Determination of Antimony in Steel by Differential Pulse Anodic Stripping Voltammetry at a Rotating Gold Film Electrode

Tatsuhiko TANAKA,[†] Takashi ISHIYAMA, and Kumi OKAMOTO

Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

A simple and rapid procedure is presented for the reliable determination of antimony in steel based on differential pulse anodic stripping voltammetry without any removal of iron matrix. Optimum conditions included a supporting electrolyte of 0.1 mol dm⁻³ nitric acid-0.1 mol dm⁻³ sulfuric acid, a pre-electrolysis of -0.5 V vs. the saturated calomel electrode for 300 s at a rotating gold film electrode, and subsequent stripping of the deposit on the electrode surface by a positive going potential scan at a rate of 40 mV s⁻¹. Antimony(V) was chemically reduced to antimony(III) by potassium iodide prior to voltammetric measurements. The interference of iron(III) was eliminated by simultaneously reducing it to iron(II) with the iodide. The generated iodine was reduced with L(+)-ascorbic acid. Arsenic(III), bismuth(III) and copper(II) interfered with the antimony determination severely. The proposed method has been successfully applied to the determination of antimony at the µg g⁻¹ level in steels within 50 min without any troublesome preconcentration steps using harmful chemicals. The detection limit (3σ) with a deposition time of 300 s was 0.19 ng cm⁻³ (1.6×10⁻⁹ mol dm⁻³).

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The accurate determination of antimony in steel is important to the steel industry, because grain boundary segregation of antimony causes the decrease in toughness of steel owing to the temper embrittlement. Spectrometric methods^{1,2} are commonly used for the determination of antimony in iron and steel, but they require a preconcentration procedure, which generally involves much skill, labor or time, and the use of toxic organic solvents such as toluene,¹ to avoid any interference from iron matrix. Furthermore, the methods exhibit poor sensitivity.

Stripping voltammetry is a powerful electroanalytical technique for the determination of trace antimony and has been extensively applied in studying antimony in various samples. It includes anodic stripping voltammetry (ASV) at mercury,³⁻²⁰ glassy carbon,²¹ gold film,²² and modified^{23,24} electrodes in acidic solutions, adsorptive stripping voltammetry with complexing agents such as triphenylmethane dyes,²⁵ catechol,²⁶ *p*-dimethylaminophenyl-fluorone,²⁷ or chloranilic acid,^{20,28} and potentiometric²⁹⁻³¹ or constant-current^{21,32} stripping analysis.

Only a few papers have been published to date on the stripping voltammetric determination of antimony in steels.³³⁻³⁵ Wang *et al.*³³ and Hofbauerova *et al.*³⁴ used ASV at mercury-based electrodes in a hydrochloric acid-alcohol medium for the determination of antimony in steels. Zhou *et al.*³⁵ developed 1.5th-order derivative linear-sweep adsorptive stripping voltammetry of antimony(III) complexed with morin (2',3,4',5,7-penta-hydroxyflavone) at a static mercury drop electrode. However, those methods involve a troublesome procedure such as filtration or require a time-consuming and laborious standard additions method because of removing interferences from coexisting elements. Furthermore, mercury, which is toxic and difficult to use, is employed exclusively as the working electrode.

The present paper describes a simple, rapid and accurate method for the direct determination of antimony at trace levels in steel based on ASV of antimony(III) at a gold film electrode

without any preconcentration step.

Experimental

Apparatus

Voltammetric determinations were performed using a BAS-50W electrochemical analyzer with an RDE-1 rotating disk electrode (Bioanalytical Systems, West Lafayette, IN, USA) and a BJC-240J printer (Canon, Tokyo, Japan). A platinum wire was used as a counter electrode. A saturated calomel reference electrode (SCE) was connected to a glass voltammetric cell (25 mm×22 mmφ) by a 4% agar-saturated potassium nitrate bridge.

Reagents

Kanto Chemicals "Ultrapure" grade mineral acids were used throughout, and other chemicals were of analytical-grade without further purification. Water was distilled from a vitreous silica sub-boiling still. An acid mixture solution was prepared by mixing one volume of 10 mol dm⁻³ nitric acid and one volume of 10 mol dm⁻³ sulfuric acid. Standard antimony(III) solutions were prepared daily by diluting a commercially available stock standard solution (1 mg cm⁻³ of antimony(III) in 2.5 mol dm⁻³ hydrochloric acid) to the desired concentration with the acid mixture solution.

Preparation of gold plated glassy-carbon electrode

The surface (7 mm² area) of a glassy carbon disk electrode (Bioanalytical Systems) was polished to a mirror finish with aluminum oxide sheets (1 and 0.3 µm particle size) and then rinsed with water. The electrode was plated in a 1 mol dm⁻³ hydrochloric acid solution containing 1 mg cm⁻³ of gold(III) and a small amount of nitric acid at -0.3 V vs. SCE for 180 s without stirring, a platinum wire serving as anode, and washed in water. In order to obtain reproducible voltammograms, the gold coating was removed from the electrode surface with a soft

[†] To whom correspondence should be addressed.

paper towel after each run, and then the electrode was plated again in the way described above.

Procedure

Approximately 1 g of a steel sample was weighed into a 100-cm³ Pyrex beaker and decomposed with 30 cm³ of the acid mixture solution on heating. After complete dissolution, the solution was boiled in order to expel nitrogen oxides. The solution was transferred to a 100-cm³ volumetric flask and diluted to the mark with the acid mixture solution. A 2-cm³ aliquot of the dilute solution was put in another 100-cm³ volumetric flask, and antimony(V) and iron(III) in the solution were reduced to antimony(III) and iron(II), respectively, by adding 20 cm³ of 4 mol dm⁻³ potassium iodide solution with gently shaking. After several minutes, 30 cm³ of water and 5 cm³ of 1 mol dm⁻³ L(+)-ascorbic acid solution were added in order to reduce the generated iodine, and then this solution was diluted to the mark with water.

A 3-cm³ aliquot of the sample solution (pH = *ca.* 0.5) was transferred in the voltammetric cell. The gold plated glassy-carbon electrode was rotated at 3000 rpm, and the solution was pre-electrolyzed at -0.5 V vs. SCE for 300 s to deposit elementary antimony on the electrode surface. The electrode rotation was then stopped. After a rest period of 10 s, the electrode potential was scanned from -0.5 to 0.1 V vs. SCE at a rate of 40 mV s⁻¹. A stripping voltammogram was recorded in the differential pulse mode, using a pulse amplitude of 50 mV, a pulse duration of 50 ms, and a pulse repetition time of 200 ms. The stripping peak area was measured, and the amounts of antimony were determined by reference to a corresponding calibration curve (peak area vs. antimony concentration) constructed with standard antimony(III) solutions containing 200 µg cm⁻³ of iron(II). All of the measurements were done at room temperature.

Results and Discussion

Selection of working electrode

Of the various electrodes (gold, glassy carbon and platinum) tried in the present work, antimony is soluble in gold, and so a gold film electrode was more suitable for the working electrode because of its excellent sensitivity and reproducibility and flatter background current curve.

A gold film was plated on the surface of the glassy carbon disk electrode in an unstirred 1 mgAu(III) cm⁻³ solution at -0.3 V vs. SCE for 180 s. The maximum stripping peak area of antimony(III) was obtained at plating potentials between -0.2 and -0.4 V vs. SCE. The peak area increased with increasing the plating time and started to level off after *ca.* 150 s, as is to be expected. Successive determinations on the same gold film resulted in poor repeatability in the antimony(III) stripping peak. Therefore, a fresh gold film should be coated before each ASV measurement in order to obtain reproducible voltammograms.

Reduction of antimony(V)

A nitric-sulfuric acid mixture was selected as supporting electrolyte. Hydrochloric acid, the most frequently used medium for steel analysis, was unsuitable, because the presence of chloride ions gave poorly reproducible peaks of antimony(III). Figure 1 shows the dependence of the peak area of antimony(III) on the concentration of the acid mixture solution. The peak area lowered at more than 3% of the acid mixture solution because of the incomplete reduction of the

Fig. 1 Dependence of the peak area of 20 ng cm⁻³ of antimony(III) on the acid mixture concentration in the solution containing 0.8 mol dm⁻³ of potassium iodide and 0.05 mol dm⁻³ of L(+)-ascorbic acid in the presence of 500 µg cm⁻³ of iron(II). Pre-electrolysis: -0.5 V vs. SCE, 300 s. Stripping: -0.5 to 0.1 V vs. SCE, 40 mV s⁻¹.

Fig. 2 Effect of the potassium iodide concentration on the peak area of 20 ng cm⁻³ of antimony(III) in the 2% acid mixture solution. Other conditions as in Fig. 1.

iodine with L(+)-ascorbic acid. A 2% acid mixture solution (0.1 mol dm⁻³ nitric acid-0.1 mol dm⁻³ sulfuric acid), which produced maximum peak areas, was used for further studies.

As only antimony(III) was reduced at the gold film electrode in the 2% acid mixture solution, preliminary reduction of antimony(V) to antimony(III) was necessary. Potassium iodide was most suitable for the reducing agent, and only a single well-defined stripping peak at around -0.12 V vs. SCE was obtained. The effect of the concentration of potassium iodide on the peak area of antimony(III) is shown in Fig. 2. The peak area increased with the iodide concentration, and 20 ng cm⁻³ of antimony(V) was completely reduced with more than 0.6 mol dm⁻³ of potassium iodide. The formed iodine interfered with the ASV determinations of antimony, so that it was re-reduced to iodide ion by adding L(+)-ascorbic acid. More than 0.1 mol dm⁻³ of L(+)-ascorbic acid caused the decrease in peak area (Fig. 3). Therefore, 0.8 mol dm⁻³ potassium iodide and 0.05 mol dm⁻³ L(+)-ascorbic acid were selected.

Fig. 3 Effect of the L(+)-ascorbic acid concentration on the peak area of 20 ng cm⁻³ of antimony(III) in the 2% acid mixture solution containing 0.8 mol dm⁻³ of potassium iodide. Other conditions as in Fig. 1.

Fig. 4 Relationship between deposition potential and the peak area of 20 ng cm⁻³ of antimony(III) in the 2% acid mixture solution containing 0.8 mol dm⁻³ of potassium iodide and 0.05 mol dm⁻³ of L(+)-ascorbic acid. Other conditions as in Fig. 1.

Optimization of ASV parameters

The best deposition potential was found at -0.5 V vs. SCE. At potentials more positive than -0.4 V vs. SCE, antimony(III) was not electrodeposited quantitatively, while at potentials less positive than -0.7 V vs. SCE, the sharp decrease in stripping peak area was due to the reduction of protons to form hydrogen gas at the electrode surface (Fig. 4). Figure 5 describes the variations in peak area with respect to the deposition time. The peak area was proportional to the deposition time up to ca. 30 min, and the surface of the electrode was completely covered by the deposits (metallic antimony) after 1 h. In the present work, ca. 16% of antimony was deposited on the rotating gold film electrode (3000 rpm) during 300 s, which yielded adequate sensitivity for antimony determinations. As expected, although the peak area increased with increasing the rotating speed of the electrode, at more than 4000 rpm the reproducibility of the ASV measurements became slightly poor.

Fig. 5 Progress of electrodeposition of 20 ng cm⁻³ of antimony(III). Other conditions as in Fig. 4.

Fig. 6 Effect of the scan rate on the stripping curve of 20 ng cm⁻³ of antimony(III). Scan rate: (a) 10, (b) 20, (c) 40, (d) 50, and (e) 100 mV s⁻¹. Other conditions as in Fig. 4.

The peak area of antimony(III) also increased with the scan rate (Fig. 6). The scan rates above 50 mV s⁻¹ led to broader and smaller peaks, so that it was impossible to determine trace amounts of antimony. The optimum scan rate was 40 mV s⁻¹. Since the peak width increased with decreasing the antimony(III) concentration, the peak height was not in proportion to the antimony(III) concentration. Therefore, the peak area, though somewhat troublesome to obtain, was used for the antimony determination.

Calibration

While the stripping peak for antimony(III) disappeared in the presence of iron(III), the presence of iron(II) only diminished the peak area of antimony(III). The addition of potassium iodide also served to reduce iron(III) to iron(II). The peak area of 20 ng cm⁻³ of antimony(III) remained constant over the concentration range 5 to 500 μg cm⁻³ of iron(II) (Fig. 7). At the presence of more than 1000 μg cm⁻³ of iron(II), a small peak appeared at around -0.2 V vs. SCE. At the moment, the

Fig. 7 Dependence of the peak area of 20 ng cm^{-3} of antimony(III) on the iron(II) concentration. Other conditions as in Fig. 4.

appearance of this peak has not been clearly explained. The maximum permissible concentration of iron(II) remained unchanged, even when potassium iodide and L(+)-ascorbic acid were added in large excess.

The calibration curve constructed in the presence of $200 \mu\text{g cm}^{-3}$ of iron(II) was linear up to at least 20 ng cm^{-3} ($1.6 \times 10^{-7} \text{ mol dm}^{-3}$) of antimony(III), with an RSD of ca. 3% for five measurements of $10 \text{ ngSb(III) cm}^{-3}$ (Fig. 8). The curve did not pass through the origin owing to the reagent blank ($0.51 \text{ ngSb(III) cm}^{-3}$) with a 300 s deposition time. The correlation coefficient and sensitivity (the slope of the calibration curve) were 0.9998 and $0.091 \mu\text{A V per ngSb(III) cm}^{-3}$, respectively. The curve was not identical with the calibration curve prepared in the absence of iron(II). The detection limit (3σ), calculated from repeated determinations ($n=10$) of a blank solution, was $0.19 \text{ ngSb(III) cm}^{-3}$. The proposed method can be applied to the determination of 2 to $4000 \mu\text{g g}^{-1}$ of antimony in steels for a deposition time of 300 s.

Interferences

In the determination of 20 ng cm^{-3} of antimony(III), 100-fold amounts of Al(III), As(V), Ca(II), Cd(II), Co(II), Cr(III, VI), Mn(II), Mo(VI), Nb(V), Ni(II), Se(IV), Si(IV), Ta(V), Ti(IV), V(V), W(VI), Zn(II), borate and phosphate; a 50-fold amount of Sn(IV); and a 5-fold amount of Pb(II) have no interference. However, the presence of 20 ng cm^{-3} of copper(II) lowered the peak area of antimony(III). Arsenic(III) and bismuth(III) also interfered severely, because the antimony(III) peak overlapped with the peaks of arsenic(III) and bismuth(III). The deaeration of the sample solution prior to the pre-electrolysis step was unnecessary.

Analytical applications

Two certified samples of steel were analyzed by the proposed method. The results summarized in Table 1 are in excellent agreement with the certified values, with a satisfactory precision. The interference from impurities in the present samples was negligible. The time required for the whole procedure was within 50 min.

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Fig. 8 Calibration curve in the presence of $200 \mu\text{g cm}^{-3}$ of iron(II). Other conditions as in Fig. 4.

Table 1 Determination of antimony in steel

Sample	Sb in sample / $\mu\text{g g}^{-1}$	RSD, %
JSS 172-7 (0.0022 mass%) ^a	21.5, 22.5, 22.1, 22.2, 22.3, 23.2, 23.4, 23.3, 23.3, 24.4 Av. 22.8	3.7
JSS 173-7 (0.0051 mass%) ^a	51.3, 54.3, 51.6, 52.8, 51.4, 51.7, 51.2, 50.9, 50.8, 51.4 Av. 51.7	2.0

JSS: The Iron and Steel Institute of Japan standard steel samples.

a. Certified values.

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