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Air segmented amplitude modulated multiplexed flow analysis with software-based phase recognition: Determination of phosphate ion



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ABSTRACT

Amplitude modulated multiplexed flow analysis (AMMFA) has been improved by introducing air segmentation and software-based phase recognition. Sample solutions, the flow rates of which are respectively varied at different frequencies, are merged. Air is introduced to the merged liquid stream in order to limit the dispersion of analytes within each liquid segment separated by air bubbles. The stream is led to a detector with no physical deaeration. Air signals are distinguished from liquid signals through the analysis of detector output signals, and are suppressed down to the level of liquid signals. Resulting signals are smoothed based on moving average computation. Thus processed signals are analyzed by fast Fourier transform. The analytes in the samples are respectively determined from the amplitudes of the corresponding wave components obtained. The developed system has been applied to the simultaneous determinations of phosphate ions in water samples by a Malachite Green method. The linearity of the analytical curve ($0.0\text{--}31.0\ \mu\text{mol dm}^{-3}$) is good ($r^2 > 0.999$) and the detection limit (3.3σ) at the modulation period of 30 s is $0.52\ \mu\text{mol dm}^{-3}$. Good recoveries around 100% have been obtained for phosphate ions spiked into real water samples.

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1. Introduction

Amplitude modulated multiplexed flow analysis (AMMFA) is a new concept of continuous flow analysis [1]. Pieces of information on sample solutions are amplitude modulated by varying their flow rates at different frequencies, and are multiplexed by merging the solutions. The pieces can be derived from a single continuous analytical signal, obtained downstream, through a frequency analysis such as fast Fourier transform (FFT) [1–4] and lock-in detection [5]. As for such application of FFT to flow analyses, Szostek and Trojanowicz [6] reported a flow injection analysis of nitrite by biamprometry, where signal-to-noise ratio and throughput rate for repeated injections were greatly improved by FFT of detector output signals. López-García et al. [7] reported a more relevant concept to the present study. Two copper solutions were simultaneously supplied to the nebulizer of a flame atomic absorption spectrophotometer at modulated flow rates. The ratio of amplitudes of interest, obtained by Fourier transform of analytical signals, was proportional to that of copper concentrations in two solutions. Thus, the analyte concentration in one solution can be determined if that in the other solution is known.

We have applied AMMFA to the simultaneous analysis of multiple samples, where analytes were food dyes [1], ferrous ion [1] and chloride ion [2]. However, amplitude damping caused by axial dispersion of sample solutions in the conduit resulted in the decrease in sensitivity of the measurement. In the previous paper [3], we introduced an air segmentation concept, which had been originated by Skeggs [8,9] in the 1950s and applied later to continuous flow analysis [10–12], monosegmented continuous flow method (segmental flow injection analysis) [13–17] and so on, to AMMFA in order to limit the axial dispersion. The air segmented AMMFA was applied to the determination of phosphate ions or nitrite ions. The effect of air segmentation on the limitation of the dispersion was more pronounced at shorter modulation period and longer flow path length. The sensitivity was increased maximally by a factor of 2.7 compared with that obtained by an AMMFA with no air segmentation. However, the air bubbles needed to be removed just before the detection through a porous membrane, because they would cause severe noises against FFT analysis of liquid signals. Considerable amplitude damping through the dispersion still occurred after the phase separation.

In the present paper, we report air segmented AMMFA with no physical deaeration. Air bubbles are not removed but directly delivered to the flow cell of a UV/vis detector together with liquid stream in order to prevent the dispersion and to preserve high amplitude. Instead, air signals are suppressed down to the level of

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liquid signals and smoothed with an in-house program. Thus processed signals are analyzed by FFT for the simultaneous determination of analytes in multiple samples. First, software parameters are optimized using Methyl Orange as an analyte, because no consideration on the coloration is necessary. The validity of the present concept is then evaluated by applying to the determination of phosphate ions, because phosphorus has been paid much attention recently with respect to the depletion of phosphorus resources [18], in addition to eutrophication. A malachite Green method [19,20] is selected due to its inherent high sensitivity. The proposed concept of air segmented AMMFA with no physical deaeration makes it possible to perform simultaneous determination of phosphate ions at $\mu\text{mol dm}^{-3}$ level in multiple samples. The method has been applied to the determination of phosphate ions in river, pond, canal and moat water samples.

2. Experimental

2.1. Flow system

Fig. 1 shows the flow system configured in the present study. The system was of five channels manifold. Teflon tubing (0.5 mm i.d.) was used as conduit unless otherwise stated. Four peristaltic pumps (P_1 , P_2 , P_3 and P_4 ; Rainin Dynamax RP-1, USA) were used for delivering solutions, and one pump (P_5 ; the same model as P_1 – P_4) was for air. Pharmed tubing with 0.51 mm i.d. was used for P_1 – P_3 and P_5 as pump tubes and the tubing with 0.79 mm i.d. was used for P_4 . The flow rates of sample solutions S_1 and S_2 delivered using P_1 and P_2 were varied in the range from 0 to $0.25 \text{ cm}^3 \text{ min}^{-1}$, but at different periods (typically, 30 and 20 s, respectively). The flow rates were controlled by sinusoidal controller output voltages (V_{c1} and V_{c2} , respectively) generated from a signal generator (SG; NF Corp. WF1974, Japan). The flow rate of color-forming reagent solution R delivered using P_3 was kept constant at $0.6 \text{ cm}^3 \text{ min}^{-1}$. Both sample solutions and reagent solution were merged at a confluence point (polypropylene joint) while the total flow rate was held constant at $1.2 \text{ cm}^3 \text{ min}^{-1}$ by P_4 . The P_4 is positioned upstream of an air-inflow joint (described below) for reliable liquid delivering and for easy comparison between air segmented AMMFA (present method) and non-segmented AMMFA (previous method [1]). The reason for the constant total flow rate is to keep the lag time between the merging the solutions upstream and the sensing the merged solution downstream. Water is, therefore, aspirated to the confluence point for compensating the difference of the total flow rate ($1.2 \text{ cm}^3 \text{ min}^{-1}$) and the sum of the flow rates of the sample solutions and the reagent solution (0.6 – $1.1 \text{ cm}^3 \text{ min}^{-1}$). Air bubbles were introduced from the fifth channel at a constant flow rate of $0.13 \text{ cm}^3 \text{ min}^{-1}$. The peristaltic pump

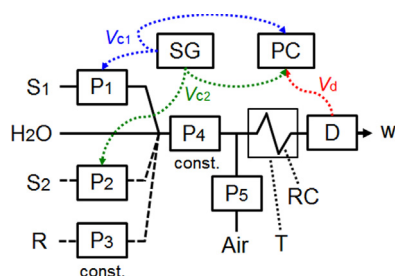


Fig. 1. Schematic diagram of flow system. A two-channel system (solid line) was used for the determination of Methyl Orange. A four-channel system (solid and broken lines) was used for the determination of phosphate ion. S, Sample solution; R, reagent solution; H_2O , water; w, waste; P_1 – P_5 , peristaltic pumps; RC, reaction coil; D, spectrophotometer; SG, signal generator; PC, laptop computer with a card type A/D–D/A converter; V_{c1} and V_{c2} , controller output voltages; V_d , detector output voltage.

(P_5) and T-shaped polypropylene joint (AS ONE, VFT 106, Japan) was used for the air introduction, because this combination had been found to give sufficiently allowable precision (RSD of air-bubble volume: $< 5\%$ [3]). The merged solution segmented by the air bubbles was led to a reaction coil (RC; 0.5 mm i.d. and 0.5 m long) in order to accelerate color reaction at elevated temperature (50°C). The temperature of RC was controlled with a temperature sensor (TOP L-TN-4-PT100, Japan), a silicon rubber heater (TOP 5099-01, $100 \times 25 \text{ mm}$, Japan) and a temperature controller (Toho BX-303, Japan). Thus reacted solution was introduced to a hand-made flow cell (quartz tubing), which was set in a spectrophotometer (D; Shimadzu SPD-10Avp or SPD-10AVvp, Japan; time constant: 0.05 s) for absorbance measurement. Analytical wavelength was 600 nm, unless otherwise stated. The incident beam is introduced not axially but perpendicularly to the cell (optical path length: 1 mm) in order to differentiate between liquid and air segments at the expense of sensitivity. The detector output voltage V_d as well as V_{c1} and V_{c2} were quantized by an A/D–D/A converter (Measurement Computing PC-CARD-DAS16/12-AO, USA). Resulting digital data were acquired in a laptop computer (PC; Toshiba DynaBook Satellite 1850 SA120C/4, Japan) as a Microsoft Excel format. An in-house program written in Visual Basic was used to acquire data, analyze them and graphically display the results automatically. Software-based phase recognition and FFT analysis will be described in Section 2.3.

2.2. Reagents and samples

Various methods such as spectrophotometry, fluorometry, chemiluminescence analysis, inductively coupled plasma atomic emission spectrometry, potentiometry, voltammetry and amperometry have been developed for the determination of phosphate ion, as reviewed by Worsfold et al. [21], Estela and Cerdà [22], Motomizu and Li [23], and Mesquita et al. [24]. In the present system with the UV/vis detector, a Malachite Green spectrophotometry [19,20] is adopted because it is inherently more sensitive than the most commonly employed Molybdenum Blue spectrophotometry by a factor of one magnitude. The color-forming reagent comprised $1.6 \times 10^{-2} \text{ mol dm}^{-3}$ ammonium molybdate, $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ Malachite Green and 1.3 mol dm^{-3} sulfuric acid. Polyvinyl alcohol of 2000 average polymerization degree (0.5% as final concentration) was added to the reagent solution as a stabilizer for the ion-pair of Malachite Green and phosphomolybdate ion, according to the recommendation by Motomizu et al. [19].

All the reagents used were of analytical reagent grade purchased from Kanto Chemicals (Tokyo, Japan), Nacalai Tesque (Kyoto, Japan) or Wako Chemical Industries (Osaka, Japan). The reagents were used without further purification. Zartorius Arrium 611 DI grade deionized water was used throughout.

Real water samples were collected from the Fukuroi Irrigation Canal, the moat of Shozui Castle, the Iio River and the Naka Pond in urban area in Tokushima Prefecture, Japan. The samples were each filtered through a disposable disk filter with a pore size of $0.45 \mu\text{m}$ (Kanto Chemical Co. 96904-00, Tokyo, Japan). Chloroform (0.5 vol% as final concentration) was added to the respective filtrates as a preservative [25], and thus prepared samples were stored in clean polypropylene bottles in a refrigerator at 4°C .

2.3. Data processing

Commercial Instrument “AutoAnalyzer”, which had been developed by Tecnicon Corporation based on the invention by Skeggs [8,9], has adopted software-based air recognition since early stages of commercialization. Independently, Habig et al. [26] reported “bubble gating”, a signal-processing based deaeration technique,

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