

New Device of Continuous Flow System for Determination of Boron in Steel by Using Both Methods of Chemiluminescent Detection and Continuous Sample Flow Injection

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Abstract

For easy, rapid and economical analysis of steel sample, a continuous flow system was developed by both methods of chemiluminescence (CL) detection and continuous sample flow injection. The system was consisted of 4 channels and analytical time required was less than 30 sec and RSD was less than 2.8 % in 5 repeated runs by using the boron standard solution. Lower detection limit and range of determination were 3×10^{-7} M and from 1.0×10^{-6} M to 9.6×10^{-4} M, respectively. Selectivity of the proposed system was good and interference by another foreign compounds such as AlCl_3 and $\text{Ni}(\text{NO}_3)_2$ was negligible small in 1000 times higher concentration of their compounds to boron. In some real steel sample analyses, their determined values agreed with their certified ones, and then the reliabilities were less than 4.4 % in terms of relative error in 3 repeated tests. Additionally, concerning the background CL determination for real steel sample, the D-sorbitol solution should be changed to the purified water, since residual acid after the steel sample preparation might be existed in the system. Also, the steel sample solution should be adjusted to the higher pH than 4.

Keywords Continuous flow system, Continuous sample flow injection, Chemiluminescent detection, Boron, Steel

1. Introduction

New devices of FIA system based on a concept of *Analytical skill free technology* [1, 2] have been actively investigated to some industrial or welfare-scientific fields such as a steel industry [3-5] or a *universal design* technology [6, 7]. Thus active research work achievements were depending on many figure of merits concerning FIA and continuous flow system like FIA: as well-known, 1) FIA and the continuous flow system are automatically operated regarding many analytical procedures; 2) an easy and/or simplified conjugation to another sensitive detection tools is much possible; 3) the system design is very easy and economical and so on. As one of supporting technologies to compensate the decreasing of skilful analytical technicians, FIA needs based on *analytical skill free technology* have been being much acute and

intensive especially in steel industry.

A boron or molybdenum analysis in steel was successfully achieved by using high sensitive color reaction reagent [3], some fluorescent reagents [4, 5] and ICP detector [8] and so on. Thus obtained systems were also much contributed to *analytical skill free technology*, but there were some problems to be improved since their systems had both complicated design and/or operation and then were expensive and so on.

The authors have developed some simplified, sensitive and/or economical flow systems such as FIA by using a wide variety of chemiluminescence (CL in abbreviation) detections [9-12].

CL research works for boron were just reported concerning vapor-gas phase emission [13], CL solvato-chromic diode sensor [14] and solvent effect on CL reaction [15], but analytical applications to FIA and the

continuous flow system by using a CL detection for boron have been insufficient yet.

Based on the needs as described above, the authors studied on a development of flow system for an easy, simple, accurate and/or precise determination of boron at less than ppm levels. In this paper, furthermore simple, economical and sensitive continuous flow system by the CL detection method was reported for the boron determination in steel sample.

2. Experimental

2.1. Previous works

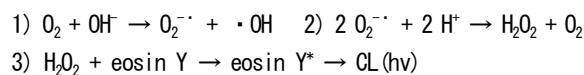
As well-known, in water phase at room temperature levels, boric acid and its derivatives easily and speedily produce a proton-dissociative complex having a cyclic ester structure through a reaction with cis-1,2-diol type sugar, and then hydrogen ion is stoichiometrically produced as the substituent. D-sorbitol of the cis-1,2-diol type sugar effectively produces the complex by a reaction with boron (H_3BO_3 ; $pK_a=9.24$ at $25^\circ C$) which is the most stable chemical species in the water phase condition.

A unique continuous flow system for boron was successfully constructed by using the CL reaction between hydrogen ion from the complex formation and alkali [19]. The system was consisted of 3 channels concerning the two for complex formation and the other for CL enhancement. However, since the system was affected by pH of the sample solution, 4 channels system was recommended for real sample analysis in stead of 3 channels one from the further detail investigation [20].

2.2. Principle of the determination

Boron was indirectly determined by a detection of hydrogen ion according to the following CL reaction scheme. Additionally, the detail CL reaction scheme between hydrogen ion and alkali (NaOH) was described in our previous reports [16–18]; that was, the CL between hydrogen ion and alkali was very weak, and then super oxide radical anion ($O_2^{\cdot -}$) played a key role for the CL production; since the weak CL should be enhanced with somewhat activation media for the analytical use, didodecyldimethylammonium bromide (DDAB) of cationic surfactant chemically producing a bilayer vesicle structure in water phase and eosin Y of xanthene dye (dye-sensitizer) were selected as the most efficient reaction media for the proposed system; The $O_2^{\cdot -}$ was also produced by a catalytic reaction of DDAB between dissolved oxygen and alkali, and then the $O_2^{\cdot -}$ reacted with hydrogen

ion to produce oxygen molecule and hydrogen peroxide as activator in the DDAB catalytic medium; finally, the hydrogen peroxide activator reacted with eosin Y and then the enhanced CL was observed through the energy transfer effect to eosin Y. Thus obtained CL scheme was as followed. Also, the possible CL mechanism model in DDAB and eosin Y media was shown in Fig. 1.



Through our previous works [16–20], the CL reaction environment was estimated to be arranged as both processes of production of super oxide radical anion and energy transfer to eosin Y could be efficiently carried out. The possible CL mechanism for the proposed system was finally as followed.

D-sorbitol + Boron → D-sorbitol/boron complex + hydrogen ion → hydrogen ion + alkali → Chemiluminescence ($h\nu$) → Xanthene dye sensitizer (Energy transfer) → Enhanced chemiluminescence ($h\nu$ detection)

Based on the CL detection method as described above, hydrogen ion (produced in sample site) and alkali should be placed to be separated each other; since the alkali/eosin Y/DDAB system was also produced to the weak CL by small amount of pollutive metallic compounds in the solvent water and/or reagents used, tetraethylenepent-amine (TEPA) of the metal scavenger was added into the system to decrease the CL till negligible small levels. Therefore, the line for the proposed system should be arranged as shown in Fig. 2.

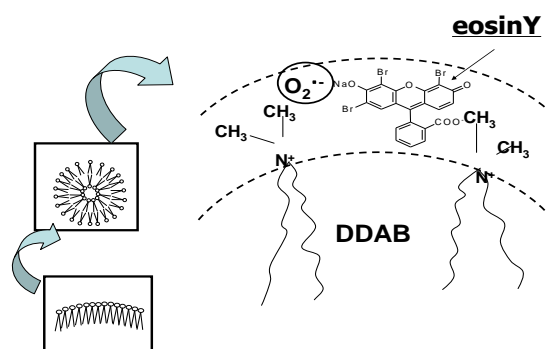


Fig. 1 Typical bilayer vesicle catalytic reaction model concerning the proposed chemiluminescence
DDAB: Didodecyldimethylammonium bromide.

2.3. Instrumentation

Based on the previous reports [17–20], an optimal flow system applicable to real steel sample analysis was devised as shown in Fig. 2. The parts of the proposed system was composed of the following tools. L₁–L₄: Flow lines (1

mm i.d., 2 mm o.d. Teflon capillary tubing), P: Pumps (SJ-1220, ATTO), M_1 - M_4 : Mixing coil (1 mm i.d., 2 mm o.d. and (M_1 : 2 m, M_2 : 1 m, M_3 : 5 cm) long Teflon tubing, D/R: Detector (PMT, R453, HAMAMATSU TV; Stabilizer, HTV-C448A; Electrometer, PM-18N, TOA DENPA; Recorder, VP-6531A, MATSUSITA DENKI).

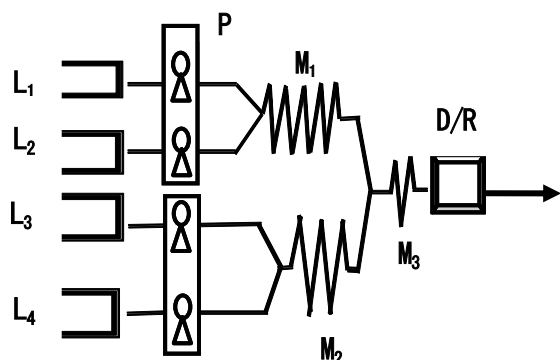


Fig. 2 The proposed continuous flow system

L_1 - L_4 : Flow lines, P: Pump, M_1 - M_4 : Mixing coils, D/R: Detector/Recorder. Recommended conditions: L_1 = Sample; L_2 = 1×10^{-3} M D-sorbitol; L_3 = 1×10^{-4} M Eosin Y, 2×10^{-3} M DDAB & 1×10^{-5} M Tetraethylenepentamine; L_4 = 1×10^{-3} M NaOH; Flow rate= 1.5 ml/min for each pump.

2.4 Reagents

All of reagents used were of analytical grade from Kanto Kagaku (Tokyo) and Wako Chemicals (Osaka). Stable 0.1 M or 0.01 M solutions of reagents were prepared and then diluted with distilled and deionized water from a water purifier (Tokyo Rikakikai, RO-10C type, Tokyo) before use. Unstable reagent solutions such as hydrogen peroxide were freshly prepared before use. Trisodium citrate recommended by M. Yamada et al. [21] was used as trapping reagent of foreign metallic compounds in steel sample.

2.4 Sample and preparation

Some steel samples were given from Dr./Prof. Kunihiko Watanabe of Tokyo University of Science. The identities (certified value of boron: m/m %) of thus obtained samples were JSS-No. 172-7 (0.0010), JSS-No. 173-7 (0.0041), JSS-No. 174-7 (0.0076), JSS-No. 363-1 (0.0027) and JSS-No. 364-1 (0.0045).

The real steel samples were prepared according to Yamane's procedure [4] as followed. 1) The steel sample of 1 g was weighted; 2) The sample was dissolved in quartz beaker with 10 ml of the aqua regia mixed solution of nitric acid - hydrochloric acid (1+3); 3) The sample solution was strongly heated till occurring white smoke

by using the 6 ml mixed solution of sulfuric acid - phosphoric acid (1+3); 4) After thus obtained sample was cooled down, it was adjusted to 50 ml with the purified water in polypropylene flask; 5) 50 ml of 0.30 M trisodium citrate was added to 20 ml of the obtained solution in Teflon beaker; 6) Thus solution was manually stirred for about 5 minutes with Teflon stick; 7) Residual acid in the prepared solution was neutralized with the 10 M ammonia solution and then the solution was adjusted to be higher pH than 4; 8) Finally, thus obtained solution was adjusted to 100 ml with the purified water in polypropylene flask.

3. Results and Discussion

3.1 Chemiluminescence profile

Typical chemiluminescence profiles observed with the proposed system were shown in Fig.3 concerning the background (BG : dotted line) and the sample (solid line). The stable profile usable for the analysis was obtained with both of highly S/N ratio based on low BG level and speedy response, since the analytical time required was less than 30 sec with the proposed system.

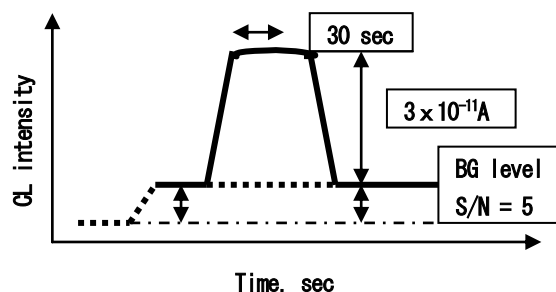


Fig. 3 Typical Chemiluminescent profiles for sample analysis and background determination with the proposed system

Experimental conditions: Sample, H_3BO_3 = ca. 3×10^{-6} M; Total flow rate = 6.0 ml/min. Dotted line: for background, Solid line: for sample.

3.2 Determination method

Boron in steel was determined by the following method. First, the BG-CL intensity was reduced from the total one in terms of current intensity (A) (see in Fig.3). Next, boron in the sample was determined by a calibration curve as shown in next section; that was, by the relationship between thus calculated CL current intensity (A) and molar concentration (M) of boron introduced. Additionally, in the case of real steel sample analysis, the D-sorbitol solution of flow line L_2 should be changed to the purified water for the BG-CL intensity observation.

3.3 Calibration graph

The experiments were performed in a range of higher pH than 4 based on the result of our previous reports [19, 20]. Also, the hydrochloric solution was used as the basic solution for pH control.

The calibration graphs obtained with the standard solution of boron was shown in Fig. 4 at three points of pH 4 to 6. All of the curves had good correlations and reproducibilities between the CL current intensity (A) and boron concentration (M). The RSDs concerning the calibrations were ranging from 2.4 to 2.8 in terms of %. Also, their lower detection limits and their ranges of determination were 3×10^{-7} M and from 1.0×10^{-6} M to 9.6×10^{-4} M, respectively. Thus obtained calibration curves were certified to be usable for the boron determination with the proposed system.

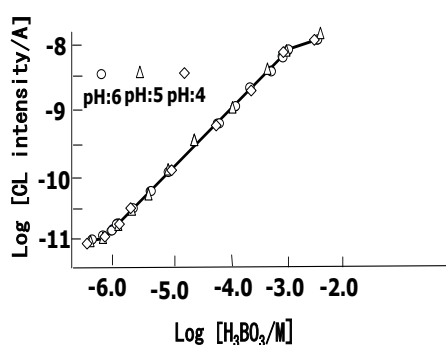


Fig. 4 Calibration graphs for boron determination

Experimental conditions: Same as in Fig. 2.

Table 1 Selectivity of the present CL reaction by the batch method

Species (1×10^{-4} M)	Relative CL [%]	Species (1×10^{-4} M)	Relative CL [%]	Species (1×10^{-4} M)	Relative CL [%]
H_3BO_3 (Reference)	—	$MgCl_2$	ND	$FeCl_3$	ND
$AlCl_3$	Trace	$Pb(NO_3)_2$	ND	$FeCl_2$	ND
$Cu(NO_3)_2$	Trace	$ZnCl_2$	ND	$K_2Cr_2O_4$	ND
$SnCl_2$	ND	$Co(NO_3)_2$	ND	$CdCl_2$	ND
$Mn(NO_3)_2$	ND	$Ni(NO_3)_2$	ND		

The test compound was dissolved in the 1×10^{-3} M D-sorbitol solution. ND: Not detected.

3.5 Interference

The investigation concerning the interference was performed to be similar to that of the selectivity. The experiment was carried out with the proposed system shown in Fig. 2. TEPA was not used for this experiment since the foreign ions used might be trapped by TEPA. Also, the test compounds were used to be dissolved in the 1×10^{-5} M H_3BO_3 solution.

As shown in Table 2, the interference concerning

3.4 Selectivity

Based on the results of our previous works [17–19] and considered to the steel sample component used, the selectivity was investigated concerning some metallic compounds probably occurring the CL reaction by using the proposed system. The experiment for selectivity study was performed with our usually use batch type CL analyzer [6], since the CL could be discussed in detail from a wide variety of observation interests. $20 \mu\text{l}$ each of 1×10^{-3} M D-sorbitol, 1×10^{-4} M test samples, 2×10^{-3} M DDAB, 1×10^{-4} M eosin Y, and 1×10^{-3} M NaOH for the experiment were introduced into the analyzer in order. Since the selectivity concerning hydrogen ion with the proposed CL system was reported in detail in our previous works [16–19], this investigation was performed through an observation of the complex formation to D-sorbitol. The result was shown in Table 1.

As shown in Table 1, the complex formation ability of boron to D-sorbitol was the highest, and then the second higher abilities of aluminum (III) and copper (II) were less than trace levels against that of boron in terms of the relative CL intensity (%). From this experiment, the proposed CL system was identified to be highly selective to the detection of boron.

listed compounds was less than 0.3 % in quenching in terms of relative error (%). The proposed system was applicable to the boron determination with negligible small interference, since the boron CL signal was not disturbed under the coexistence of tested foreign compounds in about 1000 times higher concentration to the 1×10^{-5} M H_3BO_3 solution. Additionally, the reason for their quenching CL signals were not clear now, but the authors guess either the solution pH environment or the complex formation

ability to D-sorbitol may be changed, since the proposed system was affected by the solution pH environment as

described below.

Table 2 Effect of some foreign metallic compounds on the CL intensity of boron

Species (1x10 ⁻⁴ M)	Relative error [%]	Species (1x10 ⁻⁴ M)	Relative error [%]	Species (1x10 ⁻⁴ M)	Relative error [%]
H ₃ BO ₃ (Reference)	—	MgCl ₂	- 0.2	FeCl ₃	- 0.2
AlCl ₃	- 0.3	Pb(NO ₃) ₂	- 0.2	FeCl ₂	- 0.1
Ni(NO ₃) ₂	- 0.2	ZnCl ₂	- 0.1	K ₂ Cr ₂ O ₄	0
SnCl ₂	- 0.2	Co(NO ₃) ₂	- 0.1	CdCl ₂	0

Experimental conditions: Same as in Fig. 2 except for none tetraethylenepentamine (TEPA).

3.6 pH effect

Since the determined value could be affected by the solution pH environment as described in our previous reports [19, 20], the pH effect was investigated in detail between pH of the sample solution and the CL intensity. The result was shown in Table 3 in comparison between both of the standard and the real steel samples. The operating condition was same as in Fig. 2. The standard solutions No. 1 and No. 2 were used as ca. 5x10⁻⁶ M H₃BO₃ and ca. 1x10⁻⁴ M H₃BO₃, respectively. The calculated values of the standard solutions in the Table were also shown in terms of a relative CL intensity concerning a (the response CL

intensity - the BG-CL intensity) value at each pH point vs. that of pH 6; that was, the relative value at each pH vs. the CL intensity (= 1) at pH 6. The calculated value in the real steel sample was shown in terms of a relative error (%) concerning the determined value vs. the certified one in 3 times repeated runs.

The lower pH of the sample solution shifted to strong acidic region, the higher the determined value by the proposed method was, including somewhat a CL enhancement effect; the reason was not clear now. As shown in the result, the proposed system was should be used in the weak acidic region of higher pH than 4.

Table 3 Effect of pH of the sample solution on the CL intensity of boron

Sample species	pH	6.0	5.5	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.0
Standard No. 1 (Reference)		1	1.04	1.00	—	1.00	1.20	1.20	1.40	1.60	1.70
Standard No. 2 (Reference)		1	1.00	1.01	1.00	1.00	1.01	1.02	—	1.04	1.06
Steel JSS-No. 174-7		1.3 %	—	1.0 %	—	1.3 %	—	19.7 %	—	34.2 %	—

3.7 Real sample analysis

The real steel samples were analyzed with the proposed system under the recommended operating condition (see in Fig. 2). TEPA was also added to the proposed system since the interference of another foreign compounds should be strictly excluded. The result was shown in Table 4. The determined values with the proposed system were shown in those of the three repeated tests.

As shown in Table 4, the determined values of real steel samples with the proposed system agreed with their

certified values. In higher boron content region of the test samples, the relative error against the certified value was a bit higher. The authors guess that this reason may be by what a CL behavior from the difference of the sample component tested. As the result, the proposed system was sufficiently applicable to the boron determination in real steel sample.

Table 4 Analytical result of some real steel samples by the proposed flow system

Sample	The proposed method (m/m %)	Certified value (m/m %)	Relative error [%]
JSS-No. 172-7	0.0010 ± 0.0001	0.0010	0.0
JSS-No. 173-7	0.0042 ± 0.0001	0.0041	2.4
JSS-No. 174-7	0.0079 ± 0.0003	0.0076	3.9
JSS-No. 363-1	0.0028 ± 0.0001	0.0027	3.7
JSS-No. 364-1	0.0047 ± 0.0002	0.0045	4.4

4. Conclusion

The continuous flow system with both methods of the unique CL detection and the continuous sample flow injection was successfully devised for the boron determination in steel sample. The proposed system had many figure of merits such as an easy and automatic operation, a simple and low cost design, a highly sensitive CL detection and a rapid, precise and selective determination usable for “analytical skill-free technology”. Also, the good analytical result was actually obtained in real steel samples, but the sample solution should be adjusted to the weak acidic region of higher pH than about 4. Additionally, the background observation in the real steel sample analysis should be performed by the change of the D-sorbitol solution to the purified water, since residual acid might be kept in the system after the sample preparation.

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