 1); C_s is the concentration of Sb(III) or Sb(V) in the standard solution (0.5 mg L^{-1}); V_2 and V_3 are the volumes of the field sample and the standard solution used, respectively ($V_2 = V_3 = 1$ mL).

Table S3. Spike recoveries of Sb in field-collected samples.

Sample name	Sb concentration in the spiked samples (mg L^{-1})		Recoveries of spiked standard samples (%)	
	Sb(III)	Sb(V)	Sb(III)	Sb(V)
XKS1	252 ± 6.08	417 ± 1.48	96.3 ± 2.4	98.5 ± 0.6
XKS2	264 ± 9.09	413 ± 9.51	99.0 ± 3.6	95.1 ± 3.8
SKS3	256 ± 3.22	415 ± 2.61	97.7 ± 1.3	96.8 ± 1.0

1.5 Applicable range of iron and manganese ion concentrations

To evaluate the effects of Fe^{3+}, Fe^{2+}, and Mn^{2+} on the separation behavior of Sb(III) and Sb(V), mixed working solutions containing both Sb(III) and Sb(V) were prepared with a total Sb concentration of 1 mg L^{-1} and a molar ratio of Sb(III) to Sb(V) of 1:1. Ultrapure water was used as the solvent, and the mixed working solutions were prepared by diluting Sb(III) and Sb(V) stock solutions, followed by the addition of Fe^{3+}, Fe^{2+}, or Mn^{2+} standard stock solutions to obtain final metal ion concentrations of 0, 0.1, 0.3, 0.5, 1, and 2 mg L^{-1}, respectively. Each system was prepared independently, with only one metal ion concentration varied in each experimental set while all other conditions were kept constant. After preparation, the pH of each solution was adjusted to 7, and the solutions were thoroughly mixed and allowed to equilibrate for a certain period before being subjected to the subsequent separation experiments.

2 Supplementary figures

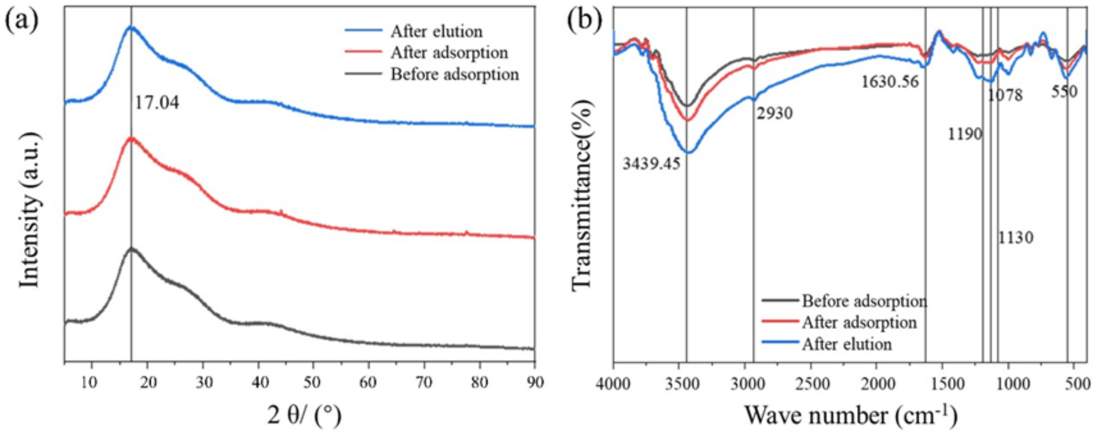

Figure S1. XRD and FT-IR patterns of SCX before, after adsorption and after elution

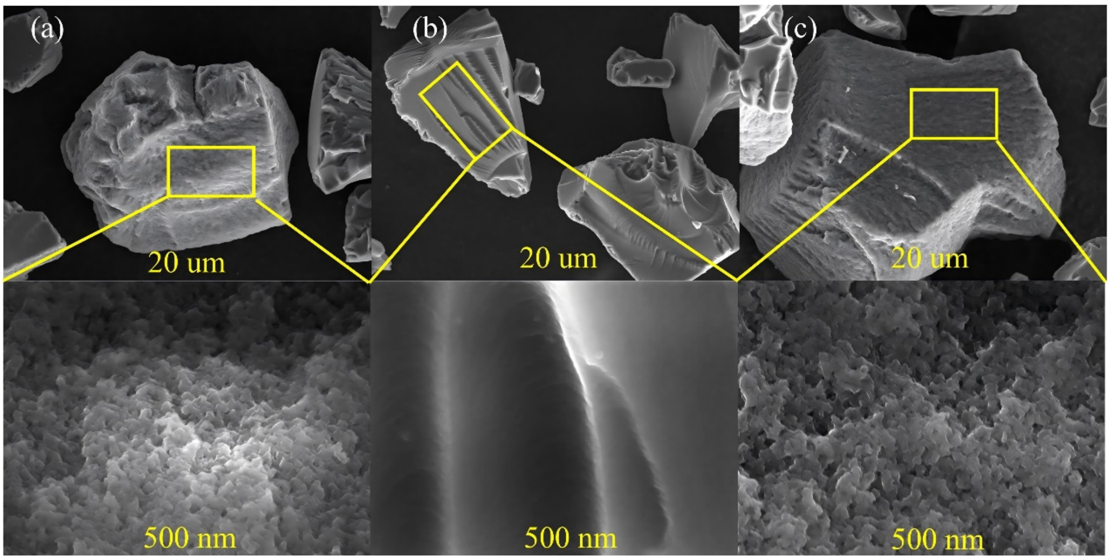

Figure S2. SEM of SCX before (a), after adsorption (b) and after elution (c)

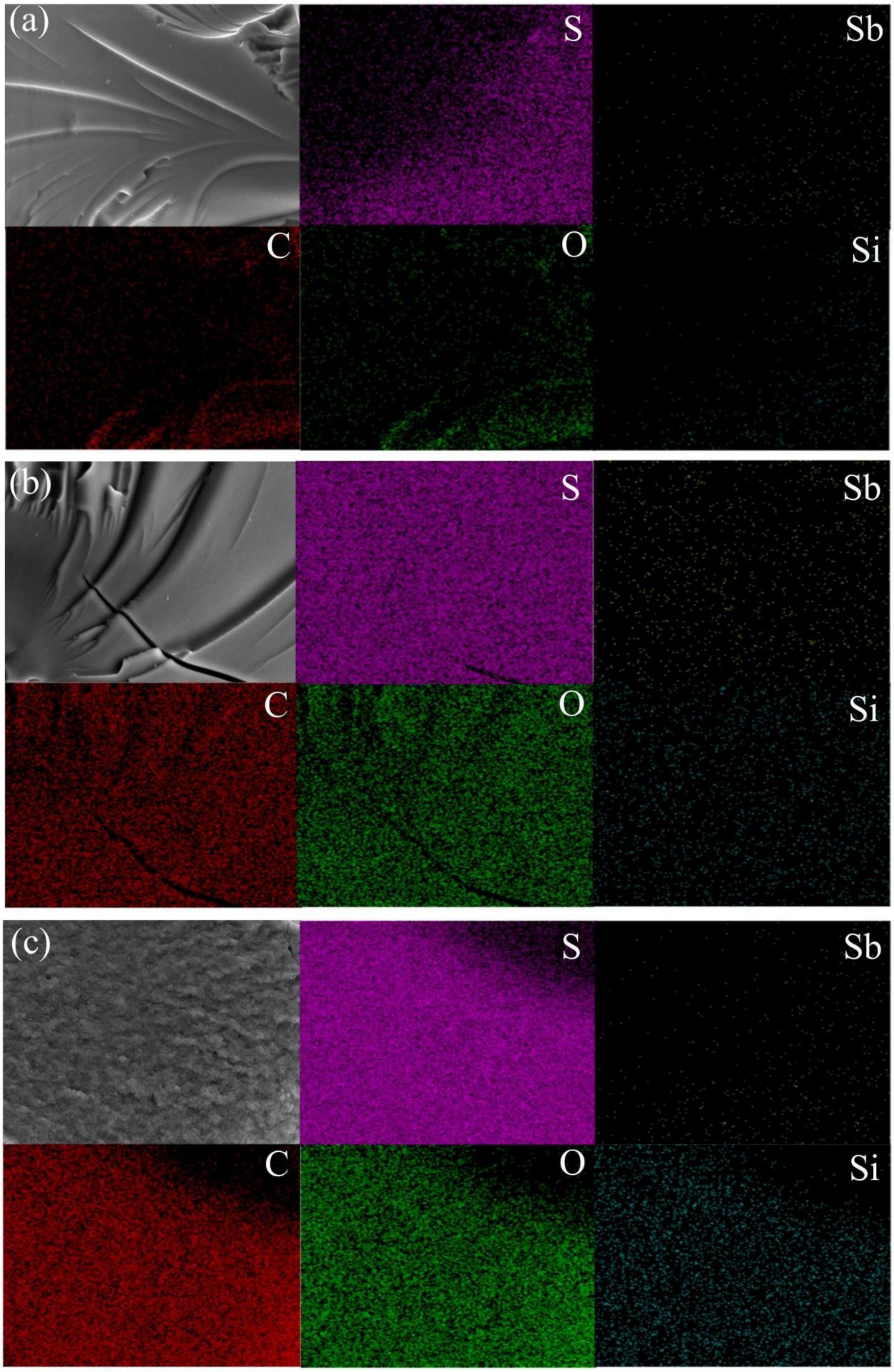

Figure S3. SEM-EDS elemental mapping images of SCX before (a), after adsorption (b) and after elution (c)

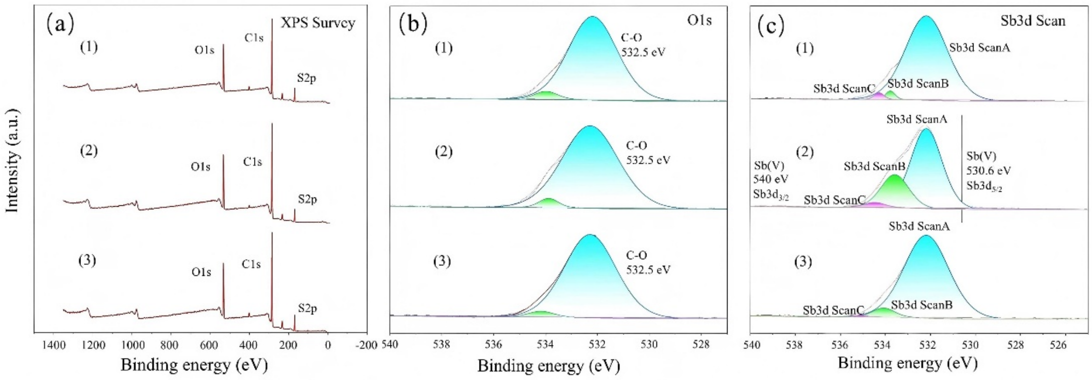

Figure S4. XPS spectra of SCX: survey scan (a), O 1s (b), and Sb 3d (c) high-resolution spectra before adsorption (1), after adsorption (2), and after elution (3)

2 Supplementary Tables

Table S4. Functional groups, particle size, and porosity of the resins

Resin ID	Porosity	Functional Group	Particle Size （mm）
SCX01	0.31	SO_3H	0.04-0.06
SCX02	0.31	COOH	0.40-1.00
SCX03	0.34	SO_3H	0.20
SCX04	0.36	SO_3H	0.40-0.60
SCX05	0.33	SO_3H	0.30-1.20

Table S5. Isotopic compositions of Sb(III) and Sb(V) in waters with varying ionic strength and pH

Ionic Strength (mol L^{-1})	δ^{123}Sb (‰)		pH	δ^{123}Sb (‰)	
	Sb(V)	Sb(III)		Sb(V)	Sb(III)
0.1	0.43 ± 0.13	1.24 ± 0.06	3	0.35 ± 0.09	1.18 ± 0.07
0.05	0.39 ± 0.03	1.22 ± 0.14	5	0.52 ± 0.09	1.19 ± 0.08
0.01	0.36 ± 0.14	1.37 ± 0.07	7	0.36 ± 0.14	1.37 ± 0.07
0.005	0.44 ± 0.14	1.33 ± 0.08	9	0.52 ± 0.13	1.22 ± 0.12
0.001	0.43 ± 0.16	1.21 ± 0.05	11	0.63 ± 0.14	1.42 ± 0.11

Table S6. Sb isotope compositions of natural samples before and after separation

Sample name	Initial sample	Samples after separation		
	δ^{123}Sb (‰)	δ^{123} Sb(V) (‰)	δ^{123} Sb(III) (‰)	δ^{123}Sb(calculated value) (‰)
XKS1	1.26 ± 0.11	1.30 ± 0.04	0.40 ± 0.06	1.25 ± 0.04
XKS2	0.40 ± 0.05	0.33 ± 0.09	0.01 ± 0.03	0.3 ± 0.08
XKS3	0.11 ± 0.04	0.05 ± 0.12	-0.11 ± 0.06	0.04 ± 0.11

Note: δ^{123}Sb (calculated value) was derived from the separated Sb(V) and Sb(III) fractions (see Eq. 2).