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Determination of trace arsenic and bismuth content in iron, steel and alloys by hydride generation－atomic fluorescence spectrometric method

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Abstracts: An analysis method for determining trace arsenic and bismuth in iron, steel and alloys by hydride generation-atomic fluorescence spectrometry (HG-AFS) is presented. The operation parameters of AFS, effects of acidity, limit of coexisting ions and concentration of reducing agent have been tested. Thiosemicarbazide-ascorbic acid and phosphoric acid were used to eliminate the interference of matrix elements. The detection limits of arsenic and bismuth are 0.04 $\mu g/g$ and 0.02 $\mu g/g$(3σ, $n=11$), respectively. The method has been applied to determine trace arsenic and bismuth in middle and low alloy steel, ferronickel-base superalloy, nickel-base superalloy, cobalt-base superalloy and copper alloy with satisfactory results. The method was proved to be sensitive, accurate, quick and convenient.

Key words: hydride generation; atomic fluorescence spectrometry; iron, steel and alloys; arsenic; bismuth

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Trace arsenic and bismuth can affect the mechanical performance of alloy, so determination of the arsenic and bismuth content in alloys is necessary. The hydride generation-atomic fluorescence spectrometric (HG-AFS) method for the determination of trace arsenic and bismuth content has high sensitivity, but the main compositions of alloy, such as iron, nickel, cobalt, copper, tungsten, molybdenum, niobium, tantalum and etc., effect the determination of arsenic and bismuth heavily. How to eliminate the interference of matrix has been studied[1-6], but it is not applicable to determination of arsenic and bismuth of superalloy. An analysis method by adding thiosemicarbazide-ascorbic acid and phosphoric acid to eliminate the interference of main constituent has been developed in this paper. The method is applicable to the determination of arsenic and bismuth contents between 0.5 $\mu g/g$ and 1 000 $\mu g/g$ in iron, steel and superalloy.

1 Experimental

1.1 Instruments

Atomic fluorescence spectrometer : AFS-2202; special arsenic and bismuth hollow cathode lamp.

1.2 Reagents

Hydrochloric acid, GR; Nitric acid, GR; Mixed acid with sulfuric acid, phosphoric acid and water, diluted 1 + 1 + 2; Mixed solution of thiosemicarbazide- ascorbic acid - hydrochloric acid, 50 g/L + 50 g/L + 200 mL /L; Potassium borohydride solution, 15 g/L (including 5 g/L potassium hydroxide); Arsenic and bismuth mixed

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standard solution, 1 μg/mL and 0.1 μg/mL; iron, nickel, cobalt, copper, tungsten, molybdenum, niobium, tantalum solution.

1.3 Experimental procedure

Put different quality of iron , nickel, cobalt, copper, tungsten, molybdenum, niobium and tantalum into several 100 mL volumetric flasks seperately. Then pipette 1.0 μg arsenic and bismuth and transfer into the 100 mL volumetric flask, then add 5.0 mL of hydrocloric acid, 5.0 mL of mixed acid with suluric acid, phosphoric a cid and water and mix. Add 50 mL of mixed solution of thiosemicarbazide- ascorbic acid, dilute with water to the mark and mixed again. Incubate for 30 mins at room temperature, then determine the fluorescence intensity of the solution.

2 Results and discussion

2.1 The parameters of apparatus

The optimal parameter of the intrusment for the determination of arsenic and bismuth is following: the current of hollow cathode lamp is 50 – 70 mA; the carrier gas is 400 mL/min; the shielding gas is 800 mL/min; the voltage of detector is 310 V; the height of tquartz atomizer is 7.5 mm; the integral time is 10 s; the delay-time is 1 s; the speed of pump is 120 r/min.

2.2 The condition of hydride generation

The experiment showed that when the concentration of hydrochloric acid , sulfuric acid and phosphoric acid is between 10% – 40% (*v/v*), 1% – 5% (*v/v*) and 1% – 5%, respectively, the intensity of the atomic fluorescence for arsenic and bismuth is strong and stable enough to measure . So 20% (*v/v*) Hydrochloric acid and 2.5% sulfuric acid and phosphoric acid were selected as medium in the paper . After the samples are decomposed with hydrochloric acid and nitric acid , the mixture of sulfuric acid and phosphoric acid is added in and evaporate the solution to remove the nitrogen oxide and the phosphoric acid combine with hydrolyzable elements, such as tungsten, molybdenum, niobium and tantalum, to eliminate the interference of this elements. In the paper, 15 g/L potassium borohydride solution (including 5g potassium hydroxide) is used as reducer.

2.3 Interference and elimination

2.3.1 Interference of nickel, cobalt and copper and elimination

Table 1 Elimination for interference of Ni, Co, Cu

Ni Added (mg/mL)	Bi Recovery (%)	Co Added (mg/mL)	Bi Recovery (%)	Cu Added (mg/mL)	Bi Recovery (%)
0.1**	78	0.1**	56	0.1**	0
0.1***	82	0.1***	88	0.1***	81
0.1	99	0.1	97	0.1	96
1	101	1	107	0.5	98
2	102	2	104	1	104
3	97	3	101	1.5	97
4	110	4	98	2	101
5	105	5	110	2.5	98
6	107	6	105	3	83

Note: The concentration of arsenic is 1 ng/mL in solution; ** denotes that there is no thiosemicarbazide and ascorbic acid in solution; *** denote that there is no thiosemicarbazide in solution

Table 2 Elimination for interference of Ni, Co, Cu

Ni Added (mg/mL)	As Recovery (%)	Co Added (mg/mL)	As Recovery (%)	Cu Added (mg/mL)	As Recovery (%)
0.1**	60	0.1**	56	0.1**	0
0.1***	82	0.1***	94	0.1***	85
0.1	101	0.1	98	0.1	98
1	98	1	101	0.5	98
2	97	2	102	1	102
3	102	3	106	1.5	98
4	97	4	97	2	101
5	104	5	98	2.5	99
6	95	6	96	3	90

Note: The concentration of bismuth is 1ng/mL in solution; ** denotes that there is no thiosemicarbazide-ascorbic acid in solution; *** denotes that there is no thiosemicarbazide in solution.

The interference of nickel, cobalt and copper has been studied and the different method to eliminate the interference has been brought forward[1-9]. The method only can be applied to the simple alloys such as middle-low-alloy steel etc but cannot be applied to the complicated samples such as ferronickel-base, nickel-base and cobalt-base superalloy and copper alloy etc. In this paper the thiosemicarbazide was selected as masking reagent from more than 20 organic reagents to eliminate the interference of the matrix. The experiment indicated that the thiosemicarbazide could eliminate the interference of plentiful nickel ion, cobalt ion and copper ion in solution effectively. The concentration of the thiosemicarbazide-ascorbic acid is 25 g/L in the solution. The results are listed in table 1 and table 2. Table 1 is the interference of nickel, cobalt and copper for the recovery of arsenic. Table 2 is the interference of nickel, cobalt and copper for the recovery of bismuth.

2.3.2 Interference of hydrolyzable elements and elimination

In the solution, tungsten, molybdenum, niobium and tantalum will hydrolyze and deposit. The deposition will absorb arsenic and bismuth ion and induce the recovery of arsenic and bismuth too low. In the paper we select phosphoric acid as masking reagent to eliminate the interference. The experiment proved that when the concentration of phosphoric acid is 2.5% (*v/v*), 1 mg/mL molybdenum, 0.5 mg/mL tungsten, niobium and tantalum have no interference for the recovery of arsenic and bismuth. The results are listed in table 3.

Table 3 Elimination for interference of W, Mo, Nb and Ta

W added (mg/mL)	As recovery (%)	Bi recovery (%)	Mo added (mg/mL)	As recovery (%)	Bi recovery (%)
0.02**	81	88	0.02**	84	90
0.02	95	97	0.02	94	98
0.2	104	102	0.2	99	97
0.3	101	98	0.4	97	101
0.4	98	101	0.6	101	99
0.5	99	96	1.0	102	96
0.6	88	99	1.2	90	94
Nb added (mg/mL)	As recovery (%)	Bi recovery (%)	Ta added (mg/mL)	As recovery (%)	Bi recovery (%)
0.02**	60	70	0.02**	64	60
0.02	92	98	0.02	97	98
0.2	101	103	0.2	101	96
0.3	104	102	0.3	99	97
0.4	99	98	0.4	98	102
0.5	101	97	0.5	102	97
0.6	91	89	0.6	94	90

Note: the concentration of arsenic is 1 ng/mL. ** denotes that there is no phosphoric acid in solution.

2.3.3 The limit of other coexistent element

For 1ng/mL arsenic and bismuth, the relative error of fluorescence intensity is less than ± 5%, the limit of other coexistent element is following: 1 mg/mL Mn, Al, Zn, Cr; 0.3 mg/mL Si, Y, La, Ce, V, Ti, Zr, Hf; 10 μg/mL Ga, In, Pd, Cd, Tl, Ag, Au, Ru, Ir. Pt ; 1 μg/mL Sb, Pb, Sn, Ge, Se, Te, Hg. Plentiful alkali metals and alkaline-earth metals have no interference for the determination of the arsenic and bismuth.

2.4 Linearity and detection limit

Under the conditions given in this paper, the cencontration of calibration graphs of arsenic and bismuth is between 0 – 0.2 μg/mL, the detection limits of arsenic and bismuth is 0.04 μg/mL and 0.02μg/mL, respectively.

3 Sample test

3.1 Treatment of samples

Weight he sample 0.100 g and place it in a 100 mL beaker. Add 10 mL of mixed hydrochloric acid and nitric acid[note], heat up to dissolve on the low temperature electric stove . when the sample is completely dissolved, cool for a little while then add 5 mL of mixed acid of sulfuric acid and phosphoric acid. Heat and evaporate until it gives off white smoke of sulfuric acid. Then cool to room temperature, add 5 mL of hydrochloric acid and mix. It is transferred into a 50 mL volumetric flask and add 25 mL of mixed solution of thiosemicarbazide- ascorbic acid-hydrochloric acid, mix again. Incubate for 30 min at room temperature (if room temperature is below 15 ℃, incubate at 30 ℃ in water bath for 20 min), flute with water to the mark and mix.

Note: According to the composition of the sample matrix, the mixed acid of hydrochloric acid and nitric acid with different ratio is used to dissolve the samples.

3.2 Test results

Using the HG-AFS method in the preceding section are presented to determine different alloy samples and compare with the corresponding certified values in table 4 and table 5. Table 5 show the results determined using the HG-AFS method agree well with the certified values.

Table 4 Results of HG-AFS determination of arsenic $n=5$

Sample/number	Certified (μg/g)	Found (μg/g)	RSD(%)
GSBH41009 - 93 crude iron	10	10	2.1
GSBH40061 - 93 constructional alloy steel	63	63	2.4
GBW01665 stainless steel	25	27	2.3
GWB01620 ferro - nickel superalloy	11	11	2.5
DZ125 - 1 nickel base superalloy	1.2	0.96	4.8

Table 5 Results of HG - AFS determination of bismuth $n=5$

Sample/number	Certified (μg/g)	Found (μg/g)	RSD(%)
GSBH40065 - 93 constructional alloy steel	67	72	2.4
GWB01620 ferro - nickel superalloy	0.4	0.6	6.4
GBW01639 nickel - base superalloy	2.0	1.9	4.7
684 H62 copper - base alloy	20	22	2.8

4 Conclusion

By studying, the optimal condition to determine trace arsenic and bismuth by HG- AFS method in alloy samples is given and good precision and accuracy have been obtained.

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