

Recovery of high-purity vanadium from aqueous solutions by a reusable primary amines N1923 associated with semiquantitative understanding of vanadium species

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Supporting Information Content:

15 pages

6 tables and **15** figures

Table S1 Identified vanadium species in aqueous solution

No.	Vanadium atom number	Molecular formula	Ionic formula	Exact parent peak mass/charge (m/z)	Refs.
1	1	H ₃ VO ₄	H ₂ VO ₄ ⁻	116.9393	¹
2	2	H ₂ V ₂ O ₆	HV ₂ O ₆ ⁻	198.8652	¹
3	2	H ₂ V ₂ O ₆	NaV ₂ O ₆ ⁻	220.8472	²
4	3	H ₃ V ₃ O ₉	H ₂ V ₃ O ₉ ⁻	298.8018	*
5	4	HV ₄ O ₁₀	V ₄ O ₁₀ ⁻	363.7250	³
6	4	V ₄ O ₁₀	NaV ₄ O ₁₀ (SO ₄) ⁻	482.6665	*
7	4	H ₂ V ₄ O ₁₁	HV ₄ O ₁₁ ⁻	380.7278	¹
8	4	H ₂ V ₄ O ₁₁	NaV ₄ O ₁₁ ⁻	402.7097	²
9	4	H ₂ V ₄ O ₁₁	V ₄ O ₁₁ ²⁻	189.8600	¹
10	4	H ₄ V ₄ O ₁₂	H ₂ V ₄ O ₁₂ ²⁻	198.8652	*
11	5	HV ₅ O ₁₃	V ₅ O ₁₃ ⁻	462.6537	¹
12	5	H ₃ V ₅ O ₁₄	H ₂ V ₅ O ₁₄ ⁻	480.6643	⁴
13	5	H ₃ V ₅ O ₁₄	NaHV ₅ O ₁₄ ⁻	502.6462	*
14	5	H ₃ V ₅ O ₁₄	Na ₂ V ₅ O ₁₄ ⁻	524.6282	*
15	5	H ₃ V ₅ O ₁₄	HV ₅ O ₁₄ ²⁻	239.8282	*
16	5	H ₃ V ₅ O ₁₄	NaV ₅ O ₁₄ ²⁻	250.8192	*
17	6	H ₂ V ₆ O ₁₆	NaV ₆ O ₁₆ ⁻	584.5722	²
18	6	H ₂ V ₆ O ₁₆	V ₆ O ₁₆ ²⁻	280.7912	¹
19	6	H ₄ V ₆ O ₁₇	H ₂ Na ₂ V ₆ O ₁₇ ⁻	624.5647	*
20	7	H ₃ V ₇ O ₁₉	HV ₇ O ₁₉ ²⁻	330.7595	*
21	7	H ₃ V ₇ O ₁₉	NaV ₇ O ₁₉ ²⁻	341.7505	*
22	10	H ₂ V ₁₀ O ₂₆	V ₁₀ O ₂₆ ²⁻	462.6537	¹
23	10	H ₆ V ₁₀ O ₂₈	H ₄ V ₁₀ O ₂₈ ²⁻	480.6643	⁴
24	10	H ₆ V ₁₀ O ₂₈	Na ₂ H ₂ V ₁₀ O ₂₈ ²⁻	502.6462	*
25	10	H ₆ V ₁₀ O ₂₈	Na ₃ HV ₁₀ O ₂₈ ²⁻	513.6372	*
26	10	H ₆ V ₁₀ O ₂₈	Na ₄ V ₁₀ O ₂₈ ²⁻	524.6282	*
27	10	H ₈ V ₁₀ O ₂₄	Na ₄ H ₂ V ₁₀ O ₂₄ ²⁻	493.6461	*
28	12	H ₄ V ₁₂ O ₃₂	Na ₂ V ₁₂ O ₃₂ ²⁻	584.5722	*
29	3	HV ₃ O ₈ (Na ₂ (SO ₄)) ₂	V ₃ O ₈ (Na ₂ (SO ₄)) ₂ ⁻	564.6537	*
30	5	H ₃ V ₅ O ₁₂ (SO ₄)	H ₂ V ₅ O ₁₂ (SO ₄) ⁻	544.6262	*
31	6	Na ₃ HV ₆ O ₁₆ (SO ₄)	Na ₃ V ₆ O ₁₆ (SO ₄) ⁻	726.5035	*

*obtained from Masslynx software.

Mass spectrometer data analysis.

(1) The relative concentrations of each species in different m/z

The intensity of each peak can reflect the relative concentration of each serial species at the same spectrum, so the relative concentrations of each peak in different m/z were described as Eq. (s1), where E_i or E_j represented the intensity of subscripted peak i, j, m was the molecular mass and z was the charge of each species. And c_i was the relative mole concentration of interested peak i.

$$c_i(\%) = \frac{E_i}{\sum_{j=1} E_j} \times 100\% \quad (s1)$$

(2) The relative concentrations of each species in the same m/z

Some species pairs (for example $V_5O_{13}^-$ and $V_{10}O_{26}^{2-}$) have the same parent peak, and must be assigned with isotopic peak (Fig. S1). Then the concentration for each species of the species pairs can be calculated as Eq. (s2)-(s3).

For certain species pairs, the isotopic models were fixed and obtained from Masslynx software (Figure S1 was an example for $V_5O_{13}^-$ and $V_{10}O_{26}^{2-}$), then the x/y referred to a fixed ratio for certain species pair as seen in Eq. (s2), and the A, B, a and b were the intensity of certain peaks described as Fig. S1. The related species pairs and its x/y ratio were listed in Table S2.

With the use of fixed x/y ratio, the relative concentrations of each species in the same m/z can be calculated using Eq. (s3), and the m and n referred to the intensity of isotopic peak of species pairs in real spectrum. Because the (x/y) was a constant for

definite species pairs, so the (mx/ny) can refer to the relative intensity ratio of the species pairs, which was also the relative concentrations of the species pairs approximately.

The calculation process was similar to internal standard method.

$$x = \frac{A}{a}; y = \frac{B}{b} \Rightarrow \frac{A}{B} = \frac{ax}{by} \quad (s2)$$

$$\frac{c_{(V_{10})}}{c_{(V_5)}} \approx \frac{E_{V_{10}}}{E_{V_5}} = \frac{mx}{ny} \quad (s3)$$

(3) Summary of the relative concentration calculation process

First, the relative concentrations of each species in different m/z were determined by Eq. (s1); Second, the relative concentrations of each species in the same m/z were determined by Eq. (s2)-(s3); Third, the relative concentrations of each species were obtained, and the total relative concentration was 100% in definite condition.

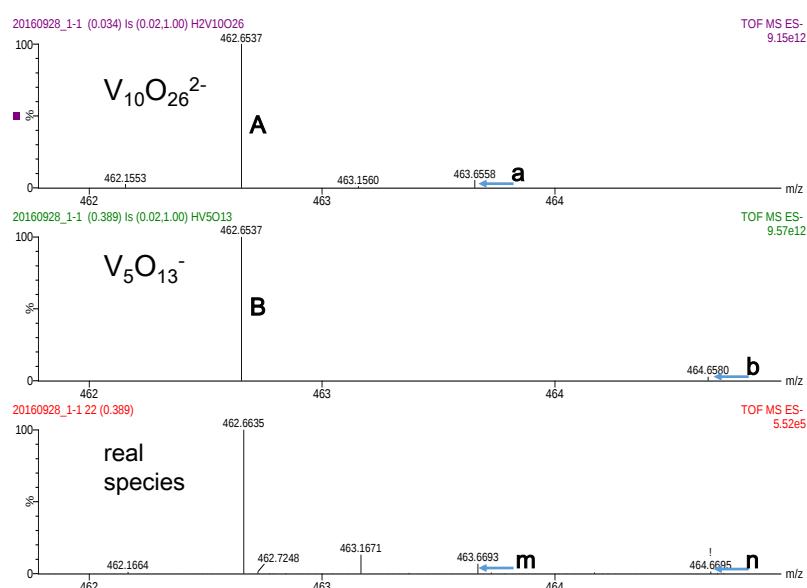


Figure S1 The mass spectra and its isotope model for $V_5O_{13}^-$ and $V_{10}O_{26}^{2-}$

Table S2 The related species pairs and its x/y ratio

N o .	Species pairs	Parent peak mass	Intensity	Isotope peak mass	Intensity	x(y)	x/y
1	HV ₂ O ₆ ⁻	198.8652	9.804e12	200.8695	1.209e11	81.09	2.00
	H ₂ V ₄ O ₁₂ ²⁻	198.8652	9.611e12	199.8674	2.371e11	40.54	05
2	Na ₂ V ₄ O ₁₂ ²⁻	220.8472	9.613e12	221.8493	2.372e11	40.53	0.49
	NaV ₂ O ₆ ⁻	220.8472	9.805e12	222.8514	1.209e11	81.10	97
3	H ₂ V ₁₀ O ₂₈ ⁴⁻	239.8282	9.104e12	240.3293	5.246e11	17.35	0.49
	HV ₅ O ₁₄ ²⁻	239.8282	9.542e12	240.8304	2.746e11	34.75	94
4	NaV ₅ O ₁₄ ²⁻	250.8192	9.543e12	251.8213	2.747e11	34.74	2.00
	Na ₂ V ₁₀ O ₂₈ ⁴⁻	250.8192	9.106e12	251.3203	5.247e11	17.35	17
5	V ₆ O ₁₆ ²⁻	280.7912	9.474e12	281.7933	3.116e11	30.40	0.50
	V ₃ O ₈ ⁻	280.7912	9.733e12	282.7954	1.601e11	60.79	01
6	V ₁₀ O ₂₆ ²⁻	462.6537	9.153e12	463.6558	4.896e11	18.69	0.49
	V ₅ O ₁₃ ⁻	462.6537	9.567e12	464.6580	2.557e11	37.41	97
7	H ₄ V ₁₀ O ₂₈ ²⁻	480.6643	9.104e12	481.6664	5.246e11	17.35	0.49
	H ₂ V ₅ O ₁₄ ⁻	480.6643	9.542e12	482.6685	2.746e11	34.75	94
8	Na ₂ HV ₅ O ₁₂ ⁻	493.6461	9.589e12	495.6504	2.366e11	40.53	2.00
	Na ₄ H ₂ V ₁₀ O ₂₄ ²⁻	493.6461	9.195e12	494.6483	4.540e11	20.25	11
9	Na ₂ H ₂ V ₁₀ O ₂₈ ²⁻	502.6462	9.106e12	503.6483	5.247e11	17.35	0.49
	NaHV ₅ O ₁₄ ⁻	502.6462	9.543e12	504.6505	2.747e11	34.74	96
1	Na ₄ V ₁₀ O ₂₈ ²⁻	524.6282	9.108e12	525.6303	5.248e11	17.36	0.21
0	Na ₂ V ₅ O ₁₄ ⁻	524.6282	9.544e12	523.6313	1.196e11	79.80	75
1	H ₂ V ₁₂ O ₃₂ ²⁻	562.5903	8.977e12	563.5923	5.907e11	15.20	0.49
1	HV ₆ O ₁₆ ⁻	562.5903	9.474e12	564.5945	3.116e11	30.40	98
1	Na ₂ V ₁₂ O ₃₂ ²⁻	584.5722	8.979e12	585.5743	5.909e11	15.20	0.49
2	NaV ₆ O ₁₆ ⁻	584.5722	9.475e12	586.5764	3.117e11	30.40	99

Table S3 the effect of pH on the separation extraction

acid/vanadium	0.01 mol/L		0.02 mol/L		0.04 mol/L		0.08 mol/L	
ratio	pH ₀	pH _e	pH ₀	pH _e	pH ₀	pH _e	pH ₀	pH _e
0.4	6.05	6.03	6.10	6.18	6.18	6.39	6.26	6.40
0.6	4.19	5.49	4.44	5.79	4.92	6.04	4.01	6.10
0.8	2.95	5.32	2.91	5.68	2.78	5.90	2.41	6.01
1.0	2.70	5.14	2.59	5.57	2.43	5.77	2.14	5.88
1.2	2.54	4.85	2.45	5.99	2.27	5.52	2.00	6.48

* pH₀ represented the initial pH in the solution, and pH_e was the equilibrium pH in aqueous solution after extraction.

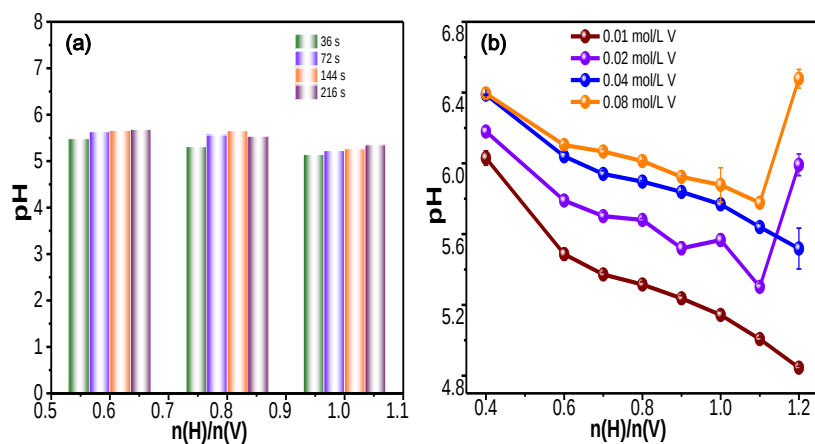


Figure S2 (a): effect of contact time (36–216 s) on the pH in equilibrium aqueous solution at 0.01 mol/L vanadium concentration; (b): effect of vanadium concentration (0.01–0.08 mol/L) on the pH in equilibrium aqueous solution at the same contact time (36 s).

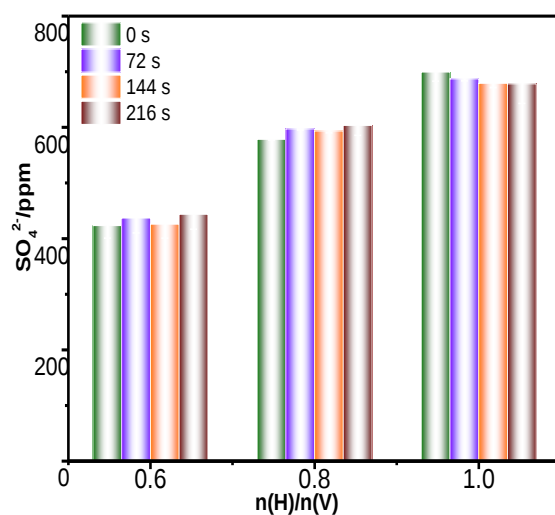


Figure S3 the concentration of SO_4^{2-} ions in aqueous solution during extraction process (0 s, 72 s, 144 s and 216 s).

Table S4 The variation relative ratio of vanadium species (0 s, 72 s, 144 s and 216 s).

Description		10 mmol L⁻¹ V n(H)/n(V)=0.6						
Time/s		0		72		144		216
Number of vanadium species	Value %	Standard error	Value %	Standard error	Value %	Standard error	Value %	Standard error
1	0.59	0.0433	5.16	0.7447	6.14	0.1388	5.46	0.1506
2	0.28	0.0209	2.95	0.8357	5.36	0.4606	3.83	0.3071
3	0.46	0.0486	0.85	0.0297	0.93	0.0462	0.84	0.0119
4	30.98	0.6563	30.70	0.4072	33.41	0.1921	31.68	0.3681
5	7.67	0.3656	6.80	0.0569	8.36	0.0940	8.01	0.2037
7	1.80	0.1927	1.76	0.0312	1.60	0.0284	1.64	0.0254
10	58.22	0.4374	51.78	1.9690	44.20	0.4278	48.54	0.6416
Description		10 mmol L⁻¹ V n(H)/n(V)=0.8						
Time/s		0		72		144		216
Number of vanadium species	Value %	Standard error	Value %	Standard error	Value %	Standard error	Value %	Standard error
1	0.69	0.1162	12.62	0.1804	6.20	0.6996	5.25	0.7949
2	0.25	0.0089	7.98	0.1360	2.07	0.3512	2.14	0.3156
3	0.55	0.0274	0.89	0.0158	0.88	0.0175	0.96	0.0528
4	31.20	0.4607	31.56	0.3107	28.46	0.0773	30.21	0.0985
5	6.88	0.2556	6.95	0.0766	8.09	0.2087	6.30	0.1308
7	1.78	0.1073	1.19	0.0155	1.54	0.0187	1.51	0.0419
10	58.64	0.5337	38.81	0.3436	52.75	0.8336	53.65	0.9481
Description		10 mmol L⁻¹ V n(H)/n(V)=1.0						
Time/s		0		72		144		216
Number of vanadium species	Value %	Standard error	Value %	Standard error	Value %	Standard error	Value %	Standard error
1	0.32	0.0155	22.33	0.3314	14.54	1.1322	17.46	0.9477
2	0.00	0.0000	7.19	0.9255	3.52	0.6195	4.19	0.2141
3	0.68	0.0202	0.81	0.0453	0.88	0.0153	0.96	0.0394
4	31.30	0.3200	31.16	0.6310	28.73	0.2982	31.39	1.0465
5	4.62	0.1521	3.89	0.6004	2.02	0.0195	2.40	0.0869
7	1.34	0.0345	0.80	0.0029	0.00	0.0000	0.00	0.0000

10	61.7	0.3773	33.8	1.4752	50.3	1.7066	43.5	1.7679
	4		2		0		9	

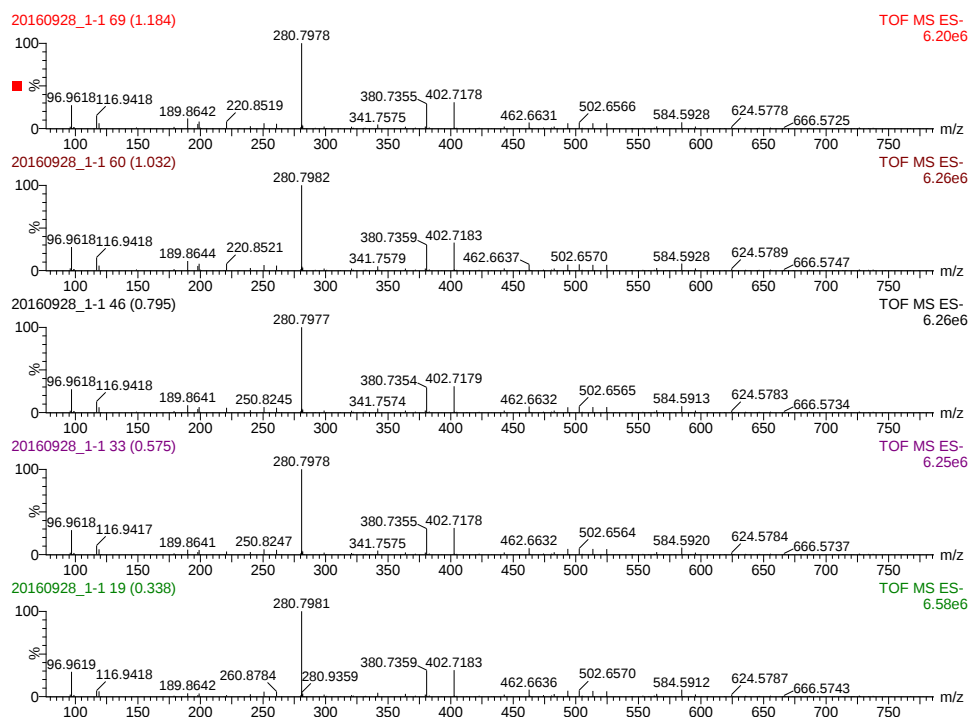


Figure S4 The mass spectra for vanadium aqueous solution after extraction from ACC at 72 s (initial $n(H)/n(V)=0.6$)

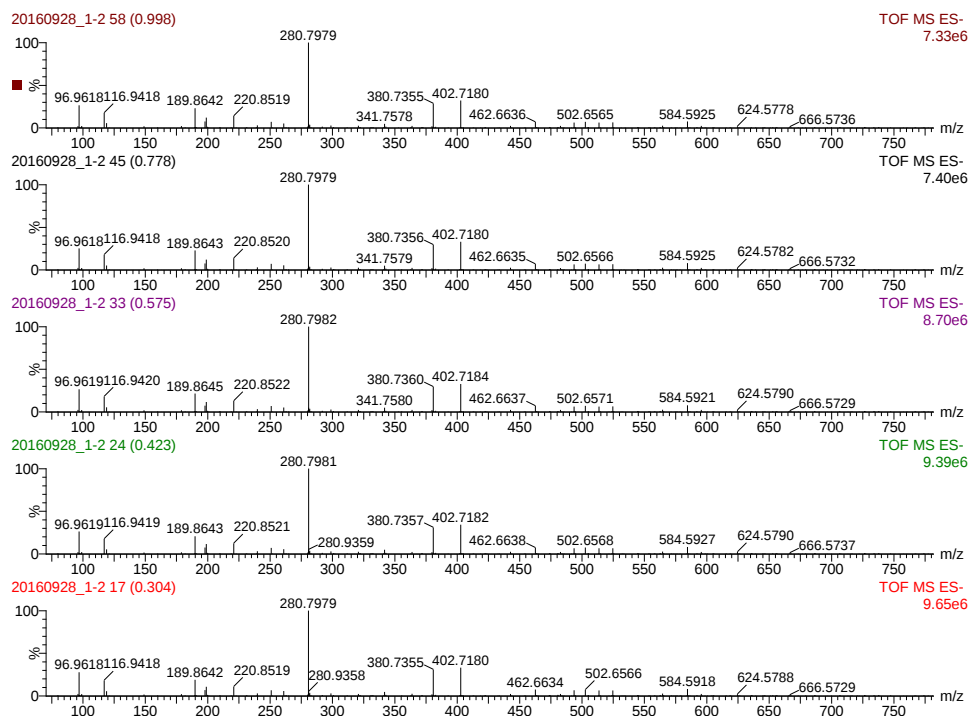


Figure S5 The mass spectra for vanadium aqueous solution after extraction from ACC at 144 s (initial $n(\text{H})/n(\text{V})=0.6$)

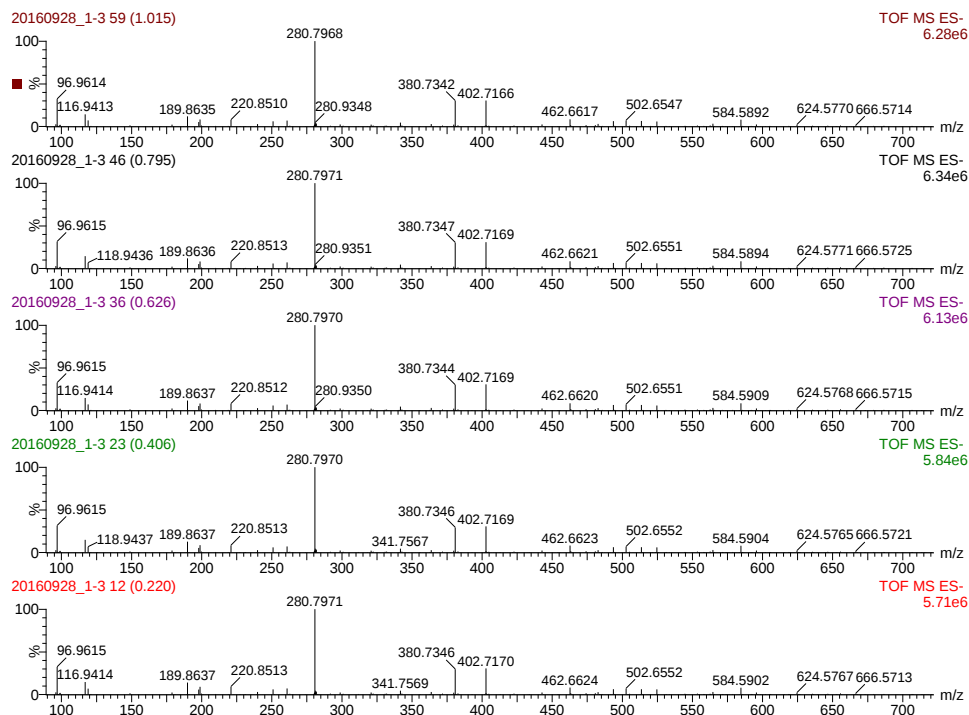


Figure S6 The mass spectra for vanadium aqueous solution after extraction from ACC at 216 s (initial $n(\text{H})/n(\text{V})=0.6$)

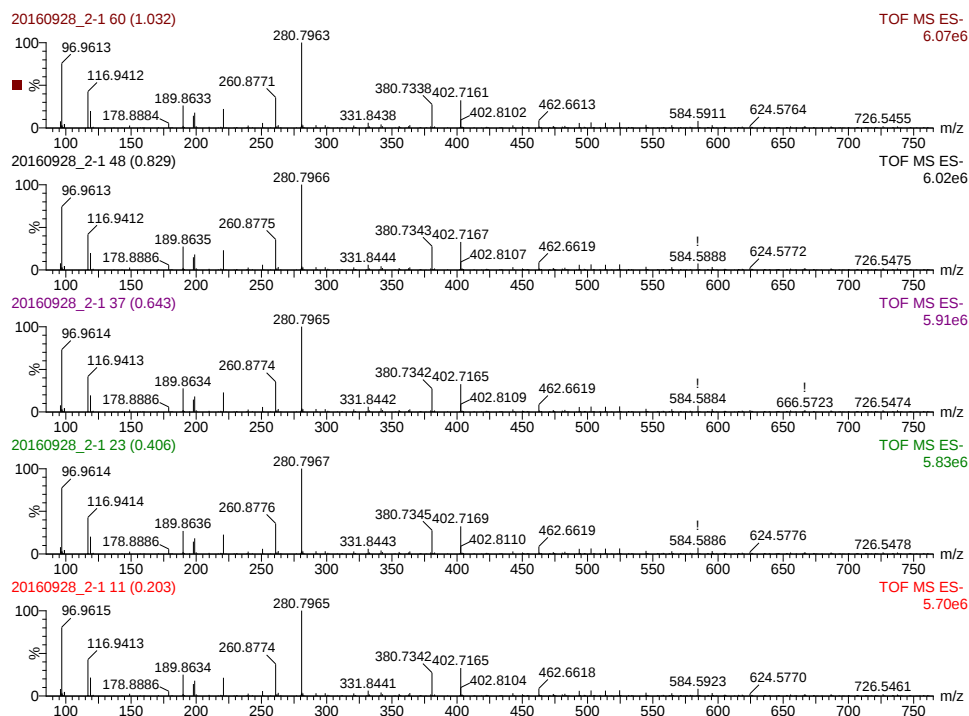


Figure S7 The mass spectra for vanadium aqueous solution after extraction from ACC at 72 s (initial $n(H)/n(V)=0.8$)

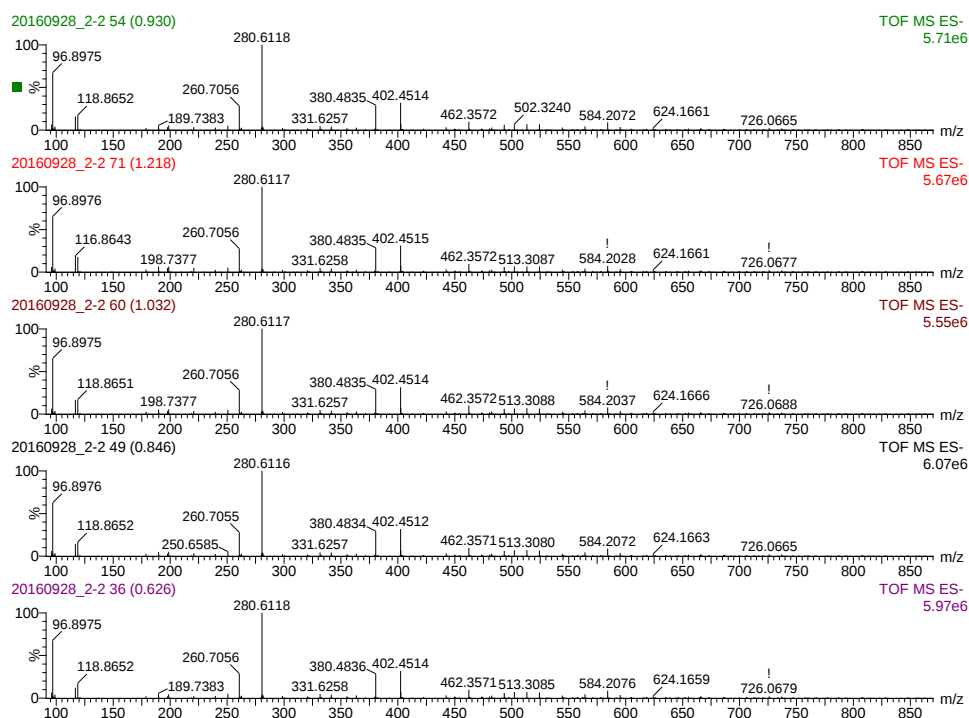


Figure S8 The mass spectra for vanadium aqueous solution after extraction from ACC at 144 s (initial $n(H)/n(V)=0.8$)

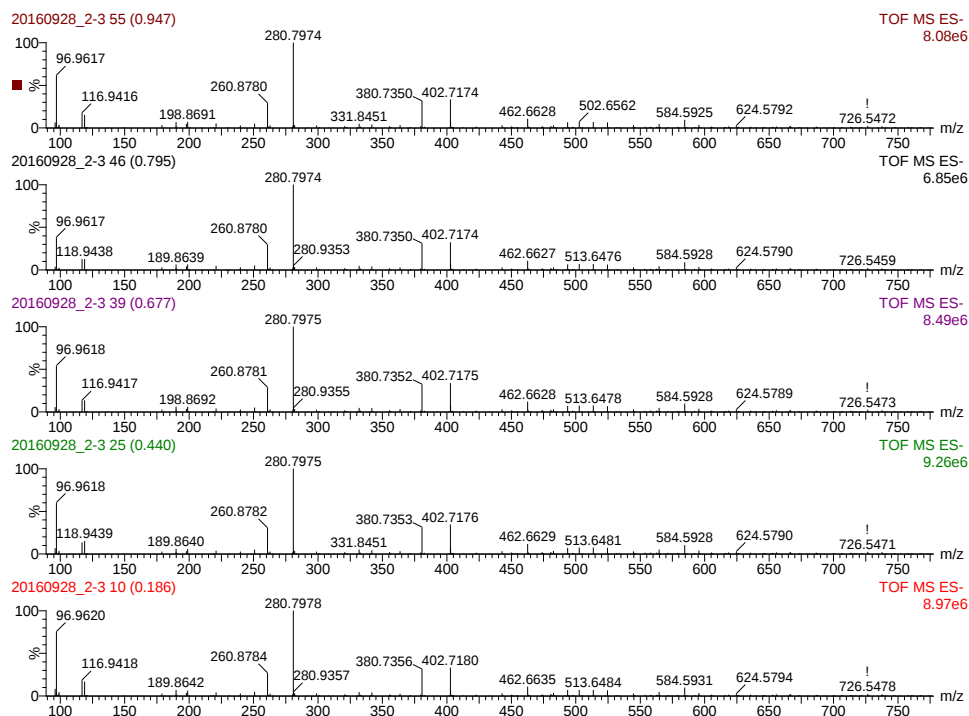


Figure S9 The mass spectra for vanadium aqueous solution after extraction from ACC at 216 s (initial $n(H)/n(V)=0.8$)

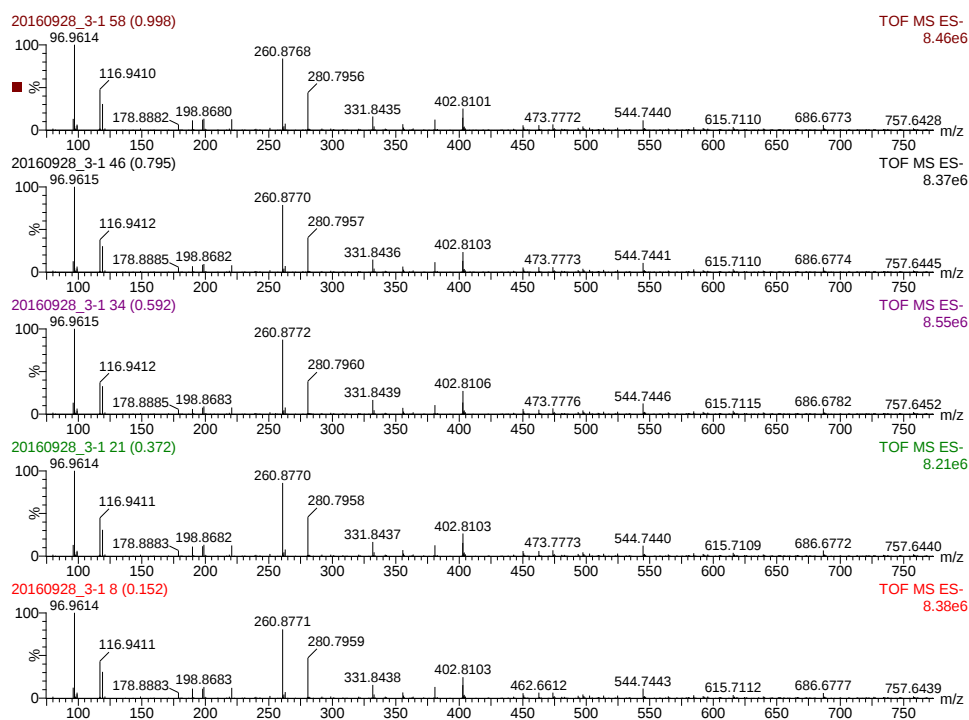


Figure S10 The mass spectra for vanadium aqueous solution after extraction from ACC at 72 s (initial $n(H)/n(V)=1.0$)

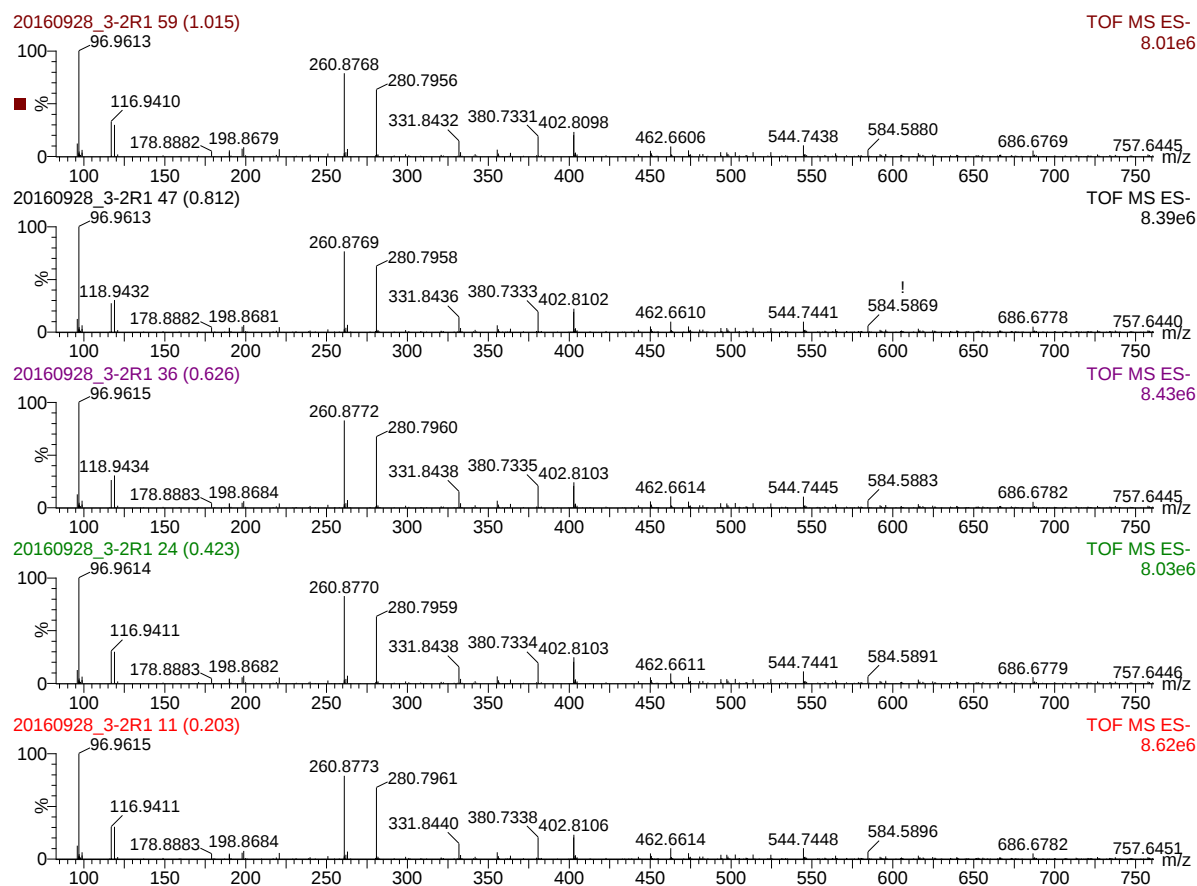


Figure S11 The mass spectra for vanadium aqueous solution after extraction from ACC at 144 s (initial $n(H)/n(V)=1.0$)

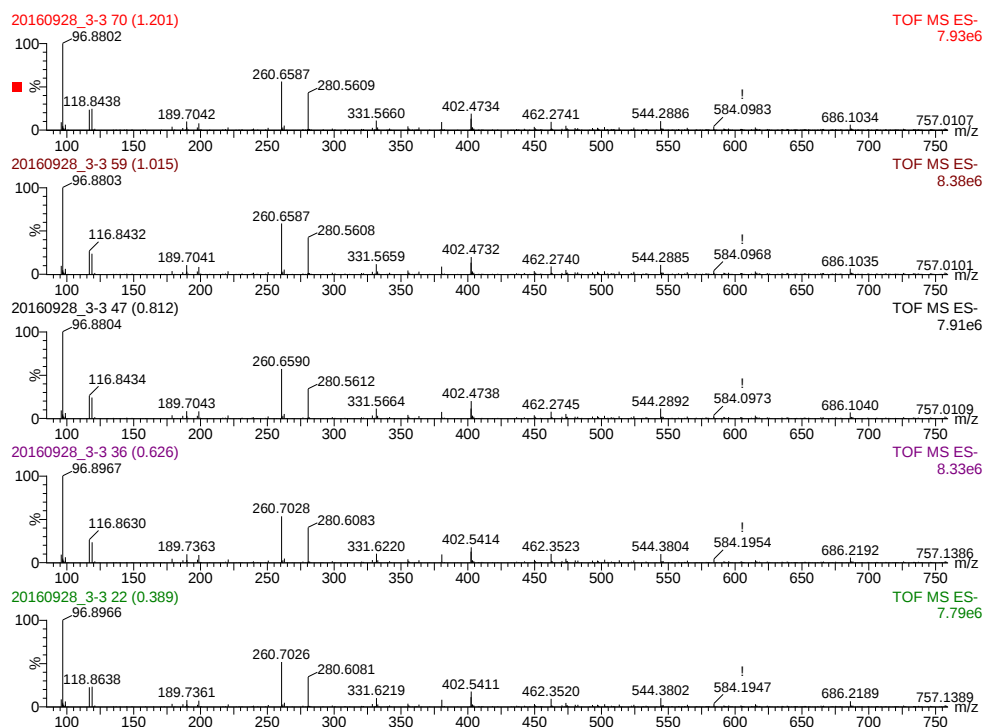


Figure S12 The mass spectra for vanadium aqueous solution after extraction from ACC at 216 s (initial $n(H)/n(V)=1.0$)

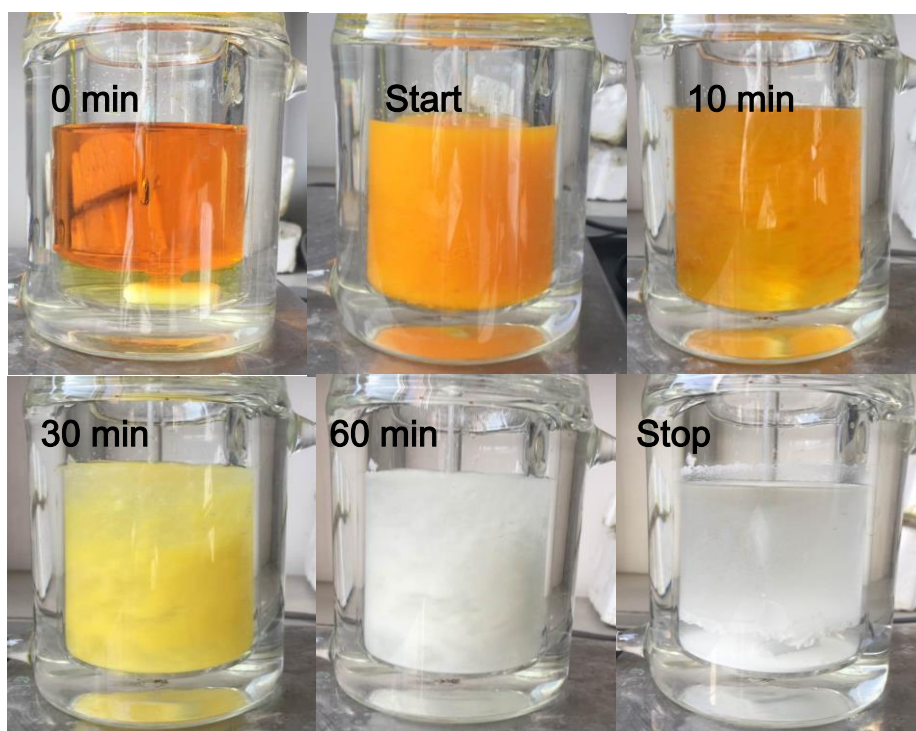


Figure S13 the images of stripping process to obtain precipitated NH_4VO_3

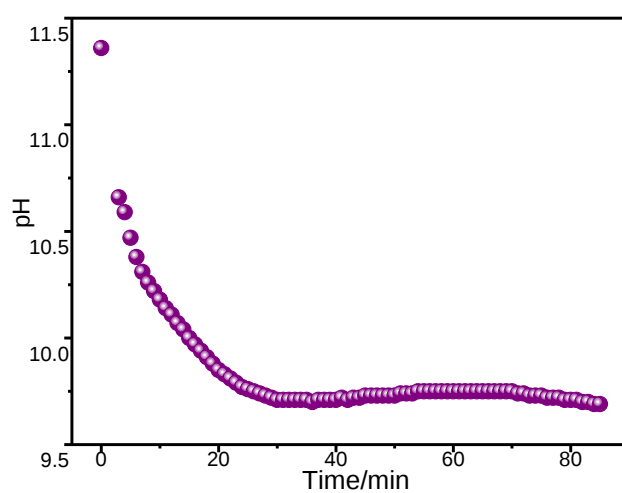


Figure S14 The variation of pH in the stripping process. .

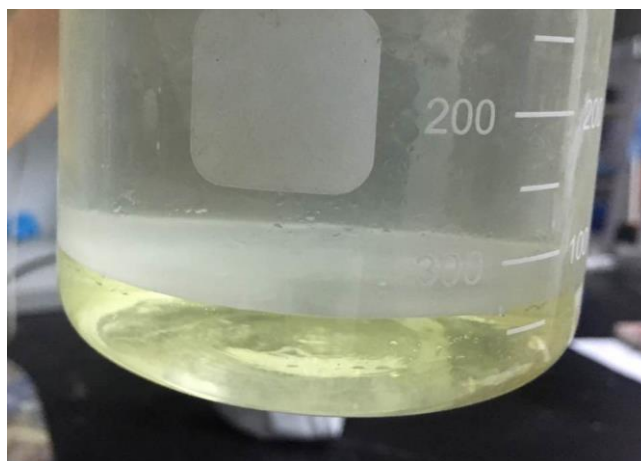


Figure S15 The stripped solution without enough ammonia solution after the same reaction time.

Table S5 the mass fraction of impurities in the obtained NH_4VO_3 by recycled extractant for first, second and third time recycle.

Content(wt.) %	Al	As	B	Ca	Co	Cr	Cu	Fe
First time	0	1.3e-5	0	3.7e-4	2.9e-5	0	0	4.2e-4
Second time	0	5.3e-5	0	9.1e-4	3.3e-5	0	0	5.5e-4
Third time	0	8.6e-5	0	1.7e-3	5.8e-5	0	0	1.0e-3
Content(wt.)%	K	Mg	Mn	Mo	Na	Ni	P	Pb
First time	6.3e-4	4.8e-5	0	0	0	0	0	0
Second time	7.3e-4	1.0e-4	0	0	1.8e-4	0	0	0
Third time	1.1e-3	3.0e-4	0	0	4.8e-3	0	0	0
Content(wt.)%	Si	Ti	W	Y	SO_4^{2-}	purity		
First time	0	0	0	0	0.0749	99.925		
Second time	1.9e-4	0	0	0	0.0597	99.940		
Third time	0	0	0	0	0.0783	99.922		

Table S6 The global recovery rate

recycle time	m _{vo} (mg/L)	m _{ve} (mg/L)	extraction yield%	vanadium-loaded in organic phase (g)
First time	4890	34.55	99.29	1.457
Second time	4991	9.647	99.81	0.747
Third time	5086	6.495	99.87	0.406
Number	obtained solid (g)	purity (%)	NH_4VO_3 solid (g)	recovery rate (%)
First time	3.144	99.925	3.142	93.93
Second time	1.626	99.940	1.625	94.72
Third time	0.870	99.922	0.870	93.18

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