Determination of traces of As, B, Bi, Ga, Ge, P, Pb, Sb, Se, Si and Te in high-purity nickel using inductively coupled plasma-optical emission spectrometry (ICP-OES)

S. Thangavel, K. Dash, S.M. Dhavile, A.C. Sahayam *

National Centre for Compositional Characterization of Materials, Bhabha Atomic Research Centre, ECIL-Post, Hyderabad-500062, India

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ABSTRACT

A method has been developed for the determination of traces of arsenic, boron, bismuth, gallium, germanium, phosphorus, lead, antimony, selenium, silicon and tellurium in nickel matrix. The sample was dissolved in $HClO_4$ ($\sim 150\ ^\circ C$) and nickel was settled as crystalline nickelperchlorate [$Ni(ClO_4)_2$] on cooling. The mixture was ultrasonicated and after the separation of $Ni(ClO_4)_2$, analytes of interest were determined in the supernatant using ICP-OES. Similarly, it was also found that, after the dissolution of nickel in perchloric acid, when the solution temperature was maintained at $\sim 100\ ^\circ C$, long needle like crystals of nickel perchlorate were formed. The crystals were separated from the mixture and trace elements in the supernatant were determined using ICP-OES. In both methods the matrix removal was $> 99\%$ and the recoveries of analytes were in the range 92–97%. The limits of detection for As, B, Bi, Ga, Ge, P, Pb, Sb, Se, Si and Te were found to be 0.18, 0.21, 0.07, 0.06, 0.25, 0.11, 0.09, 0.10, 0.17, 0.20 and 0.07 $\mu g\,g^{-1}$ respectively. The procedure was applied for the analysis of a standard reference material nickel oxide (SRM 761, Nickel Oxide No.1, NBS, USA) and the values obtained are in close agreement with the certified values.

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1. Introduction

Nickel base super alloys, by virtue of their excellent high temperature properties coupled with corrosion resistance, have been widely used in jet engine, gas turbine engine components where high strength at high temperature is needed [1,2]. The quality of nickel-base alloys is highly dependent on the amounts of trace elements present as the presence of trace elements has serious effects on the mechanical and physical properties of these high temperature alloys [3,4]. Among the impurities in nickel base alloys, low melting elements such as As, Se, Te, Pb etc. are detrimental to the strength of high temperature alloys even when present at very low concentrations [5]. Therefore it is essential to determine traces of these low melting elements (As, Se, Te and Pb) in nickel matrix.

Hydride generation atomic absorption spectrometry (HG-FAAS) and Hydride generation Inductively Coupled Plasma Optical Emission Spectrometry (HG-ICP-OES) are among the most sensitive techniques for the determination of traces of As, Se and Te [6,7]. However, due to the strong interference of nickel in hydride generation process, it is difficult to analyze nickel matrices for

low melting elements mentioned above by hydride generation [8,9]. In these techniques, the interference caused by nickel is minimized by masking the interferents [6,10] or by rapid hydride generation followed by fast separation of hydride from the liquid phase [11]. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a powerful technique for the trace multi-element analysis. The determination of traces of Te in alloys by ICP-MS suffers from severe non-spectroscopic interference when conventional pneumatic nebulizer was used for sample introduction. This problem was overcome by applying the vapor generation of Te and its introduction to ICP-MS [12]. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) methods were developed for the determination of selenium, tellurium in nickel after the matrix separation by reductive co-precipitation with palladium using ascorbic acid [13,14]. As per our knowledge, no single method has been reported to date for trace level determination of these impurities (As, Sb, Bi, B, Ga, Ge, Pb, P, Se, Si and Te) in nickel matrix.

Herein, a new method has been described for the determination of traces of As, Sb, Bi, B, Ga, Ge, Pb, P, Se, Si and Te in nickel matrix. The sample was dissolved in con.$HClO_4$ at hot condition and after cooling, the matrix (nickel) was separated from the sample solution either as crystalline precipitate or needle like crystals of $Ni(ClO_4)_2$. The crystalline precipitate was ultrasonicated

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* Corresponding author. Tel.: +91 40 27121365.
E-mail address: sahayamac@gmail.com (A.C. Sahayam).

to leach out the impurities from crystals and the concentration of trace impurities in the supernatant was measured using ICP-OES. In the second procedure, needle like crystalline $Ni(ClO_4)_2$ was prepared by maintaining the sample solution at $\sim 100\,^{\circ}C$ and the supernatant was analyzed for trace impurities by ICP-OES.

2. Experimental

2.1. Apparatus

A Horiba scientific model of ULTIMA-2 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used. The instrumental specifications are given in Table 1. A Bandelin model of SONOREX DIGITEC 35 kHz ultrasonic bath with heater (20–80 $^{\circ}C$) was used.

2.2. Reagent and standard solutions

Suprapur grade $HClO_4$ (70%,w/v) from Merck, Germany was used. Standard stock solutions of all the elements (1000 mg L^{-1}) were obtained from Merck, Germany. Working standard solutions were freshly prepared from these stock solutions as required.

2.3. Procedure

2.3.1. Matrix separation after precipitation of $Ni(ClO_4)_2$ followed by ultrasonication

Around 0.5 g of nickel sample was taken in a flat bottom quartz test tube of 25 mL capacity, 10 mL suprapur grade $HClO_4$ (70%,w/v) was added, the tube was covered with watch glass and heated over a hot plate at $\sim 150\,^{\circ}C$ (solution temperature) for 30 min. After the complete dissolution of the sample, the sample solution was allowed to cool to $\sim 60\,^{\circ}C$. Then the sample solution was sonicated at 50 $^{\circ}C$ (35 kHz) for ~ 40 min. After ultrasonication, the sample solution was taken out from the ultrasonic bath and cooled to room temperature and was centrifuged between 1000 and 1500 rpm and the supernatant was separated using a micropipette. Then the supernatant (~ 3 mL) was diluted to 25 mL and impurities present were measured using ICP-OES. If the concentration of impurities is not detectable, pre-concentration of impurities can be carried out by evaporating the supernatant on a hot plate (surface temperature of $\sim 130\,^{\circ}C$) in a fume hood till no more dense fumes came out from the sample solution. Then after cooling it was diluted to 10 mL using mill-Q water and the analytes were measured using ICP-OES.

2.3.2. Matrix separation after the formation of needle like crystals of $Ni(ClO_4)_2$

Around 0.5 g of nickel sample was dissolved in perchloric acid as described above. After complete dissolution of sample, the test tube was removed from the hot plate and temperature of the solution was maintained at 100 $^{\circ}C$ using Infra Red (IR) lamp (IR lamp was kept by the side with respect to sample solution). After the

appearance of needle like crystals, the sample solution was kept at this temperature for around 30 min. Then the IR lamp was switched off and allowed the solution to cool to room temperature ($\sim 25\,^{\circ}C$). The sample solution was carefully transferred into a clean 25 mL quartz beaker using a micropipette. Then the separated sample solution (~ 3 mL) was diluted to 25 mL and measured for the impurities using ICP-OES. To reduce the dilution factor, the separated sample solution could be diluted to 10 mL after the evaporation of excess $HClO_4$ as described in the above procedure.

3. Result and discussion

3.1. Role of $HClO_4$ on dissolution and separation of nickel

Nickel/nickel oxide reacts with con. $HClO_4$ (70%,w/v) at $\sim 150\,^{\circ}C$ (solution temperature) forming intense green color $Ni(ClO_4)_2$ solution. When this solution is allowed to cool $> 99\%$ of nickel is settled as crystalline form of $Ni(ClO_4)_2$. This unique property of $Ni(ClO_4)_2$ is utilized to separate the matrix for its trace element analysis. Due to high solubility of $Ni(ClO_4)_2$ in water, after the crystallization, any dilution of $HClO_4$ with water leads to redissolution of the matrix and decrease in matrix separation. Therefore, sample dissolution and matrix separation were carried out using concentrated $HClO_4$. The effective matrix separation was not affected when the concentration of $HClO_4$ is maintained $> 95\%$ (v/v). Any increased dilution of $HClO_4$ drastically increases the dissolution of $Ni(ClO_4)_2$ and leads to complete dissolution when the concentration of $HClO_4$ is $< 50\%$ (v/v). However, the matrix separation ($\sim 99\%$) was independent of the amount of $HClO_4$ (70%, w/v) used for the sample dissolution.

3.2. Ultrasonic extraction of analytes

Preliminary experiments were carried out for the separation of Ni as $Ni(ClO_4)_2$ precipitate and the recovery of analytes in the supernatant was found to be only 20–30%. Lower recovery of analytes could be due to the occlusion of the analytes during the formation of bulky molecule of $Ni(ClO_4)_2$ (~ 5 times the weight of nickel) precipitate. Therefore, after the precipitation of crystalline form of $Ni(ClO_4)_2$, ultrasonication was carried out to leach out the analytes from $Ni(ClO_4)_2$ precipitate. Even after the ultrasonication, the recovery of analytes was in the range of $\sim 80\%$. Increase in the temperature of the sample solution and ultrasonication bath lead to further improvement in recovery of analytes. However, it also leads to increase in the dissolution of $Ni(ClO_4)_2$ which resulted in poor matrix separation. Therefore these two parameters are required to be optimized. After the separation of nickel, a high concentration of $HClO_4$ remains in the sample solution requiring large dilution prior to the determination of impurities using ICP-OES which lead to poor limit of detection (LOD). Hence, to obviate large dilution, excess $HClO_4$ from sample solution needed to be evaporated. Due to hazardous nature of $HClO4$, it is very essential to optimize its amount to as minimum as possible.

3.3. Optimization of ultrasonic extraction of analytes

Based on the recovery of arsenic, ultrasonic extraction was optimized for each parameter, i.e., amount of $HClO_4$, temperature of the sample solution/ sonication bath and time duration of ultrasonication. To study the effect of amount of $HClO_4$ on matrix removal and analyte recovery, after the dissolution of sample, ultrasonication was carried out at a solution temperature of $\sim 60\,^{\circ}C$ and ultrasonic bath temperature of $\sim 50\,^{\circ}C$ for 30 min. The amount of $HClO_4$ was increased from 5 mL onwards (minimum 5 mL of $HClO_4$ is required for the dissolution of 0.5 g of nickel) in steps of 2 mL and when it was

Table 1
Operating conditions of ICP-OES.

Power	1.1 kW
Wavelengths (nm)	Se (196.090), As (197.198), Sb (206.833), Ge (209.426), P (213.618), Te (214.281), Pb (220.353), Bi (223.061), B (249.772), Si (251.611) and Ga (294.364)
Plasma gas flow rate	12.1 l min^{-1}
Nebulizer gas flow rate	0.83 l min^{-1}, concentrique nebulizer
Auxiliary gas flow rate	0.52 l min^{-1}
Solution uptake rate	2.0 mL min^{-1}