

Analytical Methods

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Molybdenum blue photometry method for the determination of colloidal silica and soluble silica in leaching solution

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Abstract: an improved analytical procedure has been described for the spectrophotometric determination of colloidal silica in leaching solution by means of adding fluoride to convert colloidal silica into reactive silica. The method is a variation of the classical molybdenum blue method, and has determination of optimal wavelength, temperature, ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$, pH and ammonium molybdate in the colorimetric process, and pH need to be fairly strictly controlled especially. The linear equation is established as: $C=3.15956A-0.51912$, R is more than 0.9992. Its feasibility and reproducibility has been confirmed by ICP-OES, the average relative error is 1.5%. The detection scope of silicon concentration extends almost 1000 times higher in leaching solution, so method in this paper can be used to detect the leaching samples of high silica concentration.

Keywords: molybdenum blue photometry; colloidal silica; solution; determination

1. Introduce

Determination the amount of silica in water samples is presently of special concern in such applications as semiconductors, metallurgical products, industrial and purified waters. Different analytical techniques have been proposed so far to determine silicon, including spectrophotometry [1–5], atomic absorption spectrometry(AAS) [6–7], inductively coupled plasma atomic emission spectrometry(ICP-OES) [8–10], and inductively coupled plasma mass spectrometry(ICP-MS) [11–12], ion chromatography(IC) [13–16] or capillary electrophoresis(CE) [17]. But these analytical techniques are just involved in determination of total amounts of silicon in water samples. Silica is unstable and occurs polymerization or condensation polymerization in aqueous system, which leads to exist two forms of silica in solution—colloidal silica and soluble silica. When referring to leaching solution in metallurgical technology, the concentration of silica has a significant influence on filtration performance of leaching solution, what's more, the structure of silica determines the properties of the solution and yet the basic mechanisms of particle formation and aggregation in aqueous solution remain imperfectly understood. But the formation of colloidal silica must have a crucial role on filtration performance of leaching solution [18-19]. So finding an analytical technique of determination of colloidal silica urgently need to be addressed.

Since Strickland [20] found that two forms of molybdosilicic acid can be formed in mixtures of molybdate, acid and silicate, photometry method has acquired extensive used for silicate analysis. Classical procedures for determining dissolved silicate are based on the formation of a yellow molybdosilicate acid complex, which exists in two forms depending on pH [21-22]. The α -isomer appears at pH 3.5-4.5, whereas the β -isomer, the formation of which is favoured in the pH range of 0.8-2.5 [22-25]. However, most analytical methods are based on conditions favouring the formation of the β -isomer [21-24]. In order to enhance sensitivity, the silicomolybdate complex can be reduced to a blue coloured heteropoly acid [26].

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3 Dienert and Wandenbulcke [27] and Harmon [28] have stated that “soluble silica,” but not
4 “colloidal silica” will react with molybdic acid to form the silicomolybdate complex. Weitz and
5 Schuchard [29] have thrown further light on this point by the discovery that silica in the
6 monomeric, disilicic and oligomer state will react with molybdic acid. So when taking
7 into consideration of colloidal silica, transforming colloidal silica into soluble silica is a requisite
8 procedure. Senll [30] has described an analytical method for the determination of silicate in the
9 presence of colloidal silica, which makes colloidal silica depolymerize to form reactive silica by
10 means of adding fluoride [31-33].

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13 Based on above-mentioned theories, this paper have found a convenient method to determine
14 the concentration of colloidal silica in leaching solution of high silica concentration and research
15 the influence of in all situations. This method has positive significance for further researching the
16 influence of colloidal silica on filtration performance of leaching solution.
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18 19 20 21 22 **2 Experimental**

23 24 25 26 **2.1 Reagents**

27 All chemicals used were analytical grade and stored in polyethylene bottles unless otherwise
28 stated: HCl 1M; H₂SO₄ 1M; Oxalic acid- tartaric acid 0.5M-0.5M; boric acid
29 0.5M; ammonium molybdate 5% m/v; ascorbic acid 2% m/v; NH₄F 1M. Deionized water was
30 used throughout.

31 Preparation for Si stock solution: 200mg/L. Weigh 65mg of sodium metasilicate with 1g of
32 NaOH in a polyter afuoroethyenea beaker and add two drops of absolute ethyl alcohol and 50 ml
33 of deionized water. Then above samples go through heating, stirring and dissolving. After that the
34 solution is diluted to 250ml with deionized water in a polyethylene bottle. The Si stock solution is
35 for preparing the standard work curve subsequent.

36 37 38 39 40 **2.2 Apparatus**

41 The spectrophotometric determination of silicon was then performed at 812 nm using a
42 UV-1801 ultraviolet spectrophotometer. All measurements were made using 10 mm path length
43 cuvettes. In order to verify the reliability of molybdenum blue photometry method, the ICP-OES is
44 used to determine the total concentration of silicon, the ICP-OES is proceeded in center of
45 forecasting and analysis of Kunming University of Science and Technology.

46 Water bath kettle is used to keep warm and glass calomel electrode pH meter is used to test
47 the pH of solution.

48 49 50 51 52 **2.3 Procedures**

53 Procedure of standard work curve: dilute 200mg/L of Si stock solution to 20 mg/L, take 1mL,
54 3mL, 5mL, 7mL, 9mL respectively into 5 polyter afuoroethyenea beakers, add 10ml of deionized
55 water, 10mL of HCl(1M) and 2mL of NH₄F (1M), put them in a water bath kettle and keep its
56 temperature on 298K with 30-40min until complete reaction, stirring is used throughout, then add
57 20mL of boric acid (0.5M) to keep 30min, after that, adjust the pH to 1.4, next add 10mL of
58 absolute ethyl alcohol and 15mL of ammonium molybdate (5%) to keep 20min, finally add
59 10mL of oxalic acid- tartaric acid (0.5M-0.5M) and 5mL of ascorbic acid (2%) to keep 20min and
60 transfer the solution to polyethylene bottle of 100mL. The spectrophotometric determination of
silicon is then performed at 812 nm using a UV-1801 ultraviolet spectrophotometer. All
measurements are made using 10 mm path length cuvettes. The solution absence of Si stock
solution regards as reference solution.

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3 Procedure of determination of total silica of leaching solution: dilute the concentration of
4 leaching solution to the range of standard work curve (0.2-1.8mg/L), take 2mL into a polyter
5 afuoroethyenea beaker, add 10ml of deionized water, 10mL of HCl(1M) and 2mL of NH₄F (1M),
6 put them in a water bath kettle and keep its temperature on 298K with 30-40min until
7 complete reaction, stirring is used throughout, then add 20mL of boric acid (0.5M) to keep
8 30min, after that, adjust the pH to 1.4, next add 10mL of absolute ethyl alcohol and 15mL
9 of ammonium molybdate (5%) to keep 20min, finally add 10mL of oxalic acid- tartaric acid
10 (0.5M-0.5M) and 5mL of ascorbic acid (2%) to keep 20min and transfer the solution to
11 polyethylene bottle of 100mL. The spectrophotometric determination of silicon is then performed
12 at 812 nm using a UV-1801 ultraviolet spectrophotometer. All measurements are made using 10
13 mm path length cuvettes. The solution absence of Si stock solution regards as reference solution.

14
15 Procedure of determination of soluble silica of leaching solution: all steps are same with the
16 procedure of determination of total Si of leaching solution, except omitting the process of adding
17 NH₄F. The solution absence of leaching solution and NH₄F regards as reference solution.

18
19 Procedure of determination of colloidal silica of leaching solution: the concentration of
20 colloidal silica is equal to the concentration of total silica minus the concentration of soluble silica.
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23 24 **3. Results and discussion**

25 26 **3.1 Determination the wavelength of photometry**

27 During building the standard work curve, every sample is scanned by wavelength at the range
28 of 400nm-1000nm. It is found that all wave peaks appeared at the wavelength of 812nm. That can
29 indicate silicomolybdenum blue has preferable sensitivity, so we chose to measure the absorbance
30 at the wavelength of 812nm. The detection wavelength is chose by 680nm and 740nm[3-5], but
31 through scanning by wavelength at the range of 400nm-1000nm. It was found that all wave peaks
32 appeared at the wavelength of 812nm. That can indicate silicomolybdenum blue has preferable
33 sensitivity at the wavelength of 812nm.
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36 37 **3.2 Determination the temperature of photometry**

38 Take 1mL of Si stock solution of 20 mg/L to proceed the procedure of determination of total
39 silica concentration at the temperature of 288K、298K、308K、318K respectively. The results
40 showed in figure 1. It can see that when temperature is less than 298K, the absorbance is serious
41 low, when temperature is more than 298K, the absorbance has a tendency of decreasing gradually.
42 This phenomenon is consistent with G.V.L.N.Murty's conclusion—at temperature 303K and above
43 there is a distinct decrease in the intensities of the colour in case of all the procedures [34].
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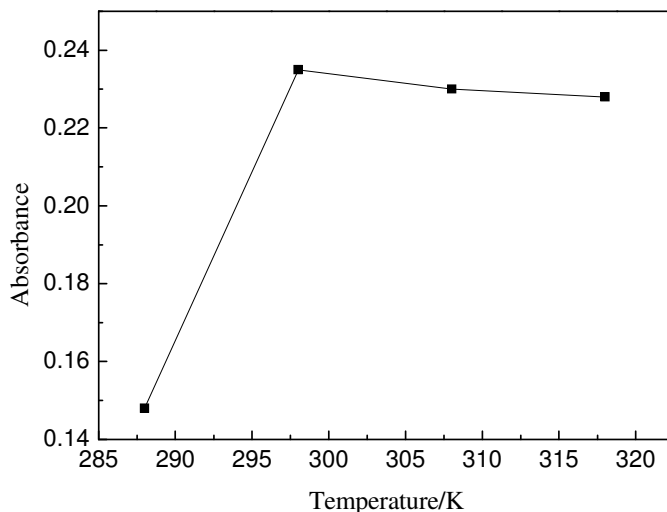


Fig.1.The relationship of absorbance with temperature

(1mL of Si stock solution of 20 mg/L, measure the absorbance under the procedure of determination of total silica concentration at the temperature of 288K、298K、308K、318K respectively)

3.3 Determination the ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$

The key to determine the colloidal silica is to convert polymer into reactive silica. So the choice of fluoride is important, K.D. Demadis[35] has investigated HF, $\text{NH}_4\cdot\text{HF}_2$, NH_4F , NaBF_4 and $\text{Na}_2\text{PO}_3\text{F}$ on the dissolution of colloidal silica. HF and $\text{NH}_4\cdot\text{HF}_2$ have more effective on the dissolution of colloidal silica, but the interference of HF and $\text{NH}_4\cdot\text{HF}_2$ is strong, which make the absorbance is serious low, and their strong toxicity bring a serious obstruction to experiments. The dissolution efficiency of NaBF_4 is very low. $\text{Na}_2\text{PO}_3\text{F}$ is monitored not by the silicomolybdate method and brings the interference element P. Under the same conditions, the absorbance of adding NH_4F is better than adding HF, which indicates the dissolution capacity of colloidal silica of NH_4F can satisfy the leaching samples of high silica concentration. So NH_4F is chose as medium of depolymerization.

Then need to determine the amount of NH_4F . Take 9mL of Si stock solution of 20 mg/L to proceed the procedure of determination of total silica concentration without the step adding boric acid, the amount of NH_4F (1M) of 1mL、2mL、3mL、4mL respectively. The results showed in figure 2. It can see that when the amount of NH_4F is 2mL, the absorbance gets maximum value. When the amount of NH_4F is more than 2mL, the absorbance decreases gradually, which can indicate that 2mL of NH_4F is enough to establish the standard work curve, at the same that, excess of fluoride is known to inhibit the color development of molybdenum blue. This interference comes from the formation of silicon–fluoride complexes, mainly is SiF_6^{2-} , these are no longer reacting to form the oligomer of Mo. The effect of F^- can be eliminated to a certain extent by adding boric acid (H_3BO_3), which can remove the fluoride ions from the solution through the formation of boron–fluoride complexes according to the following reactions [32]:





These boron–fluoride complexes are formed preferentially at the expense of the silicon–fluoride complexes, because their equilibrium constants are more than 30 orders of magnitude higher[32,36-37]. But excess of boric acid also affects the color development of molybdenum blue, so need further to determine the ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$. Take 9mL of Si stock solution of 20 mg/L to proceed the procedure of determination of total silicon concentration, the mole ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$ is 0、 2.5、 5、 7 respectively. The results showed in figure 3. It can see that boric acid also puts an upper limit to the NH_4F concentration of the analyte. So the optimal mole ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$ is 5, which corresponds with volume is 2mL of NH_4F (1M) and 20mL of H_3BO_3 (0.5M).

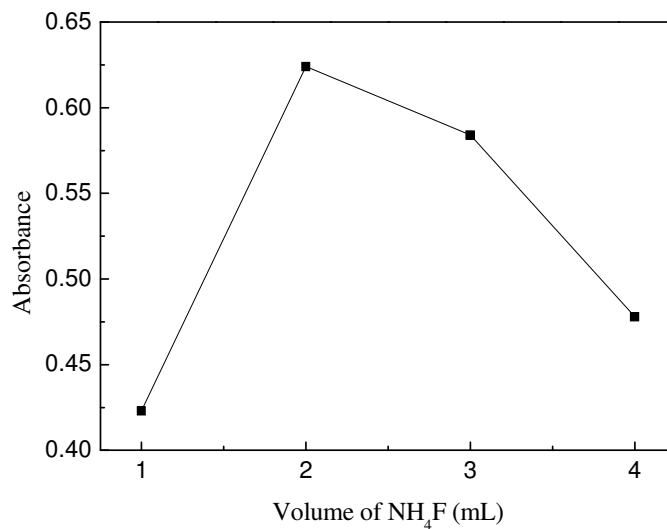


Fig.2.The relationship of absorbance with the volume of NH_4F

(9mL of Si stock solution of 20 mg/L, measure the absorbance under the procedure of determination of total silica concentration with the volume of NH_4F (1M) of 1mL、 2mL、 3mL、 3mL respectively, without the step adding boric acid)

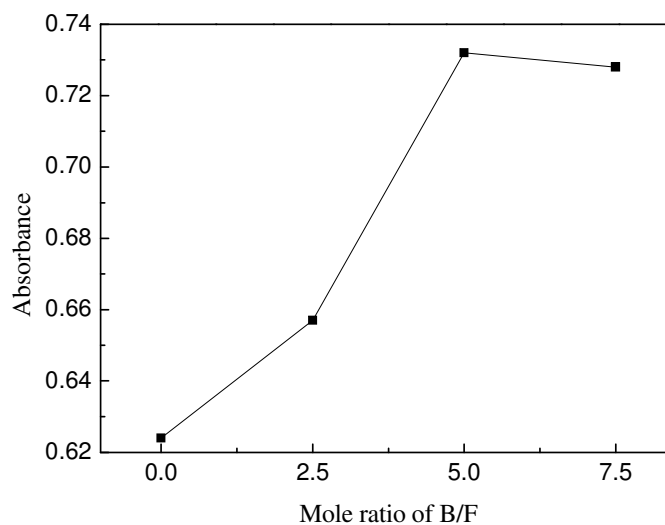


Fig.3. The relationship of absorbance with the mole ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$

(9mL of Si stock solution of 20 mg/L, measure the absorbance under the procedure of determination of total silica concentration with the mole ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$ of 0, 2.5, 5, 7.5 respectively)

3.4 Determination the pH

In previous works, most analytical methods are based on favouring to form the b-isomer, the formation pH is in the range 0.8 ± 2.5 , so before adding ammonium molybdate, need to adjust the pH to the range. Take 1mL of Si stock solution of 20 mg/L to proceed the procedure of determination of total Si concentration, pH is 1, 1.1, 1.2, 1.3, 1.4, 1.5 respectively before adding ammonium molybdate. The results showed in figure 4. It can see that pH has a dramatic influence on the formation of b-isomer, when pH is 1.4, the formation of b-isomer is fairly complete, the pH range of b-isomer formation is correct to 1.4 ± 0.04 by experiment research.

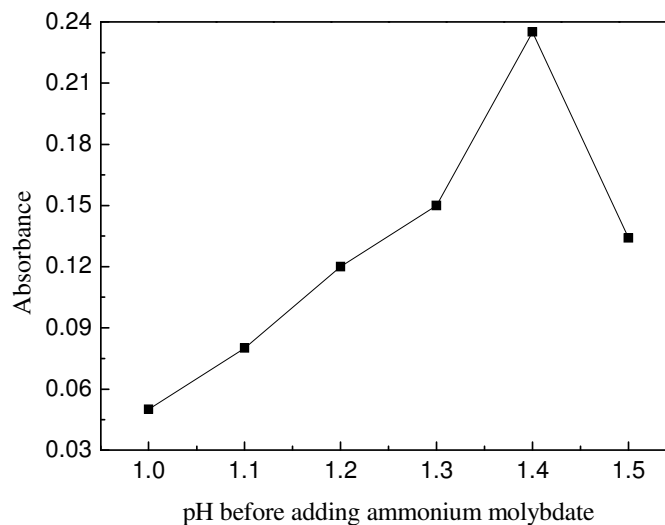


Fig.4.The relationship of absorbance with pH

(1mL of Si stock solution of 20 mg/L, measure the absorbance under the procedure of determination of total silica concentration with pH of 1、 1.1、 1.2、 1.3、 1.4、 1.5 respectively)

3.5 Determination the amount of ammonium molybdate

Before adding ammonium molybdate, absolute ethyl alcohol treats as stabilizer of b-isomer. Take 1mL of Si stock solution of 20 mg/L to proceed the procedure of determination of total Si concentration, the volume of ammonium molybdate (5%) is 5mL、 10mL、 15mL、 20mL respectively. The results showed in figure 5. It can see that when the volume of ammonium molybdate reaches 15mL, the absorbance gets the maximum value and has a fixed tendency with the volume of ammonium molybdate increasing.

After the b-isomer formation, the mixed acid of oxalic acid- tartaric acid can eliminate the interference of phosphorus and iron, although researches about this paper are without element of phosphorus and iron, the mixed acid of oxalic acid- tartaric acid also can be regarded as stabilizer among the reduction reaction of ascorbic acid.

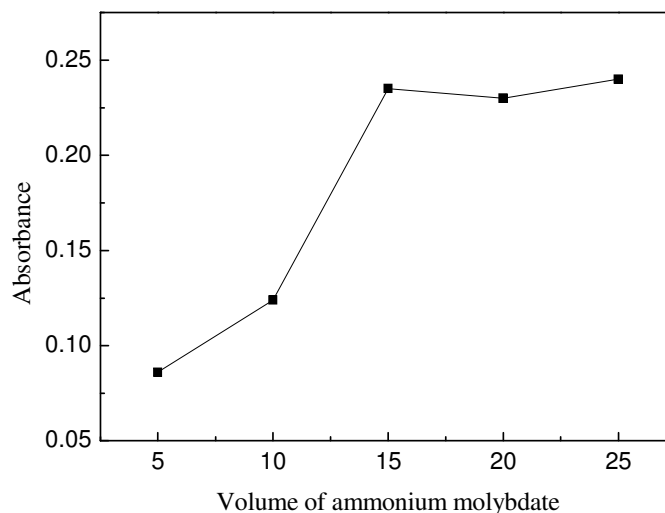


Fig.5.The relationship of absorbance with the volume of ammonium molybdate

(1mL of Si stock solution of 20 mg/L, measure the absorbance under the procedure of determination of total silica concentration with the volume of ammonium molybdate(5% m/v) of 5mL、 10mL、 15mL、 20mL、 25mL respectively)

3.6 Standard work curve

The standard work curve is established, as followed figure 6, after having proceeded in the procedure of standard work curve. The linear equation is: $C=3.15956A-0.51912$, C is concentration of Si (mg/L), the linear scope of silica concentration is 0.2mg/L-1.8mg/L, A is absorbance, the linear correlation coefficient R is more than 0.9992, however, the best linear correlation coefficient R is 0.998 [3,26,32,38], that means the linear equation have a better linear correlation and can satisfy the photometric measurement of silica.

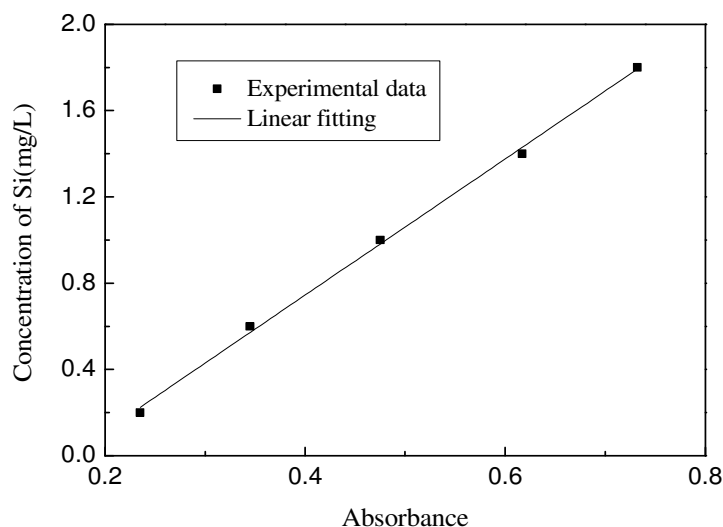


Fig.6.Linear fitting of experimental data

3.7 Verification of ICP-OES

In order to verify the feasibility of molybdenum blue photometry method in this paper, utilize the ICP-OES which is one of most convincing detection means so far to detect four samples compared with molybdenum blue photometry method, the four samples are 20mg/L of Si stock solution, 100mg/L of Si stock solution and two leaching solutions, and their serial number are 1、2、3、4 respective. The results are listed in table 1. From table 1, the minimum relative error is 0.91% and the maximum relative error is 1.89%, and the average relative error is 1.50%. These results can manifest the feasibility of molybdenum blue photometry method in this paper enough. The relative error increases with the silicon concentration increasing of sample, the reason for this phenomenon is extension of dilution ratio mainly, the dilution ratio of sample 1、2、3、4 is 20、100、200、300 respective. From table 1, the detection scope of silicon concentration almost reaches the level of g/L, this method is generally used to detect silicon concentration of nature water, which silicon concentration is general less than 10mg/L[38], the detection scope of silicon concentration extends almost 1000 times higher. So method in this paper can be used to detect the leaching samples of high silica concentration, which greatly improves the detection scope of silicon concentration.

Table 1.Relative error of detected by method in this paper with detected by ICP-OES

Sample	1	2	3	4
Method in this paper (mg/L)	19.96	99.89	177.2	438
ICP-OES (mg/L)	19.78	98.56	174	429.86
Relative error%	0.91	1.35	1.84	1.89
Average relative error%	1.50			

3.8 Determination the colloidal silica and soluble silica in leaching solution

Test the sample 3 and 4 in 3.7 by the means of procedure of determination of soluble silica of leaching solution and procedure of determination of colloidal silica of leaching solution, the results are listed in table 2. Determination the colloidal silica of leaching solution achieves easily and conveniently and this method has good sensitivity and feasibility, therefore this method can be

as a mean of detecting the concentration of colloidal silica in solution.

Table 2. Determination of colloidal silica for sample 3 and 4

Sample	3	4
Concentration of colloidal silica (mg/L)	139.2	322
Concentration of soluble silica (mg/L)	38	116
Concentration of total silica (mg/L)	177.2	438

4. Conclusions

An improved analytical procedure has been described for the spectrophotometric determination of colloidal silica in leaching solution by means of adding fluoride to convert colloidal silica into reactive silica. The method is a variation of the classical molybdenum blue method, and has determination of optimal wavelength, temperature, ratio of $\text{H}_3\text{BO}_3/\text{NH}_4\text{F}$, pH and ammonium molybdate in the colorimetric process. The detection scope of silicon concentration extends almost 1000 times higher, so method in this paper can be used to detect the leaching samples of high silica concentration. It has good sensitivity and its feasibility and reproducibility has been confirmed. So this method has built an impressive foundation for determination the colloidal silica in solution.

Acknowledgement

Financial support from the National Natural Science Foundation of China (Grant No. 51364022, 50904030, 51474117), the National Key Basic Research and Development Plan of China (973 program) (Grant No. 2014CB643404) and the Major Projects in the Scientific Research Foundation of the Education Department of Yunnan Province of China (Grant No. ZD2014003) is gratefully acknowledged.

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