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Talanta 68 (2006) 646–652
Talanta
www.elsevier.com/locate/talanta

Post-column detection of benzenediols and 1,2,4-benzenetriol based on acidic potassium permanganate chemiluminescence

Shun-Li Fan [a,b], Li-Ke Zhang [b], Jin-Ming Lin [a,*]

[a] *State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, Beijing 100085, China*
[b] *Henan Key Laboratory for Environmental Pollution Control, College of Chemistry and Environmental Sciences, Henan Normal University, Xinxiang 453002, China*

Received 22 February 2005; received in revised form 8 May 2005; accepted 8 May 2005
Available online 13 June 2005

Abstract

Based on the sensitizing effect of formic acid on the chemiluminescence (CL) reaction of polyhydroxylbenzenes with acidified potassium permanganate and the combination technique of high-performance liquid chromatography (HPLC), a sensitive, selective and simple post-column CL detection method for simultaneously determining catechol, resorcinol, hydroquinone and 1,2,4-benzenetriol is described. The optimal conditions for the CL detection and HPLC separation were carried out. The linear ranges were: 6.0×10^{-3}–1.5 mg/L for hydroquinone, 8.0×10^{-3}–1.5 mg/L for 1,2,4-benzenetriol, 1.0×10^{-2}–2.0 mg/L for resorcinol and 1.0×10^{-2}–2.5 mg/L for catechol, respectively. The detection limits are: 3.2×10^{-3} mg/L for hydroquinone, 3.9×10^{-3} mg/L for 1,2,4-benzenetriol, 4.7×10^{-3} mg/L for resorcinol and 5.2×10^{-3} mg/L for catechol, respectively. Combining with solid phase extraction, the proposed method has been successfully applied to the determination of the polyhydroxylbenzenes in river water. The recoveries for three benzentriols were 92.1–95.4% and 82.0% for 1,2,4-benzenetriol, respectively.

Keywords: Chemiluminescence detection; HPLC; Potassium permanganate; Benzenediols; 1,2,4-Benzenetriol; Solid phase extraction (SPE)

1. Introduction

Benzenediols and benzenetriols are biologically and environmentally important phenolic compounds. They are extensively used as industrial chemicals, for example, photographic developers, rubber and food antioxidants, polymerization inhibitors [1,2], and considered to be of medium toxicity. Exposure to them can result in lots of clinical symptoms, such as dermatitis, erosion of the skin, tinnitus (ringing in ears), dizziness, headache, nausea, etc. [3,4]. The International Agency for Research on Cancer (IARC) has classified catechol as a Group 2B, possible human carcinogen [3]. The U.S. Environmental Protection Agency (EPA) has calculated a provisional Reference Dose (RfD) of 0.04 mg kg^{-1} day^{-1} for hydroquinone [4] and the acute oral median lethal dose (LD_{50}) of resorcinol for rats is 301 mg/kg [5]. Benzenediols and benzenetriols have been also found having a function of blocking some amines or amides being nitrosated to *N*-nitroso compounds which are known as powerful carcinogens in vivo [6]. Due to health and ecological risks caused by long and short-term exposure to phenolic compounds, to develop a highly sensitive, selective and simple method for the low level detection is of significance for the study of toxicological analysis, foods inspection, and environmental concerns.

Various methods are available for the determination of benzenediols or benzenetriols, including chromatographic [7–11], spectrophotometric analyses [12–15] and chemiluminescent (CL) detection [16–18]. Spectrophotometric methods are employed mainly for the determination of total amount of phenolic compounds. While chromatographic methods permit selective determination of individual phe-

* Corresponding author. Tel.: +86 10 62841953; fax: +86 10 62841953.
E-mail address: jmlin@mail.rcees.ac.cn (J.-M. Lin).

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doi:10.1016/j.talanta.2005.05.004

nolic compounds, problems, such as lower sensitivity of the detector used (e.g. UV) are usually encountered and thereby greatly hamper their application from trace analysis. CL detections are proved to be much more sensitive and have advantages of wide dynamic range, simple instrumentation and rapidity in signal detection. Unfortunately, most of the methods reported can be used only for the determination of single compound in simple matrices, while the determination for complex matrices, such as biological and environmental samples is almost impossible because phenolic congeners are often present together in these samples and similar CL reactions will lead to the interference from one to another. It can be expected that the technique of combination of CL detection with high-performance liquid chromatography (HPLC) separation will provide both good sensitivity and selectivity. However, practical application of the HPLC–CL technique for the determination of phenolic compounds is still uncommon [19–21], only few investigations concerning it have been reported [21–24]. Moreover, the varieties of sample detected were limited and some of them even detected no real sample at all [21]. The reason is probably that fewer CL reactions are available, or the mobile phase of HPLC is often incompatible with the CL reactions, resulting in difficulties for determination. Therefore, it is very necessary for analysts to expand the practical application of current CL reactions and explore new CL reactions with high sensitivity, good compatibility with HPLC.

Acidic potassium permanganate is one of the most important oxidants utilized in chemiluminescent reactions and considerable numbers of the investigations have been published [19,25,26]. A detailed review reported by Hindson and Barnett [25] and a book chapter by Lin [19] showed that most of the compounds containing a phenolic and/or amine moiety elicited a chemiluminescence response in acidic potassium permanganate system. However, the majority of the investigations reported till date have been operated with a flow-injection analysis (FIA) model and focused primarily on the applications of this CL reagent for the determination of pharmaceutical, biological, cosmetic products or inorganic environmental samples [25]. In comparison, less efforts have been directed towards the purpose of organic pollutant analysis in environment [25–27]. Furthermore, only few researches have, as yet, been made on the technique of combining HPLC with this detection chemistry [28,29]. Amiott and Andrews [28] utilized the technique for the determination of morphine and monoacetylmorphine and obtained impressive detection limits (1, 15 ng/mL, respectively), but the procedure was not applied to real samples. Zhu et al. [29] also achieved similar results with almost the same system. To the best of our knowledge, no investigation concerning the determination of benzenediols and benzenetriols in real sample using the CL reaction as a post-column detection has so far been reported. In this paper, a simple and highly sensitive method for simultaneously determining catechol, resorcinol, hydroquinone and 1,2,4-benzenetriol was established, based on the combination technique of HPLC with the CL reaction of polyhydroxylbenzenes with acidified potassium permanganate and the sensitizing effect of formic acid on the CL system. The method was validated and applied to determine these polyhydroxylbenzenes in river water by means of solid phase extraction (SPE) with satisfactory results.

2. Experimental

2.1. Apparatus

Batch model BPCL luminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China) was employed to study the characteristics of the CL reaction. The flow manifold finally proposed for the HPLC–CL detection is schematically illustrated in Fig. 1. The HPLC system consisted of a model high-pressure pump (LC-10AD, Shimadzu, Japan), a manual sampling valve injector with a 50-μL loop, an analytical column (Supelco Cosil C18-DB, 150 mm × 4.6 mm i.d., 5 μm, USA) and a thermostat column compartment (CTO-10ASvp, Shimadzu, Japan). The CL detection was conducted on a flow injection chemiluminescence system (LUMFLOW LW-800, Funabashi, Japan) comprised a peristaltic pump (Chenghe, Suzhou, China), a mixing coil (1.0 mm i.d.) of 15 cm length and a glass spiral-type flow cell. CL signals were recorded and processed by a personal computer equipped with LUM-2000 data processing program (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China).

2.2. Chemicals

All chemicals employed were at least of analytical grade and the solutions were prepared with deionized ultrapure water (18.3 MΩ/cm, EasyPure^{TM} LF Barnstead, Iowa. USA). Methanol and acetonitrile were from Fisher Scientific (Fair Lawn, NJ, USA). Potassium permanganate ($KMnO_4$), catechol, resorcinol and hydroquinone were from Beijing Chemical Reagents Company (Beijing, China). 1,2,4-Benzenetriol was purchased from Aldrich (Milwaukee, WI, USA). A stock solution of 0.01 M $KMnO_4$ was prepared by dissolving 0.3951 g $KMnO_4$ in 250 mL of 1.0 M H_2SO_4

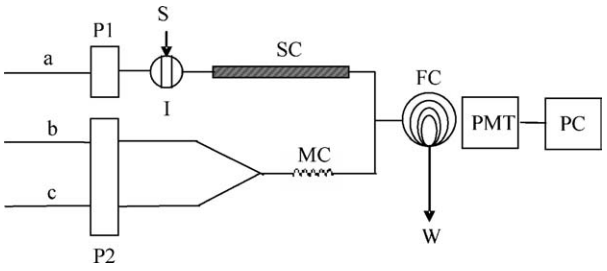

Fig. 1. Schematic diagram of HPLC–CL system. P_1, high-pressure pump; P_2, peristaltic pump; I, injector; SC, separation column; MC, mixing coil; FC, flow cell; PMT, photomultiplier; PC, personal computer; a, mobile phase; b, acidified $KMnO_4$ solution; C, formic acid; S, sample; W, waste.

solution, filtering through glass wool and stored in dark brown bottles. Stock standard solutions of 0.10 mg/mL catechol, resorcinol, hydroquinone and 1,2,4-benzenetriol were fresh weekly prepared by dissolving 0.0500 g polyhydroxybenzenes in 500 mL water, respectively, and stored at 4 °C in a refrigerator. All working solutions were prepared by diluting the stock standard solutions to the needed concentrations correspondingly. The HPLC mobile phases were fresh daily prepared, filtered through a 0.45-μm filter (Xinya, Shanghai, China), and then degassed prior to use.

2.3. Procedure

Separation of polyhydroxybenzenes was carried out on a Supelco Cosil C18-DB column at 25 °C with an isocratic elution program at a flow rate of 0.6 mL/min. The mobile phase consisted of 30% methanol and 70% phosphoric acid (0.5%). And the volume of sample injected was 50 μL in all instances (blanks, standards, and samples). Solutions of $KMnO_4$ and HCOOH were delivered by a peristaltic pump at a flow rate (per tube) of 1.0 mL/min and mixed in a mixing coil and then merged and reacted with the effluent from the HPLC column in the flow cell. The emitted light was monitored by the photomultiplier tube (operated at −800 V). The quantitative determination was based on the net CL intensity $\Delta I = I_s - I_0$, where I_s is the CL intensity of polyhydroxybenzenes and I_0 is the intensity of blank signal.

2.4. Sample preparation

Water samples were preconcentrated with Supelclean Envi-18 (3 mL) cartridges (Supelco, USA) on a set of Visiprep™ Solid Phase Extraction Vacuum Manifolds (Supelco, USA). Two hundred millilitres freshly collected water sample was filtered with 0.45-μm filter to remove suspended particles and acidified to pH 1.5 using concentrated sulfuric acid. The SPE cartridges were first conditioned with 10 mL methanol, then with 15 mL water. The water sample was passed through the cartridge at 4–6 mL/min. After the extraction was complete, the cartridge was dried by applying a vacuum. The extract was eluted with 2.0 mL methane and collected for detection.

3. Results and discussion

3.1. Optimization of CL system

To achieve maximal relative CL intensity for all analytes, a batch experiment was carried out initially to understand the kinetic characteristics of the CL reaction. Then factors that probably influence the reaction, such as reagent concentration, reaction medium, CL sensitizer and flow rate, were investigated. In the optimal processes, the mobile phase (see Fig. 1, flow line (a) was replaced with water and 0.10 mg/L standard solutions were employed for each polyhydroxybenzenes.

The batch experiment showed that the characteristics of the CL reaction appeared to be independent of the phenolic congeners tested, and at start only weak CL signal was elicited when the sample was injected immediately into the fresh mixture of formic acid and $KMnO_4$ solution, and about 15 s later much strong CL signal was observed. If the sample was injected after the mixture placed still ca. 15 s, CL signals occurred almost immediately, went to the maximum value at 4.6 s and then descended to the baseline at 5.6 s. These results suggested that the CL reaction was closely related to the reaction of $KMnO_4$ with formic acid in which an active intermediate seemed to have been produced and played an important part in the latter CL reaction. Because the latter CL reaction was obviously a fast kinetic process, the reaction of $KMnO_4$ with formic acid was the rate limiting step in the whole process. The CL mechanisms of acidified potassium permanganate oxidation with some organic compounds are still not very clear so far. Some excited or active intermediates, such as triplet dimer of carbon dioxide [30], energy transfer to fluorophore [31,32], triplet state of a Mn(II) complex [33,34], or an autocatalytic effect [35], have been speculated, whereas most of the speculations had no convincing supporting evidences. Therefore, the details of the mechanisms remain to be investigated further.

The effect of $KMnO_4$ concentration on the CL intensity was studied in the range 1.0×10^{-4} to 1.0×10^{-3} M. As shown in Fig. 2, the CL intensity increased with the increase in $KMnO_4$ concentration up to 6.0×10^{-4} M and then decreased gradually with a continuous increase in the concentration. The decrease in the signal at higher concentration of $KMnO_4$ was owing to the adsorption of light emission by the intense color of the permanganate solution. Thus, the optimal concentration of $KMnO_4$ was 6.0×10^{-4} M.

Hydrochloric acid, phosphoric acid, polyphosphoric acid, sulfuric acid and nitric acid were used, respectively, as the reaction media to study their effect on the CL intensity. The results showed that sulfuric acid was more suitable medium for all analytes since it gave the strongest light intensity and the highest signal-to-noise ratio (S/N). The effect of sulfuric acid concentration in the range 0.2–1.2 M was further

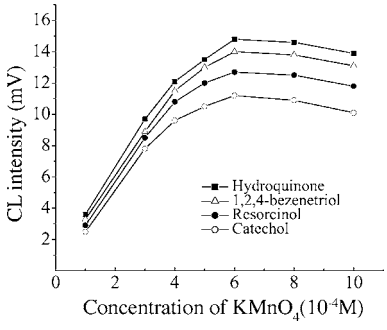

Fig. 2. Effect of $KMnO_4$ concentration on CL signal, $C_{H_2SO_4} = 1.0$ M; C_{HCOOH} = 10% (v/v); flow rate = 1.0 mL/min for each flow line.

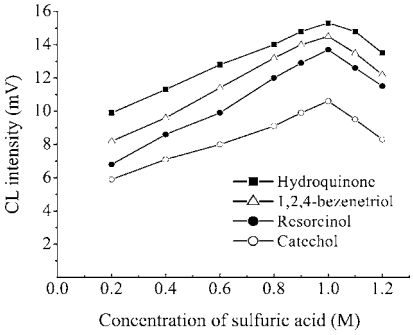

Fig. 3. Effect of sulfuric acid concentration on CL signal, $C_{KMNO_4} = 6.0 \times 10^{-4}$ M; C_{HCOOH} = 10% (v/v); flow rate = 1.0 mL/min for each flow line.

researched and the results are shown in Fig. 3. A sulfuric acid solution 1.0 M was chosen as the optimum sulfuric concentration in $KMnO_4$ solution.

Previous investigations showed that some sensitizers, such as surfactants [25], fluorescing compounds [32], formaldehyde [31], formic acid [36], significantly enhance the CL reactions. In this work, nine potential CL enhancers, including rhodamine 6G or B, uranine, riboflavin, polyethylene 400, sodium dodecyl sulfate, ethyldimethylcetylammonium bromide, formic acid and formaldehyde, were tested. The results showed that most of the compounds added produced no obviously change in the emission intensity except formic acid and formaldehyde which resulted in significantly enhancing effect in the CL signals. Formic acid was proved to be promising one for the CL reaction due to its greatest power of enhancement and lower signal-to-noise ratio. The effect of formic acid concentration varied from 2.0 to 20% (v/v) is shown in Fig. 4. It can be seen that 16% formic acid provided the maximum CL intensity. Higher concentrations caused greater noise signals and therefore resulted in lower analytical signals. So, a 16% formic acid was suitable for the detection of these polyhydroxybenzenes.

It was found that the design of flow system and its operation conditions were also significantly vital to the light emission. Thus, two main parameters, reagent flow rate and the piping length from the mixing point of $KMnO_4$ solution and formic acid to the flow cell, were examined. The influence of the flow rates for each solution was carried out at the

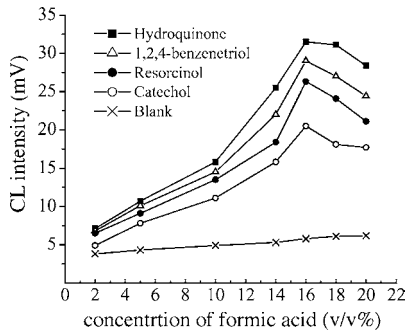

Fig. 4. Effect of formic acid concentration on CL signal, $C_{KMNO_4} = 6.0 \times 10^{-4}$ M (in 1.0 M H_2SO_4); flow rate = 1.0 mL/min for each flow line.

same flow rate in the range 0.5–2.0 mL/min (here water was used as carrier flowing through line a). The results showed that maximum CL intensity could be achieved when the flow rates held upon 0.8–1.2 mL/min; however at flow rate higher or lower than this range, an obvious decrease of CL intensity would be observed. The length of flow line was examined in the range 5–25 cm. The results showed that 15 cm flow line resulted in maximum CL intensity. So, a 15 cm mixing coil and 1.0 mL/min flow rates of the reagents were employed in the study. According to the mechanisms of the CL reaction, the influences of the reagent flow rate and the length of flow line can be simply explained by the fact that suitable parameters of them permitted $KMnO_4$ reacting fully with the formic acid to produce enough active intermediates which would enhance the CL reaction occurred between $KMnO_4$ and the analytes in the flow cell.

3.2. Optimization of HPLC system

The composition of the mobile phase and its flow rate were optimized as a compromise between the resolution and the CL intensity. Several mobile phases have been reported for the separation of phenolic compounds on C_{18} column, such as acetonitrile–water [21], methanol–H_3PO_4–KH_2PO_4–water [22] and methanol–dihydrogenphosphate–water [9]. In this case, acetonitrile and methanol have been examined as the organic part of the mobile phase, respectively, with phosphoric acid as a buffer of the inorganic part. The results showed that although both acetonitrile–phosphoric acid–water and methanol–phosphoric acid–water could almost completely separate these compounds with an isocratic elution program, the use of mobile phase containing acetonitrile greatly quenched the CL signal and produced serious background noise. So, methanol–phosphoric acid–water was chosen as the mobile phase for the further study. The concentration of methanol in the mobile phase was initially optimized by varying the methanol–water mixture ratio in the range 25–40% methanol (v/v) at a constant flow rate of 0.8 mL/min, and 30% methanol was proved to be more effective on the separation, then replaced water with 0.2–1.0% phosphoric acid, 0.5% phosphoric acid improved the resolution of the chromatograph further and the CL intensities of the compounds were almost maximal. The effect of the mobile phase flow rate was investigated in the range 0.4–1.0 mL/min. The results showed that maximum CL intensity and good resolution could be obtained when the mobile phase flow rate was 0.6 mL/min. With the optimized conditions, 30/70 (v/v) methanol/phosphoric acid (0.5%) mobile phase, flow rate of 0.6 mL/min, the four phenolic compounds were separated within ca.10 min. The results in Fig. 5 demonstrate that the CL system was well compatible with the mobile phase of HPLC and no significant baseline drift occurred which was often encountered in some other HPLC–CL detections [22]. In addition, compared with the flow injection CL detection, the HPLC–CL intensity was reduced about 12% due to the different carrier and the flow rate of mobile phase between

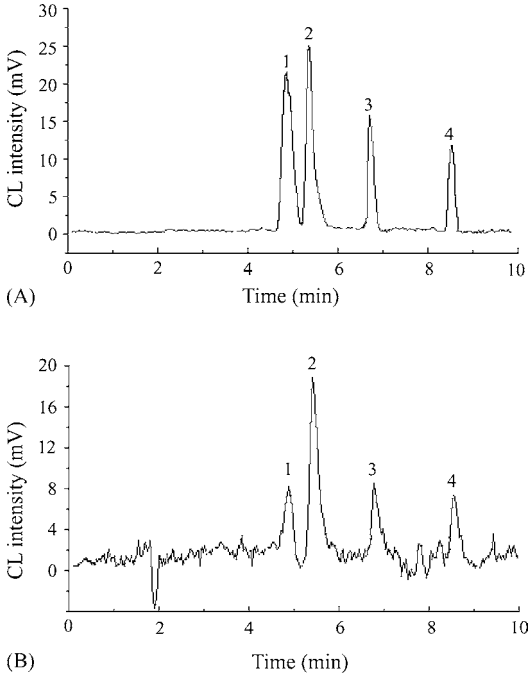

Fig. 5. Chromatograms of four polyhydroxylbenzenes with the CL detection: (A) standard mixture of the four polyhydroxylbenzenes: 0.10 mg/L for each polyhydroxylbenzenes; (B) spiked sample of river water: 200 mL river water was spiked with 0.10 μg for respective polyhydroxylbenzenes, SPE preconcentration; experimental condition: $KMnO_4$: 6×10^{-4} M (in 1.0 M H_2SO_4), 1.0 mL/min; HCOOH: 16% (v/v), 1.0 mL/min; mobile phase: 30:70 (v/v) methanol–phosphoric acid (0.5%), 0.6 mL/min. (1) 1,2,4-Benzenetriol, (2) hydroquinone, (3) resorcinol, and (4) catechol.

the cases. This is still acceptable for the high sensitivity of the method.

3.3. Analytical performance

In order to understand the analytical performance of the system, standard solution containing the four phenolic compounds was prepared over the concentration range 2.0×10^{-3}–5.0 mg/L. The calibration curves were determined under the optimized conditions. The chromatogram is shown in Fig. 5 (A). Parameters of the regression equations and the analytical characters are shown in Table 1. For all compounds, linear ranges of the CL detection were about two orders of magnitude. The limits of detection (S/N = 3) were in the range 2.2×10^{-3} to 4.2×10^{-3} mg/L ($n = 3$). Reproducibilities of the system were performed on 0.1 mg/L of respective phenols and the calculated relative standard deviations (R.S.D.) were in the range 2.8–6.5% ($n = 11$). The results showed that the HPLC–CL system is sensitive for the detection of all the polyhydroxylbenzenes tested.

Table 2
Determined results of polyhydroxylbenzenes in surface water samples ($n = 5$)

Compounds	Added (μg/L)	Found (μg/L)	Recovery (%)	R.S.D. (%)
Hydroquinone	0	0.22	95.4	6.7
	0.50	0.68		
1,2,4-Benzenetriol	0	ND	82.0	12.3
	0.50	0.41		
Resorcinol	0	0.26	92.1	4.5
	0.50	0.70		
Catechol	0	0.31	93.8	3.8
	0.50	0.76		

ND: not detected.

3.4. Method validation and application

In order to evaluate the utility of the proposed method in real samples, both spiked and non-spiked water samples were detected. Surface water sample (200 mL) was collected from the Qinghe River (Beijing, China) and preconcentrated by SPE process as has been described in Section 2.4. A typical chromatogram obtained from a spiked water sample is shown in Fig. 5(B). Table 2 shows the average values of the detections. It can be seen that good recoveries (92.1–95.4%) were obtained for the three benzenetriols and a relatively low recovery (82.0%) for 1,2,4-benzenetriol due to its higher polarity thereby poorer retention on the C18 cartridge. The relative standard deviations were in the range 3.8–12.3% ($n = 5$). Matrices in the river water did not significantly interfere with the detection. So, the proposed method was applicable for detection of these polyhydroxylbenzenes in water.

3.5. Method's figures of merit

Since various methods can be used for the determination of polyphenols, a comparison of the established method with the previous in literatures is necessary and is listed in Table 3. Obviously, the present method has some advantages over the previously reported. For the HPLC–CL methods, our method covered a wider linear range (two orders of magnitude) than all others and the detection limits were superior to the work of Cui et al. [22] and Zhou

Table 1
Regression equations and analytical characteristics for the polyhydroxylbenzenes

Compounds	Linear range (mg/L)	Regression equation ($\Delta I = Ac + B$)	Correlation coefficient (R^2)	LOD[a] (mg/L)	R.S.D.[b] (%)
Hydroquinone	0.006–1.5	$\Delta I = 243.7c + 4.1$	0.9957	3.2×10^{-3}	6.5
1,2,4-Benzenetriol	0.008–1.5	$\Delta I = 219.4c + 3.5$	0.9984	3.9×10^{-3}	4.3
Resorcinol	0.010–2.0	$\Delta I = 205.9c + 3.0$	0.9956	4.7×10^{-3}	3.4
Catechol	0.010–2.5	$\Delta I = 166.4c + 2.2$	0.9976	5.2×10^{-3}	2.8

[a] LOD: limit of detection (S/N = 3).
[b] R.S.D.: relative standard deviation 0.1 mg/L ($n = 11$).

Table 3
Comparison of detections of phenolic compounds with other methods

Compound	Methods	Samples	Linear ranges (μg/mL)	LODs (μg/mL)	References
Hydroquinone	This method	River water	0.006–1.5	3.2×10^{-3}	
	FIA–CL		0.1–1.0	0.04	[17]
	FIA–CL	Drug, photographic developer	0.1–0.15	0.03	[16]
	HPLC–CL	Oxidative hair dyes	0.01–1.0	3.2×10^{-3}	[24]
	HPLC–Coulometric	Urine	0.25–5	0.25	[9]
	Biosensor	Cosmetic cream	8.2–176	0.89	[37]
	Electrochemical	Bleach cream	0.01–0.1	0.01	[38]
	Spectrometric	Pharmaceutical formulations	100–3000		[12]
1,2,4-Benzenetriol	This method	River water	0.008–1.5	3.9×10^{-3}	
Resorcinol	This method	River water	0.01–2.0	4.7×10^{-3}	
	FIA–CL		0.06–1.0	0.02	[17]
	HPLC–CL	Rutin, tobacco[a]	1.0–10	0.68	[22]
	HPLC–CL	Pharmaceutical formulations	0.025–1.0	2.2×10^{-3}	[23]
	HPLC–CL	Oxidative hair dyes	0.1–10	0.012	[24]
	GC–FID			0.032	[7]
	Spectrometric	Pharmaceutical formulations	100–2000		[12]
Catechol	This method	River water	0.01–2.5	5.2×10^{-3}	
	FIA–CL	Cigarettes[a]	0.006–1.1	1.3×10^{-3}	[18]
	HPLC–CL		0–11		[21]
	HPLC–CL	Rutin, tobacco[a]	0.05–5	0.037	[22]
	Biosensor		0.11–5.5	0.11	[39]
	Spectrometric	Pharmaceutical formulations	250–2500		[12]

LOD: limit of detection.
[a] The target polyphenols were not analyzed in the sample.

et al. [24] with respect to resorcinol, who had employed luminol–potassium–hexacyanoferrate(III) and Ce^{+4}–Tween 20 systems, respectively, and similar to Cui et al.'s another work [23] in which luminol–dimethylsulfoxide–OH^- reaction was used or Zhou et al.'s work [24] concerning hydroquinone. Moreover, their detection samples were mainly biological [22], pharmaceutical [23], cosmetic[24] or even without at all [21]. In addition, we used an isocratic elution program for the separation purpose that overcame baseline drift which occurred in other HPLC–CL detections [22]. For the FIA–CL methods, the detection limits of the reported were apparently inferior to the current, and these methods were only used for the determination of single phenolic congener in simple matrices [19,25,16–18], whereas the current method had successfully determined benzenediols or benzenetriols in natural water with simple sample pretreatment. As the rest methods cited are concerned, they all had relative high limits of detection compared with the present although some of them, such as biosensor [37,39], were claimed having impressive selectivity. Therefore, the established method offers HPLC or CL detection an alternative, sensitive and simple approach for the determination of some phenolic compounds and is no doubt a potential tool for its routine use in various areas, such as environmental analysis, etc.

4. Conclusions

Based on the sensitizing effect of formic acid on the CL reaction of polyhydroxylbenzenes with acidified $KMnO_4$ and the combination technique of HPLC, a novel CL—post-column detection method has been established for the determination of hydroquinone, catechol, resorcinol and 1,2,4-benzenetriol. The method has been proved that the CL reaction is well compatible with isocratic elution in the HPLC separation and permits highly sensitive, selective and simultaneous determination of these polyhydroxylbenzenes in complex matrices. Furthermore, with solid phase extraction and methanol elution, only a relatively small volume (200 mL) of water sample is needed and the extract can be directly injected into the analytical system without further concentration or solvent change. This makes the determination of real samples more simple and rapid. Thus, the method is a promising alternative approach for the determination of polyhydroxylbenzenes in environmental samples.

Acknowledgements

The authors gratefully acknowledge financial support of the National Science Fund for Distinguished Young Scholars of China (No. 20125514), National Natural Science Foundation of China (No. 20437020) and Major Research Program of Chinese Academy of Sciences (KZCX3-SW-432).

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