Determination of Dissolved Oxygen in Water Samples Using Capillary Electrophoresis

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Capillary electrophoresis was successfully applied for the determination of a gaseous analyte of interest i.e., dissolved oxygen in water samples, for the first time. Each analysis was performed within 5 min and as low as 50 ppb dissolved oxygen can be determined by this method. The proposed method was successfully applied for the analysis of river water. The method is versatile for analysis of miniaturized samples and studies of reaction kinetics.

Capillary electrophoresis (CE) is a rapidly growing separation technique with diverse applications.[1] This technique which originally distinguished with high resolution ability for the analysis of biological macromolecules,[2] soon was used as a general method like HPLC in the field of separation science.[3] However, some applications appeared in which the fundamentals of capillary electrophoresis were used for the sake of other goals than separation. Electrophoretically mediated chemical analysis[4] is a representative example. This technique uses the influence of an applied electric field for electrophoretically mixing spatially distinct zones of chemical reagents inside the capillary to proceed a chemical reaction and develop a detectable product.

In this report we would like to introduce CE for the determination of dissolved oxygen (DO) in water samples. Several methods have been proposed for the determination of DO in water such as photometric,[5] gas chromatographic,[6] differential pulse voltammetric,[7] and ruthenium based polymer-immobilized sensing.[8] Up to our knowledge, there have been no reports on the application of CE for the determination of dissolved gases in water. However, intrinsic capabilities of CE i.e., short analysis time, small sample volume required, simple method development, and closed system, can be well matched with the requirements of a reliable, cheap, and rapid determination of DO and other dissolved gases in water. Pyrogallol reacts with oxygen in alkaline solution to form a product absorbing at 440 nm.[9,10] This reaction was used for the determination of DO. The alkaline water samples (pH=12) were injected into capillary electrophoresis column,[11] which was filled with a degassed solution of 0.5 M(1M=1mol dm^{-3}) pyrogallol,[12] and 0.05 M sodium dihydrogen phosphate buffer at pH=5.6. An electropherogram was obtained after 5 min (RSD of migration time was 2.5% for 5 measurments) and was used for the quantification of DO in water samples (Figure 1B). Air saturated water at different temperatures were used to prepare standard samples of oxygen. At any temperature the concentration of oxygen can be calculated by the equation:[13]

$$C_{(ppm)} = 14.161 - 0.3943t + 0.007714t^2 - 0.0000646t^3 \quad (1)$$

A linear relationship up to 10 ppm oxygen was observed with a linear regression equation of $Y = 1.067 + 6.006X$ ($R^2 = 0.996$). Detection limit for the method was calculated to be 50 ppb which can be improved in the expense of increased analysis time by the off-field modified method. In this method one minute after injection of sample into capillary column, the power supply was turned off for a certain time and the reaction between pyrogallol and oxygen was left for the completion. The peak area of the resulted electropherograms increased by the increase of the off-field time up to 6 min (see Figure 1A). Since the sensitivity is defined as the slope of the calibration curve, the off-field method has an obvious effect on the improvement of method sensitivity.

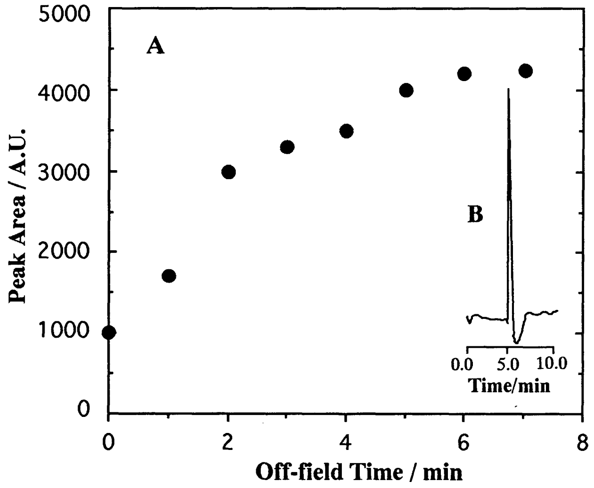

Figure 1. **(A):** Effect of off-field time on enhancement of method sensitivity. **(B):** A typical electropherogram obtained by the reaction between pyrogallol and dissolved oxygen.

A brief investigation was made of the influence of common inorganic compounds which usually interfere in the determination of DO (see Table 1). Some oxidizing/reducing agents interfered and should be removed before analysis. Due to the working pH of the sample, metal cations (if present) remove as precipitates and do not interfere in analysis. Effect of different matrices on determination of 8.2 ppm DO was studied by some few synthetic samples and acceptable results were obtained. In the presence of formate (0.1 M), EDTA (0.05 M), and urea (0.3 M), the obtained DO by the proposed method was 7.6 ppm. In the presence of binary components: iodine and chloride (each 0.5 M), formate (0.1 M), and bicarbonate (0.2 M), and EDTA (0.05 M), and urea (0.3 M), DO was found as 8.1, 7.5, and 7.6 ppm respectively.

For the analysis of a real sample, the water of the Kyobashi river in Hiroshima city was analyzed by the proposed method. Using the calibration graph, the amount of DO was found to be 9.1 ppm at 10 °C. The reliability of the method was evaluated by comparing the results obtained by the standard method,[14] and the proposed method(see Table 2).

In addition to the possibility of applying the proposed method for the determination of DO in miniaturized samples, one can use this method even for the kinetic and mechanistic studies of the reaction between dissolved oxygen and pyrogallol. By changing the capillary length, pH of the carrier electrolyte, pyrogallol concentration and capillary column temperature, different necessities for such studies are accessible. This approach is currently underway in our laboratory. Furthermore, assay of other dissolved gases in water by capillary electrophoresis and possibility of simultaneous determination is now under investigation.

Table 1. Interference effects of common ions on the determination of 8.2 ppm of DO in air-saturated water

Ion	Salt	Concentration(M)	Recovery(%)
Borate	$Na_2B_4O_7$	0.10	97
Tartrate	Tartric acid	0.10	104
Formate	Formic acid	0.10	92
EDTA	Na salt	0.05	95
Hydrogen Phosphate	Na_2HPO_4	0.40	86
Citrate	Citric acid	0.05	98
Iodide	KI	0.50	98
Chloride	NaCl	0.50	100
Carbonate	Na_2CO_3	0.20	100
Thiosulfate	$Na_2S_2O_3$	0.20	104
Hydrogen Sulfate	$NaHSO_4$	0.004	99
		0.02	96
		0.20	64
Nitrite	$NaNO_2$	0.20	136
Nitrate	$NaNO_3$	0.50	104
Sulfide	Na_2S	0.07	69
Sulfite	Na_2SO_3	0.25	63

Table 2. Comparison between Winkler's (I) and the proposed method(II) for the determination of DO

Sample	Method	DO found(ppm)[b]
Distilled Water[a]	I	8.4 ±0.1
	II	8.2 ±0.1
Kyobashi river	I	9.5 ±0.1
	II	9.1 ±0.2

[a] 20 °C. [b] Average of four measurments ± SD.

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11 Capillary electrophoresis system and apparatus used in this study: A high voltage power supply (model HCZE-30 Mastsusada precision devices, Japan) was used for generation of 30 KV (25 μA) electric field. Peak detection was performed using a CE UV-VIS. detector operated at 440 nm (Jasco, Japan). Electropherograms were recorded and processed on a Chromatopac model C-R3A (Shimadzu, Japan). Fused silica capillary tubes, 50 cm long, 30 cm to detector with 50 μm i.d. and 375 μm o.d.(G.L. Sciences, Japan) was used. Injection was performed hydrodynamically for 10 sec. Methanol was eluted after 3.2 min and used as neutral marker for the measurment of electroosmotic flow mobility ($\mu_{eof} = 2.60 \times 10^{-4}$ cm^2 sec^{-1} V^{-1}).

12 This solution is stable for at least 5 hours but care should be made to avoid contamination from sample vial due to its high pH which can promote air oxidation of pyrogallol.

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