Determination of Trace Nitrogen by Gas-Diffusion Flow Injection-Waveguide Capillary Cell Spectrophotometry

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Abstract:

A simple method for determining nitrogen in steel with high sensitivity has been developed by combining flow injection analysis (FIA) and waveguide capillary cell (WCC) spectrophotometry. A steel sample was decomposed by hydrochloric acid and turned into a sample solution. When the solution was made strongly alkaline, the nitrogen dissolved in the solution changed to gaseous ammonia (NH3). The ammonia was separated from the matrix through a porous membrane, reacted with a color reagent, and examined for light absorbance. The detector used was a WCC system capable of detecting light absorbance with high sensitivity. When four standard reference materials were analyzed by this method, the analyzed values agreed with the certified values. When two steel samples were analyzed by the proposed method, the analyzed values agreed well with the analyzed values of the steel samples by JIS methods.

1. Introduction

The remarkable progress of steel refining technology in recent years has allowed the manufacture of high-purity steel with a low concentration of impurity elements. For example, nitrogen, one of the impurity elements, has an adverse effect on the deep drawability of steel, an important property required of automotive steel sheet. The lowest nitrogen content of steel accomplished by refining was 30 µg/g in the 1970s, but is now 10 µg/g and is predicted to fall to 6 µg/g after the year 2000[1].

The inert gas fusion-thermal conductivity method, presently used as nitrogen process control analysis, lacks the analytical sensitivity to analyze steel samples with a nitrogen content of 10 µg/g or less. The wet analytical chemistry method specified in Japanese Industrial Standard (JIS) G 1228[2] guarantees analytical values to a nitrogen content of 5 µg/g. However, it is complicated to operate, calls for high skills, and takes more than 20 min of analytical time, so that it is not applicable to process control analysis. Improvement in the level of analytical techniques for trace components calls for the study and solution of many factors. These factors include optimization of sampling methods at the operating field, control and reduction of sample contamination during sample preparation before analysis, increase in sensitivity, accuracy and speed of analyzers, and reduction in blank and contamination. Conventional analytical methods are likely to be inadequate for improvement in productivity and development of new products. Thus, it is necessary to establish new analytical systems that are faster, simpler, and more sensitive than conventional methods.

A new method of analysis for trace nitrogen has been successfully developed by combining simple and accurate flow injection

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analysis (FIA) with ultrahigh-sensitivity waveguide capillary cell (WCC) spectrophotometry.

FIA is an analytical technique whereby addition, mixing, and reaction of samples and reagents are performed in a continuous flow in a capillary. It can analyze samples continuously and accurately. Since this analysis is conducted in a closed system, it excels in speed and simplicity, and involves little sample contamination from the surrounding environment. It also emits few spent solutions and imposes a low environmental burden. Under the FIA method a steel sample was dissolved in hydrochloric acid. Nitrogen present as NH_4^+ in the resultant solution was converted to the gaseous form NH_3 under a strongly alkaline environment. The NH_3 gas was separated by diffusion from a large amount of the sample matrix and reacted with a color reagent to form a chromophore[3-6].

WCC spectrophotometry is a technique to obtain high sensitivity by increasing the light path length in Lambert-Beer's law. When the capillary is filled with a solution whose refractive index is greater than that its material, it becomes a WCC of the optical fiber type with the solution as the core. That is, since light from a light source is transmitted by total reflection through the capillary with the solution as the core, the effective path length in spectrophotometry can be easily increased. As compared with a conventional spectrophotometer (cell length of 10 to 50 mm), sensitivity can be enhanced by a small factor up to a few hundred times. The capillary was made of tetrafluoroethylene-co-hexafluoro-propylene (FEP) with the refractive index $n_D = 1.338$[7]. Water with its refractive index ($n_D = 1.333$) lower than that of FEP cannot be used as solution, but acetone ($n_D = 1.357$) can be used if mixed with water.

Analytical parameters were examined in the new analytical method or FIA-WCC combination, and an analytical system was built. Certified ferrous reference materials were analyzed for nitrogen by the new method, and the analyzed values were confirmed to agree well with the certified values. When steel samples were also analyzed for nitrogen by the new method, it was confirmed that the analyzed values closely agreed with those measured by a comparable JIS method. The minimum limit of determination by the new analytical method was 0.4 µg/g, and the repeatability was 3% when samples with a nitrogen content of 2 µg/g were analyzed by the new method. This means that the new analytical method is sharply improved in both sensitivity and accuracy as compared with the conventional analytical method.

2. Experimental

2.1 Analytical system and conditions

The new analytical system is schematically illustrated in **Fig. 1**, and its measuring conditions are listed in **Table 1**. Reagents C_1 to C_4 are supplied by double-plunger pumps (Nihon Seimitsu Kagaku Co., Ltd., SP-D-2502U, SP-D-3201U, and NP-FX-3U). The solution sample is introduced into the flow path of the system at a constant rate of 0.5 mL with good reproducibility by a loop
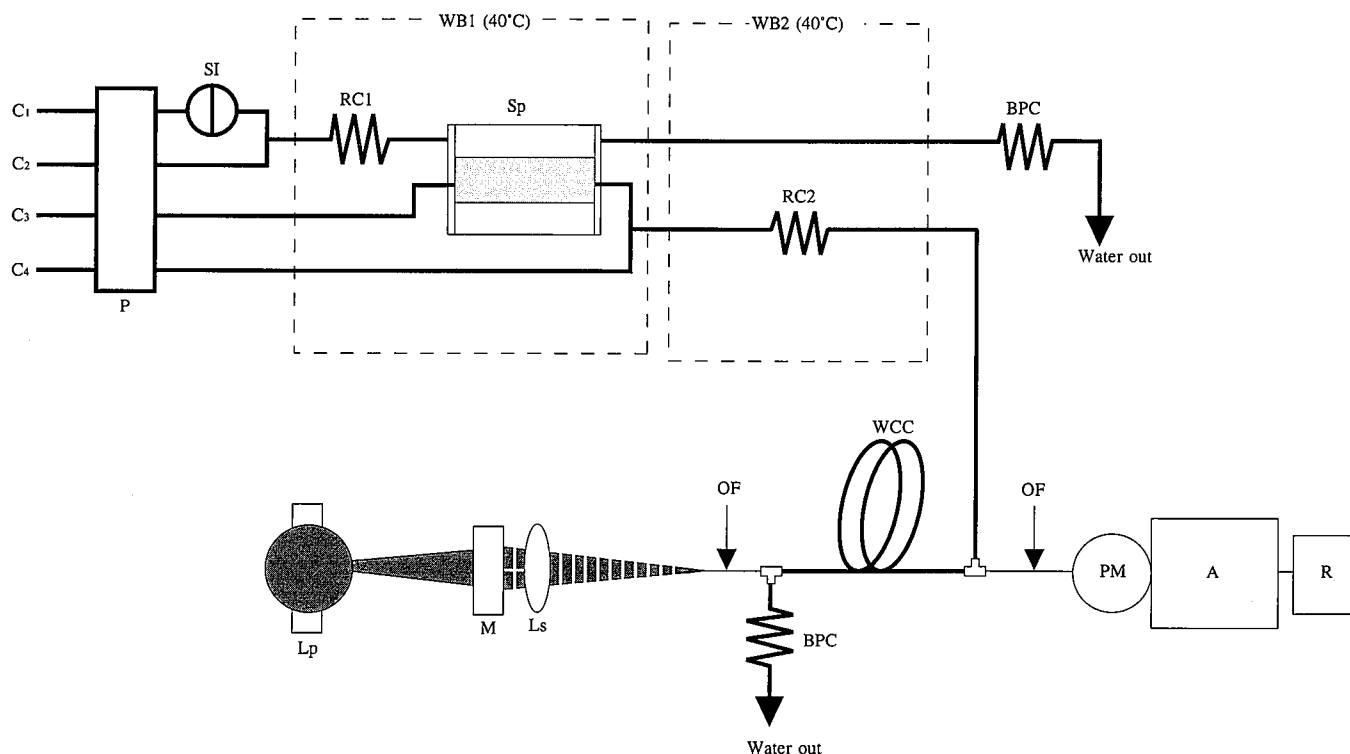
SI: Sample solution loop injector (0.5 mL); P: Pump; Sp: Gas-liquid separation membrane; WB1: Thermostat 1; WB2: Thermostat 2; RC1: Reaction coil (100 cm long, 0.5 mm ID); RC2: Reaction coil (300 cm long, 0.5 mm ID); BPC: Back pressure coil (300 cm long, 0.5 mm ID); WCC: Waveguide capillary cell (50 cm long, 0.68 mm ID, 1.18 mm OD); Lp: Xenon lamp; M: Monochrometer (732 nm); Ls: Lens; OF: Optical fiber; PM: Photomultiplier tube; A: Lock-in amplifier; R: Recorder

Fig. 1 Schematic diagram of system

Table 1 Measuring conditions

Reagent flow rate	C_1, C_2	0.4mL/min
	C_3, C_4	0.3mL/min
Reagent composition	C_1	Ultrapure water
	C_2	6mol/L NaOH, 150g/L tartaric acid
	C_3	NaOCl (effective Cl concentration 0.05%) 0.2mol/L NaOH
	C_4	0.5% a-naphthol, 45 (v/v)% acetone
Sample injection rate		0.5mL
Gas-liquid separation membrane length		30cm

injector. The injected sample is transported together with the carrier solution C_1 and mixed with the strongly alkaline solution C_2. Nitrogen present as NH_4^+ in the solution sample is converted to gaseous ammonia (NH_3).

The separation membrane[4,6] consists of the outer tube of glass (2.5 mm inside diameter and 30 cm long) and the inner tube of poly-tetrafluoroethylene (PTFE) formed into a porous membrane (2 mm outside diameter, 100 μm thick, and 1 μm pore diameter). NH_3 in the solution is separated from the matrix by the diffusion phenomenon, reacted with NaOCl in the solution to form monochloroamine, and absorbed in the C_3 solution. This monochloroamine reacts with a-naphthol in the C_4 solution and forms an indophenol-type blue color with an absorption wavelength of 732 nm through naphthoquinone chloroamine. Spectrophotometry using a-naphthol[8] differs from spectrophotometry using thymol blue, for example, in that it is little affected by the hydrogen ion concentration and allows reagents to be handled with greater ease[6]. The separation membrane and the mixing and reaction coils were maintained at constant temperature using thermostats, in order to prevent the diffusion separation and reaction from being influenced by the outside air temperature.

The WCC was connected by T-joints to the light introduction and sample solution discharge devices at one end and to the photo-detection and sample solution introduction devices at the other end. First, light of the 732 nm wavelength was extracted from the light source of a xenon lamp (Hamamatsu Photonics K.K.) by a monochromator (Shimadzu Model AT-100MD), sampled with an optical fiber (Ensign-Bickford Optics Model HR-S-FB400, 0.37 mm numerical aperture), and introduced into the FEP tube of the WCC. The light from the WCC was transmitted through another optical fiber and converted into voltage by a photomultiplier tube detector (JASCO Model DH-AP). The signal was amplified and printed on a recorder.

The flow path comprising the system was made of 0.5 mm diameter PTFE tubes and joints (Flon Industry Co., Ltd.), and the WCC was made of semitransparent FEP (Chukoh Chemical Industry Co., Ltd.) with an 0.68 mm inside diameter. The length of the WCC was set at 50 cm, providing sensitivity about 50 times higher than that of a conventional 10-mm flow cell specrophotometer.

2.2 Reagent and sample preparation

The four sample solutions C_1 to C_4 listed in **Table 1** were used. Commercial guaranteed reagents were used as chemicals for preparing reagents without distillation or other refining operations.

Solution C_1 as carrying steel sample solution: Ultrapure water with a minimum resistivity of 18.3 MΩ·cm was used.

Solution C_2 for converting NH_4^+ to NH_3: Ultrapure water was added to 240 g of NaOH and 150 g of tartaric acid to a volume of 1,000 mL. When the solution sample contains a large amount of

Fe as matrix, ferric hydroxide forms and settles in the strongly alkaline condition, severely interfering with measurement. Tartaric acid is added to mask ferric hydroxide. When tartaric acid is added to the sample solution, NH_3 as impurity in the tartaric acid is added to blank values. When tartaric acid is added to the solution C_2, NH_3 can be removed and vented beforehand.

Solution C_3 for absorbing NH_3: Ultrapure water was added to 8 g of NaOH and about 8 mL of NaOCl water solution (effective chlorine concentration of 0.05% or more) to a volume of 1,000 mL.

Solution C_4 containing color reagent: Five grams of a-naphthol were dissolved in 450 mL of acetone, and ultrapure water was then added to a volume of 1,000 mL. The amount of acetone added was changed in the experiment conducted to study the changes in light transmission and absorbance with the difference in the acetone concentration that greatly affects the light transmission and absorbance of the WCC.

Four steel samples with different nitrogen contents were used: three reference materials certified by the Iron and Steel Institute of Japan, or JSS 001-3, 003-3 and 366-4, and one European certified reference material, or ECRM 097-1. Two additional samples were used for comparative study with a JIS method. Each steel sample was accurately weighed to 1 g, pyrolyzed with 20 mL of 6 mol/L hydrochloric aid, and filtered with No. 5B paper. Ultrapure water was added to a volume of 100 mL, and the resultant solution was dispensed and used for measurement purposes.

3. Results and Discussion

3.1 Study of FIA parameter

The sensitivity of analytical methods utilizing continuous flow is intimately influenced by such factors as the solution transport speed, membrane separation efficiency, reagent mixing degree, and reaction time. An NH_4Cl water solution with a nitrogen concentration of 100 ng/mL was prepared and used as a test sample solution to study properties and optimize analytical conditions.

The experiment was basically conducted under the conditions listed in **Table 1**. The solution flow rate, thermostat temperature, and acetone concentration of the solution C_4 were changed. The effects of the parameters on the light absorbance and transmission were studied.

Fig. 2 shows the absorbance of the test sample solution when the test solution flow rate was changed and the WCC light transmission of the blanks. With the a-naphthol spectrophotometric method adopted in this study, the coloring reaction greatly proceeds for 0 to 10 min after the addition of the color reagent when the analysis is manually made on a batch basis[8]. From **Fig. 2**(a) it is evident that the absorbance increases with decreasing reagent flow rate. This may be explained as follows. Since the time during which the sample is mixed with the reagent and carried to the detector is prolonged, the effect of the resultant increase in the reaction time accelerating the color development surpasses the effect of the diffusion of the sample in the flow path broadening the peak. The net result is the increase in the absorbance. From **Fig. 2**(b) it is evident that the light transmission decreases with decreasing reagent flow rate.

The refractive index of the solvent depends on the absorbance and light transmission to a great extent. **Fig. 3** shows the absorbance of the solvent and the light transmission of the blank measured by changing the acetone concentration of the solution C_4 from 25 to 45% (v/v). Increasing the acetone concentration
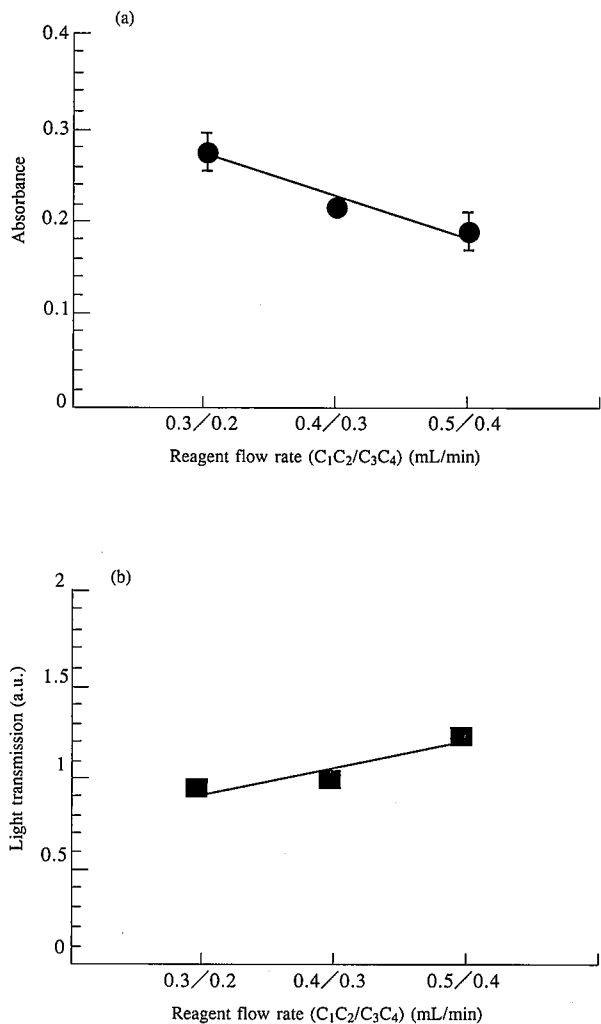
Fig. 2 Effects of reagent flow rate on absorbance (a) and light transmission (b)

Fig. 3 Effects of acetone concentration of reagent solution C_4 on absorbance (a) and light transmission (b)

markedly increases the light transmission and slowly decreases the absorbance. Given the stability of light transmission, the acetone concentration of the solution C_4 was set at 45% (v/v).

The gas diffusion separation efficiency and color development reaction are temperature dependent[4,8]. Thermostats 1 and 2 were installed in the sample-alkali mixing coil/gas separation membrane section and in the coloring reaction coil section, respectively. While one thermostat was held at a temperature of 40°C, the temperature of the other thermostat was raised in 5°C increments from 15 to 60°C. The absorbance and the light transmission of the blank in that process were measured. The results are shown in Figs. 4 and 5. When the temperature of the thermostat 1 was changed, the light transmission remained almost constant. That is, in the NH_3 formation/gas diffusion reactions, there occur no such phenomena as to diminish the light transmission. The absorbance increases at temperatures up to 25°C and remain practically constant at higher temperatures. The NH_3 formation/gas diffusion reactions are almost constant in the temperature range of 25 to 60°C. When the temperature of the thermostat 2 is changed, the light transmission decreases with increasing temperature. This
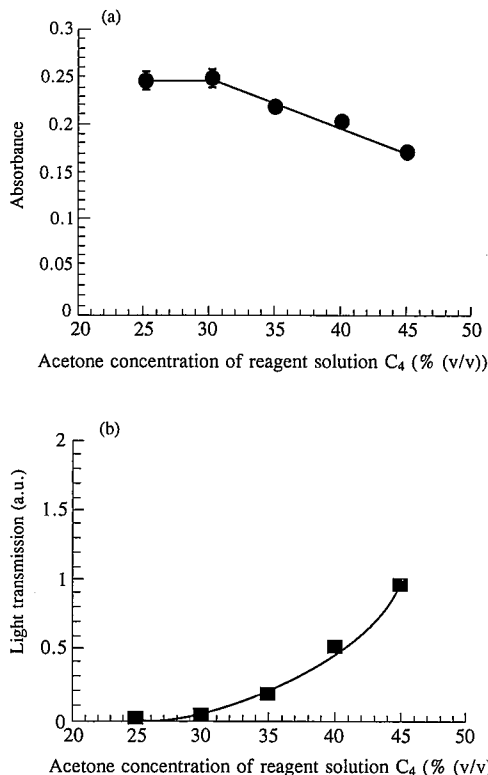
indicates that some phenomenon occurs that reduces the light transmission as the temperature of the reaction coil section rises.

The absorbance is practically constant regardless of temperature rise to 35°C, and decreases at higher temperatures. The formation of substances that obstruct the transmission of light, the change in the refractive index of the solvent with temperature and pressure, and the misalignment of the optical axis due to these physical changes are considered as factors responsible for changing the light transmission when the temperature of the thermostat 2 and the reagent flow rate are changed. It was confirmed that turbidity was clearly produced in the analysis spent solution both when the temperature of the thermostat 2 to promote the coloring reaction, and when the reagent flow rate were reduced. It was thus inferred that the coloring reaction formed some background material to interfere with the transmission of light. The variation of the light transmission with the temperature of the thermostat 2, irrespective of the change in the absorbance, can be attributed to the fact that the formation of the interfering material has its own time and temperature dependence. Given the ease of temperature control and the reproducibility of absorbance, the temperature of both thermostats 1 and 2 was set at 40°C for analysis of actual samples.

Experiments were performed by changing the separation membrane length to 15, 30, and 40 cm, but the absorbance and light transmission did not exhibit large changes. This means that the gas diffusion already reaches equilibrium when the membrane length is 15 cm. Under this method, the membrane length was set at 30 cm. The sample injection volume was varied from 0.2 to 2.0 mL. The absorbance increases as the sample injection volume increases to 1.5 mL but increases no further as the sample injection volume
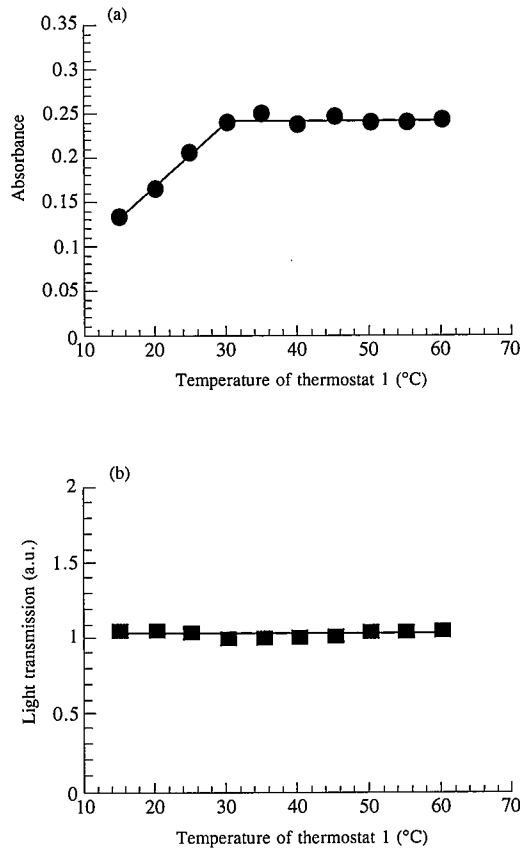
Fig. 4 Effects of temperature of thermostat 1 on absorbance (a) and light transmission (b)
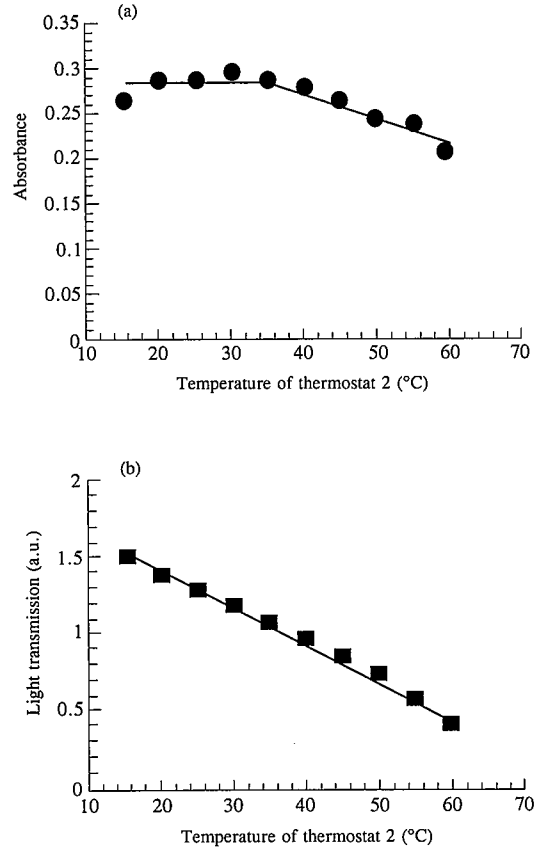

Fig. 5 Effects of temperature of thermostat 2 on absorbance (a) and light transmission (b)

exceeds 1.5 mL. The sample injection volume was set at 0.5 mL to determine nitrogen in a suitable concentration range.

3.2 Calibration curve

The correlation between the absorbance and the nitrogen concentration of an NH_4Cl water solution was studied in a nitrogen concentration range of 5 to 500 ng/mL. The results are shown in **Fig. 6**. An extremely good straight line with the correlation coefficient R of 0.999 or more was obtained as the calibration curve. When a solution with a nitrogen concentration of 5 ng/mL was analyzed, repeatability was 9% (n = 5).

3.3 Determination of nitrogen in steel samples

3.3.1 Analysis of certified reference materials for nitrogen

Four types of certified reference materials were analyzed for nitrogen. The analytical results are shown in **Table 2**. The measured values agree well with the certified values. When a sample with a nitrogen content of 2 μg/g was analyzed, repeatability was 3% (n = 3). When a conventional spectrophotometer is used as detection method for FIA, repeatability is about 7% (n = 5)[6]. More accurate results were successfully obtained by using WCC spectrophotometry as detection method for FIA.

3.3.2 Comparison with JIS method

The results of nitrogen determination by the new method were compared with those by a method specified in JIS G 1228 or titrimetry with sulfonamide after separation by distillation[2]. The JIS method used 10 g of steel sample for one analysis. The results are given in **Table 3**. The values measured by the new method agree well with those obtained by the JIS method and confirm
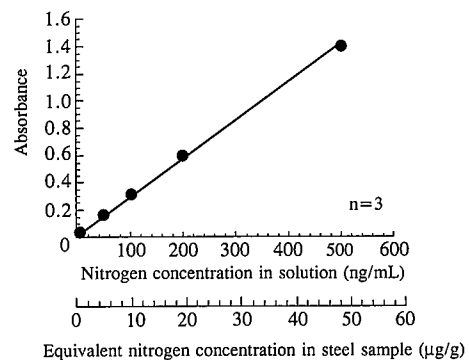

Fig. 6 Calibration curve for nitrogen

Table 2 Nitrogen in certified reference materials as determined by new method

(μg/g)

Certified reference material		Certified value	Value measured by new method (n = 3)
JSS	001-3	2*	2.7±0.1
ECRM	097-1	7	7.3±0.4
JSS	366-4	9	8.4±0.2
JSS	003-3	14	13.5±0.5

*Reference value

Table 3 Nitrogen in steel samples as determined by new method (μg/g)

Sample	JIS method (n = 3)	New method (n = 3)
Steel A	9±0.6	8.6±0.1
Steel B	11±0.6	12.0±0.3

Table 4 Comparison of new method with JIS method

	Steel sample weight	Analytical time	Detection limit[*1]
JIS G 1228 Ammonia distillation	–	–	–
Titrimetry with sulfonamide	5g	>11min	8μg/g[*2] 20μg/g[*3]
Spectrophtometry with bis(1-phenyl-3-methyl-5-pyrazolone)	4g	>40min	5μg/g[*3]
Spectrophotometry with indophenol blue	2g	>25min	5μg/g[*3]
Gas-diffusion separation FIA-WCC α-naphthol spectropho-tometry	1g	5min	0.4μg/g[*4]

[*1] Repeatability ≤ 15% [*2] ISO 10702 [*3] JIS G 1228-1994 [*4] BEC

that the new method is effective in determining the nitrogen content of steel samples. The new method has higher analytical accuracy than the JIS method and exhibits excellent determination capability for all the samples analyzed. The new method and the JIS method are compared in **Table 4**. The detection limit of the new method as determined from the background equivalent concentration (BEC) of the calibration curve is 0.4 μg/g, representing extremely high sensitivity as compared with the JIS method. The new method uses only 1 g of sample for one analysis and can analyze one sample in about 5 min as compared for 10 min or more for the JIS method.

4. Conclusions

Flow injection analysis (FIA) with a built-in gas separation membrane and spectrophotometry with a waveguide capillary cell (WCC) have been combined and applied for determination of nitrogen in steel. As compared with a JIS method in widespread use for the same purpose, the new method can automatically analyze steel samples for nitrogen. It is a simple and useful method for determining nitrogen in steel with fewer samples at higher speed, sensitivity, and accuracy.

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