Interference correction in analysis of stainless steel and multi-element determination by glow discharge quadrupole mass spectrometry

Yu Xing *, Li Xiaojia, Wang Haizhou

Chemistry Department, Central Iron and Steel Research Institute, No. 76, Xueyuan Nan Lu, Beijing 100081, China

Abstract

Multi-element determination in stainless steel has been carried out by glow discharge mass quadrupole spectrometry (GD-QMS). According to the influences on relative intensity of analytical elements and their stability, glow discharge parameters such as current, voltage and pre-burn time were investigated. Mass interferences of analytical elements were researched, as well as appropriate isotopes were selected for analysis. Correction formulas were established for interfered isotopes of Ti and Mo. Fifteen elements in solid samples of stainless steel were directly determined, and the method has satisfactory accuracy and precision.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Glow discharge quadrupole mass spectrometry; Stainless steel; Interference correction; Multi-element

1. Introduction

The stainless steel is widely used in industry due to its excellent corrosion resistant performance. It has a large range of the category and composition since the variation of its application. In the practical analysis, it is necessary to establish a direct and accurate method to determine the multi-elements in stainless steel, on account of the high matrix effect, the serious interference between elements and the complicated chemical analysis process.

Glow discharge mass spectrometry (GDMS) is an efficient direct solid analysis method [1–6]. In the glow discharge, the atomization and ionization processes are separated in space and time, resulting in only minor variation in sensitivities, and little matrix effect [7]. The technique shows most of the ideal virtues [8,9], such as wide element coverage, rapid sequential multi-element determination capability at the major, minor, trace and ultra-trace concentration levels under the same operating conditions, superior detection limits and wide linear dynamic range.

Quadrupole mass spectrometers are typically more compact and less expensive than magnetic sectors, which result in the commercial availability of GD-QMS [10]. However, the low

resolution of GD-QMS makes it impossible to separate molecular ion interferences from analytical ions with the same nominal mass [11]. In practical application, GDMS is used to determine the high pure metal and semiconductor material [10,12–21], but seldom applied in steel analysis. In this study, 15 elements of stainless steel were determined by GD-QMS, and the sample analysis has obtained the satisfactory results.

As another important direct solid-state analytical technique, LA-ICP-MS, which is powerful, simple and fast, has been gained great development in recent years [22–24], and used for the analysis of high-purity metals, alloys, semiconductors and insulators increasingly [25]. The main problem of LA-ICP-MS is the serious matrix effect [26].

2. Experimental

2.1. Instrumentation

2.1.1. GD-QMS

A quadrupole GD-MS, Model GloQuad (VG Elemental, UK), is used for the analysis. The selected instrumental conditions are listed in Table 1. The system is operated in the direct current mode. The discharge gas is argon of 99.999% purity. The dual detector system utilizes an electron multiplier for ion counting for trace elements (ion currents $<3 \times 10^{-13}$ A) and a Faraday cup for the measurement of major and minor elements

* Corresponding author. Tel.: +86 10 62182481; fax: +86 10 62182584.
  E-mail address: yuxingnacis@yahoo.com.cn (X. Yu).

Table 1
Operating parameters

Parameters	Values
Discharge voltage (kV)	1.0
Discharge current (mA)	2.0
Argon gas flow rate (sccm)	19.6
Temperature during discharge (°C)	−162
Vacuum at quadrupole region (mbar)	5×10^{-7}
Resolution ($M/\Delta M$)	300

(ion currents $>3 \times 10^{-13}$ A). The peak jump mode is used for the data acquisition. A flat sample holder is used for the sample analysis, and the aperture is 10 mm in diameter. The GD cell in the instrument is cryogenically cooled with liquid nitrogen in order to minimize the residual gas contaminants and the interferences caused by C, N, O and hydrocarbons. The matrix's intensity should be tuned to a count rate of around 1 MHz by adjusting the lens stack to optimize the extraction and focus of the ions from the cell into the quadrupole system.

2.1.2. Mass calibration

A stainless sample (NBS C1154) was chosen for mass calibration using the strong and characteristic peaks at 14, 20, 36 (lower masses), 50–64, 80, 93 (mid masses), 181, 206–208 (higher masses). All of them are generated from nitrogen, argon, chromium, iron, nickel, niobium, tantalum and lead.

2.1.3. Collector calibration

The Faraday cup and electron multiplier detectors were cross-calibrated by measuring the signal intensity at mass 76 ($^{36}Ar^{40}Ar^+$). Detector calibration factor was adjusted to 3000 ± 200 as recommended by the manufacturer by adjusting the HT voltage to the electron multiplier before the scanning. The collector calibration was done with a mass step of 0.01 amu and 120 points in peak scan.

2.2. Samples

In this study, certified reference samples, such as NCS HS11709-1–NCS HS11709-7 (7 pieces), NCS HS23702-1–NCS HS23702-7 (7 pieces), 219-2, 221-4, NBS C1154, were used. Sample surface was polished by utilizing 6 μm diamond sandpaper. The polished surface should be washed with acetone to remove any surface contaminants and to present a dry surface prior to sample introduction.

2.3. Analysis procedure

Each sample was introduced into the GD system and evacuated to a vacuum of around 1×10^{-2} mbar prior to the analysis for the removal of surface atmospheric contaminants. A pre-burning time of 30 min was applied to all analysis to ensure to reach stable conditions for all elements. The sample NCS HS23702-6 was used for the optimization of the discharge conditions. The analytical measurements were carried out at a mass step of 0.01 amu with 120 points peak scan. Coarse integra-

tion time for Faraday cup (major and minor elements) was set as 40 ms and fine integration time for electron multiplier (trace elements) was set as 1 ms. Three scans for Faraday cup and 30 scans for electron multiplier were used for each measurement. More than 30 scans can be used for electron multiplier to improve the signal-to-noise ratio of the elements to be determined at ultra trace levels. Five repetitive measurements were recorded for each sample. The signal of $^{57}Fe^+$ was served as internal standard in analysis to reduce effects of difference among analytical samples and fluctuation of discharge conditions on analysis results. Elements were determined by using the isotopes ^{12}C, ^{27}Al, ^{31}P, ^{34}S, ^{48}Ti, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{75}As, ^{100}Mo, ^{118}Sn, ^{184}W, ^{208}Pb.

3. Results and discussion

3.1. Optimization of the discharge conditions

The quality of the determination results correlate directly with the parameters adopted in the experiment, therefore the influences of discharge current, voltage and pre-burn time on the relative intensity of analytical elements (intensity ratio of analytical element to matrix element Fe) and the stability of the relative intensity were investigated. The relative intensity is the average value of five repetitive measurements in a sample analysis without removing the sample from the instrument, and the relative standard deviation (R.S.D.) value is calculated from five repetitive measurements data (internal precision).

3.1.1. Discharge current

The discharge voltage was kept constant at 1000 V, and the discharge current was changed from 1 to 5 mA in turn by adjusting the flow rate of argon. Figs. 1 and 2 show that the relative intensity of analytical elements and the R.S.D. of relative intensity changed with discharge current.

The total trend is that the fluctuation of relative intensity of analytical elements is little, except Cr, when the discharge current is more than 2 mA; the values of R.S.D. reached the lowest point at 2 or 3 mA of discharge current, meanwhile the fluctuation range is wider and R.S.D. values are higher when the discharge current is at 1–2 and 4–5 mA.

The relative intensity is influenced by discharge current, discharge voltage, atom ionization energy, ion diffusivity and so
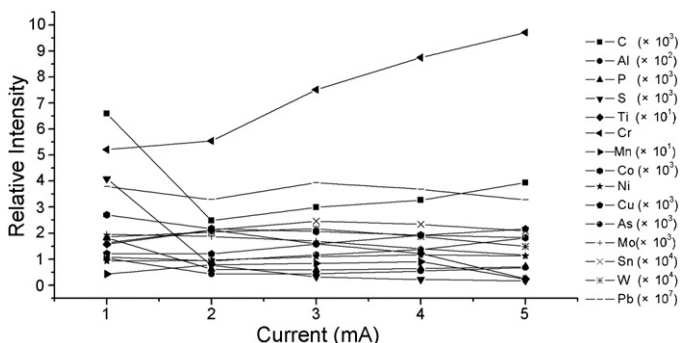

Fig. 1. Influence of discharge current on relative intensity of analytical elements.