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# Simultaneous Detection of Protocatechuic Acid, Chlorogenic Acid and Caffeic Acid in Honey by HPLC with Ultraviolet and Electrochemical Detectors

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A rapid and sensitive method for the detection of protocatechuic acid (PA), chlorogenic acid (CLA) and caffeic acid (CAA) has been developed by high-performance liquid chromatography (HPLC) with an ultraviolet detector (UV) and an electrochemical detector (ECD). HPLC with UV detection was performed on a $C_{18}$ column (250×4.6 mm, 5 μm) with methanol (pH 4.0) - acetic acid (v/v, 85/15) as the mobile phase at a flow rate of 1.0 mL/min. ECD detection was performed on a three-electrode system, with a glassy carbon electrode, a platinum foil and a saturated calomel electrode (SCE) as the working electrode, the auxiliary electrode and the reference electrode, respectively. Compared with individual HPLC-UV and ECD methods, the presented HPLC (UV-ECD) technique had the advantage of enhanced capture of electroactive PA, CLA and CAA and achieved obvious detection sensitivity. Under the optimized conditions, the linear concentration ranges were from 0.0005 to 6 mg $L^{-1}$ for PA and CAA, and from 0.0015 to 18 mg $L^{-1}$ for CLA, with limits of detection of 10 ng $L^{-1}$ for PA, 30 ng $L^{-1}$ for CLA and 13 ng $L^{-1}$ for CAA (S/N = 3), which were clearly lower than those obtained with the HPLC-UV method. The approach was also successfully applied to detection in honey samples with satisfactory recoveries.

**Keywords:** HPLC-UV method; HPLC-ECD method; HPLC (UV-ECD) technology; protocatechuic acid; chlorogenic acid; caffeic acid

## 1. INTRODUCTION

Protocatechuic acid (PA), chlorogenic acid (CLA) and caffeic acid (CAA) are widely distributed in commonly consumed fruits, natural products and other foods [1-4]. The molecular

structures of the three compounds are shown in Fig. 1. Pharmaceutical investigations have demonstrated that the three compounds exhibit antioxidant, anticancer and anti-carcinogenic properties [5-9]. Therefore, the development of a fast and sensitive method for the simultaneous detection of the three compounds is important. Over the past few years, many methods have been devoted to the detection of one of PA, CLA, or CAA of mixtures of the three compounds, including liquid chromatography-mass spectrometry (LC-MS) [10-12], gas chromatography-mass spectrometry (GC-MS) [13], and capillary electrophoresis (CE) [14,15]. Although these technologies possess fairly high selectivity, the processes for sample pretreatment are complex and lengthy. HPLC is an effective technology for quantitatively analyzing complex compounds in natural products because of its high separation efficiency and reproducibility [16-19].

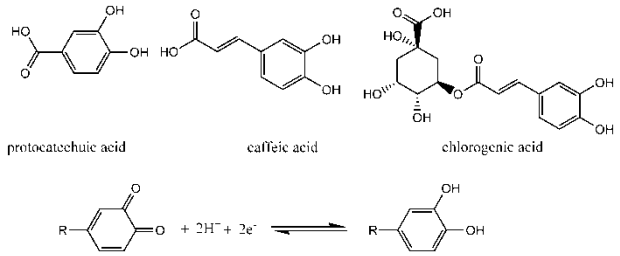



**Figure 1.** The molecular structures of PA, CLA and CAA, and the redox reaction mechanism of PA, CLA and CAA using HPLC (UV-ECD)

However, HPLC also has higher detection limit and needs more analytical time than electrochemical detection methods (ECDs). ECDs are adopted to detect the three species due to the advantages of rapidity, low-cost and high sensitivity [20-24]. Unfortunately, the oxidation potentials of PA, CLA and CAA are too close to be determined by using separate ECD method.

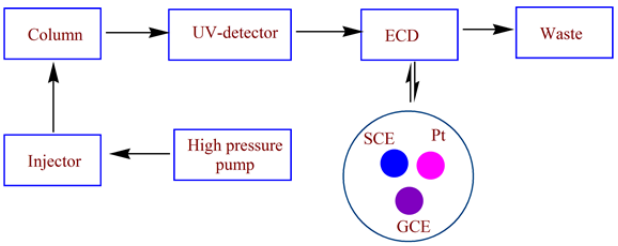
To date, there have been a few reports about the determination of these organic compounds by using HPLC (UV-ECD) method. Chen [25] proposed a method using HPLC (UV-ECD) to detect four alkaloids of *Coptis chinensis* in real samples, and the limit of detection for berberine was lower than the value obtained by only HPLC-UV detection. Zhou [26] used HPLC with wall-jet/thin-layer ECD to successfully separate DA and homovanillic acid (HVA) with satisfactory recoveries. Hang [27] prepared a self-fabricated HPLC (UV-ECD) system to measure four 5-hydroxy polymethoxyflavones with wide concentration ranges and low detections. Wu [28] developed a quantification method using HPLC combined with ECD to identify monofloral honeys. As far as we know, there has not been a published report using HPLC (UV-ECD) methods to simultaneously detect PA, CLA and CAA [25-31].

In this work, we provide a strategy to establish a method using the advantages of HPLC-UV and ECD, that can be utilized to the quantitatively detect PA, CLA and CAA in real samples. The method exhibited excellent responses to PA, CLA and CAA, and three well-defined separated peaks were observed. More importantly, HPLC (UV-ECD) possessed the advantages of easy electrode treatment and improved analytical performance. Furthermore, the selectivity and sensitivity of the method can be obviously improved by using new technology. When the method was applied for

determining the content of PA, CLA and CAA in real samples, satisfactory recoveries were obtained. Moreover, excellent responses were achieved due to the reproducibility of HPLC and low detection limit of ECD.

## 2. MATERIALS AND METHODS

PA, CLA and CAA were purchased from Alfa Aesar (Shanghai). Acetic acid and methanol were obtained from Aladdin Chemistry Co., Ltd. (Shanghai). All other reagents were at least of HPLC grade and were filtered through 0.22 μm filters.




**Scheme 1.** The schematic diagram of the self-assembled HPLC (UV-ECD) instrument system.

The HPLC (UV-ECD) system consisted of a binary pump, an autosampler, a UV-vis spectrophotometric detector (Agilent Corp., Waldbronn, Germany) and an ECD system (Chenhua Corp., Shanghai, China). A schematic diagram of the HPLC (UV-ECD) instrument is shown in scheme 1. The HPLC analysis were performed on an Agilent 1100 system equipped with a binary pump, a UV-vis spectrophotometric detector and a manual injector with a 20.0 μL autosampler. ECD was performed on an electrochemical analyzer with a layer flow cell composed of a three-electrode system of glassy carbon electrode, platinum foil and saturated calomel electrode (SCE) as the working electrode, the auxiliary electrode and the reference electrode, respectively.

The HPLC experiments were carried out on a Diamonsil $C_{18}$ (i.d. 5 μm 250×4.6 mm) column at a flow rate of 1.0 ml $min^{-1}$. The temperature of the column was controlled at 25 ºC and the ECD system was placed behind the UV detector operating at 254 nm.

The active GCE was prepared by using cyclic voltammetry (CV) in borax buffer solution (pH 9.18) with a potential range from -0.2 to +1.3 V, and a scan rate of 0.10 V/s. After the GCE was scanned for 10 cycles, the electrode was rinsed by deionized water. The electrochemical method is helpful for enhancing the sensitivity of HPLC (UV-ECD).

The 2 g $L^{-1}$ standard solutions of PA, CLA and CAA were prepared by dissolution in methanol. The solutions were stored at 4 ºC after they were filtered through a 0.22 μm membrane and were diluted to the required concentrations with mobile phase before use.

The honey samples were prepared [28,32] by mixing 1.0 g of honey with 5 mL of buffer and 4 mL of ethyl acetate. After it was centrifuged, the supernatant was collected and put into an Oasis HLB SPE, which was pretreated with 5 mL of methanol and 10 mL of HCl (pH=2.0). Afterwards, 10 mL of

distilled water was used to rinse the SPE, and the eluent was collected after the SPE was eluted with methanol. After the collected solution was evaporated to dryness, the solid residue was redissolved in methanol. Then, the solution was passed through a membrane filter, and 20 μL of the prepared solution was injected into the HPLC (UV-ECD) instrument. In this paper, the electrochemical behaviors of PA, CLA and CAA were investigated by using differential pulse voltammetry (DPV).

## 3. RESULTS

### *3.1. Electrochemical performance of PA, CLA and CAA*

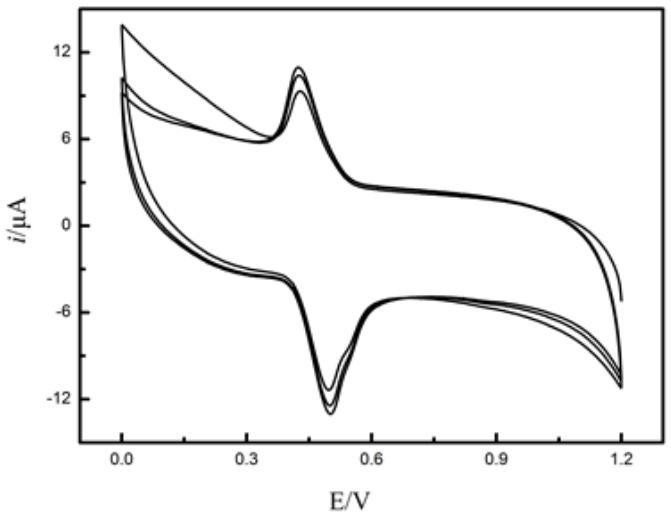



**Figure 2.** Cyclic voltammetry of the bare GCE in 1 g $L^{-1}$ PA, CLA and CAA solution after being immersed in borax buffer solution (pH 9.18) . Potential range: -0.2 - +1.3 V. Scan rate: 0.10 V/s.

Fig. 2 shows the CV responses of PA, CLA and CAA obtained by using the ECD method. It was found that the current peaks of the three small molecules overlapped when using the individual method. To achieve ideal, well-separated peaks, the combination of the good separation efficiency of HPLC with ECD in the HPLC-UV detector was used for the simultaneous detection of the three small molecules in further experiments.

### *3.2. Optimization of the experimental conditions*

A series of conditions were tested for optimization and for achieving good reproducibility and high sensitivity. These parameters include mobile phase composition, pH value and voltage. The DPV method was used to investigate all the influencing factors.

*3.3. Effect of mobile phase compositions*

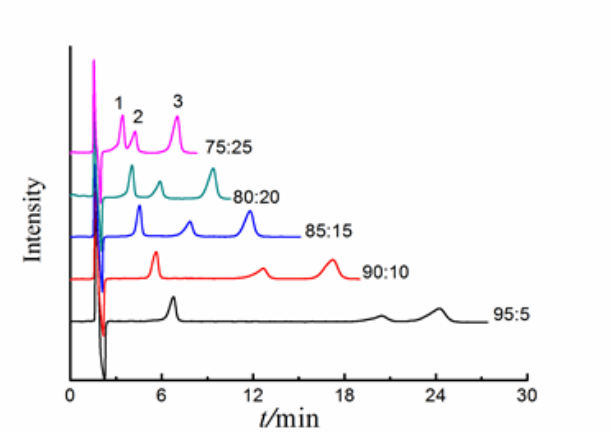



**Figure 3.** Effects of different mobile phase compositions on the current of the HPLC (UV-ECD) method for the three organic acids (the mobile phase compositions of 4% acetic acid and methanol were 75:25; 80:20; 85:15; 90:10; 95:5; 1. PA 2. CLA 3. CAA). Supporting electrolyte: methanol (pH 4.0) - 4% acetic acid.

Since the composition of the mobile phase is the main factor in HPLC, different ratios of the mobile phase component were investigated in this paper [33-34]. It can be seen in Fig. 3 that the overall time of analysis decreased as the methanol content increased from 5% to 25%, while the separation efficiency decreased and well-separated peaks could not be observed with increasing methanol in the mobile phase. To obtain good peak shapes for PA, CLA and CAA and ideal results in a short time, a mobile phase consisting of 15% methanol was selected for further studies.

*3.4. Effect of pH value*

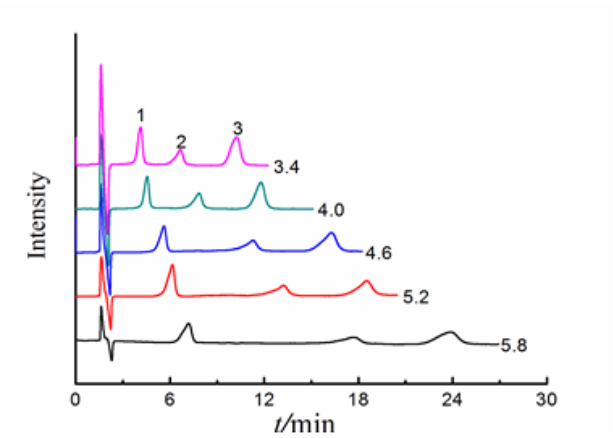



**Figure 4.** Effect of mobile phase pH on the current of the HPLC (UV-ECD) method for the three organic acids. (pH values were 5.8, 5.2, 4.6, 4.0, 3.4; 1. PA 2. CLA 3. CAA). Supporting electrolyte: methanol- 4% acetic acid (v/v, 85/15).

The pH value of the mobile phase has an important influence on the current peaks and retention time of the analytes[35,36]. Different pH values of the mobile phase ranging from 3.4 to 5.8 were investigated in this work. As shown in Fig. 4, the adsorbed PA, CLA and CAA molecules showed different electrochemical behavior and overall retention times at different pH values. Although well-separated peaks could be obtained within the pH range tested, the mobile phase at pH 4.0 exhibited the strongest current signal and the optimal retention time. Therefore, the mobile phase consisting of methanol - 4 % acetic acid (pH 4.0) was chosen for separating the three compounds.

### *3.5. Effect of potentials*

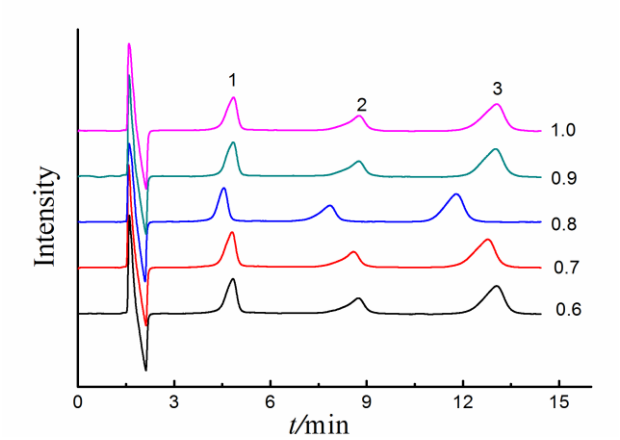



**Figure 5.** Effect of voltage on the current of the HPLC (UV-ECD) method for the three organic acids. (voltage values were 0.6 V, 0.7 V, 0.8 V, 0.9 V, 1.0 V; 1. PA 2. CLA 3. CAA). Supporting electrolyte: methanol (pH 4.0)- 4% acetic acid (v/v, 85/15).

To investigate the effect of suitable settings for the potential on the electrochemical performance of PA, CLA and CAA, a series of potentials set at 0.6-1.0 V were chosen in the optimized experiments. As shown in Fig. 5, all of the three compounds could be separated, and they exhibited the maximum current signals and the shortest retention time at 0.8 V. To obtain high sensitivity, the potential of 0.8 V was applied in the following experiments using the HPLC (UV-ECD) method.

## 4. DISCUSSION

### *4.1. Simultaneous determination of PA, CLA and CAA*

A series of concentrations of PA, CLA and CAA were investigated to prove the analytical performance of the HPLC (UV-ECD) method (Fig. 6a). The experiments indicated that the peak currents of the three compounds rapidly increased with increases in their concentrations. The linear ranges for PA, CLA and CAA obtained with the self-fabricated HPLC (UV-ECD) system were 0.0005-6 mg $L^{-1}$, 0.0015-18 mg $L^{-1}$ and 0.0005-6 mg $L^{-1}$, with correlation coefficients of 0.993, 0.993 and 0.997, respectively.

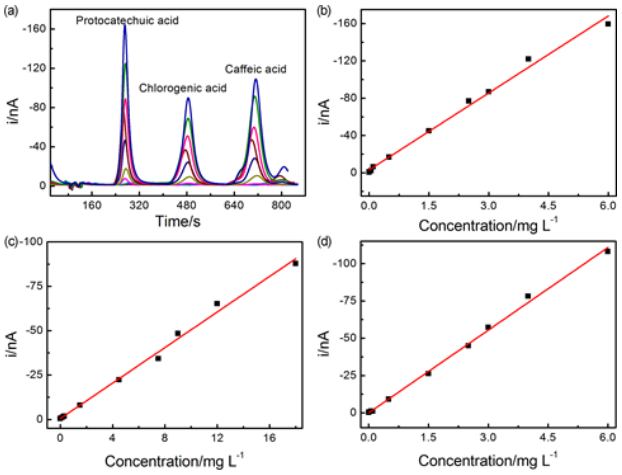



**Figure 6.** DPVs of different concentrations of PA and CAA, 0.0005, 0.05, 0.1, 0.5, 1.5, 2.5, 3.0, 4.0, and 6.0 mg $L^{-1}$, and different concentrations of CLA, 0.0015, 0.15, 0.3, 1.5, 4.5, 7.5, 9.0, 12, and18 mg $L^{-1}$ by using the HPLC (UV-ECD) method. The linear relationship between the peak current and PA (b), CLA (c) and CAA (d) concentration. Other conditions are the same as those in Fig. 5.

The corresponding linear equations were expressed as $I_{pA}$ (nA) =-3.15-27.50 $C_{PA}$ (mg $L^{-1}$), $I_{CLA}$ (nA) =-0.52-5.00 $C_{CLA}$ (mg $L^{-1}$) and $I_{CAA}$ (nA) =-0.07-18.46 $C_{CAA}$ (mg $L^{-1}$). The limits of detection were estimated to be 10 ng $L^{-1}$ for PA, 30 ng $L^{-1}$ for CLA and 13 ng $L^{-1}$ for CAA (Fig. 6b-d). Furthermore, the good separation of the three compounds by HPLC and the high sensitivity to the three electroactive analytes of ECD made our method highly sensitive and selective (Table 1).

**Table 1.** The parameters of the linear regression by using HPLC-ECD with ECD and UV-detection.

| Analyte | Regression equation | RSD (%, n=3) | Linear range (mg $L^{-1}$) | $R^2$ | LOD (ng $L^{-1}$) |
|---|---|---|---|---|---|
| | | ECD | | | |
| PA | i = -3.15-27.50 c | 1.5 | 0.0005-6 | 0.993 | 10 |
| CLA | i = -0.52-5.00 c | 1.6 | 0.0015-18 | 0.993 | 30 |
| CAA | i = -0.07-18.46 c | 1.5 | 0.0005-6 | 0.997 | 13 |
| | | UV-detection | | | |
| PA | i = -29.57+1.26 c | 2.1 | 7.0-1500 | 0.995 | 2000 |
| CLA | i = -24.56+1.28 c | 1.8 | 21.0-4500 | 0.993 | 5000 |
| CAA | i = -2.67+0.79 c | 1.9 | 7.0-1500 | 0.994 | 1600 |

The redox reaction mechanism of PA, CLA and CAA was explained by the fact the three compounds are phenolic acids. According to the literature [37], the redox processes of phenolic acids

proceed with two electron transfers and two proton transfers to form the corresponding phenolic aldehydes. The first explanation is that the aldehyde compounds can be accounted for by an electron transfer followed by a proton transfer. Afterwards, the compounds are accounted for by a second electron transfer with subsequent proton transfer to reversibly generate phenolic acids. The other explanation is that the aldehyde compounds are accounted for by an initial electron transfer, followed by two consecutive proton transfers and a final electron transfer to reversibly generate phenolic acids (Fig. 1).

### *4.2. Reproducibility of the HPLC (UV-ECD) method*

The reproducibility of the HPLC (UV-ECD) method was investigated by performing repeated injections of PA, CLA and CAA on one day or on three consecutive days. The different concentrations of the three compounds were calculated both intra-day (n=6) and inter-day (n=3), and the results are summarized in Table 2.

**Table 2.** Intra-day and inter-day variability of PA, CLA and CAA detection with the HPLC-ECD method.

| Analyte | Concentration (mg $L^{-1}$) | RSD (%) | |
|---|---|---|---|
| | | Intra-day (n=6) | Inter-day (n=3) |
| PA | 0.01 | 2.4 | 3.6 |
| | 0.1 | 2.8 | 3.8 |
| | 1.0 | 3.2 | 4.1 |
| CLA | 0.1 | 3.0 | 4.2 |
| | 1.0 | 3.5 | 4.9 |
| | 10 | 4.2 | 5.2 |
| CAA | 0.01 | 2.6 | 3.1 |
| | 0.1 | 2.9 | 3.9 |
| | 1 | 3.7 | 4.4 |

ECD method possessed the advantages of the rapid response, good stability and high sensitivity in the determination of PA, CLA and CAA. However, it also suffered from the low selectivity and poor separation effect. HPLC can make up for the drawback of ECD method for it can provide the excellent accuracy and high selectivity. Combined ECD together with HPLC, the HPLC (UV-ECD) method exhibited good reproducibility.

The intra-day relative standard deviation (*RSD*) ranged from 2.4 % to 4.2 %, and the inter-day *RSD* ranged from 3.6 % to 5.2%, suggesting the method possessed excellent reproducibility. The excellent reproducibility of the method can be attributed to the synergistic effect of the ECD and HPLC.

*4.3. Real sample analysis*

To study the viability of HPLC (UV-ECD), the technology was used to detect PA, CLA and CAA in honey samples. The concentrations of the three compounds were directly detected and the standard addition method was used to calculate the recoveries of the three compounds. Spiked samples of PA, CLA and CAA were added to the prepared honey samples. Afterwards, the experiments were repeated three times, and the results are presented in Table 3.

**Table 3.** Contents of PA, CLA and CAA in honey samples obtained by using the HPLC-ECD method.

| Samples | Detected (mg $L^{-1}$) | Added (mg $L^{-1}$) | Found (mg $L^{-1}$) | Recovery (%) | RSD (%) (n=3) |
|---|---|---|---|---|---|
| PA | 0.228 | 0.1 | 0.30 | 93.8 | 5.0 |
| | | 1.0 | 1.19 | 97.5 | 4.2 |
| | | 4.0 | 4.25 | 100.7 | 3.8 |
| CLA | 0.075 | 0.01 | 0.084 | 98.8 | 4.7 |
| | | 0.1 | 0.17 | 97.1 | 4.1 |
| | | 1.0 | 1.04 | 96.7 | 4.5 |
| CAA | 0.25 | 0.1 | 0.34 | 97.1 | 4.3 |
| | | 1.0 | 1.24 | 99.2 | 4.5 |
| | | 4.0 | 4.26 | 100.2 | 4.2 |

It can be seen that the RSD was in the range of 3.8 %-5.0 % and that the recovery was between 93.8 % and 100.7 %. The results indicated that this HPLC (UV-ECD) method had high accuracy and sufficient precision.

**Table 4.** Comparison with other reported methods for the detection of PA, CLA and CAA.

| **Methods** | **Linear range (mg $L^{-1}$)** | | | **Detection limit (ng $L^{-1}$)** | | | **References** |
|---|---|---|---|---|---|---|---|
| | PA | CLA | CAA | PA | CLA | CAA | |
| **ECD** | / | / | 0.005-169 | / | / | 1080 | [38] |
| | / | / | 0.001-2.70 | / | / | 486 | [39] |
| | / | 0.053-21.250 | / | / | 15945 | / | [40] |
| | 0.0008-0.0650 | / | 0.0004-0.0900 | 208 | / | 121 | [41] |
| **HPLC-UV** | / | 50-200000 | / | / | 10 | / | [42] |
| **HPLC (UV-ECD)** | 0.0005-6 | 0.0015-18 | 0.0005-6 | 10 | 30 | 13 | **This Work** |

The results of the HPLC (UV-ECD) method were compared with some other literatures, as shown in Table 4. The minimum concentrations of PA, CLA, and CAA and the detection limits of this paper are lower than that of those previously reported methods. These results confirmed that the method was a promising technique for the high selective, sensitive and reproducible detection of the three biomolecules.

## 5. CONCLUSIONS

In this paper, a new strategy for using a self-fabricated HPLC (UV-ECD) system to simultaneously determine PA, CLA and CAA was presented for the first time. The developed method exhibited high sensitivity and a low detection limit. Notably, the method was successfully applied to the detection of the contents of the three compounds in honey samples with satisfactory recoveries. Furthermore, we found that the three compounds can adsorb on the electrode and that the HPLC (UV-ECD) system is sensitive to the ternary mixture of PA, CLA and CAA. This technology provides a more accurate and reliable analytical method to analyze other electro-active compounds.

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