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# Lab-on-valve (LOV) system coupled to irreversible biamperometric detection for the on-line monitoring of catechol

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ABSTRACT

The analytical performance of lab-on-valve (LOV) system using irreversible biamperometry for the determination of catechol was evaluated. By integrating miniaturized electrochemical flow cell (EFC) designed and processed which is furnished with two identical polarized platinum electrodes, into the LOV unit, the lab-on-valve system combines sampling with analysis, realizing automated on-line analysis for catechol in a closed system. The biamperometric detection system was established to record the relationship between oxidation current and time by coupling the irreversible oxidation of catechol at one pretreated platinum electrode with the irreversible reduction of platinum oxide at the other pretreated platinum electrode. Factors influencing the analytical performance were optimized, including the potential difference ($\Delta E$), buffer solution and pH, and flow variables in the LOV. A linear calibration curve was obtained within the range of $1.0 \times 10^{-6}$–$5.0 \times 10^{-4}$ mol $L^{-1}$ of catechol with the detection limit ($3\sigma$) of $5.09 \times 10^{-7}$ mol $L^{-1}$. The relative standard deviation (R.S.D.) was 2.39% for 11 successive determinations of $1 \times 10^{-5}$ mol $L^{-1}$ catechol and the sample throughput was 35 $h^{-1}$. Moreover, this proposed method was applied to the analysis of catechol in beer sample, which was testified by high-performance liquid chromatography (HPLC).



## 1. Introduction

As the third generation of flow injection analysis (FIA), the sequential injection lab-on-valve (SI-LOV) system, which was introduced by Ruzicka [1], has opened up a host of prospects in the sample pretreatment, on-line monitoring and biochemistry assays [2–4]. The microconduit LOV unit is a single monolithic structure mounted atop of a multiposition valve of a sequential injection network. The flexible channel design of LOV unit integrated with a multi-purpose flow cell offers much more versatility over the FIA and sequential injection analysis (SIA) systems. Up to now, the LOV analytical system can serve as versatile "front ends" to various detection techniques with micro-miniaturized sample processing, such as molecularspectroscopy [5], fluorescence [6], chemiluminescence [7], atomic spectrometry [8,9], electrochemistry [10] and chromatography [11,12]. The exploitation of LOV system not only significantly minimized sample and reagent consumption, but also offered an improved analytical frequency and minimized the risk of sample cross-contamination, which provided an automatic, rapid, and accurate protocol for the determination of analytes [13,14].

The irreversible biamperometric detection can be well established, which relies on the presence of two irreversible and independent redox reactions that have inverse electrode processes. The irreversible biamperometry not only provides high sensitivity and signal-to-noise ratio (S/N), but also broadens the application fields of reversible biamperometry [15,16]. In addition, the method can be applied to the determination of analytes at very small potential difference, even down to 0 V. Since the external potential difference is very small with small background current in the testing process, the proposed method shows high selectivity, making biamperometry a much more attractive technique [17].

With increasing demands for faster, more automated, and less reagent-intensive analytical systems, the lab-on-valve system was developed for the first time in conjunction with the biamperometric technology in this paper. And taking catechol as a concrete example, the feasibility of the testing system was demonstrated. As an important fine chemical, catechol is the basic organic ingredients or intermediates in the process of producing a variety of chemical products and pesticides, as well as during the natural decomposition of the humic and lignocellulosic substances [18]. Moreover, the presence of catechol in drinking water and food poses a safety concern due to its toxic and possibly carcinogenic effects. So it is of great practical significance to analyze the catechol. Many electrochemical methods have been employed for the determination of catechol, such as differential pulse voltammetry (DPV) based

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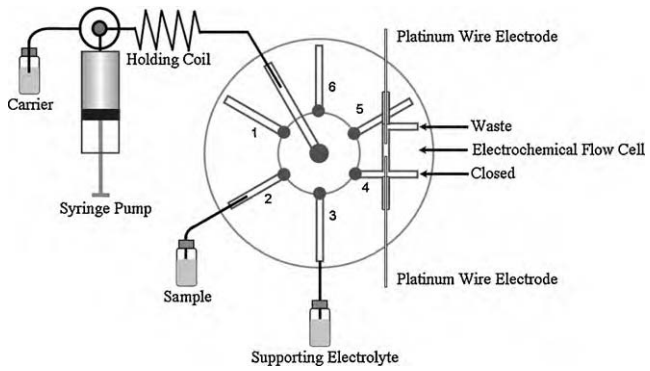


**Fig. 1.** Schematic diagram of the SI-LOV manifold coupled with irreversible biamperometry for the determination of catechol.

on molecular imprinting technology [19], series dual-band amperometric detection in the flow injection analysis [20], mediated electrochemical detection by tyrosinase-based poly(dicarbazole) electrodes [21], and a new tyrosinase/DNA biosensor with flow injection [22]. Although much research efforts have been made to explore flow injection procedures coupled with amperometric detectors for reducing sample consumption [23–25], due to its continuous flow character, still needs large amounts of reagent. The biamperometry provides several advantages in hyphenation with LOV format. To begin with, the experimental procedure is not complicated with no need for electrode modifications. Second, the system is easy and simple to handle because reference electrode is not required in the course of biamperometric analysis. Last but not the least, the proposed method is characterized by high selectivity with biamperometry owing to very small potential difference applied.

In this work, by integrating appropriate electrochemical flow cell (EFC) into LOV format, the biamperometric detection scheme was built based on the irreversible electrochemical oxidation of catechol and the irreversible reduction of platinum oxide when potential difference of 0 V was applied. The present work developed new field in application and research of the electrochemistry for the LOV technology in terms of automation and minimum for solution handing for the first time, by implementing irreversible biamperometric measurement.

## 2. Experimental

### 2.1. Apparatus

The LOV system controlled by FIAlab software for Windows 5.0 is shown schematically in Fig. 1. The experiments were carried out via employing a FIAlab-3000 sequential injection system (FIAlab, Instruments, Bellevue, WA, USA) equipped with a 2500 μL syringe pump (Cavro, Sunnyvale, CA, USA) and a six-position selector valve. The LOV itself is a microconduit mounted atop of a multiposition valve with 6 external ports. The central flow-through channel, via which the other individual ports are connected, is used to communicate with a syringe pump.

A homemade LOV unit incorporated an EFC with a two platinum wire electrodes system. The volume of the electrochemical flow cell was equivalent to approximately 230 μL. All the used tubes were made of 0.8 mm i.d. PTFE tubing (Upchurch Scientific, OakHarbor, WA, USA) and the capacity of holding coil (HC) was 2.5 mL. A LK2005 electrochemical workstation (LANLIKE Tianjin Chemistry and Electron High Technology Co. Ltd., China) was used for the biamperometric detection. The model Surveyor HPLC apparatus (FINNIGAN) with PDA detector was employed for the analysis of catechol in real sample. And the chromatographic conditions were the following. Flow rate of mobile phase: 1.0 mL/min; UV detection wavelength: 278 nm; sampling volume: 20 μL; column temperature: 30 °C; analytical column: Agilent TC – $C_{18}$ column (150 mm × 4.6 mm interior diameter (I.D.), 5 μm); mobile phase: 90% A and 10% B (A: an aqueous solution of 0.5% acetic acid; B: methanol).

### 2.2. Chemicals and reagents

Stock solution of $1 \times 10^{-2}$ mol $L^{-1}$ catechol was prepared daily in 0.05 mol $L^{-1}$ phosphate buffer solution (PBS, pH 6.6). The working standard solutions were obtained by step-wise dilution in the same background electrolyte solution to avoid any differences in ionic strength of the sample. PBS (0.05 mol $L^{-1}$, pH 6.6) and de-ionized water were used that acted as the supporting electrolyte and carrier solution, respectively. 0.2 mol $L^{-1}$ sodium hydroxide solution was prepared for the electrode polarization. All the reagents used were at least of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Double de-ionized water (18 MΩ) was used throughout the experiments.

### 2.3. Fabrication of two electrodes

The two platinum electrodes were fabricated from Pt wire 0.5 mm in diameter with 99.9% purity, which were sealed in the screw connectors with epoxy resin with the exposed length of 1.0 cm to the flowing solution. After immersed in the concentrated nitric acid for 5 min and rinsed with double de-ionized water, the two finished platinum electrodes were polarized at applied potential difference of 1.5 V (*vs.* SCE) for 600 s in 0.2 mol $L^{-1}$ sodium hydroxide solution. Then rinsed with double de-ionized water, the two activated platinum electrodes were assembled into the LOV unit for biamperometric detection. Such pretreatment was repeated daily to maximize the sensitivity.

### 2.4. Operating procedure

The schematic diagram of LOV system for biamperometric determination of catechol was illustrated in Fig. 1. The central channel was connected to 2500 μL high-precision syringe pump via HC. Port 4 was acted as a detection port where a multi-purpose flow cell was integrated. First, 1000 μL of carrier from the reservoir and 600 μL of PBS and 150 μL of catechol solution were aspirated from the ports 3 and 2 sequentially at a flow rate of 50 μL $s^{-1}$ into the HC, where the various zones were stacked and stored. Thereafter, the mixed sample/reagent zones were propelled forward into the EFC at the flow rate of 40 μL $s^{-1}$, where the biamperometric system was built. At the same time, the resulting current was recorded based on the two irreversible couples when the external potential difference of 0 V was imposed across the two platinum electrodes. Finally, the remaining 1000 μL of carrier was dispensed into port 4 to cleanse both the EFC and the tubes.

## 3. Results and discussion

### 3.1. The construction of biamperometric system

The cyclic voltammetry (CV) was performed in order to establish the irreversible biamperometric system with a three-electrode system, namely, a platinum wire electrode as working electrode (WE), a small-sized platinum electrode as counter electrode (CE), and a saturated calomel electrode (SCE) as reference electrode (RE). When the pretreated electrode was placed in phosphate buffer medium with no catechol present, an irreversible reduction peak $P_1$ appeared at ca. 0.02 V (all potentials *vs.* SCE in CV), which is related to the reduction of PtO formed at the Pt electrode surface

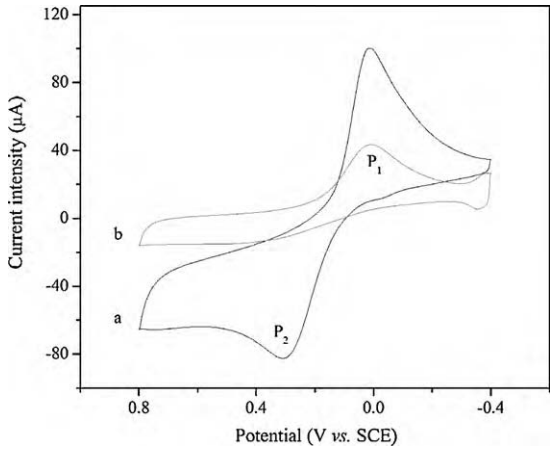


**Fig. 2.** Cyclic voltammograms on pretreated platinum electrode in the presence (a) and absence (b) of $5.0 \times 10^{-5}$ mol L$^{-1}$ of catechol in 0.05 mol L$^{-1}$ PBS (pH 6.6) solution. Initial potential −0.4 V, reversal potential 0.8 V, scan rate $\nu = 100$ mV s$^{-1}$.

through pre-anodization. This wave has been described and the result was consistent with the published one [26]. After the addition of catechol, an irreversible oxidation peak $P_2$ was present at ca. 0.29 V, corresponding to the oxidation of catechol, together with the basically identical reduction peak potential. Furthermore, the influence of pH on peak potential was also studied by CV. It can be seen that the oxidation peak potential shifts negatively with increasing solution pH within the range from 2.0 to 8.0, obeying the equation $E_p = 0.7080 - 0.0633$ pH with $R^2 = 0.9983$. The slope of −63.3 mV pH$^{-1}$ was obtained, which suggests that the number of proton and electron involved in the oxidation of catechol is equal. In the meantime, the constant potential coulometry for catechol was carried out at the potential of 0.5 V. And the electron transfer number was found to be 2.09. So the oxidation reaction formula is as follows:

$$\text{catechol} \rightarrow o\text{-quinone} + 2H^+ + 2e^-$$

Moreover, there was only one anodic peak, indicating that the oxidation reaction of catechol at platinum electrode contained only one step and was achieved in the irreversible process. The peak $P_1$ and $P_2$ were, respectively, in cathodic and anodic curves with the inverse electrode processes. Therefore, biamperometric system consisting of the two irreversible and independent couples, was well-established on the basis of the irreversible biamperometric measurement principle. When the applied potential difference ($\Delta E$) was 0 V, this method was applied to the determination of catechol and biamperometric currents were related to its concentrations. As can be seen in Fig. 2, when the $\Delta E$ of 0 V was implemented, the actual potentials of the two platinum electrodes were between 0.02 and 0.29 V and were kept the same value because anodic and cathodic currents were equivalent to each other. Meanwhile, the potential of two platinum electrodes may not reach limit currents of both reactants, but the current response was generated in the under-potential situation. The magnitude and the flow direction of the current are decided by the smaller one among anodic and cathodic currents. At the same time, increasing the applied $\Delta E$ will make the potentials of two electrodes move to the limiting current direction of one or the other reactant, which will lead to the increase of sensitivity [27].

The good current response was obtained at the applied potential of 0 V when catechol solution got through the EFC. It can be seen that the biamperometric system has produced an obvious result by coupling the reduction of platinum oxide with the oxidation of catechol. The coupling system can work in an under-potential situation based on the irreversible biamperometric mode without any potential difference $\Delta E$ imposed artificially between two electrodes, which is different from that in reversible couple system in which no current response can be obtained at $\Delta E$ of 0 V, such as $I_2/I^-$ and $Fe^{3+}/Fe^{2+}$ [28].

### 3.2. Effect of applied potential difference

The external potential difference ($\Delta E$) imposed between two platinum electrodes appeared to be a predominant parameter in biamperometric measurement, which had an influence on sensitivity, selectivity and linear range. With respect to irreversible biamperometry, the potential difference $\Delta E$ dependents on the $\Delta E_{1/2}$ (or $\Delta E_p$) of the half-wave potential $E_{1/2}$ (or peak Potential $E_p$) of two irreversible couples. When the $\Delta E_{1/2}$ (or $\Delta E_p$) is large, the increasing of the applied $\Delta E$ leads to the increase of sensitivity. However, the increase of the $\Delta E$ was accompanied by the decrease of both selectivity and S/N ratio, which did not contribute to the practical analysis [29].

The effects of the $\Delta E$ on signal magnitude were investigated ranging from −0.3 to 0.3 V in $5 \times 10^{-5}$ mol L$^{-1}$ catechol solution (not shown). With increasing $\Delta E$, the current response was improved along with a high relatively sensitivity. However, larger background current were also obtained, which caused the selectivity to decrease. When $\Delta E$ of 0 V was applied, the method showed high S/N and selectivity with the company of small background level and noise, which made it possible to increase the dynamic range available for the signal current. At the same time, the well-shaped peak and more stable baseline were obtained. Therefore, applied $\Delta E$ of 0 V was chosen as a compromise between the sensitivity and selectivity for the further experiment.

In amperometric and biamperometric detection mode, because the working potential difference is fixed at a constant value, the background current is mainly faradic current rather than charging current, which is mainly caused by other introduced electroactive substances. In this method, because the applied $\Delta E$ is 0 V, it is difficult for co-existed electoractive compounds to be electrolyzed and produce current. As a result, a steady baseline was obtained. This is impossible with conventional amperometry in which baseline is high and easy to shift because the applied potential is generally high.

### 3.3. Effects of buffer solution and pH

The supporting electrolyte played an important role in the biamperometric analysis, which was selected based on the effect of pH on the peak height and peak shape. Under the condition of $\Delta E$ of 0 V, influences of various buffer systems on resulting currents were tested in $5 \times 10^{-5}$ mol L$^{-1}$ catechol standard solution, including 0.2 mol L$^{-1}$ HAc–NaAc (pH 3.0–5.5), 0.05 mol L$^{-1}$ $Na_2HPO_4$–$KH_2PO_4$ (pH 3.4–7.7) and 0.1 mol L$^{-1}$ $NH_3 \cdot H_2O$–$NH_4Cl$ (pH 7.5–9.8). The results showed that the current response of catechol in PBS was significantly higher than other two kinds of mediums, and well-shaped peaks and stable current signals were achieved. Therefore, phosphate buffer solution was chosen as the reaction medium.

A more detailed study of the effect of pH on the biamperometric response was performed using PBS (0.05 mol L$^{-1}$) between the pH level of 3.4–7.7. The biamperometric current responses of the catechol are presented in Fig. 3. It can be seen that the peak height increased with the pH value of PBS up to about 6.6, above which it decreased, and at which a maximum signal was obtained. As a result, phosphate buffer solution of pH 6.6 was used throughout the biamperometric experiments.

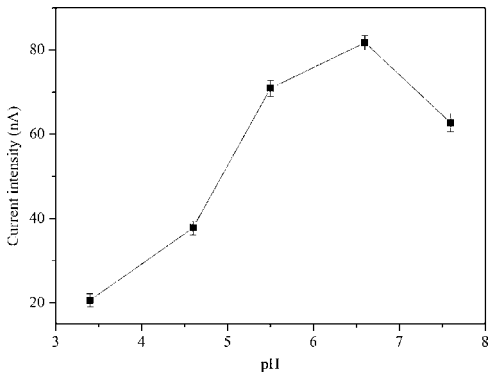


**Fig. 3.** The effect of pH upon the biamperometric response signal.

### 3.4. Optimization of LOV parameters

LOV parameters were optimized by the univariate method so as to achieve a compromise between the peak height, sample throughput and reproducibility. The optimization of dynamical parameters containing sample volume and flow rate was carried out.

It was found that the injection volume had a strong effect on current response in peak height and peak width, which was varied from 50 to 400 μL. As illustrated in Fig. 4(A), the peak height and peak width increased with the sample volume up to 150 μL, above which it leveled off, demonstrating the improvement of detection sensitivity by increasing the sample volume within a certain range. No significant differences were observed above 150 μL except for a decrease in the sample throughput. This phenomenon could be attributed to the fact that the amount of reactant was increased with the increment of the injection volume, resulting in an increase of the peak height. However, when an excessive amount of sample zone was introduced into the EFC, the catechol could only disperse/penetrate into a certain length of reagent zone, which contributed very little to the reaction in fact, and thus an unchanged signal was obtained. Therefore, a 150 μL sample volume was assumed as the optimum.

The flow rate was investigated taking into account the change in signal intensity as well as the peak shape and reproducibility, on which the sample throughput was strongly dependent. As shown in Fig. 4(B), the signal intensity increased with the flow rate from 10 to 40 μL $s^{-1}$ and reached a maximum at the flow rate of 40 μL $s^{-1}$, thereafter it decreased. With regard to the adjacent sample/reagent zones in a flow channel, the extent of dispersion is one of the most important factors affecting the reaction and the sensitivity of the detection system. On the one hand, when lower flow rate was implemented, a broader peak and small peak height were obtained because the higher degree of dispersion of the sample zone into the carrier stream would result in the decrease of the concentration of the detectable sample. On the other hand, higher flow rate would lead to an unstable signal with poor reproducibility due to lack of adequate reaction time. When the flow rate of 40 μL $s^{-1}$ was applied, the maximal peak height was achieved with satisfactory sample throughput. Hence 40 μL $s^{-1}$ was chosen as the optimum flow rate.

### 3.5. Stability of the biamperometric system

It was suggested that the anodic oxidation of some aromatic substances on the solid electrodes resulted in the loss of electrode response and precision since the formation of polymeric films on electrode surfaces. However, no loss of electrode response was obtained for detection at low concentration of aromatic compounds [30]. The two pretreated Pt electrodes were applied to the determination of $1.0 \times 10^{-5}$ mol $L^{-1}$ catechol for 70 measurements, and the current response remained about 98.0% of the initial value, indicating that the electrode system had good durability. The good durability of the electrodes is mainly related to two facts. On the one hand, large amounts of platinum oxide have been produced on platinum surface after the proposed pretreatment step [31]. On the other hand, as mentioned above, the true potential of the cathode actually has not reached the limiting current plateau of platinum oxide. Therefore, the depletion of platinum oxide is a slow process. The platinum oxide depleted can be easily recovered by next pretreatment. Because the formation and reduction of platinum oxide is reversible, the detector can be repetitively used with no loss of platinum from the electrode surface.

### 3.6. Investigation of interferences

The tolerance of the analytical method to foreign species was investigated by using standard solutions containing $1.0 \times 10^{-5}$ mol $L^{-1}$ catechol and adding various concentrations of the interfering substances. The tolerable ratio of each foreign species concentration was as follows: 1000-fold for $K^+$, $Na^+$, $Cl^-$, $SO_4^{2-}$, $Mg^{2+}$; 500-fold for $Zn^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ca^{2+}$, $NH_4^+$, $PO_4^{3-}$; 300-fold for $Cu^{2+}$, $Mn^{2+}$, ethanol, salicylic acid; 200-fold for $Cd^{2+}$, $Ni^{2+}$; 100-fold for $Pb^{2+}$, $Sn^{2+}$, thiamine hydrochloride, riboflavin, glucose, resorcinol; 50-fold for gallic acid, benzoic acid; 30-fold for hydroquinone. In this study biamperometric detection technology was carried out at potential difference of 0 V, which avoided interference from other redox species that could react directly at the electrode surface. Meanwhile, it can be seen

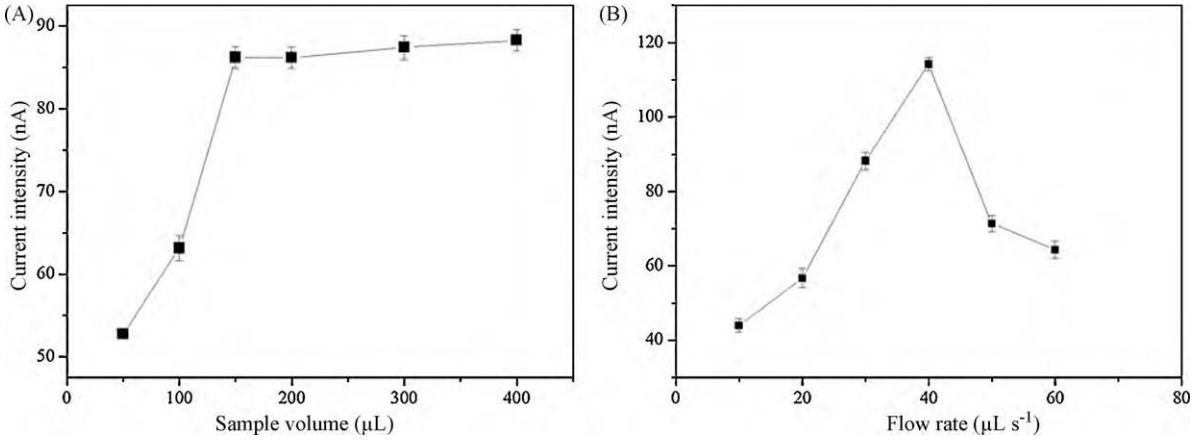


**Fig. 4.** The effects of sample volume and flow rate upon the biamperometric response signal.

**Table 1**
Determination of trace level concentrations of catechol in beer sample by LOV system-biamperometric detection and HPLC ($n = 3$).

| Sample | Found by LOV-biamperometry ($mol\,L^{-1}$) | Found by HPLC ($mol\,L^{-1}$) |
|---|---|---|
| A | $6.64 \pm 0.57$ | $6.89 \pm 0.42$ |
| B | $7.83 \pm 0.64$ | $8.02 \pm 0.50$ |

that common substances caused no significant interference with catechol during analysis, which meant this method possessed good anti-interference ability. Therefore, it can be applied to the determination of catechol in real samples with good selectivity.

### 3.7. Analytical characteristics

A study of the analytical application of the LOV procedure was carried out to establish the application range, reproducibility, detection limit and sample throughput. Under the optimal experimental conditions, a calibration graph was plotted based on the relationship between the peak height and the concentration of catechol. The calibration graph was linear over the range $1.0 \times 10^{-6}$–$5.0 \times 10^{-4}\,mol\,L^{-1}$ of catechol with $R^2 = 0.9998$. Regression equation of the calibration curves was $i_p = 1.5629C + 15.854$ ($i_p$: $10^{-9}$ A, C: $\mu mol\,L^{-1}$) along with a sampling frequency of $35\,h^{-1}$. The limit of detection (LOD) is evaluated using $3\sigma/s$, where $\sigma$ is the standard deviation of the blank signals and s is the slope of the linear calibration graph. And the LOD for catechol was calculated to be $5.09 \times 10^{-7}\,mol\,L^{-1}$, along with a precision of 2.39% relative standard deviation at the level of $1 \times 10^{-5}\,mol\,L^{-1}$ catechol for 11 repeated cycles.

Compared with the traditional flow analysis, volume of injected sample was only 150 μL along with a higher sampling frequency in LOV format. At the same time, the proposed method shows a wider linear range and a lower LOD. Moreover, the sample cross-contaminations were eliminated, because all the manipulations were carried out in a closed system. Therefore, using biamperometry with LOV makes an ideal combination of the methods and uses the best characteristics of both of them.

### 3.8. Determination of catechol in real sample

The catechol content of beer was determined by the established system, and the results were validated by HPLC. The beer sample was degassed by ultrasonic device for 30 min, and then was filtered through a 0.45 μm millipore filters before use. The results obtained by two methods were in good agreement, suggesting that the proposed method is feasible and effective with high accuracy for the determination of catechol. The obtained results were summarized in Table 1.

## 4. Conclusions

Based on the analysis of catechol, it was demonstrated that LOV as the solution-handling and automation system gives additional possibilities in biamperometric measurements by integrating the appropriate EFC into LOV unit. The method is superior to the conventional batch method in that it provides fully automation, cost effectiveness with less reagent and sample consumption, rapidity and small waste generation. By means of pre-anodic polarization, electrode contamination was removed to maximize the sensitivity, along with getting enough platinum oxide coupling with catechol. These results show that biamperometric measurements can well be used with the LOV technique.

With respect to the analysis of some real world samples, e.g., body fluids including urine and blood, the content of catechol could not be detected because of the complex matrix interferences. At this time, bead Injection (BI) technique [32–34], that is, the renewable surface scheme, could be introduced and implemented in an LOV fluidic manifold, so that the matrix effect of the complicated samples can be on-line eliminated before biamperometric detection, and the related work is performed. Moreover, in order to further downscale the reagent/sample consumption, a smaller flow cell can be designed and the electrode size can be reduced such as microelectrodes based on the actual demands, which is especially useful for bioassays.

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