

Determination of 18 kinds of trace impurities in the vanadium battery grade vanadyl sulfate by ICP-OES

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Abstract. The method that direct determination of 18 kinds of trace impurities in the vanadium battery grade vanadyl sulfate by inductively coupled plasma atomic emission spectrometry (ICP-OES) was established, and the detection range includes 0.001% ~ 0.100% of Fe, Cr, Ni, Cu, Mn, Mo, Pb, As, Co, P, Ti, Zn and 0.005% ~ 0.100% of K, Na, Ca, Mg, Si, Al. That the influence of the matrix effects, spectral interferences and background continuum superposition in the high concentrations of vanadium ions and sulfate coexistence system had been studied, and then the following conclusions were obtained: the sulfate at this concentration had no effect on the determination, but the matrix effects or continuous background superposition which were generated by high concentration of vanadium ions had negative interference on the determination of potassium and sodium, and it produced a positive interference on the determination of the iron and other impurity elements, so that the impacts of high vanadium matrix were eliminated by the matrix matching and combining synchronous background correction measures. Through the spectral interference test, the paper classification summarized the spectral interferences of vanadium matrix and between the impurity elements, and the analytical lines, the background correction regions and working parameters of the spectrometer were all optimized. The technical performance index of the analysis method is that the background equivalent concentration $-0.0003\%(\text{Na}) \sim 0.0004\%(\text{Cu})$, the detection limit of the element is $0.0001\% \sim 0.0003\%$, $\text{RSD} < 10\%$ when the element content is in the range from 0.001% to 0.007%, $\text{RSD} < 20\%$ even if the element content is in the range from 0.0001% to 0.001% that is beyond the scope of the method of detection, recoveries is 91.0% ~ 110.0%.

1. Introduction

With the worldwide continuous development of the new energy technologies which can save energy and protect the environment, the application field of all vanadium redox flow battery has been increasingly expanded because it is able to discharge more depth and high current density, rapid charge and higher energy density and other characteristics, and the vanadium battery is harmless to the environment and can be recycled in the whole process of the manufacture, use and disposal. At present, the all vanadium redox flow battery has been used as energy storage device for solar energy, wind energy and other clean power generation system, it also can provide power for submarines, ships and was used as a backup power supply in the building, the airport and etc. The vanadium battery is composed of three parts that includes the stack, electrolyte and control system, and because the impurity elements in vanadium electrolyte solution will seriously affect its long-term stability and charge discharge efficiency, so that the quality standards for vanadium battery grade vanadyl sulfate



that is necessary used in the manufacture of vanadium electrolyte has a very strict limits on the chromium iron nickel silicon aluminum calcium and other trace impurities, but there are rare reports for the analytical method is applied to the determination of trace impurity elements in vanadium battery vanadyl sulfate. The similar detection techniques include that determination of phosphorus, potassium, sodium, arsenic, iron and other impurity elements in the vanadium pentoxide or ammonium metavanadate by the atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry [1-5].

This paper established the analytical methods which be used for direct simultaneous determination of 18 trace impurity elements in the vanadyl sulfate is used in the ICP-OES, and the detection range includes 0.001% ~ 0.100% of Fe, Cr, Ni, Cu, Mn, Mo, Pb, As, Co, P, Ti, Zn and 0.005% ~ 0.100% of K, Na, Ca, Mg, Si, Al. In this paper, the influence of the matrix effects, spectral interferences and background continuum superposition in the high concentrations of vanadium ions and sulfate coexistence system had been studied, and then it also summarized the spectral interferences of vanadium matrix and between the impurity elements, so, the analytical lines, the background correction regions and working parameters of the spectrometer were all optimized, then the impacts of high vanadium matrix were eliminated through the application of matrix matching and simultaneous background correction. The method has the advantages of simple operation, less interference effect, short analysis flow, excellent technical performance, so it fully meet the needs of quality inspection of impurity elements in various vanadyl sulfate including vanadium battery level.

2. Experimental

2.1. Instruments and reagents

iCAP 6300 full spectrum of direct-reading plasma atomic emission spectrometer, Elix water purifier. Excellent level of pure HCl, HNO₃, H₂SO₄. Vanadium pentoxide (> 99.99%). Standard stock solution of the Fe, Cr, Ni, Cu, Mn, Co, Ti, Si, Al, Ca, Mg, K, Na, Pb, As, Mo, P, Zn: 1mg/mL.

2.2. Working conditions of ICP spectrometer

RF power is 1100 W, auxiliary gas flow rate (Ar) is 1.0 L/min, nebulizer pressure is 0.22MPa, peristaltic pump speed is 60r/min, observation height is 11.8mm, detection integration time is 25 s (wavelength > 220 nm) or 30 s (wavelength less than 220 nm).

2.3. Test method

0.5000g vanadyl sulfate sample was weighted and put into a 250mL PTFE beaker, rinse the beaker wall and disperse samples with 10mL water, then add 5mL hydrochloric acid and until the digestion reaction is completed at a low temperature heating conditions and boiled to produce a uniform large bubbles, the test solution after cooling is diluted with water in 100mL volumetric flask. And the test solution is measured in plasma atomic emission spectrometer according to the working conditions of instrument in paragraph.

2.4. The calibration curve

The high-purity vanadium pentoxide was digested in accordance with the 2.3 test methods and became the pure matrix reagent solutions whose vanadium ion concentration was 1.6 mg/mL, then used it as blank correction and matrix matching bottoming solution. The element standard solutions were added in the matrix matching bottoming solutions, in order that were formulated into a series of concentration gradient of the mixed standard solutions whose matrix composition were consistent with the sample solution of the vanadyl sulfate and the measured elements contents were 0.00%, 0.001%, 0.002%, 0.005%, 0.010% and 0.100%, finally use its to draw calibration curve.

3. Results and Discussion

3.1. Spectral interference test of the matrix elements vanadium and sulfurs

According to the content of matrix components in vanadyl sulfate sample solution which prepared by the test method 2.3, the paper tested spectral interference effect of matrix elements vanadium and sulfur through the containing vanadium ion 1.6mg/mL, 3.0mg/mL sulfate and their mixed solution.

The test showed: sulfur does not produce spectral interference on the impurity elements sensitive spectral line, because the 3.0mg/mL sulfate showed no peak signal in the each element analysis spectral line scanning window, its signal baseline is straight and almost completely coincide with the water blank solution. However, high strength vanadium line produced severe spectral overlap interference on the part of analytical spectral lines of elements, for example V 279.483nm on Mn 279.482nm and V 212.411nm on Si 212.412nm produce serious spectral overlap interference, vanadium interference peak and measured peak are overlapped together and cannot be distinguished within the line integration region, the test results are the sum of the vanadium interfere with the analyte peak signal intensity, so these lines cannot be used as elemental analysis spectrum. Shown in Figure 1, Figure 2.

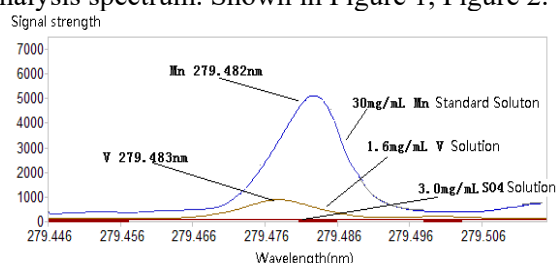


Fig1 Mn 279.482nm interference test chart

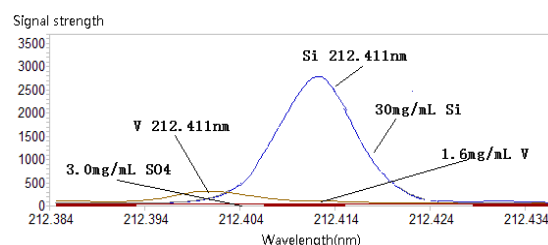


Fig2 Si 212.411nm interference test chart

Moreover, a strong side peak of the vanadium element appear next to a few spectral lines of impurity elements, although the measured element peak can substantially be separated from vanadium interfering peak and do not overlap in the integral region, but because the signal strength of the vanadium side peak is much higher than the measured element peak spectral, the vanadium side peak still resulted in a serious spectral interference, then usually do not recommend the use of such line as the analysis line for determination of micro or trace impurity elements in the vanadyl sulfate. Such as, Al 309.271nm and Ni 361.939nm are respectively interfered by the side peaks of V 309.311nm and V 361.893nm, shown in Figure 3, Figure 4.

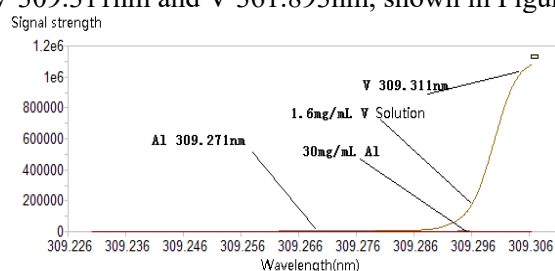


Fig3 Al 309.271nm interference test chart

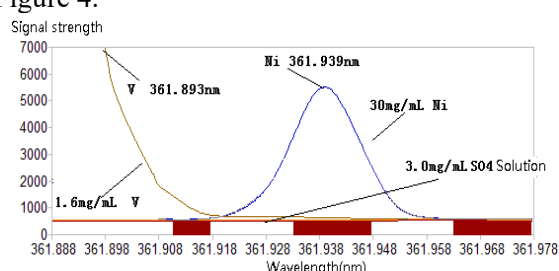


Fig4 Ni 361.929nm interference test chart

In addition, it has been reported the V 251.612nm spectral existed spectral overlapping interference on Si 251.611nm in some literature, but the test have showed that the 1.6mg/mL vanadium standard solution produced no significant V 251.612nm peaks at Si 251.611nm position, and the signal baseline respectively generated by vanadium standard solution and reagent blank solution are completely coincide. At the same time, Si 251.611nm is the sensitive spectral line and the sensitivity of V Si 251.611nm is about 400 times more than Si 251.612nm according to the literatures. Therefore, the interference of V to Si 251.611nm can be ignored, Si 251.611nm still can be used as determination of silicon in the vanadyl sulfate samples, see figure 5.

Most other high sensitivity spectral line of the measured impurity elements were not affected by the spectral interference of matrix elements of vanadium and sulfur effect in the vanadyl sulfate sample. For example, Al: 396.152nm、Al 167.079nm、As 189.042nm、Ca 183.801nm、Ca315.887nm、Ca317.933nm、Co 228.616nm、Co 230.786nm、Co 237.862nm、Co 238.892nm、Cr 205.560nm、Cr 267.716nm、Cr 283.563nm、Cu 327.396nm、Cu 224.700nm、Cu 219.958nm、Fe 240.488nm、Fe 239.562nm、Fe 238.204nm、Fe 259.940nm、K 766.490nm、Mg 202.582nm、Mg 285.213nm、Mg 279.553nm、Mg 280.270nm、Mn 257.610nm、Mn 259.373nm、Mn 293.306nm、Mn 293.930nm、Mn 403.307、Mo 281.615nm、Mo 202.030、Mo 203.844nm、Mo 204.598nm、Na 589.592nm、Ni 221.647nm、Ni 231.604nm、Ni 232.003nm、Ni 341.476nm、Pb 220.453nm、P 177.495nm、P 178.284、P 185.942nm、P 213.618nm、Si 221.667nm、Si 198.898nm、Si 251.611nm、Ti 323.904nm、Ti 334.941nm、Ti 337.280nm、Zn 202.548nm、Zn 213.856nm、Zn 334.502nm、Etc, they can be used as the analysis lines for the determination of impurity elements in vanadium sulfate, and because the vanadium and sulfur are all no spectral peaks and their signal baseline is straight in line scanning window, so it can flexibly select the background correction region on the left and right sides of the measured spectral peak, see figure 6.

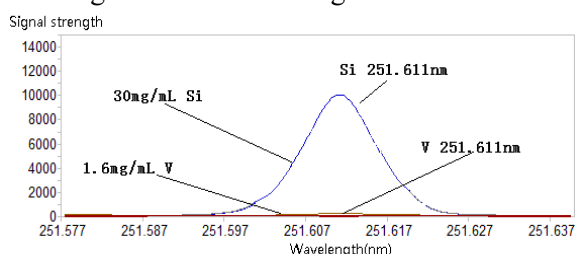


Fig5 Si 251.611nm interference test chart

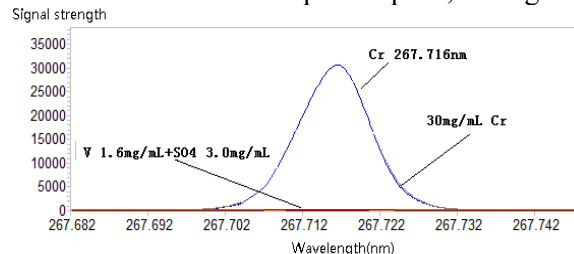


Fig6 Cr 267.716nm interference test chart

3.2. Spectral interference between the coexist impurities

Experiments show that there is influence of adjacent spectral peaks between part of coexist impurities, Such as, lines affected by beside peak included Mg 202.582nm by Zn 202.548nm, P 213.618nm by Cu 213.598nm, Pb261.418nm by Co 261.436nm, Si 226.667nm affected by Ni 221.647nm. However, the measured peak completely separated from the interfering beside peaks within the detection integration area and the signal strength of the interfering beside peak is usually relatively low, then the influence of side peaks can be eliminated if you choose a background correction area to avoid the side peak position. Therefore, these lines are also selected as analysis spectrum for the determination of trace elements in the vanadyl sulfate. Of course, the interference coefficient correction method can be used to further eliminate spectral influence between impurity elements. Shown in figure 7, figure 8.

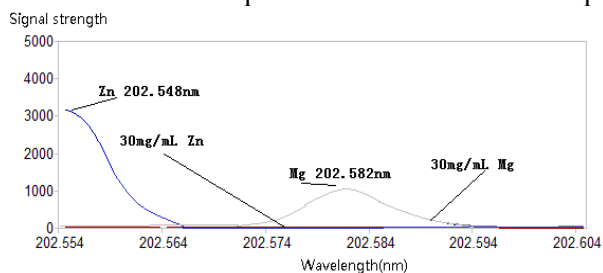


Fig7 Mg 202.582nm interference test chart

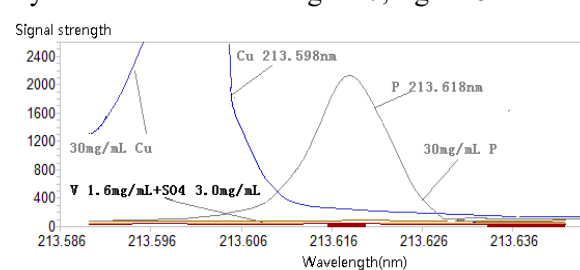


Fig8 P 213.618nm interference test chart

According to the above test, this paper optimized the elemental analysis wavelength and background correction position, shown in Table 1.

Table 1 The element analysis wavelength and the background correct position

Element	Wavelength	Left background correction points		Right background correction points		Integral regional center width	Integral position
	nm	pixel	pixel	pixel	pixel	pixel	pixel
Al	396.152	1	11	6	2		
As	189.042	1	12	7	1		
Ca	317.933	2	11	6	2		
Co	228.616	1	11	7	2		
Cr	267.716	1	10	6	2		
Cu	324.754	1	12	6	2		
Fe	238.204	2	11	6	2		
K	766.490	1	11	7	1		
Mg	285.213	1	10	6	2		
Mn	293.930	1	10	6	2		
Mo	281.615	2	10	7	2		
Na	589.592	2	11	7	2		
Ni	221.647	1	/	7	2		
P	231.618)	/	11	7	1		
Pb	220.353	1	11	6	2		
Si	251.611	3	10	7	1		
Ti	334.911	/	12	6	2		
Zn	202.518	2	10	6	2		

3.3. The interference test of the matrix effect

First, two standard solutions with a concentration of 10mg/L are prepared, one of which contains no vanadium and sulfur, the other contains 1.6mg/mL vanadium and 3.0mg/mL sulfate whose matrix composition is consistent with the sample solution of the vanadyl sulfate, and then the signal strength, the background intensity and the net signal intensity of the analysis lines were all scanned, in order to conduct impact tests of the matrix effect and the continuous background superimposed, the results shown in Table 2.

Table 2 The vanadium matrix affect test

Wavelength (nm)	The element standard solution not containing vanadium and sulfate			The element standard solution containing vanadium and sulfate		
	signal strength	background intensity	net signal intensity	signal strength	background intensity	net signal intensity
Al396.152	4800.67	744.14	4056.53	5025.79	815.54	4210.26
As 189.042	137.64	13.78	123.86	191.88	29.2	162.88
Ca 317.933	6494.85	271.21	6223.64	7495.5	448.97	7046.53
Co 228.616	3215.02	68.38	3146.64	2705.71	91.57	2614.14
Cr 267.716	6384.02	155.65	6228.37	6972.03	388.53	6583.5
Cu 324.754	8672.10	493.99	8178.11	9336.88	492.42	8844.45
Fe 238.204	5672.49	75.06	5597.43	6005.22	78.14	5927.09
K 766.490	9586.25	4856.11	4730.14	8394.64	3993.9	4400.73
Mg 285.213	44322.31	148.12	44174.19	47485.47	511.7	46973.77
Mn 293.930	6013.39	129.05	5884.34	6585.02	309.49	6275.53
Mo 281.615	2736.97	128.25	2608.72	3175.52	199.47	2976.05
Na 589.592	19890.41	3778.16	16112.25	18938.1	3261.28	15676.82
Ni 221.647	3106.48	117.88	2988.60	3139.71	115.26	3024.45
P 231.618	458.47	71.38	387.09	544.52	139.58	404.93
Pb 220.353	591.67	60.62	531.05	707.47	99.03	605.44
Si 251.611	3260.25	97.21	3163.04	3511.7	138.4	3373.29
Ti 334.911	25381.39	197.74	25183.65	28118.85	305.32	27813.52
Zn 202.518	4750.01	79.80	4670.21	5332.94	57.96	5274.98

Experiments show that the matrix effect and the continuous background superimposed produce a negative interference on the determination of potassium and sodium, and simultaneously produce positive interference with the remaining elements to be measured, so the method needs to use the vanadium matrix matching and simultaneous background correction to eliminate its influence.

3.4. The calibration curve

The vanadium pentoxide was digested in accordance with the 2.3 test methods and became the pure matrix solutions whose vanadium ion concentration was 1.6 mg/mL, then used it as blank correction

and matrix matching solution. The element standard solutions were added in the matrix matching solutions, so that were formulated into a series of concentration gradient of the mixed standard solutions whose matrix composition were consistent with the sample solution and the measured elements contents were 0.00%, 0.001%, 0.002%, 0.005%, 0.010% and 0.100%, finally used to draw calibration curve. The results showed a good linear relationship of the calibration curve of each element, the correlation coefficient is not less than 0.999, shown in Fig 9, Fig 10.

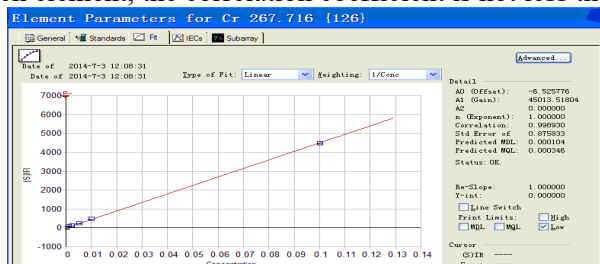


Fig 9 Cr 267.716nm calibration curve

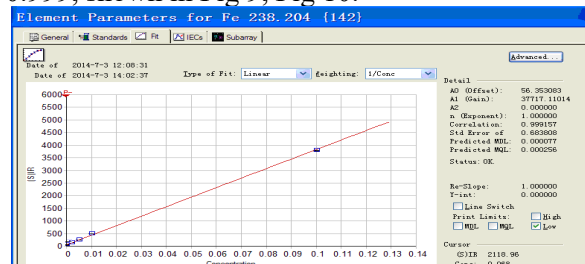


Fig 10 Fe 238.204nm calibration curve

3.5. The background equivalent concentration and detection limit test

According to the content of matrix components in the vanadyl sulfate sample solution that prepared by the test method, the mixed solution containing 1.6mg / mL vanadium and 3.0mg / mL sulfate was used as a blank matrix solution, and then that blank solution was continuously measured 11 times and three times the standard deviation was used as the element detection limits, in the meantime, the blank solution was continuously measured 20 times and it was used to calculate the background equivalent concentration, shown in Table 3.

Table 3 The method background equivalent density and the element Detection limit (%)

Element	BEC	Detection limits	Element	BEC	Detection limits	Element	BEC	Detection limits
Al	0.0001	0.0003	Mn	0.0000	0.0002	Fe	-0.0001	0.0001
As	-0.0001	0.0003	Mo	0.0000	0.0001	K	0.0003	0.0003
Ca	-0.0001	0.0003	Na	-0.0003	0.0003	Mg	-0.0002	0.0002
Co	0.0000	0.0001	Ni	0.0000	0.0001	Si	0.0001	0.0003
Cr	0.0001	0.0001	P	-0.0001	0.0003	Ti	0.0000	0.0002
Cu	0.0004	0.0001	Pb	0.0001	0.0003	Zn	0.0000	0.0001

Table 3 shows the background equivalent concentration is -0.0003% (Na) to 0.0004% (Cu) in the lower range, this show that the matrix matching and simultaneous background correction effectively eliminates the influence of reagents blank and the high vanadium high sulfur matrix, the positive or negative interference of sample matrix on the detection results are very small. The detection limits are in the range of 0.0001% ~ 0.0003%, that fully meet the needs of the determination of 0.001% to 0.100% nickel, iron, chromium, molybdenum, lead, arsenic, copper, manganese, cobalt, titanium, zinc, phosphate, and 0.005% to 0.100% of potassium, sodium, calcium, magnesium, silicon, aluminum in the vanadium battery level or other level of vanadyl sulfate sample.

3.6. The precision test

This paper randomly selected tow sample of vanadium battery grade vanadyl sulfate, and each sample was separately prepared into eight test solutions. Each solution was measured and the eight test results' relative standard deviation was calculated. The precision of the method are shown in Table 4.

Table 4 The method accuracy experiments

Element	Sample 1			Sample 2		
	Average (W/%)	Standard deviation	RSD (%)	Average (W/%)	Standard deviation	RSD (%)
Al	0.0048	0.00012	2.49	0.0009	0.00005	6.29
As	0.0020	0.00009	4.50	0.0003	0.00005	16.83
Ca	0.0054	0.00023	4.20	0.0008	0.00008	9.45
Co	0.0011	0.00005	4.31	0.0003	0.00004	12.30
Cr	0.0013	0.00005	3.49	0.0008	0.00004	4.35
Cu	0.0007	0.00007	10.09	0.0003	0.00005	14.24
Fe	0.0038	0.00019	4.94	0.0035	0.00024	6.84
K	0.0013	0.00012	8.88	0.0006	0.00007	11.67
Mg	0.0015	0.00005	3.14	0.0007	0.00006	8.99

Mn	0.0027	0.00005	1.94	0.0012	0.00004	2.92
Mo	0.0015	0.00005	3.04	0.0004	0.00005	11.83
Na	0.0029	0.00028	9.75	0.0012	0.00011	8.91
Ni	0.0016	0.00012	7.60	0.0012	0.00007	6.02
P	0.0010	0.00010	9.79	0.0003	0.00005	16.83
Pb	0.0006	0.00005	8.12	0.0004	0.00005	14.28
Si	0.0061	0.00041	6.77	0.0013	0.00009	6.85
Ti	0.0026	0.00009	3.38	0.0003	0.00005	16.83
Zn	0.0039	0.00019	4.93	0.0002	0.00004	18.86

Table 4 shows that: when the element content is in the range from 0.001% to 0.007%, the RSD<10%, even if the element content is in the range from 0.0001% to 0.001% that is beyond the scope of the method of detection, the RSD is still not more than 20%. This indicates the precision and repeatability are all good and the method has strong operability, the method is applicable determination of micro and trace impurity elements in the vanadyl sulfate.

3.7. Recovery of the method test

The actual Vanadium battery grade vanadyl sulfate samples are analyzed in accordance with the experimental methods and the spike recovery is tested, in order to assess the accuracy of the method. The results the results are shown in Table 5.

Table 5 Recoveries test

Element	Sample 3				Sample 4			
	Found before add standard	Added	Found after add standard	Recovery	Found after add standard	Added	Found after add standard	Recovery
Al	0.00242	0.00100	0.00352	110.0	0.00184	0.00200	0.00381	98.5
As	0.00031	0.00100	0.00122	91.0	0.00030	0.00200	0.00223	96.5
Ca	0.00424	0.00100	0.00530	106.0	0.00151	0.00200	0.00339	94.0
Co	0.00095	0.00100	0.00189	94.0	0.00000	0.00200	0.00200	100.0
Cr	0.00153	0.00100	0.00259	106.0	0.00002	0.00200	0.00205	101.5
Cu	0.00093	0.00100	0.00195	102.0	0.00091	0.00200	0.00300	104.5
Fe	0.00061	0.00100	0.00152	91.0	0.00060	0.00200	0.00260	100.0
K	0.00035	0.00100	0.00132	97.0	0.00000	0.00200	0.00195	97.5
Mg	0.00411	0.00100	0.00521	110.0	0.00318	0.00200	0.00503	92.5
Mn	0.00052	0.00100	0.00156	104.0	0.00000	0.00200	0.00198	99.0
Mo	0.00030	0.00100	0.00125	95.0	0.00030	0.00200	0.00224	97.0
Na	0.00030	0.00100	0.00121	91.0	0.00177	0.00200	0.00358	90.5
Ni	0.00010	0.00100	0.00118	108.0	0.00010	0.00200	0.00211	100.5
P	0.00020	0.00100	0.00121	101.0	0.00043	0.00200	0.00230	93.5
Pb	0.00081	0.00100	0.00180	99.0	0.00086	0.00200	0.00272	93.0
Si	0.00021	0.00100	0.00121	100.0	0.00039	0.00200	0.00220	90.5
Ti	0.00007	0.00100	0.00101	94.0	0.00006	0.00200	0.00219	106.5
Zn	0.00040	0.00100	0.00132	92.0	0.00010	0.00200	0.00220	105.0

In Table 5, the recovery is between 91.0% and 110.0%, which indicates the results of the method are accurate and reliable.

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