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Separation and determination of phenolic compounds by capillary electrophoresis with chemiluminescence detection

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Abstract

Phenolic compounds were analyzed by means of capillary electrophoresis with chemiluminescence detection. Peroxyoxalate chemiluminescence reagent was used together with dansyl chloride as a labeling reagent. The reagent concentrations, the labeling procedures, and the performance of chemiluminescence detection cells were examined for sensitive detection of phenolic compounds. Six kinds of phenolic compounds (phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol) were determined over a range of three orders of magnitude with detection limits of the order of 10^{-7} *M*; their detection limits were ca. 10 times as low as those obtained by an ordinary fluorescence detector. A running buffer solution containing sodium dodecylsulfate and acetonitrile provided satisfactory results in the separation of 15 kinds of phenolic compounds. The combination of capillary electrophoresis with chemiluminescence detection and column concentration procedure supported the possibility that the present system could be applied to real samples such as surface and reused waters.
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Keywords: Chemiluminescence detection; Detection, electrophoresis; Buffer composition; Chlorophenols; Nitrophenols; Phenols

1. Introduction

The influences of endocrine-disrupting chemicals for animals, humans, and environments have attracted a great deal of public attention [1,2]. Endocrine-disrupting chemicals have been mainly analyzed with GC–MS. However, this analytical method is expensive and several days are required to obtain analytical results, because the pretreatment or the derivatization of this analysis is complicated [3,4].

We have developed capillary electrophoresis (CE) with chemiluminescence (CL) detection [5]. Several CL reagents such as luminol [6], peroxyoxalate [7], 1,10-phenanthroline [8], and Ru(II) complex [9] have been utilized. The method can offer excellent selectivity and sensitivity. Furthermore, it features easy and rapid operation as well as inexpensive reagents and instruments.

Some phenolic compounds are well-known as endocrine-disrupting chemicals. One sensitive detection method is fluorescence detection through

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derivatization with dansyl chloride. Halvax et al. analyzed dansyl phenolic compounds by liquid chromatography with fluorescence detection [10]. On the other hand, Kwakman et al. reported sensitive liquid chromatographic determination of alkyl-, nitro-, and chlorophenols by precolumn derivatization with dansyl chloride and peroxyoxalate CL detection [11]. The sensitivity of the CL detection was reported to be ~1 or 2 orders of magnitude larger than that of the fluorescence detection [12,13].

Several groups have reported an analysis of phenolic compounds by CE using absorption detection [14,15]. In this study, we tried for the first time to apply CE with CL detection using peroxyoxalate reagent to the analysis of dansyl phenolic compounds. Two batch-type CL detection cells, which were originally developed by the authors, were examined. Fifteen kinds of phenolic compounds were successfully separated and detected by use of a running buffer solution containing sodium dodecylsulfate (SDS) and acetonitrile. The present method was applied to the analysis of phenolic compounds in surface and reused waters by being combined with column concentration.

2. Experimental

2.1. Reagents

All of the reagents used were of commercially available special grade. Ion-exchanged water was distilled for use. Bis[2-(3,6,9-trioxadecanyloxycarbonyl)-4-nitrophenyl]oxalate (TDPO) and tetrabutylammonium bromide (TBABr) were purchased from Wako. Sodium dodecylsulfate (SDS), dansyl chloride (Dns-Cl), phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4-dinitrophenol (2,4-DNP), 2,5-dinitrophenol (2,5-DNP), 2,6-dinitrophenol (2,6-DNP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,6-trichlorophenol (2,3,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP), nonylphenol (NoP), bisphenol (BiP), 4-octylphenol (OcP), and pentachlorophenol (PeP) were purchased from Nacalai Tesque.

2.2. Labeling of phenolic compounds with Dns-Cl [16,17]

Derivatization of phenolic compounds with Dns-Cl was carried out by two kinds of procedures (methods 1 and 2). Phenolic compounds were dissolved in organic solvent (method 1) and in aqueous solvent (method 2). Methods 1 and 2 were typically carried out as follows: method 1, a stock solution of 10 m*M* phenolic compounds was prepared by dissolving them in acetone. One mg ml^{-1} Dns-Cl methylene chloride solution (5 ml) and 10 m*M* Na_3PO_4 aqueous solution (pH 11.2) (0.5 ml) were added to a phenolic compound solution (5 ml) which was prepared by diluting the stock solution with acetone. After being stirred for ca. 10 s and left in a dark place for ca. 10 min, the mixture was subjected to CE–CL detection.

Method 2 (two-phase system with TBABr as a phase transfer catalyst): a stock solution of 10 m*M* phenolic compounds was prepared by dissolving them in methanol–water (1:1) solution. One mg ml^{-1} Dns-Cl methylene chloride solution (0.6 ml) and 30 mg ml^{-1} TBABr alkaline solution (10 m*M* NaOH) (0.1 ml) were added to a phenolic compound solution (0.5 ml) which was prepared by diluting the stock solution with methanol–water (1:1) solution. The mixture solution was stirred for ca. 2 min. The organic phase obtained after the centrifugation was used for CE measurement.

2.3. Column concentration

A solid-phase extraction column (MERCK LiChrolut® EN/3 ml/200 mg) was used in this study. The column was pretreated with 3 ml acetone (two times), subsequently with 3 ml water (two times). Sample solution (1000 ml) was fed to the column with a flow-rate of 10 ml min^{-1}. After that, the column was cleaned up with 3 ml water. The phenolic compounds which were adsorbed onto the column were extracted with 1 ml acetone. The acetone solution was subjected to a labeling procedure similar to method 1.

2.4. CL detection cell

Two batch-type CL detection cells were used for

the CE–CL detection using peroxyoxalate CL reaction. The concepts of the cells were originally proposed by the authors in previous papers [7,18]. One of them is an optical-fiber type CL detection cell [7]. The cell was made of PTFE, with a 4-cm O.D., 2.5 cm in height, and 8-ml inner volume. An optical-fiber (a core diameter of 2 mm; PGR-FB2000, Toray Industries), a fused-silica capillary, and a platinum wire as a grounding electrode were fixed to the cell. That is, the cell also worked as an outlet reservoir. The optical-fiber was set up straight to the capillary with a distance of 0.3 mm between them. CL reagent was added into the cell. When analytes emerged from the capillary, they reacted with the CL reagent at the capillary outlet to produce visible light. The light was transported through the optical-fiber to a photosensor module (PM).

The other one is a glass-cuvette type CL detection cell [18]. The cell had an inner diameter of 5 mm and an inner volume of about 0.7 ml. A capillary and a platinum wire as a grounding electrode were inserted into the cell through an upper silicon rubber. The detection cell also worked as an outlet reservoir. The cell was put just in front of a PM. The CL light at the tip of the capillary was directly detected by the PM.

2.5. Apparatus and analytical procedure

A high voltage was applied to electrodes using a d.c. power supplier (Model HCZE-30PNO. 25, Matsusada Precision Devices). A fused-silica capillary of 50 cm×50 μm I.D. (GL Sciences) was used. An aliquot of CL reagent (2 m*M* TDPO acetonitrile solution containing 50 m*M* H_2O_2) was added into the cell. A 10 m*M* phosphate buffer solution (pH 8.0), the buffer solution containing SDS, or the buffer solution containing SDS and acetonitrile were used as a running buffer solution. Sample injections were performed by siphoning from a height of 30 cm for 15 or 25 s. The sample solution migrated in the running buffer solution toward the CL detection cell and mixed with the CL reagent. The resulting CL at the capillary outlet was captured by the optical-fiber or glass-cuvette type CL detection cell. The output from the detector was fed to an integrator.

A modified Shimadzu RF-535 fluorescence detector was also used for fluorescence detection (ex. 335 nm and em. 480 nm) in CE.

3. Results and discussion

3.1. Reagent concentration and labeling procedure

Firstly, we examined the effect of TDPO and H_2O_2 concentrations on the S/N ratio of 2-CP by use of an optical-fiber type CL detection cell. It was found that around 2 m*M* TDPO and 50 m*M* H_2O_2 provided the maximum CL intensity. Their concentrations were used for CL reagent preparation in this study.

As described in Section 2, the derivatization with Dns-Cl was carried out with two different procedures (methods 1 and 2). Phenolic compounds as endocrine-disrupting chemicals in the environment exist mostly in an aqueous solution, such as rivers and lakes. Therefore, it is important that method 2 (two-phase system) indicates the same performance for labeling as does method 1. We examined the labeling performance of the two methods by use of 18 kinds of phenolic compounds. There was little difference in the labeling performance between them. However, 2,4-DNP, 2,5-DNP, and 2,6-DNP, which have two electron-withdrawing groups in their molecules, were not detected in both methods.

3.2. Comparison of optical-fiber and glass-cuvette type CL detection cells

Six kinds of dansyl phenolic compounds (Ph, 2-CP, 4-CP, 2,4-DCP, 2,6-DCP, and 2,4,6-TCP) were examined by use of the optical-fiber type CL detection cell. The sample injection time must be optimized for CE–CL detection [19]. Siphoning from a height of 30 cm for 15 s was recommended for the optical-fiber type by examining the relationships between the sample injection time and the peak area as well as the theoretical plate number. All of them indicated linear relationships between the concentration and the CL intensity. Their linear determinable ranges were more than three orders of magnitude. They were detected with a good reproducibility; the relative standard deviation was within 2%. The obtained results concerning detection limits

Table 1
Detection limits, linear detection ranges, and correlation coefficients of dansyl phenolic compounds by use of the optical-fiber CL detection cell

Dansyl phenolic compounds	Detection limit ($S/N=3$)		Linear detection range (M)	Correlation coefficient
	Concentration (M)	Mass (fmol)		
Ph	1×10^{-6}	7.0	1×10^{-5}–5×10^{-2}	0.995
2-CP	1×10^{-6}	7.0	1×10^{-5}–5×10^{-2}	0.996
4-CP	1×10^{-6}	7.0	1×10^{-5}–5×10^{-2}	0.990
2,4-DCP	4×10^{-6}	27	5×10^{-5}–1×10^{-2}	0.996
2,6-DCP	1×10^{-6}	7.0	1×10^{-5}–5×10^{-2}	0.992
2,4,6-TrCP	1×10^{-6}	7.0	1×10^{-5}–5×10^{-2}	0.998

Conditions: capillary, 50 cm×50 μm I.D. fused-silica; applied voltage, 15 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0); CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution.

and correlation coefficients are summarized in Table 1. As the sample injection volume was ca. 7 nl, the detection limits ($S/N=3$) were ca. 7–30 fmol.

We also examined six kinds of phenolic compounds by use of the glass-cuvette type detection cell. Siphoning from a height of 30 cm for 25 s was recommended for the glass-cuvette type by preliminary experiments. All of them indicated linear relationships between the concentration and the CL intensity and were detected with a good reproducibility (the relative standard deviation was ≤2%). Their linear determinable ranges were more than three orders of magnitude. The obtained results are summarized in Table 2. As the sample injection volume was ca. 12 nl, the detection limits ($S/N=3$) were ca. 1–6 fmol.

The detection limits obtained using the glass-cuvette type were better than those obtained using the optical-fiber type. However, the resolution when using the former was inferior to that of the latter. The experimental results were consistent with those reported in the previous papers [5,7,16] that the glass-cuvette type indicated higher sensitivity but lower resolution in comparison with the optical-fiber type. In this study the authors determined to use the glass-cuvette type which provided better sensitivity. When a mixture sample solution of 15 kinds of phenolic compounds was subjected to CE–CL detection using 10 m*M* phosphate buffer solution (pH 8.0) as a running buffer solution, we could see ~9 peaks on the electropherogram. Improving the resolution is explained in the next section.

3.3. Separation and determination of phenolic compounds

In order to improve resolution, we examined the effect of SDS and acetonitrile in a running buffer solution on the electropherogram. Firstly, the effect of SDS concentration of up to 100 m*M* was examined with respect to the migration time, the peak height of 2-CP, and the resolution between 2-CP and

Table 2
Detection limits, linear detection ranges, and correlation coefficients of dansyl phenolic compounds by use of the glass cuvette CL detection cell

Dansyl phenolic compounds	Detection limit ($S/N=3$)		Linear detection range (M)	Correlation coefficient
	Concentration (M)	Mass (fmol)		
Phe	2×10^{-7}	2.3	5×10^{-6}–1×10^{-3}	0.998
2-CP	2×10^{-7}	2.3	5×10^{-6}–1×10^{-3}	0.994
4-CP	2×10^{-7}	2.3	1×10^{-6}–1×10^{-3}	0.996
2,4-DCP	5×10^{-7}	5.8	5×10^{-6}–1×10^{-3}	0.998
2,6-DCP	2×10^{-7}	2.3	5×10^{-6}–1×10^{-3}	0.998
2,4,6-TrCP	1×10^{-7}	1.1	5×10^{-6}–1×10^{-3}	0.998

Conditions: capillary, 50 cm×50 μm I.D. fused-silica; applied voltage, 15 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0); CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution.

4-CP (Fig. 1). The migration time of 2-CP increased with increasing SDS concentration. The increase of migration time must be due to the partition of analyte into the micellar phase. The resolution between them was improved significantly by increasing the SDS concentration. However, the peak height decreased with increasing SDS concentration; SDS might interfere with the CL reaction.

Next, the effect of acetonitrile volume percentage of up to 70% (v/v) in a running buffer was examined with respect to the migration time, the peak height of 2-CP, and the resolution between 2-CP and 4-CP (Fig. 2). The migration time of 2-CP increased with increasing acetonitrile volume percentage. The increase in the migration time of 2-CP might be due to a change in the electroosmotic flow. While the peak height was almost constant up to ca. 50% (v/v) acetonitrile, the resolution between them was improved with increasing the acetonitrile volume percentage.

In order to achieve the best resolution and sensitivity possible, a running buffer solution containing 2 m*M* SDS and 50% (v/v) acetonitrile was recommended for use. As shown in Fig. 3, 15 kinds of phenolic compounds were successfully separated and detected under the conditions. In all likelihood, the additions of SDS and acetonitrile in the running buffer decreases the mobility of electroosmotic flow, and increases the solubility of analytes. The effects of such additives would lead to successful separation of 15 kinds of phenolic compounds as shown in Fig. 3, although the exact separation mechanism is unknown. It was also found that the conditions provided the same analytical performance as described in Table 2. CL detection was ca. 10 times as sensitive as fluorescence detection.

3.4. Application

As described above, the detection limits of the present method were of the order of 10^{-7} *M*. The sensitivity was not enough to apply the method to real samples in the environment, because water quality standards of phenolic compounds in the environment have been regulated as 0.005 mg l^{-1} (ca. 5×10^{-8} *M* for Ph) by a law since 1992 in Japan. Therefore, we tried to combine CE with CL de-

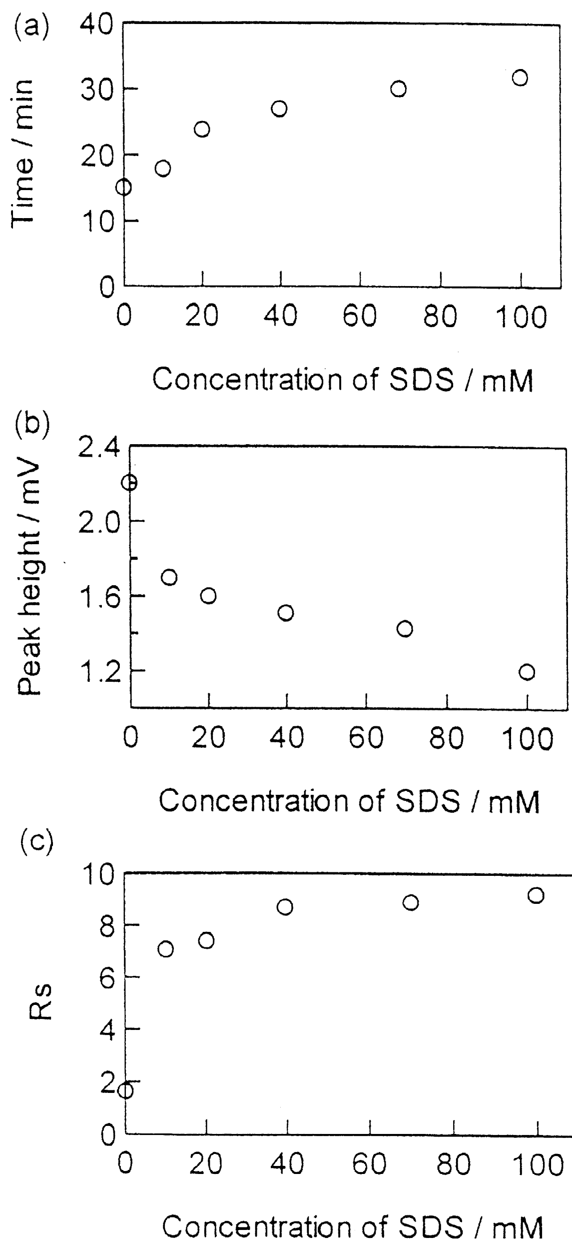

Fig. 1. The effect of SDS concentration in a migration buffer solution on (a) migration time of 2-CP, (b) peak height of 2-CP, and (c) resolution between 2-CP and 4-CP. Conditions: capillary, 50 cm×50 μm I.D. fused-silica; applied voltage, 12 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0) containing SDS; CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution; sample, 1×10^{-5} *M* 2-CP and 4-CP.

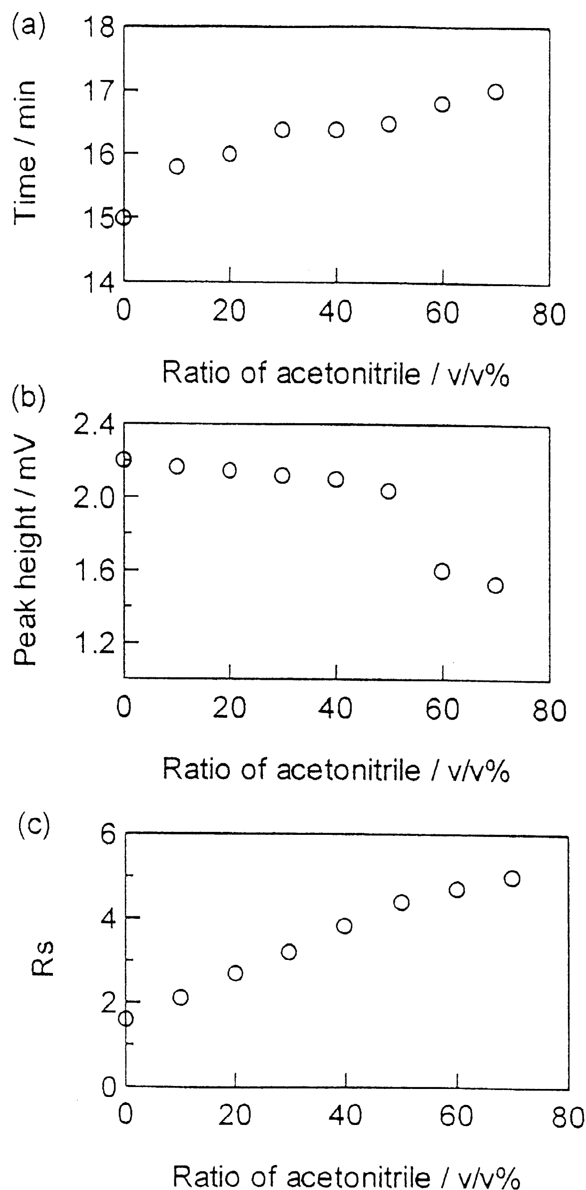

Fig. 2. The effect of acetonitrile volume percentage in a migration buffer solution on (a) migration time of 2-CP, (b) peak height of 2-CP, and (c) resolution between 2-CP and 4-CP. Conditions: capillary, 50 cm×50 μm I.D. fused-silica; applied voltage, 12 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0) containing 2 m*M* SDS and acetonitrile; CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution; sample, 1×10^{-5} *M* 2-CP and 4-CP.

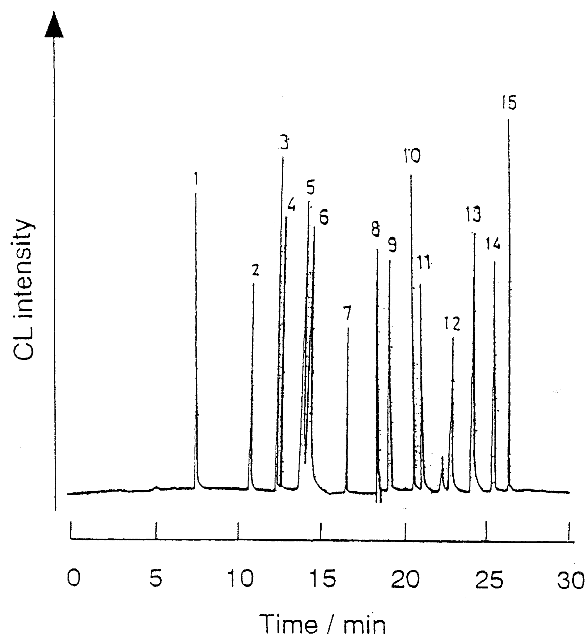

Fig. 3. The electropherogram of a mixture solution of dansyl phenolic compounds. Peak identification: 1, Ph; 2, 2-CP; 3, 4-CP; 4, 2-NP; 5, 2,6-DCP; 6, 4-NP; 7, BiP; 8, NoP; 9, 2,3,6-TCP; 10, 2,4,6-TCP; 11, 2,3,4,6-TeCP, 12, OcP; 13, PeP; 14, 2,4-DCP; 15, 2,3,4,5-TeCP. Conditions: capillary, 50 cm×50 μm I.D. fused-silica; applied voltage, 12 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0) containing 2 m*M* SDS and 50% acetonitrile; CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution; sample, 1.0×10^{-5} *M* Ph, 2-CP, 4-CP, 2-NP, 2,6-DCP, and 4-NP; 1.0×10^{-4} *M* BiP, NoP, 2,3,6-TCP, 2,4,6-TeCP, and 2,3,4,6-TCP; as well as 5.0×10^{-5} *M*, OcP, PeP, 2,4-DCP, and 2,3,4,5-TeCP.

tection and a column concentration procedure for measurement of real samples.

The sample solution (1000 ml) containing 1.0×10^{-8} *M* Ph was fed with various flow-rates (5–20 ml min^{-1}) into the concentration column. The recovery decreased with increasing flow-rate. A flow-rate of 10 ml min^{-1} was recommended for use by considering the recovery and the analytical time. Also, 15 kinds of phenolic compounds were examined with regard to recovery under the conditions used. Six kinds of phenolic compounds were recovered with 67–92% as shown in Table 3, while other compounds were not recovered enough under the present conditions. For others, the flow-rate and the solvent for extraction must be examined in detail to improve the recovery. Fig. 4 shows the relationships between

Table 3
Recovery of dansyl phenolic compounds in column concentration procedure

Dansyl phenolic compound	Recovery (%)
Ph	84.2
2-CP	92.2
4-CP	90.9
2-NP	76.3
2,6-DCP	73.8
4-NP	67.1

Conditions: capillary, 50 cm×50 μm I.D. fused-silica; applied voltage, 15 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0) containing 2 m*M* SDS and 50% (v/v) acetonitrile; CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution; sample, 1000 ml of 1.0×10^{-8} *M* phenolic compound was concentrated to 1 ml acetone through column concentration.

the concentration of phenolic compounds (Ph, 2-CL, and 4-CP) and the CL intensity which was observed by CE–CL detection through column concentration. Clearly, the system combined with column concentration could analyze these phenolic compounds with concentration less than the water quality standards of 0.005 mg l^{-1} (ca. 5×10^{-8} *M* for Ph, 2-CL, and 4-CP).

Tentatively, we examined surface water (for drinking) and reused water (for experiment, which is supplied by purifying used water in our University) in our laboratory by the present method together with column concentration. We could not see any peaks on both electropherograms. In order to confirm that the system was not influenced by any co-existences in surface and reused waters, we added phenolic compounds (1.0×10^{-8} *M* Ph, 2-CP, and 4-CP) to the surface and reused waters and analyzed them. Three obvious CL peaks due to their phenolic compounds were seen on both electropherograms. As examples, the electropherograms obtained for the reused water and that to which phenolic compounds were added are shown in Fig. 5. The change of baseline as shown in Fig. 5 was always observed for the samples of surface and reused waters treated with the concentration column. However, the reason for this is unknown. The combination of CE with CL detection and column concentration supported the possibility that the present system could be applied to real samples in the environment.

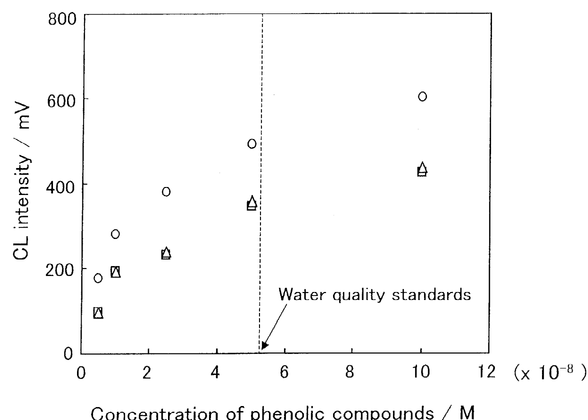

Fig. 4. The relationships between the concentration of phenolic compounds and the CL intensity. Conditions: capillary, 50 cm× 50 μm I.D. fused-silica; applied voltage, 15 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0) containing 2 m*M* SDS and 50% (v/v) acetonitrile; CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution; sample, 1000 ml of 1×10^{-8} *M* Ph, 2-CP, and 4-CP was concentrated to 1 ml acetone through the column procedure.

4. Conclusion

Phenolic compounds, some of which are well-known as endocrine-disrupting chemicals, were analyzed by means of CE–CL detection. Peroxyoxalate CL reagent was used together with Dns-Cl as a labeling reagent. The performance of the two labeling procedures was examined by use of 18 kinds of phenolic compounds. There was little difference in the labeling performance between them. Two batch-type CL detection cells, which were originally developed by the authors, were also examined. The detection limits obtained using the glass-cuvette type were better than those obtained using the optical fiber type. The authors determined that use of the glass-cuvette type provides better sensitivity. Six kinds of phenolic compounds were determined over a range of three orders of magnitude with detection limits of the order of 10^{-7} *M*; the detection limits were about 10 times as low as those obtained by an ordinary fluorescence detector. Fifteen kinds of phenolic compounds were successfully separated and detected by use of a running buffer solution containing SDS and acetonitrile. The present method was applied to the detection of phenolic compounds

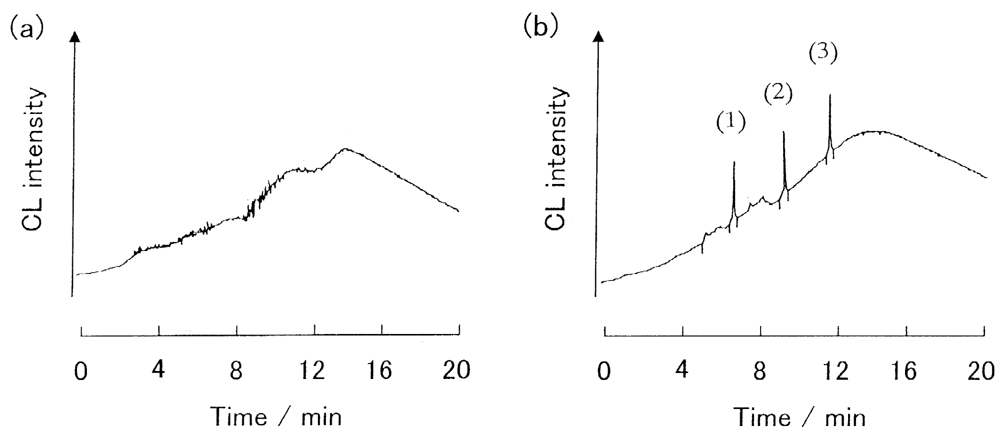

Fig. 5. The electropherograms of (a) reused water and (b) that to which phenolic compounds were added. Peak identifications: 1, Ph; 2, 2-CP; 3, 4-CP. Conditions: capillary, 50 cm×50 μm I.D. fused-silica; applied voltage, 15 kV; migration buffer, 10 m*M* phosphate buffer solution (pH 8.0) containing 2 m*M* SDS and 50% (v/v) acetonitrile; CL reagent, 2 m*M* TDPO and 50 m*M* H_2O_2 acetonitrile solution; sample, 1000 ml of reused water and that to which 1.0×10^{-8} *M* Ph, 2-CP, and 4-CP were added were concentrated to 1 ml acetone through the column procedure.

in surface or reused water combined with column concentration.

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