Flow Injection Simultaneous Determination of Copper and Iron in Lubricating Oil Using a New Spectrophotometer with Dual Light-Emitting Diode

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Abstract

A dual light-emitting diode-based spectrophotometer was newly designed for the determination of two components by a flow injection (FI) method. The FI system was demonstrated for the simultaneous determination of copper and iron in lubricating oil used for marine diesel engines. The chemistry relied on the complex formations of copper(II) and iron(II) with 2-(5-Bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)aniline (5-Br-PSAA). Copper(II)- and iron(II)-5-Br-PSAA complexes were detected at 560 and 710 nm. The analytical results obtained by the proposed method are compared with those obtained by inductively coupled plasma atomic emission spectrometry.

1. Introduction

Ferrography is one of techniques for analyzing particles present in lubricating oils used for various diesel engines. This technique is used to monitor wear condition for marine diesel engines [1]. Hashimoto *et al.* [2] measured wear metals such as copper and iron in the cylinder lubricating condition of two stroke marine diesel engine by ferrographic analysis. However, there is a limit to the information obtained by ferrographic analysis, for instance, chemical concentrations are unavailable.

Spectrometric oil analysis program (SOAP) is of importance for surveillance of various engines [3,4]. SOAP has been accomplished by the determination of wear metals in lubricating oils using mainly atomic absorption spectrophotometry (AAS) [5,6] or inductively coupled plasma atomic emission spectrometry (ICP-AES) [7,8]. However, these instruments are expensive and require skillful operators.

Flow injection analysis (FIA) reported by Ruzicka and Hansen [9] has become an important and versatile technique for a laboratory automation, and many simple, rapid, sensitive and reproducible procedures have been investigated in various fields [10,11]. FIA technique has been coupled with AAS [12, 13] and ICP-AES [14] for lubricating oil analysis.

UV-vis spectrometric methods represent the majority of FIA-based researches. In such cases, FIA systems are usually assembled for single element detection. However, some FIA methods for simultaneous determination of metal ions have been reported [15–18]. Sakai and co-workers have reported simultaneous spectrophotometry for copper and iron determination using 2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)aniline (5-Br-PSAA) by flow injection analysis [19]. The flow system consists of a double-beam

spectrophotometric detector with the double flow-cell. And also, we proposed a multi-compartment flow cell which allowed the simultaneous determination of copper, iron and zinc with a single injection and a double beam spectrophotometer [20,21].

In this paper, a dual light-emitting diode (LED)-based spectrophotometer is newly designed, and the applicability is demonstrated for the determination of copper and iron in lubricating oil used for marine diesel engines.

2. Experimental

2.1. Reagents

All reagents used were of analytical-reagent grade, and de-ionized water purified by a Milli-Q PLUS system was used throughout.

Stock standard solutions (10 mg L^{-1}) of copper and iron were prepared by suitable dilutions of commercially available 1000 mg L^{-1} copper and iron standard solutions for atomic absorption spectrometry (Wako, Osaka) with 0.01 M hydrochloric acid. Working solutions were prepared daily by diluting the solutions with 0.01 M hydrochloric acid.

5-Br-PSAA and ascorbic acid solutions were prepared according to the reference [19].

2.2. Apparatus

The manifold of the flow injection system is represented in Fig. 1. Two double-plunger pumps were used to pump the carrier (0.01 M HCl), reagent (2×10^{-3} M 5-Br-PSAA, pH 4.2) and ascorbic acid (5×10^{-3} M, pH 4.2) solutions. The flow rate of pump 1 was 0.9 mL min^{-1} and that of pump 2, 0.3 mL min^{-1}. The sample volume was 100 µl. The reaction coils 1 (1.5 m long) and 2 (5 m long) were made with 0.5 mm i.d. Teflon tubing. The reaction temperature in reaction coil 2 was set at

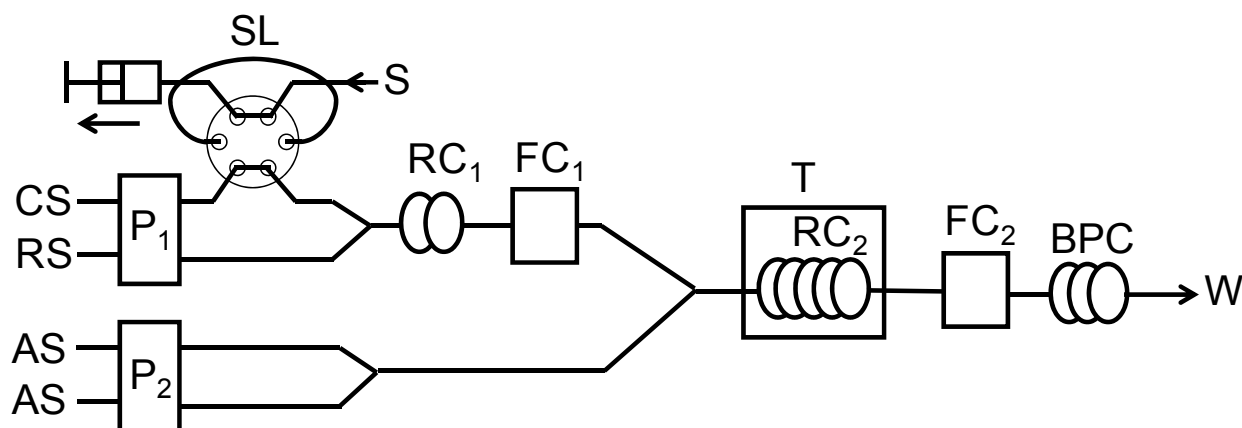*Corresponding author.
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Fig. 1 Schematic diagram of the flow injection system. CS, carrier solution (0.01 M HCl); RS, reagent solution (5-Br-PSAA, pH 4.2); AS, ascorbic acid (pH 4.2); P_1, pump 1 (0.9 mL min^{-1}); P_2, pump 2 (0.3 mL min^{-1}); SL, sample loop (100 µl); RC_1, reaction coil 1 (0.5 mm i.d., 1.5 m long); FC_1, flow cell 1(560 nm); RC_2, reaction coil 2 (0.5 mm i.d., 5 m long); T, temperature control unit (50°C); FC_2, flow cell 2 (710 nm); W, waste.
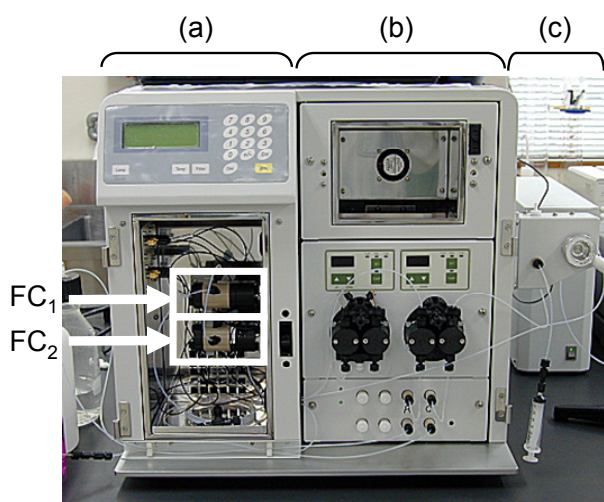

Fig. 2 Front view of the flow system. (a), newly designed spectrophotometer equipped with two LED-based flow cells; (b), pumps with degassers; (c) injector.
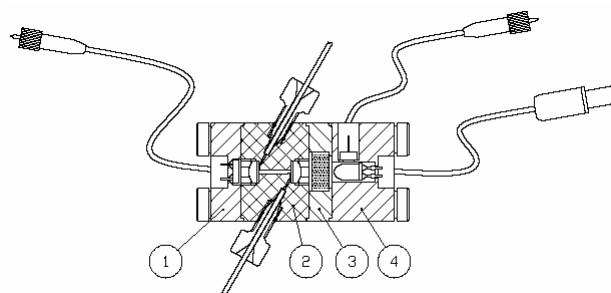

Fig. 3 Light emitting diode-based flow cell. (1), photodiode; (2), cell unit; (3), filter; (4), light-emitting diode.

50°C. The detection wavelengths were 560 nm for the flow cell 1 (FC_1) and 710 nm for the flow cell 2 (FC_2). As depicted in Fig. 2, one box unit containing two double-plunger pumps, a degassor, a reactor with air thermostat (30–70°C), a sample injector and an air thermostat with two flow cells was manufactured and the conditions for measurements are selected on the programming panel. The box size lengths including two pumps, sample injector and LED-based detector are 530(W), 418(H), and 440(D) mm and the weight is 32 kg. The size lengths of the LED-based detector are 200(W), 200(H) and 250(D) mm.

2.3. Procedure

In the flow system as shown in Fig. 1, an aliquot (100 µL) of standard/sample solution is introduced into the carrier stream (CS) by a six-way injection valve. An injected sample merges with the reagent solution (RS) buffered at pH 4.2, and copper(II)-5-Br-PSAA complex is detected at FC_1. The sample zone then merges with the ascorbic acid solution (AS) to detect the absorbance of iron(II)-5-Br-PSAA complex at FC_2. As such,

two peaks are obtained by a single injection.

3. Results and discussion

3.1. New spectrophotometer

In this study, a newly designed detector was developed. The proposed detector consists of two small flow cells with LEDs as the light sources. Each signal can be independently detected by each photodiode. The uses of LEDs and photodiodes make it possible to design a compact detection system. The flow cell configuration is illustrated in Fig. 3. Each flow cell consists of photosensor unit, flow cell unit, wavelength selecting unit and light source unit. The light sources were a white LED for copper detection and a red LED (700 nm with a half bandwidth of ±12 nm) for iron. The measuring wavelengths at 560 and 710 nm were selected using each interference filter which has a half bandwidth of ≤15 nm with a center wavelength tolerance of ±3 nm. The flow cell unit with 20 mm light path is made of PEEK. The output signals from reference and sample can be detected by each photodiode. The flow cells are set in the air
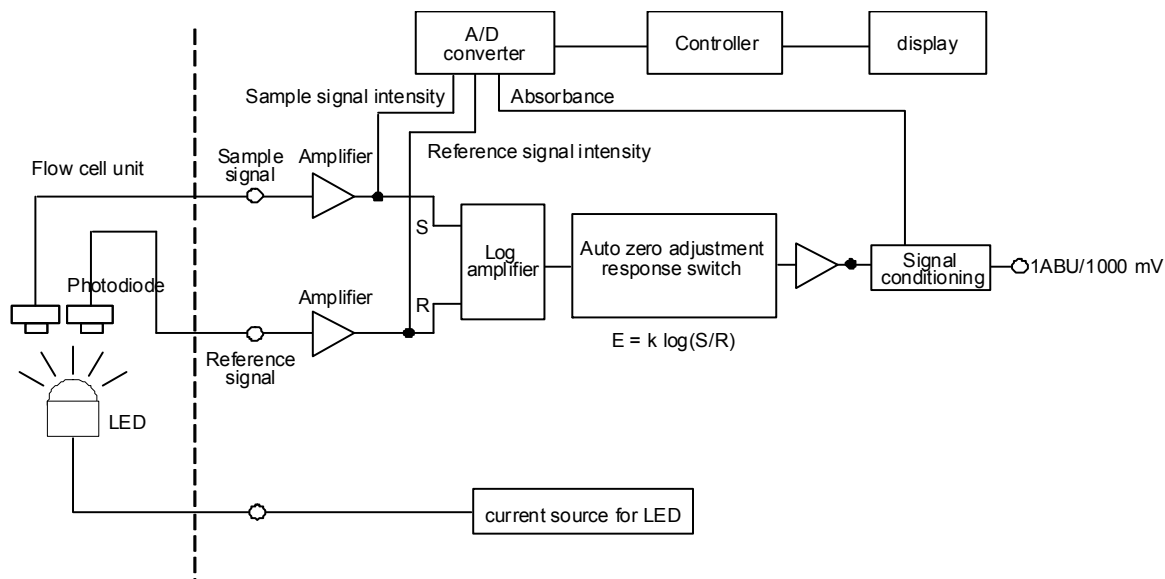
Fig. 4 Electronics of the spectrophotometer.

Table 1 Analytical performances of this work and a previous work [19]

		Limit of detection / μg L^{-1}	Relative standard deviation / % (n = 5)	Sample throughput / h^{-1}
This work				12
	Copper	0.77	1.0[a]	
	Iron	0.85	0.59[a]	
Ref. 19				12
	Copper	1.00	0.60[b]	
	Iron	1.00	0.99[b]	

a. Each tested metal concentration was 25 μg L^{-1}.
b. Each tested metal concentration was 30 μg L^{-1}.

thermostat with Pertier element to obtain stable absorbance. The electric of the detector is illustrated in Fig. 4. Each electric signal produced by photodiode is amplified by low noise amplifier and then converted into absorbance unit by log amplifier.

3.2. Analytical performances

In a previous paper [19], chemical and physical parameters for the complex formations of copper and iron with 5-Br-PSAA have been optimized in the flow system. Thus, the analytical performance of the proposed flow system equipped with the dual LED detector was compared with our previous study [19]. As summarized in Table 1, the analytical performances between these two methods are comparable. The results ensured the reliability of the newly designed spectrometer.

3.3. Pre-treatment of oil samples

An aliquot (4 g) of used lubricating oil in a platinum crucible was incinerated at 550°C. The white ash was obtained from the incineration of the oil sample, and was ground to a powder in the mortar. Ten mL of nitric acid (its concentration is described below) was added to a 0.1 g of ash and the mixture was heated on the plate heater at 120°C for 60 min.

The effect of nitric acid concentration mentioned above was investigated for complete dissolution of ash. The results are shown in Table 2. Over 0.8 M nitric acid, the ash was completely dissolved. Eventually 1 M nitric acid was chosen.

Table 2 The effect of nitric acid concentration on the dissolution of ash

Nitric acid concentration / M	Dissolution conditions
8	Very good
1.6	Very good
0.8	Good
0.32	Not complete
0.16	Not complete
0.016	Not complete

The ash (0.1 g) dissolved in 10 mL of 1 M nitric acid was put into the 100 mL volumetric flask, and the solution was diluted to the mark with water. The resulting solution was again diluted to 10 times with de-ionized water to match the pH of the solution with that of the carrier. As a result, the ghost peak disappeared.

3.4. Determination of copper and iron in lubricating oil ash

The resulting solutions (100 μL) obtained after the pre-treatment were injected in the flow system in Fig. 1. Table 3 shows the found values (in ppb) and the converted concentra-

Table 3 Simultaneous determination of copper and iron in lubricating oil used with crude fuel oil

Incinerated sample weight / g	C_{Cu}		C_{Fe}	
	Found / ppb	In oil / ppm[a]	Found / ppb	In oil / ppm[b]
0.0968	21.2	9.91	62.9	29.4
0.1064	22.9	9.74	70.3	29.9
0.0984	20.6	9.48	64.4	29.6
	Ave. 21.6±1.2	9.71±0.22	65.9±3.9	29.6±0.25

4.0250 g of lubricating oil sample were incinerated, and then 1.822 g of ash was obtained.
[a] 8.00 ppm by ICP-AES method employed routinely at the laboratory of Mitsui Engineering & Shipbuilding Co., Ltd.
[b] 25.0 ppm by ICP-AES (the same instrument as the above).

Table 4 Simultaneous determination of copper and iron in lubricating oils used with high quality fuel oil

Sample	Proposed method / ppm		ICP-AES / ppm	
	Cu	Fe	Cu	Fe
A	0.65±0.00	5.24±0.02	0.77	5.47
B	0.59±0.01	6.10±0.08	0.68	6.25
C	0.62±0.00	6.25±0.02	0.66	6.38

tions (in ppm) in the running oil. As shown in Table 3, reproducible results were obtained; the copper content was 9.71±0.22 ppm and iron was 29.6±0.25 ppm in the running oil. On the other hand, the contents obtained by ICP-AES were 8.00 ppm for copper and 25.0 ppm for iron.

We analyzed three more lubricating oils. The results are summarized in Table 4. Including the above mentioned data (Table 3), the experimental t-values between the proposed method and ICP-AES were 0.813 for copper and 0.857 for iron. These t-values were smaller than the critical t-value (3.182) for three degrees of freedom at the 95% confidence level. The simple and compact analytical system is sufficient to monitor rapidly and reproducibly metal contents in lubricating oil.

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