On-line deoxygenation in reductive (and oxidative) amperometric detection: environmental applications in the liquid chromatography of organic peroxides

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Cyclic voltammetry was used qualitatively to characterize and determine the feasibility of the oxidation and reduction of selected organic peroxides and hydroperoxides at a glassy carbon electrode. Organic peroxides were determined using reversed-phase high-performance liquid chromatography with simultaneous reductive and oxidative amperometric detection in a thin-layer dual parallel–adjacent electrode configuration. An on-line deoxygenator allowed the removal of molecular oxygen from the mobile phase and this resulted in an extension of the negative potential range of the glassy carbon electrode by approximately 750 ± 50 mV vs. the Ag/AgCl reference electrode. Chromatographically assisted hydrodynamic voltammetric measurements, in the dual parallel–adjacent electrode configuration, provided confirmation of the feasibility of simultaneously monitoring two independent redox reactions, for a single analyte, and allows for both the qualitative and quantitative analysis of organic peroxides (and hydroperoxides). The reductive amperometric responses were, on average, 2–5 times greater, depending on the particular organic peroxide, than the corresponding oxidative amperometric responses. An empirically determined parameter was evaluated and developed, \([i_{\text{ox}}/i_{\text{red}}]^{-1}\) or \([i_{\text{ox}}/i_{\text{red}}]^{-1}\), from two independent electrode reactions, that allows the qualitative identification of organic peroxide analytes by comparison of samples with standard injections. Estimated method detection limits (MDLs) for butan-2-one (butan-2-one) peroxide (2-BP), tert-butyl hydroperoxide (t-BHP) and cumene hydroperoxide (CHP) in reductive amperometry are approximately 0.8, 0.4 and 5 ppb, respectively and the oxidative amperometric MDLs are about 3, 2.5 and 12 ppb, respectively. The reductive amperometric responses for 2-BP, t-BHP and CHP are linear over 4–5 orders of magnitude of concentration, extending from ca. 1 µg l\(^{-1}\) to ca. 100 mg l\(^{-1}\), and the corresponding correlation coefficients are of the order of 0.9997–0.99994.

Introduction

The presence of dissolved molecular oxygen in solution has presented liquid chromatographers and other researchers with challenges that have essentially frustrated reductive amperometric measurements in flow injection analysis and liquid chromatography. Because of the problems associated with oxygen interference, the chemical literature contains little information with regard to the determination of organic peroxides and hydroperoxides using high-performance liquid chromatography (HPLC) with reductive mode amperometric detection. Funk et al.\(^{1}\) determined selected organic peroxides at a gold/mercury amalgam electrode\(^{1,2}\) and a polarographic detector used in the hanging mercury drop electrode mode.\(^{2,3}\) Xi and Baldwin\(^{4}\) employed a chemically modified carbon paste electrode containing iron phthalocyanine (FePC) to reduce organic peroxides at potentials 100 mV more positive than that required for oxygen reduction. Chou and Locke\(^{5}\) reported the determination of benzoyl peroxide at an amalgam electrode with a working potential of −0.15 V vs. the reference. A series of long chain peroxyxcarboxylic acids in commercial detergents were determined by Kirk et al.\(^{6}\) at a platinum working electrode. Yamada et al.\(^{7}\) reported the determination of phospholipid hydroperoxides extracted from rat liver at a glassy carbon electrode.

This paper, in part, reports on the evaluation of the performance of an on-line deoxygenator\(^8–10\) for the removal of dissolved molecular oxygen from both the eluent and sample in HPLC. The major objective was to determine the feasibility of measuring organic peroxides and hydroperoxides in a flowing stream using reductive amperometry, with applications to analyses of drinking water. Consequently, reversed-phase (RP) HPLC coupled with parallel–adjacent dual amperometric detection (PADAD) was employed to monitor simultaneously the oxidation and reduction of each organic peroxide and hydroperoxide in a thin-layer amperometric cell. The PADAD configuration,\(^{11–20}\) providing spatial but not temporal resolution, allowed co-instantaneous measurements of the selected peroxide analytes. To our knowledge, this is the first report of an application of this redox behavior of organic peroxides and hydroperoxides in a flowing stream. Also, it may be the first application of PADAD to a chemical system in which a single form of an analyte can undergo co-instantaneously an oxidation and a reduction reaction. An empirically determined composite parameter was also evaluated and developed, from the hydrodynamic voltammogram for the two independent electrode reactions, that allows the qualitative identification of organic peroxides and hydroperoxides. The advantages of PADAD coupled with liquid chromatography are further demonstrated by enhanced sensitivity and selectivity and the ability to...
generate quantitative information from two independent redox processes.

**Experimental**

**Apparatus**

Cyclic voltammetry was performed with a Bioanalytical Systems (BAS) (West Lafayette, IN, USA) CV-27 (cyclic voltammograph, interfaced to a C2 cell stand (MF-9064)) (BAS) with built-in gas control. A BAS Model VC-2 (MF-1082, 1.0–20 ml) single compartment glass electrochemical cell was employed to perform the bulk solution experiments, which were conducted at room temperature. The three electrode system (BAS) consisted of (a) working electrode; glassy carbon disk (3 mm diameter) voltammetric electrode (MF-2012); (b) reference electrode; silver/silver chloride (Ag/AgCl) electrode (MF-2063, Model RE-5); and (c) counter/auxiliary electrode; platinum wire electrode (5 cm, MW-1032) with a gold plated connector mounted in a Kel-F cylinder.

HPLC was performed with a Model 200A liquid chromatograph (BAS) equipped with a Rheodyne (Cotati, CA, USA) Model 7125 injector employing a 20 µl sample loop and a built-in flow-through thin-layer dual channel amperometric detection system. The amperometric detector consisted of (a) a dual glassy carbon working (0.069 cm², geometric area) electrode (MF-1000), (b) an Ag/AgCl reference electrode (MF-2021, Model RE-4), (c) a stainless-steel counter/auxiliary electrode and (d) a 0.002 in thin-layer gasket (MF-1046). The liquid chromatograph was controlled by a Gateway (North Sioux City, SD, USA) 2000 386SX/33 computer system, employing the Microsoft (Seattle, WA, USA) Windows 3.1 operating system and BASControl and ChromGraph software (BAS).

Deoxygenation was, in part, performed with a Model 100 on-line deoxygenator (NovaTech, Westtown, PA, USA), with a knitted membrane tube (NT-110) (300 mm × 3.8 mm id), inserted between the column and the detector.

**Chromatography**

The reversed-phase analytical column used was a Luna (ODS, C₁₈, 5 µm) 250 mm × 4.6 mm id (Phenomenex, Torrance, CA, USA). The mobile phases were acetonitrile–water mixtures (5:95–50:50 containing 0.05 M phosphate buffer, pH ≈ 7). The flow rate was 1.0 ml min⁻¹ unless stated otherwise, and the column backpressures at this flow rate ranged from ca. 1800 to 2400 lb in⁻². The pump(s) performed at optimum efficiency when the flow rate was 1.0 ml min⁻¹.

The system was operated in a dual amperometric detector configuration (parallel–adjacent) in order to perform reductive and oxidative amperometry to monitor simultaneously two independent redox reactions. The electrode potentials, E<sub>ARP</sub> (−1.250 ± 0.05 and +1.150 ± 0.05 V vs. Ag/AgCl reference electrode) selected for detection were the optima for the simultaneous reductive and oxidative amperometric determination of the three organic peroxides/hydroperoxides. All amperometric measurements were performed by applying the specified operating potentials and allowing the transient current(s) to decay to steady state values.

**Voltammetry**

Current–potential curves were obtained by performing representative cyclic voltammetric experiments in (a) 0.05 M potassium phosphate buffer (pH 7) (b) 10% v/v methanol–0.05 M potassium phosphate buffer, (c) 40% v/v acetonitrile–0.05 M potassium phosphate buffer and (d) other combinations of organic modifiers and aqueous solutions. The potential (E<sub>app</sub>) was cycled, in two sets of experiments, from an initial value of −0.20 to +1.4 to −0.6 V and from −0.2 to −1.4 to +0.6 V (vs. Ag/AgCl reference electrode) and back to the initial setting(s). The voltammetric scan rate was 50 mV s⁻¹.

Response–potential curves [hydrodynamic voltammograms (HDVs) and/or chromatovoltammograms] were also obtained by performing liquid chromatographic experiments with reductive and oxidative amperometry under constant potential conditions (manually stepped simultaneously and sequentially) from ~ ±0.0 to ~ ±1.40 V vs. Ag/AgCl reference electrode and a constant eluent flow rate of 1 ml min⁻¹. Known amounts of organic peroxide analytes were injected after the potentials had been applied and the resultant currents reached steady state values.

**Reagents and chemicals**

HPLC grade acetonitrile (OPTIMA) was obtained from Fisher Scientific (Fairlawn, NJ, USA). In-house distilled water was passed through a four-bowl (two Ion-Ex cartridge filters, one carbon cartridge, one Organex-Q cartridge, one Millipak 0.22 µm filter for final filtration) Milli-Q water system (Millipore, Bedford, MA, USA). The organic peroxide, 2-BP, and hydroperoxides, t-BHP and CHP (Aldrich, Milwaukee, WI, USA) were used as received. Certified ACS grade potassium dichromate and dipotassium hydrogenphosphate (Fisher Scientific) were used, without additional purification, to prepare buffered eluent solutions of ca. pH 7. High purity helium, 99.995% (Matheson Gas Products, Secaucus, NJ, USA) was used to purge/deoxygenate the chromatographic eluent solutions. The purge gas employed for the cyclic voltammetric experiments was pre-purified nitrogen, 99.999% (Matheson Gas Products). A non-indicating oxygen trap, copper oxide and aluminum oxide catalyst (Oxy-Purge N) (Alltech, Deerfield, IL, USA), was used to remove any residual (trace) oxygen from the nitrogen gas prior to flowing through the on-line deoxygenator chamber.

**Caution.** Organic peroxides may be extremely toxic and are potential mutagens and teratogens. Pure standard material (liquid and solid) and stock standard solutions of these compounds should be handled with suitable protection for the skin, eyes, nasal passages and clothing.

Acetonitrile is an extremely toxic organic solvent and may constitute an environmental hazard. Proper care should be exercised when disposing of chromatographic wastes.

**Results and discussion**

**Cyclic voltammetry**

Cyclic voltammetry (CV) was used to examine qualitatively the feasibility of oxidizing and reducing 2-BP, t-BHP and CHP at glassy carbon electrodes in aqueous buffer solutions and buffered aqueous–organic solutions. Fig. 1 shows the oxidation of (a) CHP, (b) t-BHP and (c) 2-BP in phosphate buffered acetonitrile. A single anodic peak was observed for the oxidation of each organic peroxide and hydroperoxide over the potential range investigated and under the specified conditions. In addition, no cathodic peaks were observed on the reverse scan. In fact, this was found to be the case under all other conditions investigated. For comparable relative concentrations, it appears that the magnitude of the faradaic oxidative response was 2-BP > t-BHP > CHP, irrespective of the
particular organic solvent system. The difficulty in verifying this order of response is masked by the merging of the analyte oxidation peaks with the solvent system oxidation wave.

Cyclic voltammetric experiments were also conducted to determine if it was possible to reduce the selected peroxides. The potential was scanned at 50 mV s$^{-1}$ from $-0.2$ to $-1.4$ to $+0.6$ V (vs. Ag/AgCl reference electrode) and back to the initial setting. Even with very high concentrations of analytes, under the prevailing conditions, the resultant voltammograms were either non-existent or ill-defined and virtually indistinguishable from the background or baseline signal. However, a small low, broad wave or peak was observed at ca. $-1.2$ V vs. Ag/AgCl reference electrode when CHP was added to the cell. The reductive current response occurred at the potential limits of the electrode and merged with the rising signal that may have been due to the reduction of the solvent or other system components. On reversal of the scan, a corresponding oxidative peak was not observed for any of the solution analytes.

**Deoxygenation**

The on-line deoxygenator$^8$–$^{10}$ was placed between the outlet of the liquid chromatographic column and the amperometric detector. The efficiency of the deoxygenation process was enhanced by the continuous flow of nitrogen through the chamber. It appeared that even without pre-sparging the mobile phase the efficiency of the on-line deoxygenator was satisfactory. No noticeable differences were observed in the baseline responses when the deoxygenator was employed exclusively for sample and mobile phase deoxygenation.

The HDV for sample oxygen (Fig. 2) shows that the glassy carbon electrode is not large enough to allow the reductive amperometric detection of organic peroxides and hydroperoxides without interference from oxygen. With the deoxygenator on, the apparent range of the glassy carbon electrode is extended to ca. $-1.450$ ± $0.05$ V vs. the Ag/AgCl reference electrode with the contribution of oxygen to the non-faradaic or background current being virtually negligible. Fig. 2(a) and (b) show the analytes in the presence and absence of sample oxygen, respectively. The deleterious effect of sample oxygen on the analyte peaks becomes more apparent as the current sensitivity is increased.

With the deoxygenator inserted in the system, the retention times of the analytes increased by approximately 1.2 ± 0.25 min. Also, recycling of the mobile phase was problematic with respect to CHP because the deoxygenator membrane tubing is permeable not only to oxygen but also apparently to acetonitrile.$^{10}$ With recycling of the mobile phase over a period of 2–3 d, the retention times for CHP varied from about 2 to 6 min.

**Hydrodynamic voltammetry**

Since cyclic voltammetry yielded minimal information with regard to the reduction of the organic peroxides and hydroperoxides, voltammetric data were generated via chromatographically assisted HDV. Preliminary results indicated that the selected peroxides may each have the electrochemical ability to be co-instantaneously oxidized and reduced. Therefore, to investigate and exploit the potential of such redox behavior, the desirable spatial, but not temporal, resolution may be achieved with a parallel–dual electrode configuration. This arrangement permits the monitoring of two independent redox reactions, is independent of the degree of reversibility of the analytes and allows simultaneously both oxidative and reductive amperometry.

Fig. 3 shows the chromatographically assisted HDVs or chromatovoltammograms generated for each organic peroxide and hydroperoxide using PADAD. Fig. 3 confirms that the negative potential range of the glassy carbon electrode is extended by at least 700 ± 50 mV vs. Ag/AgCl reference electrode (cf., Fig. 2). The glassy carbon surface therefore offers an extended activation overpotential range for both electrochemical oxidations and reductions. Also, the organic peroxides and hydroperoxides, having high positive and negative overpotentials, are both oxidized and reduced with the maxima in their analytical signals occurring near the potential limits of the electrodes. The analytical signals for the organic peroxides and hydroperoxides increased with both positive and negative potential steps, from $+0.650$ to $+1.200$ V and from $-0.500$ V to $-1.250$ V vs. Ag/AgCl reference electrode, respectively. However, with further increases in the potential step, in either the positive or negative direction, the analytical signals decreased gradually for each analyte, resulting in peak-shaped HDVs. The electrode potentials, $E_{\text{APP},p}$ = $-1.250$ ± 0.05 and $+1.150$ ± 0.05 V vs. Ag/AgCl reference electrode, selected for the further determinations were the optima for the simultaneous reductive and oxidative amperometric responses of the three organic peroxides. Background current considerations were more significant for the oxidative (Fig. 3) measurements than for the corresponding reductive measurements. The baseline response for the reductive amperometric measurements increased slightly with increase in potential, $E_{\text{APP},p}$, up to ca. $1.400$ V vs. the Ag/AgCl reference electrode, and contributed minimally to the analytical signal. The reductive amperometric signals were estimated from the HDVs (Fig. 3) to be 2–5 times larger than the corresponding oxidative amperometric signals.

A composite empirical parameter, $[i_{\text{Ox,Red}}^{-1}]$ or $[i_{\text{Red}}^{-1}]$]

Parallel multiple electrodes may be utilized to enhance detection selectivity and peak identification via voltammetric

**Fig. 1** Cyclic voltammograms of (a) cumene hydroperoxide, (b) tert-butyl hydroperoxide, and (c) butan-2-one peroxide. Supporting electrolyte: 40% v/v acetonitrile-0.05 M phosphate buffer. Curve numbers and concentration of analyte: (1) blank response; (2) 58.8; (3) 115.3; (4) 169.8; and (5) 222.2 mg l$^{-1}$ of each analyte. Potential range: $+1.4$ to $-0.6$ V vs. Ag/AgCl reference electrode. Scan rate: 50 mV s$^{-1}$.
characterized. These spatially resolved electrodes placed side-by-side are operated at two potentials on the HDV of the analyte of interest. The two potentials are poised on the diffusion-limited current plateau and another point along the rising portion of the HDV, respectively. Co-instantaneous chromatovoltammograms result from this electrode configuration, and the ratios of their peak currents may be used to calculate an empirical parameter that may be employed to assess peak purity by comparing samples with standards. Lunte and Kissinger employed parallel-adjacent dual electrodes in a chemical system containing both oxidizable and reducible pterins to enhance peak identity assignments and selectivity. Shoup and Mayer, also seeking to enhance detector selectivity and confirm peak identities, described applications of parallel multiple electrodes to a complex mixture of neurochemicals in brain tissue and phenols in industrial wastewater, shale oil and other environmental samples.

The empirical parameter evaluated and developed in this work, unlike the parameters reported previously in the literature, is derived from two different areas of the HDV. Each organic peroxide and hydroperoxide had the ability to undergo co-instantaneously two different redox reactions, an oxidation and a reduction. The parallel-dual electrodes poised at a single potential, the optimum positive and negative potential, +1150 and -1250 mV vs. Ag/AgCl reference electrode, on each HDV, provided two unique chromatovoltammograms. The ratio of the two currents was used to calculate a composite parameter that provided real-time information on each analyte in the aqueous matrix. Current ratios were established for samples and also for standard solutions for calibration purposes. Table 1 presents data for measurements on organic peroxides and hydroperoxides in Cincinnati tap water samples and standards of each analyte added to laboratory reagent water. For nominal concentrations of 0.2 and 0.5 ng ml\(^{-1}\) for the analytes, the calculated composite parameters for standards versus samples show good agreement. Hence we are able to confirm peak identity by two independent parameters: chromatographic retention time and the calculated composite parameter from the HDV. The data in Table 1 further indicate that the average analytical signal ratios for the three analytes are ca. 2.2, 3.8 and 4.2, respectively. Because of the detector electrode configuration, with one electrode poised at a negative potential and the other electrode poised at a positive potential, and the nature of the electrode reactions, we inherently have the ability to calculate two additional parameters that will further allow unequivocal confirmation of peak identities for organic peroxides and hydroperoxides in drinking water matrices. Therefore, a combination of chromatographic and amperometric/voltammetric data should provide selectivity and peak identification assignments with a high degree of certainty.

**Detection limit, linear range and sensitivity**

The MDLs\(^{21}\) for the reductive and oxidative amperometric determination of the organic peroxide and hydroperoxide analytes are given in Table 2. These MDL data were obtained from peak current measurements by injecting 20 \(\mu\)l of the spiked reagent water solutions. When these data were obtained, the lowest possible measurements were hampered by the superposition of a sinusoidal wave on the baseline signal. This intermittent phenomenon may be peculiar to thin-layer amperometric cells having non-isolated reference electrodes. With a successful resolution of this problem it may be possible to measure each organic peroxide analyte at the lower parts-per-trillion level using reductive amperometry.

Calibration curves for the reductive amperometric measurement of 2-BP, t-BHP and CHP were linear over nearly 4–5 orders of magnitude of concentration (Table 3) from ca. 1 \(\mu\)g l\(^{-1}\) to 100 mg l\(^{-1}\). Concentrations greater than the upper limits cited in Table 3 were not pursued. The calibration curves [peak current (nA) vs. concentration (ng ml\(^{-1}\))], had correlation coefficients (\(r\)) ranging from 0.9997 to 0.9994, and deviated minimally from the origin as indicated by the \(y\)-intercept values.

**Table 1**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentrations ng ml(^{-1})</th>
<th>Analytes (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-BP</td>
<td>t-BHP</td>
</tr>
<tr>
<td>Standard</td>
<td>0.2</td>
<td>0.467 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.452 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>RSD (%)</td>
<td>2.04/1.09</td>
</tr>
<tr>
<td>Sample</td>
<td>0.2</td>
<td>0.453 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.436 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>RSD (%)</td>
<td>0.96/0.99</td>
</tr>
</tbody>
</table>

\(^a\) Ratio \(E_i^{APP}/E_i^{OxAPP}\), i.e., +1150/–1250 mV vs. Ag/AgCl reference electrode. \(^b\) Composite parameter measurements obtained from two single-point hydrodynamic voltammograms for oxidative amperometry and reductive amperometry. \(^c\) Relative standard deviation for 0.20/0.5 ng ml\(^{-1}\) respectively.

Fig. 2 Hydrodynamic voltammogram of oxygen on glassy carbon. Conditions: eluent, 40% v/v acetonitrile–0.05 M phosphate buffer; detection mode, reductive amperometric detection; electrode, glassy carbon; column, Luna (ODS, C\(_{18}\), 5 \(\mu\)m), 250 × 4.6 mm id; flow rate, 1 ml min\(^{-1}\); \(E_{APP}\), variable; and temperature, ambient. (a) Sample oxygen: (1) butan-2-one peroxide; (2) tert-butyl hydroperoxide and (3) cumene hydroperoxide, deoxygenator removed; (b) same as (a) with deoxygenator installed and on.

Fig. 3 Hydrodynamic voltammograms. Effect of potential \((E_{APP})\) on the peak current of some organic peroxides and hydroperoxides. Conditions: eluent, 40% v/v acetonitrile–0.05 M phosphate buffer; detection mode, parallel-adjacent dual amperometric detection (PADAD); electrode, glassy carbon; column, Luna (ODS, C\(_{18}\), 5 \(\mu\)m), 250 × 4.6 mm id; flow rate, 1 ml min\(^{-1}\); concentration, 100 ng each; \(E_{APP}\), variable. Each HDV was corrected for the baseline contribution.
Calibration sensitivities ranging from about 34 to 152 nA ng μl⁻¹ were also obtained for each analyte from typical calibration curves.

Applications

Cincinnati tap water containing the three organic peroxides and hydroperoxides was analyzed using RP-HPLC under isocratic elution conditions with PADAD. The results were obtained by using the analytical signals from both the oxidative and reductive detection measurements. Because of the ability to acquire two signals for each analyte co-instantaneously, it is possible to confirm the accuracy of the recoveries without performing additional measurements. Another potential advantage may be the increased selectivity offered by PADAD, especially in a complex sample matrix. Operating at potentials poised at negative and positive potentials, combined with the chromatographically assisted hydrodynamically stable measurement, the electrodes poised at negative and positive potentials, combined with the redox behavior of organic peroxides and hydroperoxides. PADAD, in conjunction with RP-HPLC, is a convenient, efficient, economical and selective approach for the detection and determination of organic peroxides and hydroperoxides in aqueous environmental matrices. PADAD measurements, with the electrodes poised at negative and positive potentials, combined with the redox behavior of organic peroxides and hydroperoxides permits (1) the monitoring of two independent redox reactions of the same analyte, (2) the simultaneous performance of reductive and oxidative amperometric detection, (3) the evaluation and development of an empirical composite parameter that allows the qualitative identification of the analytes and (4) the acquisition of quantitative results, for the same analyte, from two independently measured analytical signals.

Conclusion

An on-line deoxygenator provides an efficacious and simple means of removing molecular oxygen from liquid chromatographic mobile phases and sample solutions. The effective negative potential range of the glassy carbon electrode was extended to approximately −1.450 ± 0.05 V vs. the Ag/AgCl reference electrode, thus allowing the reductive amperometric detection of organic peroxides and hydroperoxides. PADAD, in conjunction with RP-HPLC, is a convenient, efficient, economical and selective approach for the detection and determination of organic peroxides and hydroperoxides in aqueous environmental matrices. PADAD measurements, with the electrodes poised at negative and positive potentials, combined with the redox behavior of organic peroxides and hydroperoxides permits (1) the monitoring of two independent redox reactions of the same analyte, (2) the simultaneous performance of reductive and oxidative amperometric detection, (3) the evaluation and development of an empirical composite parameter that allows the qualitative identification of the analytes and (4) the acquisition of quantitative results, for the same analyte, from two independently measured analytical signals.

Table 2  Method detection limita

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Concentration/μg l⁻¹</th>
<th>Reductive amperometry</th>
<th>Oxidative amperometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-BP</td>
<td>0.8</td>
<td>3.0</td>
<td>12.0</td>
</tr>
<tr>
<td>t-BHP</td>
<td>0.4</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>CHP</td>
<td>5.0</td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

a Data obtained for each analyte simultaneously using parallel–adjacent dual amperometric detection (PADAD). Experimental conditions: 40% v/v CH₃CN–0.05 M phosphate buffer (pH = 7); flow rate, 1 ml min⁻¹; column, Luna, (ODS, C₁₈, 5 μm), 250 × 4.6 mm id; dual glassy carbon working (0.069 cm²) electrode (MF-1000); 20 μl sample loop; ambient temperature. For the MDL determinations seven replicate measurements were made on a solution (reagent water) containing each individual analyte at a level of about five times the estimated MDL.  b E°Red,APP = −1.250 V vs. Ag/AgCl reference electrode.  c E°Ox,APP = +1.150 V vs. Ag/AgCl reference electrode.

Table 3  Calibration data for the glassy carbon electrode

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Linear range/ ng μl⁻¹</th>
<th>Calibration sensitivity/ nA ng⁻¹ μl⁻¹</th>
<th>Intercept/ nA</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-BP</td>
<td>0.001–40</td>
<td>152.04</td>
<td>2.294</td>
<td>0.99994</td>
</tr>
<tr>
<td>t-BHP</td>
<td>0.005–100</td>
<td>38.994</td>
<td>5.544</td>
<td>0.99973</td>
</tr>
<tr>
<td>CHP</td>
<td>0.010–100</td>
<td>33.679</td>
<td>−10.395</td>
<td>0.99991</td>
</tr>
</tbody>
</table>

a Data for redox amperometric detection of organic peroxides. See ref. 22 for calibration data for oxidative amperometric detection of organic peroxides. Conditions: 40% v/v CH₃CN–0.05 M phosphate buffer; E°APP = −1.250 mV vs. Ag/AgCl reference electrode; column, RP-18 (5 μm), 25 × 0.46 cm id; 20 μl sample loop. b Slope of analytical curve. c Based on measurement of the peak height.

Table 4  HPLC–reductive and oxidative amperometric analysis of spiked Cincinnati tap water

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Amount added/ng</th>
<th>Amount determined/ng (mean ± SD)</th>
<th>Recovery % (mean ± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-BP</td>
<td>2</td>
<td>2.2 ± 0.1</td>
<td>108.6 ± 4.2</td>
</tr>
<tr>
<td>t-BHP</td>
<td>2</td>
<td>2.1 ± 0.1</td>
<td>104.3 ± 7.4</td>
</tr>
<tr>
<td>CHP</td>
<td>2</td>
<td>2.1 ± 0.1</td>
<td>95.3 ± 2.1</td>
</tr>
<tr>
<td>2-BP</td>
<td>4</td>
<td>4.1 ± 0.1</td>
<td>103.3 ± 2.5</td>
</tr>
<tr>
<td>t-BHP</td>
<td>4</td>
<td>4.1 ± 0.1</td>
<td>102.5 ± 2.6</td>
</tr>
<tr>
<td>CHP</td>
<td>4</td>
<td>3.6 ± 0.1</td>
<td>91.0 ± 2.8</td>
</tr>
<tr>
<td>2-BP</td>
<td>7</td>
<td>6.4 ± 0.3</td>
<td>90.9 ± 3.7</td>
</tr>
<tr>
<td>t-BHP</td>
<td>7</td>
<td>6.0 ± 0.2</td>
<td>85.9 ± 2.7</td>
</tr>
<tr>
<td>CHP</td>
<td>7</td>
<td>6.6 ± 0.0</td>
<td>94.2 ± 0.6</td>
</tr>
<tr>
<td>2-BP</td>
<td>10</td>
<td>10.2 ± 0.4</td>
<td>101.7 ± 3.5</td>
</tr>
<tr>
<td>t-BHP</td>
<td>10</td>
<td>10.5 ± 0.5</td>
<td>104.7 ± 4.7</td>
</tr>
<tr>
<td>CHP</td>
<td>10</td>
<td>9.5 ± 0.5</td>
<td>95.1 ± 4.9</td>
</tr>
</tbody>
</table>

a Three to four determinations were performed on each Cincinnati tap water solution. The second line of data at each concentration level is the oxidative amperometric measurement. Analysis performed in 40% v/v CH₃CN–0.05 M phosphate buffer; flow rate, 1 ml min⁻¹; working electrodes, glassy carbon; PADAD: E°Red,APP = +1.150 V vs. Ag/AgCl reference electrode; sample loop, 20 μl; column, Luna, RP-18 (5 μm), 25 × 0.46 cm id; temperature, ambient.

Disclaimer

The mention of commercial products does not constitute endorsement or recommendation for use by the US Environmental Protection Agency.

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References


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