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Determination of Trace Amounts of Sulfur in Steels by Inductively Coupled Plasma Atomic Emission Spectrometry in the Vacuum Ultraviolet Spectral Region

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A simple and rapid method for the determination of trace amounts of sulfur by inductively coupled plasma atomic emission spectrometry in the vacuum ultraviolet region of the spectrum is described. For measuring sulfur lines in the vacuum ultraviolet region, the monochromator and the optical path between the plasma torch and the entrance slit have been purged with nitrogen to reduce light absorption by oxygen. In the determination of sulfur, three major sulfur lines at 180.73, 182.04 and 182.63 nm have been compared in terms of line-to-background intensity ratio, detection limit, background equivalent concentration and spectral interference. The detection limits obtained under the optimized experimental conditions are 0.92, 1.13 and 3.19 μgS/ml at S(I) 180.73, 182.04 and 182.63 nm, respectively. A sulfur atomic emission line at 180.73 nm has been by far the most suitable of the three lines because of its freedom from spectral interferences as well as its low detection limit. For accurate determination of sulfur, the use of closely matrix-matched standard solutions is recommended for the construction of analytical working curves for sulfur. The present method has been applied to the determination of sulfur in several steel standard reference materials without any prior-separation procedure. The results obtained are in good agreement with the certified values.

1. Introduction

Inductively coupled plasma atomic emission spectrometry (ICP-AES) continues to grow in popularity as a powerful analytical technique for a wide variety of samples owing to its simultaneous multi-element determination capability, low detection limits for most elements, large linear dynamic range, high tolerance to matrix effects and relative ease of operation. However, it has limitations for the determination of the non-metals including sulfur. The resonance lines of many of the non-metals lie in the vacuum ultraviolet (VUV) spectral region less than 200 nm. Observation of these resonance lines with conventional instrumentation is complicated by absorption of radiation by oxygen in the atomosphere and by the mirrors and/or windows employed in the optical transfer system.

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The ICP-AES technique has been used for the determination of sulfur (or sulfate) in water[1-5], brine[2], biological sample[6], polymeric materials[7] and coal products[8-10] by the measurement of sulfur emission intensity at 180.73, 182.04 and/or 182.63 nm mostly with the aid of a vacuum scanning monochromator or polychromator. To the knowledge, relatively little has been described on the determination of trace concentrations of sulfur in steel samples by ICP-AES without prior separation and/or pre-concentration procedures. This communication deals with the VUV ICP-AES determination of trace sulfur in several steel standard reference materials by employing a conventional monochromator with relatively low resolving power.

2. Experimental

2.1. Instrumentation

A Nippon Jarrell-Ash Model ICAP-50SM inductively coupled argon plasma emission spectrometer was employed in combination with a Rikadenki Model R-21 strip chart recorder. Specification of the instrument and the detailed description of the nitrogen-purged optical system for the VUV ICP-AES measurement, based on essentially the principle described by Kirkbright and co-workers[11], have been depicted in our previoius papers[12,13]. The nitrogen used to purge the optical system from the ICP source to the entrance slit of the monochromator and inside the monochromator installed with the photomultiplier tube (PMT) housing box was supplied from a cylinder of the compressed gas and its flow rates were continuously monitored and precisely regulated. The flow of nitrogen purge gas flowing both in the region from the ICP source to the monochromator and in the PMT housing box is referred to as the light cell purge gas flow[12,13]. This purge system permits extension of the operating range to the VUV spectral region between 170 and 190 nm.

2.2. Reagents

The stock solution of sulfur (1000 μgS/ml) was prepared by dissolving analytical-reagent grade sodium sulfate which was found to be somewhat preferable in terms of background-corrected sulfur emission intensity to ammonium sulfate. Standard sulfur solutions were prepared by dilution of the stock solution with distilled, deionized water (Milli-Q water). Sulfur-free high-purity iron metal (99.999% pure) was used to prepare matrix solutions. The content of sulfur in the iron metal was checked and found to be far below the detection limit of the present method. Other solutions of diverse elements were prepared from analytical-reagent grade compounds. Acids were added to match the standards with sample solutions. Nitrogen (99.99% pure) was used as a purge gas to reduce light absorption by oxygen.

2.3. Procedure

All emission intensities, when stabilized, are integrated at least triplicate over a fixed period of time. Background emission intensity, integrated over the same period of time, is subtracted from all line emission data to obtain the net line emission intensities. The optimized experimental conditions used throughout this investigation are summarized in Table 1. Some of the optimum operating conditions shown in Table 1 are discussed below.

3. Results and Discussion

3.1. Optimization of experimental conditions

In order to obtain a maximum line-to-background intensity ratio, I_n/I_b (I_n, net analyte emission intensity; I_b, background emission intensity) for the sulfur determination, a variety of operating parameters were investigated and optimized individually while the other parameters were kept at their optimum values. The parameters examined were radio-frequency (RF) power, analytical wavelength, observation position in the ICP, argon flow rates of coolant, plasma and carrier gases and nitrogen purge gas flow rates. Standard solutions with 10 μgS/ml were, unless otherwise stated, used to provide the best line-to-background ratios.

The vacuum ultraviolet sulfur emissions from a standard solution obtained with the nitrogen-purged monochromator and optical path were observed at 180.73, 182.04 and 182.63 nm. The net analyte intensity (I_n), line-to-background emission intensity ratio (I_n/I_b) and background equivalent concentration (BEC) expressed in μgS/ml obtained for major three lines of sulfur in the VUV spectral region are given in Table 2. All these sulfur lines at 180.73, 182.04 and 182.63 nm were used as analytical lines for optimization of the operating conditions as shown in Table 1. Nitrogen purge gas flow rates in the light cell and the monochromator were optimized precisely and are also described in Table 1. The optimized operating conditions shown in Table 1 were, unless otherwise noted, used for the remainder of this

Table 1 Optimized operating conditions for sulfur determination

Wavelength (nm)	S(I)180.73	S(I)182.04	S(I)182.63
RF power forward (kW)	1.3	1.2	1.2
Coolant gas flow rate (l/min)	16.0	16.0	16.0
Plasma gas flow rate (l/min)	0.5	0.4	0.4
Sample gas flow rate (l/min)	0.5	0.5	0.5
Observation height (mm) (above work coil)	16.0	16.0	16.0
Nitrogen purge gas flow rates			
Light cell (l/min)	6.0	6.0	6.0
Monochromator (l/min)	8.0	8.0	8.0

investigation.

3.2. Analytical working graph and detection limit

Under the optimized experimental conditions described in Table 1, analytical working graphs for sulfur at the three VUV lines investigated were established and

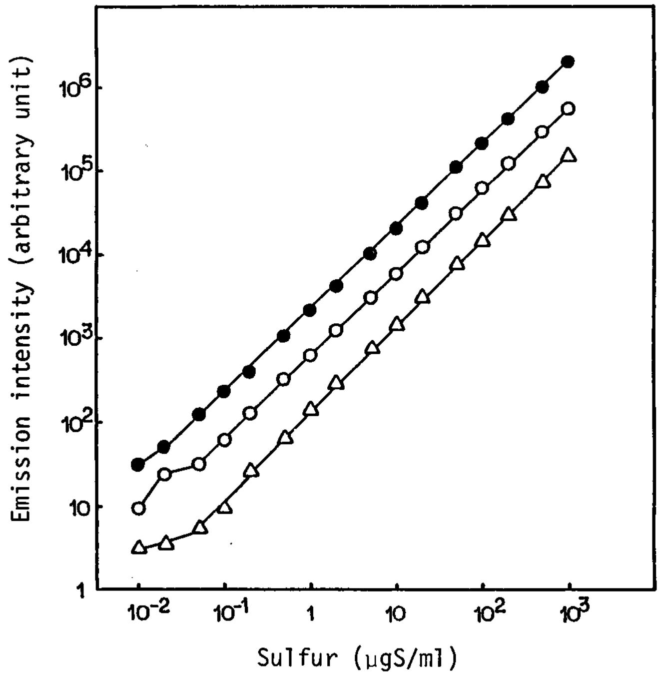

Fig. 1 Analytical working graphs for sulfur at (○) S(I)180.73 nm, (●) S(I)182.04 nm and (△) S(I)182.63 nm obtained under the optimized experimental conditions by VUV ICP-AES.

Table 2 Emission characteristics of major sulfur lines

Wavelength (nm)	I_n*	I_n/I_b*	BEC** (μg/ml)
S(I)180.73	1.00	1.00	0.92
S(I)182.04	0.96	0.81	1.13
S(I)182.63	0.39	0.29	3.19

* I_n = background-subtracted sulfur intensity, I_b = background intensity, relative to the I_n and I_n/I_b of the 180.73-nm line taken as 1.00.

** Background equivalent concentration.

Table 3 Comparison of detection limits for sulfur

Wavelength (nm)	Detection limit in pure water (μg/ml)	Detection limit in matrix	
		In 0.5% w/v iron (μg/ml)	In steel sample (μg/g)
S(I)180.73	0.024	0.061	12.2
S(I)182.04	0.036	0.062	12.4
S(I)182.63	0.11	—	—

— Not measured.

are shown in Fig. 1. Each data point in Fig. 1 is an average of at least five consecutive intensity measurements. The lowest quantitatively determinable concentrations of the analyte corresponding to the lower limits of the linear dynamic range were found to be approximately 0.05, 0.02 and 0.05 μgS/ml at 180.73, 182.04 and 182.63 nm, respectively.

Detection limits for sulfur were extrapolated from the linear parts of the analytical working graphs (Fig. 1). The detection limits reported here correspond to the concentration of the analyte required to give a net intensity, *i.e.*, background-corrected line intensity, equal to three times the standard deviation of the background in accordance with IUPAC recommendation[14]. The detection limits obtained at 180.73, 182.04 and 182.63 nm are shown in Table 3. Of the three sulfur lines investigated, a detection limit of the VUV line at 182.63 nm is by approximately one order of magnitude worse than those of the other two VUV lines. This may be partly due to the larger BEC values as compared with those of the other two lines, as shown in Table 2.

3.3. Interference from diverse elements

Under the optimized experimental conditions, spectral and matrix interferences at the sulfur lines even in the VUV spectral region that may be encountered during the determination of sulfur in various samples of steel are listed in Table 4. These have been characterized by scanning in the vicinity of each analyte emission line. A spectral interference can be obtained which is described by the relative intensity compared to 1.00 for sulfur (5 μg/ml) alone in the presence of diverse elements added at 100-fold ratio to sulfur and by the critical concentration ratio (CCR). The CCR is defined as a ratio of the concentrations of interferent to analyte, at which the ratio of the intensities of the interfering line and the analytical line within the spectral window of the analytical line is equal to unity[15]. Therefore, the smaller the CCR, the more severe the interference. The most severe interference was observed at S(I) 182.63 nm in the presence of boron. Boron gave an extraordinarily large spectral interference owing to spectral overlap of B(I)182.64 nm. These lines, S(I)182.63 nm

Table 4 Effect of diverse elements

Wavelength (nm)	Interfelent	Interfering line (nm)	R.I.*	CCR**
S(I)180.73	Ca	180.77	1.95	110
	Si	180.73+180.80	1.92	110
	Ti	#	1.95	110
S(I)182.04	Mo	181.97	1.75	130
	Si	182.03	1.96	100
	W	#	2.12	90
S(I)182.63	B	182.64	1040	0.05
	Ca	—	2.06	95
	Cu	182.54	1.97	100
	La	#	2.27	80
	Mo	#	1.96	100
	Pt	#	8.19	14
	Si	182.64	2.50	67
	Sr	—	1.96	100
	Ti	—	2.34	75
	W	#	2.06	94
	Y	#	1.93	110
	Zr	—	2.09	100

* Relative intensity in the presence of interferent (500 μg/ml), compared to 1.00 for sulfur (5 μg/ml) alone.

** Critical concentration ratio.

Interference from unknown line(s).

— No existence of interfering line(s).

and B(I)182.64 nm, could not be separated with the monochromator employed in this work. As a consequence, the use of S(I)182.63-nm line as an analytical one was abandoned for the continuation of this investigation because of severe spectral interference from boron frequently included in steel samples as shown in Table 3. However, even though most of spectral interferences from most elements can be circumvented by selecting the sulfur 180.73- and 182.04-nm lines, the presence of minor elements such as calcium, silicon, titanium, molybdenum and tungsten in the steel samples may cause more or less spectral interference with the sulfur determination. Therefore, the use of closely matrix-matched standards or the method of standard additions is highly recommended to compensate for these interferences which otherwise would produce an error in the analysis of such practical samples as steels used in this study.

3.4. Application of the VUV ICP-AES method to the determination of sulfur in several steel standards

The accuracy and precision of the present method were established by analyzing several steel standard reference materials. To this end, on the basis of the observations described above, the following procedure was examined and proposed for the determination of sulfur in some standard reference materials of mild steel, carbon steel and stainless steel, *i.e.*, British Chemical Standards (BCS) and Japan Standards of Iron and Steel (JSS) prepared and issued by Bureau of Analysed Samples Ltd. and the Iron and Steel Institute of Japan, respectively.

3.4.1. Effect of acids

In general, hydrochloric and nitric acids and a mixture of both acids are mostly used for dissolution of steel samples[16]. At first, therefore, the effect of hydrochloric and nitric acids in the range of 0.2−3.0 M on the ICP-AES intensity of sulfur was investigated. The relative emission intensity for sulfur was slightly decreased with an increase in acid concentration. There was little or no significant difference in the relative intensity between hydrochloric and nitric acids. The relative intensities for sulfur were 0.98, 0.95 and 0.90, relative to 1.00 for sulfur alone, in the presence of 1.0, 2.0 and 3.0 M hydrochloric or nitric acids, respectively. As a result, therefore, sulfur standard solutions should be matched to contain hydrochloric and/or nitric acids concentrations close to the levels expected in digested steel sample solutions.

3.4.2. Effect of matrix element

Furthermore, the effect of iron as a major matrix element in steel samples was examined in the sulfur determination. Recovery studies were made by adding known amounts of sulfur to the solution of 0.5% w/v iron prepared from high-purity iron metal and acidified with 0.8 M HCl and 0.8 M HNO_3. As a consequence, the mean recoveries of added sulfur was found to be 96.4 and 94.3% by using S(I)180.73- and S(I)182.04-nm lines, respectively. It can be concluded from these recovery data that the sulfur in steel standard reference materials can not be determined precisely by using a calibration curve constructed with simple sulfur standard solutions.

Next, analytical working graphs for sulfur at 180.73 and 182.04 nm were obtained in the presence of 0.5% w/v iron (0.8 M HCl and 0.8 M HNO_3). Linear dynamic ranges of the calibration graphs (not shown here) were in the concentration ranges of 0.1−5 μgS/ml with a correlation coefficient of 0.99989 and 0.2−10 μgS/ml with a correlation coefficient of 0.99883 at 180.73 and 182.04 nm, respectively. Detection limits obtained from the linear analytical working graphs obtained in the presence of 0.5% w/v iron are shown in Table 3.

3.4.3. Comparison of different digestion mixtures

In an attempt to select the most appropriate digestion mixture for dissolution of the steel samples used in this work, the sulfur in three selected steel standard reference materials (0.1-g sample) preliminarily determined by using ten kinds of

Table 5 Comparison of various digestion mixtures

Digestion mixture for 0.1-g sample	Sulfur content (μg/g)		
	BCS 452 (250)*	BCS 453 (340)*	BCS 454 (460)*
A: 6M HCl (5 ml)	125.8(2)**	223.0(2)**	297.3(2)**
B: 6M HCl/6M HNO_3 (2/1, 5 ml)	228.6(1)	315.7(1)	396.0(1)
C: 6M HCl/6M HNO_3 (1/1, 5 ml)	260.8(3)	346.6(3)	457.4(3)
D: 6M HCl/6M HNO_3 (1/2, 5 ml)	211.1(1)	302.0(1)	432.5(1)
E: 6M HNO_3 (5 ml)	204.2(2)	281.6(2)	306.3(2)
F: 6M HCl (8 ml)	97.2(1)	185.4(1)	301.3(1)
G: 6M HCl/6M HNO_3 (2/1, 8 ml)	243.9(2)	344.9(2)	446.2(2)
H: 6M HCl/6M HNO_3 (1/1, 8 ml)	248.5(6)	335.0(6)	457.5(6)
I: 6M HCl/6M HNO_3 (1/2, 8 ml)	246.3(2)	338.7(2)	449.7(2)
J: 6M HNO_3 (8 ml)	218.2(1)	271.2(1)	400.8(1)

* Certified value.

** Number of determinations.

digestion mixtures of hydrochloric and/or nitric acids. The results obtained at S(I) 180.73 nm by use of analytical working graphs constructed employing closely matrix-matched standard solutions are shown in Table 5. The digestion mixture H gave the best analytical results of the digestion mixtures investigated (Table 5). However, the digestion mixtures having higher concentrations in hydrochloric acid, typically the digestion mixtures, A, B, F and G, gave the worse analytical results as shown in Table 5. This probably results from the fact that the sulfur in the steel samples may be lost in its gaseous form (H_2S) during the sample digestion procedure, resulting in producing much lower results compared with the certified values.

Consequently, the digestion mixture H (Table 5) was used for dissolution of the steel samples in the following work.

3.4.4. Determination of sulfur in steel standard reference materials

Steel sample (0.1 g) was weighed out, transferred into a borosilicate glass beaker, dissolved in 8 ml of the digestion mixture H (Table 5) by heating gently on a hot plate, after cooling to room temperature, diluted to volume in a 20-ml calibrated flask with Milli-Q water and finally nebulized into the ICP source. For accurate determination of sulfur, closely matrix-matched standard sulfur solutions were used for construction of the analytical working graphs for sulfur measured at 180.73 and 182.04 nm, taking into consideration not only spectral interference from matrix element, *viz.*, iron, but also other kinds of interferences from hydrochloric and nitric acids. For a sample of stainless steel (JSS 653-3), a series of closely matrix-matched standard sulfur solutions were prepared and used, taking account of nickel and

Table 6 Determination of sulfur in several steel standard reference materials by VUV ICP-AES

Sample*	Sulfur content (μg/g)		
	Certified value	Present method**	
		S(I)180.73 nm	S(I)182.04 nm
BCS 452 (A)	250	248.5± 4.9 (6)	253.8±14.6 (6)
BCS 453 (A)	340	335.0±13.5 (6)	355.8±10.9 (6)
BCS 454 (A)	460	457.5±14.8 (6)	472.5±16.2 (6)
JSS 030-3 (B)	150	141.2±10.4 (7)	150.4± 8.7 (7)
JSS 050-1 (B)	130	127.7± 6.5 (7)	131.7±11.5 (7)
JSS 158-1 (B)	70	64.3± 5.9 (5)	79.6± 7.7 (7)
JSS 159-1 (B)	80	77.7± 3.6 (7)	87.9± 8.9 (7)
JSS 653-3 (C)	60	57.3± 5.3 (7)	87.5±11.1 (7)

* (A) : mild steel, (B) : carbon steel, (C) : stainless steel.

** The mean ± standard deviation (number of determinations).

chromium as well as iron. The results from the determination of sulfur in several standard reference materials of mild steel, carbon steel and stainless steel are summarized in Table 6. All the results obtained at S(I)180.73 nm are in excellent agreement with the certified values. However, all the results obtained at S(I)182.04 nm are somewhat higher than the certified values. This may result from another spectral interference of the minor constituents such as manganese and silicon whose concentrations in the sample solutions were not matched those in the sulfur standard solutions.

4. Conclusion

This investigation has demonstrated that trace amounts of sulfur in steels can be determined by inductively coupled plasma atomic emission spectrometry in the vacuum ultraviolet spectral region in combination with a simple nitrogen-purged optical system and a relatively low-resolution monochromator. Most spectral interferences from major and minor constituents such as iron, nickel and chromium have almost completely circumventerd by selecting the S(I)180.73-nm line as an analytical one. However, some spectral interferences at S(I)182.04 nm from such trace elements as manganese and silicon in the samples remain with use of the present ICP-AES instrument. These types of spectral interferences would be eliminated or minimized by using a higher-resolution ICP-AES system9,17).

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