Determination of Sub-ppm Levels of Silver in Heat-Resisting Alloys by Graphite Furnace Atomic Absorption Spectrometry*

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A rapid and simple analytical method has been developed for the determination of sub-ppm levels of Ag in Ni- and Co-base heat-resisting alloys by graphite furnace atomic absorption spectrometry. Nickel or Co, a base element of heat-resisting alloys, did not affect the absorbance of Ag. The effects of the other elements and acids on the absorbance of Ag were also studied. As a result, the acid solutions of Ag were used as the calibration solutions for the determination of sub-ppm levels of Ag in complex heat-resisting alloys. The results obtained by the calibration curve method agreed well with those by the standard addition method. The detection limit of Ag was 0.005 ppm in the sample by the method described. This method, however, can not be applied for the determination of Ag in Co-base heat-resisting alloys containing large quantities of Al and Ti because of the interferences.

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I. Introduction

It has been known that the impurities having a low melting point have harmful effects on the mechanical properties of heat-resisting alloys even if present at very low concentrations. Silver is one of them. Burke⁽¹⁾ studied solvent extraction-flame atomic absorption spectrometry for the determination of trace quantities of Ag in Ni-base alloys. Kirk *et al.*⁽²⁾ determined trace quantities of Ag in high-Ni alloys by ion exchange-flame atomic absorption spectrometry. These methods are sensitive but their procedures are complicated and time-consuming. Moreover, the nebulization and combustion of organic solvents in flame atomic absorption spectrometry may be harmful to the health and the environmental preservation. Graphite furnace atomic absorption spectrometry has advantages of the high sensitivity and the simplified procedure over flame atomic absorption spectrometry and allows chemical separation to be avoided. Dulski and Bixler⁽³⁾ determined trace impurities in Ni-base heat-resisting alloys by graphite furnace atomic

absorption spectrometry, but they did not determine Ag. They used a single-point method of standard addition rather than a calibration curve method to avoid the matrix effects. Recently, the present authors⁽⁴⁾ have studied the direct determination of trace quantities of Pb and Bi after the acid dissolution of Ni- and Co-base heat-resisting alloys by graphite furnace atomic absorption spectrometry.

This paper describes the application of graphite furnace atomic absorption spectrometry for the determination of sub-ppm levels of Ag in Ni- and Co-base heat-resisting alloys.

II. Experimental

1. Equipment

A Perkin-Elmer Model 403 atomic absorption spectrophotometer, equipped with a Model HGA-2100 graphite furnace and a deuterium arc background corrector, was used. A Hamamatsu TV hollow cathode lamp was used as the Ag light source. Absorbance was recorded with a Hitachi Model 056 recorder. Argon was used as the purge gas. A thermocouple or an optical pyrometer was used for the furnace temperature measurements.

2. Reagents and solutions

Nitric acid and hydrofluoric acid used were of analytical reagent grade. Stock standard

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Table 1 Chemical composition of heat-resisting alloys used. (wt%)

Alloy	Ni	Cr	Co	Al	Ti	Mn	Fe	Nb	Mo	Ta	W
NBS 349 (Waspaloy)	57.2	19.5	14.0	1.2	3.1				4.0		
Inconel 738 LC	61.6	15.8	8.3	3.4	3.4				1.8	1.7	2.6
MAR-M 246	57.7	10.1	9.9	5.5	1.5				2.6	1.5	10.9
Udimet C0263	50.9	20.1	19.9		2.2				5.8		
NBS 168 (S-816)	20.3	20.3	41.2			1.5	3.4	3.0	4.0	1.0	4.0
WI-52		21.2	62.5				2.0	1.8			10.4
Modified S-816	20.0	20.2	45.6					4.0	4.1		3.7

solution containing 1000 $\mu\text{g}/\text{ml}$ of Ag was prepared by dissolving high-purity metal of Ag (Johnson Matthey Chemicals Ltd.) in dilute nitric acid and was stored in the dark. Working standard Ag solutions of lower concentrations were prepared daily to avoid the loss of Ag due to adsorption⁽⁵⁾ by diluting the stock standard solution with dilute nitric acid. The other standard solutions were also prepared by the dissolution of high-purity metals Al, Ti, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Ta, and W. The concentrations of Ag added to the sample solutions or matrix solutions were 0.005~0.01 $\mu\text{g}/\text{ml}$. Solutions containing total metal concentrations of 10~20 mg/ml were used to select optimum analytical conditions.

3. Heat-resisting alloys used

Table 1 shows the chemical composition of the heat-resisting alloys used. NBS 349 (Waspaloy), Inconel 738 LC, MAR-M 246, and Udimet CO263 are Ni-base heat-resisting alloys. NBS 168 (S-816), WI-52, and modified S-816 are Co-base heat-resisting alloys. Standard alloys containing known amounts of Ag were not available. However, standard alloys such as NBS "benchmark" standards seem at present to be one of the most suitable samples for a comparison of the analytical results.

4. Proposed procedure

Dissolve 0.5 g of a heat-resisting alloy in 12 ml of a 1:1:1 mixture of nitric acid, hydrofluoric acid and water by warming in a Pt beaker. After the complete dissolution of the alloy, cool and transfer the solution into a 50-ml polyethylene volumetric flask. Dilute the solution to the mark with distilled water. Prepare calibration solutions by diluting the

Table 2 Operating parameters.

Analyte	Ag
Wavelength (nm)	328.07
Spectral band width (nm)	0.7
Lamp current (mA)	12
Ar flow rate (ml/min)	ca. 60
Drying temperature ($^{\circ}\text{C}$)	80
Drying time (s)	30
Ashing temperature ($^{\circ}\text{C}$)	500
Ashing time (s)	60
Atomizing temperature ($^{\circ}\text{C}$)	2400
Atomizing time (s)	7
Solution volume (μl)	20

stock standard Ag solution and adjusting the kind and concentration of acids. Pipette 20 μl of the solutions into the graphite furnace by an Eppendorf micropipette with plastic disposable tip. Operate the set program of the HGA controller under the conditions shown in Table 2. Interrupt the flow of the purge gas during the atomization for the increase in sensitivity. After the atomization, operate the high temperature (nominal temperature 2500 $^{\circ}\text{C}$) treatment of the furnace for several seconds under the flow of the purge gas to remove the residual metals in the graphite furnace. Prepare a calibration curve and calculate the concentration of Ag.

III. Results and Discussion

1. Optimum analytical conditions

The drying temperature and time had little effect on the absorbance of Ag and were set to be 80 $^{\circ}\text{C}$ and 30 s, respectively. The ashing temperature curves were investigated for Ag in the acid solution and in the solutions contain-

ing the Ni matrix, the Co matrix, and Ni- and Co-base heat-resisting alloys. NBS 349 or Inconel 738 LC, and NBS 168 were, respectively, used for representatives of Ni- and Co-base heat-resisting alloys. The optimum ashing temperature was selected to be 500°C, which was a little below the temperatures where the loss of Ag began. The ashing time had no effect on the absorbance of Ag between 60 s and 180 s, and was therefore decided to be 60 s. The atomizing temperature curves for Ag were also investigated in the same solutions used for the study of the optimum ashing temperature. The optimum atomizing temperature was selected to be 2400°C, which provided a maximum sensitivity for Ag in all the solutions used. The atomizing time of 7 s was sufficient for the determination of Ag.

It is the most useful to use nitric acid and hydrofluoric acid for the dissolution of a wide variety of complex Ni- and Co-base heat-resisting alloys. The effects of the amounts of acids on the absorbance of Ag in the acid solution and in the solutions containing the Ni matrix, the Co matrix, and Ni- and Co-base heat-resisting alloys were investigated. As a result, the effects of acids were constant when 2~4 ml of nitric acid or hydrofluoric acid was contained in 50 ml of the solution. It was, therefore, decided to use 12 ml of a 1:1:1 mixture of nitric acid, hydrofluoric acid and water for the dissolution of 0.5 g of the chips of heat-resisting alloy.

2. Effects of base elements and the other elements

The chemical composition of heat-resisting alloys varies from alloy to alloy. The calibration curve method is more suitable than the standard addition method for the determination of Ag in a wide variety of heat-resisting alloys because of the simplicity. The effect of Ni or Co, a base element of heat-resisting alloys, on the absorbance of Ag was investigated and is shown in Table 3. It is shown that the same absorbance of Ag was seen in the acid solution and in the solution containing 10 mg/ml of Ni or Co as a matrix element. The effects of the other elements, which are contained generally in complex Ni- and Co-base heat-resisting

Table 3 Effect of Ni or Co matrix element* on the relative absorbance of Ag. (Ag added: 0.01 µg/ml)

Analyte	Relative absorbance		
	Without matrix	Ni	Co
Ag	1.00	0.99	1.00

* Concentration of matrix element is 10 mg/ml.

Table 4 Effect of Cr on the relative absorbance of Ag in solutions containing Ni or Co as a main matrix element. (Ag added: 0.01 µg/ml)

Main matrix	Relative absorbance			
	Without Cr*	10 wt% Cr*	20 wt% Cr*	30 wt% Cr*
Ni	1.00	1.02	1.03	0.98
Co	1.00	0.99	0.99	0.95

* Concentration of Cr is 0.1X mg/ml and that of Ni or Co is (10-0.1X) mg/ml, where X means wt% of Cr in solutions containing Ni or Co as a main matrix element.

alloys, on the absorbance of Ag were also investigated. The experimental errors of the relative absorbance were within $\pm 5\%$. Table 4 shows that Cr did not affect the absorbance of Ag up to 30 wt% of the total matrix concentration in the solutions containing Ni or Co as a main matrix element. The effects of the diverse elements on the absorbance of Ag were investigated up to 10 wt% of the total matrix concentration of 10 mg/ml. Table 5 shows that the diverse elements did not affect the absorbance of Ag in this concentration range in the solutions containing Ni or Co as a main matrix element except for Al and Ti in Co solutions. Aluminum and Ti decreased the absorbance of Ag in the solutions containing Co as a main matrix element. However, except for such cases, the acid solutions of Ag can be used as the calibration solutions for the determination of sub-ppm levels of Ag in Ni- and Co-base heat-resisting alloys.

3. Determination of Ag in the samples

Maximum sampling concentration of heat-resisting alloy was investigated by using MAR-M 246 Ni-base alloy. It was possible to dissolve the chips up to 1 g in 50 ml of the solution

Table 5 Effects of diverse elements on the relative absorbance of Ag in solutions containing Ni or Co as a main matrix element. (Ag added: 0.01 $\mu\text{g}/\text{ml}$)

(1) Ni

Wt% of diverse element	Relative absorbance									
	Without diverse element*	Al	Ti	Mn	Fe	Zr	Nb	Mo	Ta	W
5*	1.00	1.02	1.01	1.00	1.00	1.01	0.99	1.01	1.01	1.02
10*	1.00	1.01	0.99	1.01	1.00	1.02	0.98	1.04	1.02	1.01

(2) Co

Wt% of diverse element	Relative absorbance									
	Without diverse element*	Al	Ti	Mn	Fe	Zr	Nb	Mo	Ta	W
5*	1.00	0.99	0.92	1.02	0.97	1.01	1.04	1.03	1.04	1.01
10*	1.00	0.94	0.85	0.99	0.97	0.96	0.99	0.99	1.03	0.98

* Concentration of diverse element is 0.1X mg/ml and that of Ni or Co is (10-0.1X) mg/ml, where X means wt% of diverse element in solutions containing Ni or Co as a main matrix element.

Table 6 Comparison of the results obtained by the calibration curve method and the standard addition method.

Alloy	Concentration of Ag (ppm)		
	Calibration curve method	Standard addition method	Solvent extraction-flame AAS ⁽¹⁾
NBS 349	0.14	0.15	0.2
Inconel 738 LC	0.17	0.17	
MAR-M 246	0.04	0.04	
Udimet C0263	0.09	0.09	
NBS 168	0.89	0.91	0.9
WI-52	0.53	0.53	
Modified S-816	0.23	0.22	

(20 mg/ml). However, at higher concentrations, the precipitate was observed and the absorbance of Ag largely increased. The detection limit was 0.005 ppm on the basis of 1 g sampling, which was defined as the concentration of Ag in the sample that produced the absorbance twice the fluctuation of background.

Sub-ppm levels of Ag in Ni- and Co-base heat-resisting alloys were determined by the calibration curve method. Table 6 compares the results by this method with the results by the standard addition method, together with those by Burke⁽¹⁾. The results indicated that Ag could be determined with good precision by the calibration curve method. The method

described above is of course applicable to determine Ag in Ni or Co metal and in high-Ni or high-Co alloys. For example, Ag in high-purity Ni and Co sponge (Johnson Matthey Chemicals Ltd., JMC 891 and JMC 870, respectively) was determined to be 0.05 and 0.18 ppm, respectively, by this method.

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