DETERMINATION OF MANGANESE, NIOBIUM, PHOSPHORUS, SULFUR, AND
TITANIUM IN NIOBIUM-CONTAINING PIG IRONS BY INDUCTIVELY COUPLED
PLASMA EMISSION SPECTROMETRY

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A simple and fast analytical method has been established for the determination of Mn, Nb, P, S, and Ti in niobium-containing pig irons by inductively coupled plasma emission spectrometry. A vacuum spectrometer was used and the optical path between the spectrometer and plasma was purged with Ar. Samples for the determination of Mn, Nb, P, and Ti were dissolved in hydrochloric acid, nitric acid, and hydrofluoric acid. Samples for the determination of S were dissolved in the same acids after the samples had been mixed with potassium chlorate. Excessive hydrofluoric acid was masked by boric acid. Yttrium was added as an internal standard element.

Demand of Nb is increasing as an alloying element in steels, aerospace materials, atomic power plants, and superconductors. The greater part of Nb resources is produced in Brazil. There are a lot of complex iron ores which contain Nb in the Peoples' Republic of China. Niobium, however, remains in the pig iron which has been refined from the complex iron ore. Hence, it is necessary to determine Nb in the niobium-containing pig iron. Wet chemical techniques for the determination of Nb involve time-consuming and complicated separation procedures¹⁾²⁾. Inductively coupled plasma (ICP) emission spectrometry is suitable for the determination of Nb and was applied to the analysis of steels for Nb³⁾⁴⁾. Low alloy and high alloy steels were dissolved in aqua regia³⁾. Carbon steels were dissolved in aqua regia, sulfuric acid, and phosphoric acid. Tartaric acid was added after fuming the solutions to avoid the hydrolysis of Nb⁴⁾. Dissolution method is an important problem.

In the analysis of pig iron, C, Mn, P, S, Si, and Ti are essential elements to be determined. Of these elements, ICP emission spectrometry may be applied to the determination of Mn, P, S, and Ti. Manganese and Ti in irons and steels have often been determined by ICP emission spectrometry. Phosphorus suffers from spectral interferences from Cu and Fe at longer wavelengths⁵⁾⁶⁾, but P in steels can be determined without spectral interferences by using echelle monochromator, wavelength modulation, and lock-in amplification⁷⁾. Studies on the determination of P in irons and steels at shorter wavelengths are few⁸⁾⁹⁾, because the vacuum spectrometer and the purge of optical path with Ar or N₂ are necessary to measure the analytical wavelengths in the vacuum ultra-violet region. Sulfur in irons and steels has been scarcely determined by ICP emission spectrometry.

In the present study, Mn, Nb, P, S, and Ti in the niobium-containing pig irons have been determined by ICP emission spectrometry.

EXPERIMENTAL

Apparatus

An ICP source (Model Shimadzu ICPV-1000) was used under the operating conditions tabulated in Table 1. A polychromator, which was kept under a pressure below

Table 1 Operating conditions

Frequency (MHz)	27.12	
Output power (kW)	1.2	
Coolant gas ($\text{dm}^3 \text{ min}^{-1}$)	16	
Plasma gas ($\text{dm}^3 \text{ min}^{-1}$)	1.5	
Carrier gas ($\text{dm}^3 \text{ min}^{-1}$)	1.0	
Purge gas ($\text{dm}^3 \text{ min}^{-1}$)	4	
Sample uptake ($\text{cm}^3 \text{ min}^{-1}$)	2.3	
Observation height above coil (mm)	15	
Pre-sampling time (s)	60	
Integration time (s)	20	
Cleaning time (s)	60	
Wavelength (nm)	Mn II 257.61	Nb II 319.50
	P I 178.29	S I 180.73
	Ti II 334.94	Y II 371.03 ⁺

+ Internal standard element

0.13 Pa, was a Paschen-Runge mounting type (focal length, 1 m) with a grating of 2160 grooves mm^{-1} (linear dispersion, 0.46 nm mm^{-1}). The optical path between the spectrometer and plasma was purged with Ar. The widths of entrance and exit slits were 30 and 50 μm , respectively. A wavelength scanning controller (maximum, $\pm 1.0 \text{ nm}$) was installed. Argon carrier gas was moistened with water to avoid the clogging of the nebulizer. The Pyrex glass nebulizer used was of a concentric type. Sample and synthetic standard solutions were introduced into the plasma by an autosampler. Each solution was analyzed twice and the average value was used for the calculation. Internal standard method was used.

Reagents

Hydrochloric acid (35 %), nitric acid (60 %), hydrofluoric acid (46.5 %), boric acid, potassium chlorate, potassium dihydrogen phosphate, and ammonium sulfate were of analytical reagent grade unless otherwise mentioned. For the determination of S, hydrochloric acid and nitric acid of super special grade were used to decrease the reagent blank. High-purity iron was previously confirmed not to contain detectable amounts of Mn, Nb, P, and S. Titanium was detected in the high-purity iron and was corrected.

Stock standard solutions of Mn, Nb, and Ti ($1000 \mu\text{g cm}^{-3}$) were prepared from high-purity metals. Stock standard solutions of P and S ($1000 \mu\text{g cm}^{-3}$) were prepared

from potassium dihydrogen phosphate and ammonium sulfate, respectively. Working standard solutions of Mn and Nb were prepared by diluting the stock standard solutions with dilute acids. Working standard solutions of P and S were prepared by diluting the stock standard solutions with distilled water. Working standard solutions of Ti were prepared by diluting the stock standard solution with (1 + 1) hydrochloric acid to avoid hydrolysis.

Yttrium solution ($1000 \mu\text{g cm}^{-3}$) was prepared from high-purity yttrium oxide.

Proposed procedure

Determination of Mn, Nb, P, and Ti

Sample: Weigh 0.5 g of the chips of pig iron into a 100-cm^3 PTFE beaker. Cover the beaker and add 5 cm^3 of water. Add 12 cm^3 of a (5 + 5 + 2) mixture of hydrochloric acid, nitric acid, and hydrofluoric acid. Heat the solution on a hot-plate. After the complete dissolution, add 1.5 g of boric acid and dissolve it by gentle heating. Filter off the residue through Toyo Roshi No. 5B filter paper. Wash the filter paper with dilute acid containing 5 cm^3 of hydrochloric acid and 1 cm^3 of hydrofluoric acid in 500 cm^3 . Combine the filtrate and washings in a 100-cm^3 polypropylene volumetric flask. Add 10 cm^3 of Y solution and dilute the solution to 100 cm^3 with distilled water. Use this solution for ICP measurement.

Synthetic standard: Add appropriate volumes of the working standard solutions of Mn, Nb, and P to 0.5 g of the powder of high-purity iron. Follow the same procedures for the sample. Prepare Ti synthetic standard solutions separately to avoid spectral interferences from Nb.

Determination of S

Sample: Weigh 0.5 g of the chips of pig iron and 0.3 g of potassium chlorate into a 100-cm^3 PTFE beaker and mix them. Process the sample in the same manner for Mn, Nb, P, and Ti, but add 2 g of boric acid.

Synthetic standard: Weigh the powder of high-purity iron which is equivalent to the amount of iron in the sample and 0.3 g of potassium chlorate, and mix them. Add appropriate volumes of the working standard solution of S to the mixture. Follow the same procedures for the sample.

RESULTS AND DISCUSSION

Sample treatment and internal standard element

In the sample treatment, hydrofluoric acid was necessary to keep Nb in the solution. Boric acid was added to mask excessive hydrofluoric acid in order to prevent the nebulizer, chamber, and torch from being attacked. In the determination of S, potassium chlorate was added to oxidize S completely. Otherwise, lower S value was obtained in the sample. Internal standard method was more accurate and precise than constant-time integration method¹⁰). Internal standard element and analytes should behave similarly. Yttrium was chosen as the internal standard element. Yttrium 371.03 nm is an ionic line and the analytical wavelengths of Mn, Nb, and Ti are also ionic lines. Yttrium is absent in the niobium-containing pig iron and shows few spectral interferences. The analytical wavelengths of P and S are atomic lines, but P could be determined precisely by using the ionic line of Y internal standard element¹⁰).

Operating conditions

Conditions which show higher relative signal intensity and lower relative background equivalent concentration (BEC) were generally chosen by using synthetic standard solutions. Main points were as follows. Flow rate of purge gas was varied from 0 to 4 dm³ min⁻¹. The relative signal intensities of P and S, which have analytical wavelengths in the vacuum ultra-violet region, increased with purging the optical path with Ar. Observation height was varied from 5 to 20 mm above the coil. In the cases of P, S, and Ti, the relative signal intensities were higher at lower observation height. The lower observation height, however, produced less accuracy and precision because the plasma distorted and fluctuated owing to the purge gas. Output power was varied from 1.0 to 1.6 kW. The relative signal intensities of P and S increased with increasing output power, but the relative BECs of P and S also increased. Flow rate of carrier gas was varied from 0.7 to 1.2 dm³ min⁻¹. The relative signal intensities of P and S increased with decreasing flow rate of carrier gas, but the relative BECs of Nb, P, and S also increased with decreasing flow rate of carrier gas. Flow rates of coolant gas and plasma gas did not affect the relative signal intensities and relative BECs of the five analytes from 14 to 18 dm³ min⁻¹ and from 1.3 to 1.5 dm³ min⁻¹, respectively. The optimum operating conditions chosen for Mn, Nb, P, and Ti are shown in Table 1. The optimum operating conditions for S were the same as in Table 1.

Spectral interferences

Wavelength scan was carried out to investigate spectral interferences from the elements on the five analytes in the niobium-containing pig iron. Niobium interfered with Ti and the interferences were corrected by calculation. In addition, iron continuum background interfered with the analytical wavelength of S. The concentration of iron in the synthetic standard solutions should be equal to that in the sample solutions. The interferences from OH band on Nb 319.50 nm¹¹⁾¹²⁾ are corrected by synthetic standard solutions.

Effect of reagents

Effect of iron matrix on the relative signal intensities and relative BECs of the five analytes was studied from 0 to 10 mg cm⁻³. Little change of the relative signal intensities and relative BECs was found for Mn, Nb, P, and Ti. For the determination of Mn, Nb, P, and Ti, the change of sample uptake rate due to the difference in the iron concentration was corrected by the internal standard method. However, the relative signal intensity and relative BEC of S increased with increasing concentration of iron because of the spectral interferences. The volumes of hydrochloric acid and nitric acid were varied from 3.5 to 7 cm³ and from 3 to 7 cm³, respectively. The relative signal intensities and relative BECs of the five analytes were not affected in the range studied. The relative signal intensities of Mn, Nb, P, and Ti decreased slightly with increasing volume of hydrofluoric acid from 1 to 3 cm³. The relative signal intensity and relative BEC of S increased when the volume of hydrofluoric acid exceeded 2 cm³. The amount of boric acid was varied from 1 to 3 g. The relative signal intensities of Mn, Nb, P, and Ti were almost constant from 1.5 to 3 g, but the relative signal intensity and relative

BEC of S increased with increasing amount of boric acid. The amount of potassium chlorate from 0.1 to 0.5 g did not affect the relative signal intensity and relative BEC of S.

Effects of the concentration of Y on the accuracy and precision of the five analytes were investigated from 10 to 200 $\mu\text{g cm}^{-3}$ in the solutions of niobium-spiked standard pig iron. Good accuracy and precision were obtained in the concentration range studied for the five analytes. Yttrium did not form the precipitate of yttrium fluoride in the presence of boric acid.

Analytical application

The established analytical method was applied to the determination of Mn, Nb, P, S, and Ti in niobium-containing pig irons. Analytical results are shown in Tables 2, 3, 4, 5, and 6. Average value ($\bar{x}$), standard deviation (σ), and relative standard deviation ($100\sigma/\bar{x}$) were obtained from 8 independently dissolved samples. The results by ICP emission spectrometry agreed well with those by the other methods.

When the niobium-containing pig iron was dissolved, insoluble residue was formed. The residue on the filter paper was analyzed to check the possible carbides of Nb and Ti. Niobium was extracted as thiocyanate complex into MIBK and was spectrophotometrically determined at 388 nm¹⁾. Diantipyrylmethane complex of Ti was spectrophotometrically determined at 385 nm¹³⁾. As a result, Nb and Ti in the residue were negligible. Niobium and P formed precipitate when the sample contained more than 1 % of Nb and more than 0.5 % of P at a time. The precipitate was dissolved by washings. However, lower analytical values for Nb and P were often

Table 2 Determination of manganese in niobium-containing pig irons (%)

Sample	$\bar{x}$	σ	$100\sigma/\bar{x}$	Other method ⁺
1	0.015	0.001	6.8	0.017
2	0.11	0.002	1.4	0.11
3	0.50	0.003	0.60	0.50
4	1.00	0.004	0.35	0.99
5	1.96	0.005	0.24	1.96

+ Flame atomic absorption spectrometry

Table 3 Determination of niobium in niobium-containing pig irons (%)

Sample	$\bar{x}$	σ	$100\sigma/\bar{x}$	Other method
1	0.013	0.0008	6.1	0.015 ⁺
2	0.019	0.0011	5.9	0.019 ⁺
3	0.091	0.0017	1.9	0.090 ⁺
4	1.02	0.024	2.4	1.03 ⁺⁺
5	1.04	0.012	1.2	1.02 ⁺⁺

+ Phytin separation-sulfochlorophenol S extraction spectrophotometry

++ JIS G1237-1981: sulfochlorophenol S spectrophotometry

Table 4 Determination of phosphorus in niobium-containing pig irons (%)

Sample	$\bar{x}$	σ	$100\sigma/\bar{x}$	Other method
1	0.004	0.001	27	0.0042 ⁺
2	0.047	0.0022	4.6	0.047 ⁺
3	0.098	0.0015	1.5	0.098 ⁺
4	0.48	0.0018	0.38	0.46 ⁺
5	0.88	0.0058	0.65	0.85 ⁺⁺

+ JIS G1214-1980: molybdenum blue spectrophotometry

++ JIS G1214-1980: volumetric titration

Table 5 Determination of sulfur in niobium-containing pig irons (%)

Sample	$\bar{x}$	σ	$100\sigma/\bar{x}$	Other method ⁺
1	0.011	0.0013	11.7	0.014
2	0.017	0.0013	7.5	0.019
3	0.021	0.0016	7.7	0.022
4	0.057	0.0017	3.0	0.057
5	0.105	0.0019	1.8	0.105

+ Combustion-infrared absorption spectrophotometry

Table 6 Determination of titanium in niobium-containing pig irons (%)

Sample	$\bar{x}$	σ	$100\sigma/\bar{x}$	Other method ⁺
1	0.003	0.00014	4.4	0.003
2	0.008	0.00011	1.5	0.008
3	0.013	0.00016	1.3	0.012
4	0.058	0.0024	4.2	0.058
5	0.12	0.0049	4.1	0.12

+ JIS G1223-1981: diantipyrylmethane spectrophotometry

obtained because of the incomplete dissolution of the precipitate. In this case, the sample weight should be decreased to 0.1 g.

Detection limits were calculated from the concentration equivalent to twice the standard deviation of the background in 5 mg cm⁻³ of high-purity iron solutions (n = 8). Detection limits were 0.0003, 0.0010, 0.0012, 0.0021, and 0.0001 % for Mn, Nb, P, S, and Ti, respectively, in the niobium-containing pig iron.

The established analytical method was also applied to the analysis of 16 standard samples. Five pig irons, 5 cast irons, and 6 low alloy steels were used to extend the range to be covered. One per cent of Nb was spiked to 16 standard samples. Table 7 shows the results that the ICP values agree with the certified values for Mn, P, S, and Ti. Titanium in low alloy steels is not certified. Niobium in 16 standard samples was 0.99% with relative standard deviation, 1.1 %. Iron

Table 7 Determination of manganese, phosphorus, sulfur, and titanium in niobium-spiked standard pig irons, cast irons, and low alloy steels (%)

Sample	Type	Value	Mn	P	S	Ti
JSS 102-3	Pig iron	ICP	0.53	0.086	0.024	0.053
		Certified	0.54	0.089	0.024	0.054
JSS 110-6	Pig iron	ICP	0.48	0.085	0.046	0.049
		Certified	0.48	0.085	0.047	0.049
JSS 111-9	Pig iron	ICP	0.49	0.084	0.028	0.053
		Certified	0.48	0.085	0.030	0.053
JSS 112-3	Pig iron	ICP	0.17	0.078	0.017	0.041
		Certified	0.17	0.075	0.022	0.041
JSS 113-1	Pig iron	ICP	0.41	0.080	0.020	0.041
		Certified	0.40	0.077	0.023	0.040
NBS SRM 4i	Cast iron	ICP	0.79	0.13	0.053	0.029
		Certified	0.793	0.13	0.054	0.026
NBS SRM 5k	Cast iron	ICP	0.53	0.265	0.097	0.028
		Certified	0.536	0.263	0.099	0.028
NBS SRM 6f	Cast iron	ICP	0.49	0.518	---	0.061
		Certified	0.499	0.530	0.105	0.063
NBS SRM 7g	Cast iron	ICP	0.61	0.785	---	0.046
		Certified	0.612	0.794	0.060	0.044
NBS SRM 107b	Cast iron	ICP	0.51	0.059	0.067	0.018
		Certified	0.52	0.058	0.068	0.016
JSS 150-4	Low alloy steel	ICP	0.32	0.025	0.028	---
		Certified	0.31	0.026	0.030	---
JSS 151-4	Low alloy steel	ICP	1.52	0.024	---	---
		Certified	1.50	0.026	0.023	---
JSS 152-4	Low alloy steel	ICP	0.42	0.015	---	---
		Certified	0.42	0.016	0.022	---
JSS 153-4	Low alloy steel	ICP	0.83	0.017	---	---
		Certified	0.83	0.016	0.022	---
JSS 154-4	Low alloy steel	ICP	1.17	0.014	0.022	---
		Certified	1.16	0.014	0.019	---
JSS 155-4	Low alloy steel	ICP	0.28	0.022	---	---
		Certified	0.27	0.022	0.024	---

concentration in the synthetic standard solutions for S was 4.65 mg cm^{-3} , which was close to the average (4.68 mg cm^{-3}) of iron concentrations in 10 standard samples used. These results show that the complex cast irons and low alloy steels can be analyzed for Mn, Nb, P, and S by the above-mentioned synthetic standard solutions. This method was also applied to the determination of the other elements certified in the standard irons and steels shown in Table 7. As a result, Co, Cr, Cu, Mo, Ni, and V could be determined by the same synthetic standard solutions used for Mn, Nb, P, and Ti.

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Keyword phrases

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