Determination of chromium cobalt nickel gallium niobium scandium and zirconium in the blast furnace slag of vanadium titanium magnetite by inductively coupled plasma atomic emission spectrometry

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Abstract. In order to recover the precious metal elements in vanadium-titanium blast furnace slag, the analytical method that direct determination of the range from 0.001% ~ 0.300% chromium, cobalt nickel, gallium, niobium, scandium and zirconium in the blast furnace slag of vanadium titanium magnetite by inductively coupled plasma atomic emission spectrometry was established. Sample digestion reagent consists of hydrofluoric acid, hydrochloric acid, nitric acid and sulfuric acid, and their ratio, dosage and reaction control condition are all optimized, so make sure that the blast furnace slag of vanadium titanium magnetite can be quickly completely digested. At the same time, the high content of silicon dioxide can be removed by volatilization to simplify the sample solution matrix composition, and because of the titanium ion and sulfate ion complex reaction generating oxygen titanium sulfate ion so as to solve the high concentration of titanium matrix easy hydrolysis problem in low acidity medium, thus it greatly reduce the acidity of sample solution to reduce the matrix effect. That the influence of the spectral interferences and matrix effects in the high concentrations of titanium, iron, vanadium, aluminum, calcium and magnesium coexistence matrix system had been studied, then the test results are classified summary. The influence of substrate composition were eliminated by the matrix matching and synchronous background correction measures, and then the analytical lines, the background correction areas and working conditions of the spectrometer are all optimized according to the spectral interference test. The technical performance reached: calibration curve correlation coefficient of 0.998 or higher, detection limit of element is 0.0001% ~ 0.0003% and the measuring elements content in lower 0.0003% ~ 0.0009%, RSD is less than 15% when the element content in the range from 0.001% to 0.05%, the actual sample testing results are consistent with ICP-MS.

1 Introduction
The total vanadium titanium magnetite had proven reserves of 7.337 billion tons only in the Sichuan Province, China, and were accompanied by precious metal elements such as chromium, cobalt, nickel, gallium, niobium, scandium, zirconium. In order to recover the precious metal elements associated with vanadium-titanium magnetite, we are studying their distribution, direction and enrichment in the blast furnace smelting process, so it needs to test analysis method which used for determination of trace element chromium, cobalt, nickel, copper, gallium, niobium, scandium, zirconium in the blast furnace slag of vanadium titanium magnetite.
According to the literature, there are some analysis methods used to determine the amount of the substrate or impurity elements in the vanadium titanium magnetite, for example, determination of iron, vanadium, titanium, magnesium, manganese, potassium, sodium, phosphorus and other elements by AAS or ICP-AES, and the methods that determination of trace gallium in vanadium titanium magnetite by GF-AAS and determination of chromium cobalt nickel copper gallium in vanadium titanium magnetite by ICP-MS have been reported [1-5], but did not see analysis method which is used to determine of chromium, cobalt, nickel, gallium, niobium, scandium and zirconium in the blast furnace slag of vanadium titanium magnetite. The vanadium titanium blast furnace slag has complex matrix, usually respectively contains about 20% of SiO₂, Al₂O₃, TiO₂, CaO, and about a few percent of V₂O₅, MgO, MnO, TFe. This paper established the analytical method that direct determination of the range from 0.001% ~ 0.300% chromium, cobalt, nickel, gallium, niobium, scandium and zirconium in the blast furnace slag of vanadium titanium magnetite by ICP-AES. In this paper, the sample digestion method was developed, the influence of spectral interferences and matrix effects of complex matrix components had been studied and eliminated, and then the analytical lines, the background correction regions and working parameters of the spectrometer were all optimized. The method has the advantages of simple operation, less interference effect, short analysis flow, excellent technical performance, so that it satisfies the need for the determination of chromium, cobalt, nickel, gallium, niobium, scandium and zirconium in vanadium-titanium blast furnace slag.

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 HF, HCl, HNO₃, H₂SO₄.

Standard stock solution of the Cr, Co, Ni, Ga, Nb, Sc, Zr: 1mg/mL.

2.2 Working conditions of ICP spectrometer

RF power is 1200 W, auxiliary gas flow rate (Ar) is 1.0 L/min, nebulizer pressure is 0.24 MPa, peristaltic pump speed is 65r/min, observation height is 12.0mm, detection integration time is 20 s (wavelength > 220 nm) or 30 s (wavelength less than 220 nm).

2.3 Test method

1.0000g vanadium-titanium blast furnace slag sample was weighted and put into a 250mL PTFE beaker, rinse the beaker wall and disperse samples with 5~10mL water, then add 2.5mL hydrofluoric acid, 15mL of hydrochloric acid, 5mL of nitric acid and 5mL (1+1) sulfuric acid, then the solution is heated to boiling until sulfur trioxide white smoke is produced and maintained for 3 to 5 minutes, the solution was cooled and transferred to a 100 mL volumetric flask and mixed with water to volume. Measurements were performed under instrument operating conditions.

2.4 The calibration curve

The standard solution of the measured element was added to a solution containing 1.5 mg/mL titanium, 1.5 mg/mL calcium, 1 mg/mL aluminum, and 0.5 mg/mL magnesium, iron, and vanadium, the contents of chromium, cobalt, nickel, niobium, tantalum, niobium, and zirconium in the solution respectively were 0.000%, 0.0005%, 0.001%, 0.010%, 0.100% and 0.300%, and then draw a calibration curve with this series of standard solutions.

3 Results and Discussion

3.1 Sample digestion

The method preferably uses hydrofluoric acid, hydrochloric acid, nitric acid and sulfuric acid as a combination reagent for digesting vanadium and titanium blast furnace slag samples. among them, the
effect of hydrofluoric acid is not only the effect of volatilizing to remove the high content of silica matrix in the sample, but also acts together with the sulfuric acid to promote the complete digestion of the titanium dioxide matrix. Simultaneously, stable titanyl sulfate ions are formed through the complexation of sulfate and titanium matrix, thus eliminating the problem that high concentration titanium is easily hydrolyzed in a low acidity medium. Then, the solution was evaporated to remove low boiling point volatile substances such as hydrofluoric acid, hydrochloric acid, nitric acid and silicon tetrafluoride by evaporating and decomposing sulfuric acid until sulfur trioxide fumes are generated, so the final sample preparation solution is less than 2.5% sulfuric acid, which effectively simplifying or reducing the acidity of the sample solution and matrix composition, thereby reducing the acidity effect of the matrix effect on the determination of elements.

3.2 Spectral interference test

3.2.1 Spectral interference effects of matrix composites. Firstly, several candidate analytical lines were selected based on the principle of sensitivity as high as possible, and according to the approximate content of the matrix components in the sample solution prepared in Test Method 1.3, the effect of matrix composition on the spectral interference of the candidate analytical lines were tested using standard solutions of 1.5 mg/mL titanium, 1.5 mg/mL calcium, 1 mg/mL aluminum and 0.5 mg/mL magnesium, iron and vanadium and their mixed solution.

The test showed that: some spectral lines are strongly interfered by the matrix components. In the detection integration region of these analytical lines, the measured spectral peak of the element is completely or partially overlapped with the interfering peak of the matrix component, both of which can not be clearly distinguished, thus the detection result is the sum of the signal intensity of the interference line and the spectral line, and the signal intensity of the interference peak is usually much higher than that of the spectrum to be measured, so these spectral lines can not be used as the analytical lines for the detection of vanadium-titanium blast furnace slag samples. For example, Ti 228.618nm on Co 228.616nm, Fe 283.546nm on Cr 283.563nm, V 287.417nm on Cr 357.869nm, Fe 287.417nm on Ga 287.424nm, Ti 287.411nm on Ga 287.424nm, Ti 417.191nm on Ga 417.206nm, V 309.420nm on Nb 309.418nm, Ti 313.081nm on Nb 313.079nm, Ti364.268nm on Sc 364.279nm, V 335.378nm on Sc 335.373nm, V 327.303nm on Zr 327.305nm, all produce serious spectral overlap interference, these lines cannot be used as elemental analysis lines. See Figure 1 to Figure 4.
background correction areas all avoid the location of the side peaks, so their effects are further eliminated, these spectrum can still be used as the analysis line. See Figure 5 and Figure 6.

Fig5  Co 237.862nm interference test chart         Fig6  Nb 316.340nm interference test chart

Many of the analytical lines are also unaffected by the spectral interferences of the matrix components. For example, Co 230.786nm, Cr 205.560nm, Cr 267.716nm, Ga 294.364nm, Ga 403.298, Nb 316.340nm, Ni 216.556nm, Ni 231.604nm, Ni 341.476nm, Sc 357.635nm, Sc 361.384nm, Zr 339.198nm, Zr 343.823nm and Zr 349.621nm. The high concentration of the matrix components did not show any peaks in their analytical line scan window, the signal baseline of matrix blank solution is flat and almost completely coincide with the reagent blank solution, so it also can flexibly select the background correction region on the left and right sides of the spectral peak. Therefore, it is possible to preferentially select as the analysis line, in combination with the requirement that the sensitivity thereof be as high as possible. See Figure 7 and Figure 8.

Fig7  Sc 361.384nm interference test chart         Fig8  Zr 339.198nm interference test chart

3.2.2 Spectral interference between the tested elements. The single element standard solution of chromium, cobalt, nickel, gallium, niobium, scandium, zirconium and its mixed standard solution with concentration of 0.5mg / L were used to test the spectral interference between the tested elements. The experiments show that there is a weak line overlap between the lines of the elements to be measured. For example, Ni 231.604 nm by Co 231.616nm, Ni 232.003nm by Cr 232.008nm, Ni 341.476nm by Co341.474nm, Sc 335.373nm by Zr 335.366nm, Zr 347.621nm by Sc 349.627nm, Ga 403.298nm by Mn 403.307nm, Co 237.862nm by Sc 237.862nm. Cr 205.560nm by Ni 205.550nm, Cr 283.563nm by Co 283.563nm, Cr 357.869nm by Sc 357.848nm, Ga 287.424nm by Zr 287.422nm.

However, the selected analytical line are the main sensitive or sub-sensitive lines, its sensitivity is usually higher than the interference line about 2 to 3 orders of magnitude, so for the determination of trace elements below 0.3% chromium, cobalt, nickel, gallium, niobium, scandium, and zirconium, the spectral interference between the elements to be measured is negligible.

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           |
| Cr     | 267.716    | 1     | 11               | 7               | 1               |
| Co     | 237.862    | 1     | 12               | 6-7             | 2               |
| Ni     | 231.604    | 2     | 11               | 6-7             | 2               |
| Ga     | 294.364    | 1     | 12               | 6-7             | 2               |
| Nb     | 316.340    | 4     | 10               | 6-7             | 2               |
| Sc     | 361.384    | 1     | 11               | 6-7             | 2               |
| Zr     | 339.198    | 1     | 12               | 7               | 1               |
3.3 The interference test of the matrix effect
The matrix-matching solution and the blank solution of the sample digestion reagent were respectively used to scan the analytical lines listed in Table 1, then the matrix effect of vanadium-titanium blast furnace slag was tested by comparing the signal scans produced by the two solutions in the analysis wavelength window. The matrix matching solution is basically the same as the matrix composition of the titanium blast furnace slag sample detection solution, and consists of 1.5 mg/mL Ti, 1.5 mg/mL Ca, 1 mg/mL Al and 0.5 mg/mL Mg, Fe and V. See Figure 9 and Figure 10.

![Fig9 Nb 316.340nm interference test chart](image_url)

![Fig10 Sc 361.384nm interference test chart](image_url)

The experiments showed that within the scan window of the preferred analytical lines, the signal intensity of the matrix solution was higher than that of the blank solution, and the matrix effect lifted the background line of the analysis line, the intensity of the element detection signal was enhanced and the positive interference was produced. Therefore, the matrix matching and synchronous background correction are used to eliminate the influence of matrix effect.

3.4 The calibration curve and detection limit test
The mixture solution of 1.5 mg/mL Ti, 1.5 mg/mL Ca, 1 mg/mL Al and 0.5 mg/mL Mg, Fe and V was used as matrix blank solution and standard solution matrix matching solution, then cobalt, nickel, gallium, niobium, scandium and zirconium were respectively added into the standard solution, so, the contents of the tested elements in the solution were respectively 0.000%, 0.0005%, 0.001%, 0.010%, 0.100% and 0.300%. The calibration curves were drawn from this series of standard solutions.

The matrix blank solution was measured 11 times consecutively and the standard deviation was 3 times as the limit of detection, The low limit of determination was 3 times of the detection limit, shown in Table 2.

| Element | Wavelength | Regression equation | Correlation coefficient | Detection limits w/\% | Low limit of determination w/\% |
|---------|------------|---------------------|-------------------------|-----------------------|-------------------------------|
| Cr      | 267.716    | y=174045.420x-31.8870 | 0.998 82                | 0.0002                | 0.0006                        |
| Co      | 237.862    | y=49308.7377x+184.7202 | 0.998 31                | 0.0001                | 0.0003                        |
| Ni      | 231.604    | y=46462.1918x-35.8141 | 0.998 12                | 0.0002                | 0.0006                        |
| Ga      | 294.364    | y=8792.8933x+42.7275  | 0.999 74                | 0.0003                | 0.0009                        |
| Nb      | 316.340    | y=65230.7107x-23.8005 | 0.999 79                | 0.0003                | 0.0009                        |
| Sc      | 361.384    | y=110391.82x-99.1775  | 0.999 92                | 0.0001                | 0.0003                        |
| Zr      | 339.198    | y=434274.349x+201.5294 | 0.999 96                | 0.0001                | 0.0003                        |

The results showed the correlation coefficient is not less than 0.998, the low limits of detection are in the range of 0.0003% ~ 0.0009%.

3.5 The precision test
This paper randomly selected two sample 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 3.
Table 3  The method accuracy experiments

| Sample | Element | Average (W/%) | Standard deviation | RSD(%) |
|--------|---------|---------------|--------------------|--------|
| 1      | Cr      | 0.0172        | 0.0168             | 0.0175 | 0.0165 | 0.0179 | 0.0165 | 0.0173 | 0.0185 | 0.0158 | 0.0172 | 0.0008 | 4.86   |
| 1      | Co      | 0.0003        | 0.0002             | 0.0003 | 0.0000 | 0.0003 | 0.0002 | 0.0003 | 0.0003 | 0.0002 | 0.0003 | 0.0001 | 19.72  |
| 1      | Ni      | 0.0022        | 0.0018             | 0.0024 | 0.0017 | 0.0020 | 0.0025 | 0.0022 | 0.0026 | 0.0022 | 0.0003 | 14.90  |
| 2      | Ga      | 0.0498        | 0.0475             | 0.0414 | 0.0438 | 0.0466 | 0.0443 | 0.0469 | 0.0505 | 0.0464 | 0.0031 | 6.63   |
| 2      | Nb      | 0.0001        | 0.0001             | 0.0002 | 0.0001 | 0.0010 | 0.0002 | 0.0001 | 0.0002 | 0.0001 | 0.0001 | 37.64  |
| 2      | Sc      | 0.0040        | 0.0033             | 0.0045 | 0.0038 | 0.0043 | 0.0038 | 0.0042 | 0.0036 | 0.0041 | 0.0040 | 9.86   |
| 2      | Zr      | 0.0141        | 0.0155             | 0.0127 | 0.0119 | 0.0108 | 0.0110 | 0.0133 | 0.0109 | 0.0134 | 0.0127 | 0.0018 | 13.97  |

Table 3 shows that: the RSD is less than 15% if the element content is more than 0.001%, this indicates the precision and repeatability are all good.

3.6 Comparison of different methods of testing

In order to assess the accuracy of the method, the four samples of vanadium-titanium blast furnace slag were determined according to the experimental method (ICP-AES), and the results were compared with the inductively coupled plasma mass spectrometry (ICP-MS). The results the results are shown in Table 4.

Table 4  Comparison of different methods of testing w/%

| Element | Sample3 ICP-AES | Sample4 ICP-MS | Sample5 ICP-AES | Sample6 ICP-MS |
|---------|-----------------|----------------|-----------------|----------------|
| Cr      | 0.0172          | 0.0158          | 0.0148          | 0.0161          | 0.0152          | 0.0138          | 0.0125          | 0.0141          |
| Co      | 0.0003          | 0.0004          | 0.0001          | 0.0001          | 0.0001          | 0.0001          | 0.0004          | 0.0003          |
| Ni      | 0.0022          | 0.0019          | 0.0008          | 0.0009          | 0.0010          | 0.0013          | 0.0035          | 0.0030          |
| Ga      | 0.0498          | 0.0530          | 0.0001          | 0.0001          | 0.0001          | 0.0001          | 0.0001          | 0.0001          |
| Nb      | 0.0001          | 0.0001          | 0.0034          | 0.0029          | 0.0001          | 0.0001          | 0.0001          | 0.0001          |
| Sc      | 0.0040          | 0.0037          | 0.0049          | 0.0055          | 0.0039          | 0.0045          | 0.0046          | 0.0040          |
| Zr      | 0.0141          | 0.0150          | 0.0101          | 0.0095          | 0.0155          | 0.0162          | 0.0134          | 0.0146          |

Table 4 shows that the method and ICP-MS method is basically the same test results.

4 Conclusions

The analytical method that simultaneous determination of Cr, Co, Ni, Ga, Nb, Sc, Zr in the blast furnace slag of vanadium titanium magnetite by ICP-AES was established. It solved the problem of sample digestion and the easy hydrolysis of high concentration titanium in low acidity media. The effects of matrix effects and spectral interferences were all studied and summarized, and then the interference effects of matrix coexisting components were eliminated by using matrix matching, simultaneous background correction method and optimal detection parameters. The method has the characteristics of simple operation, less interference and good precision, which meets the need of recovery of noble metal elements in vanadium-titanium blast furnace slag.

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