Comparative Investigation of Pulsed Electrochemical and Ultraviolet Detections in the Determination of Flavor-Active Aldehydes Separated by HPLC

Elisabeth Le Fur,[†] Jean-Marie Meunier,[‡] and Patrick X. Etievant*[,†]

Laboratoire de Recherche sur les Arômes, INRA, 17 rue Sully, 21034 Dijon Cedex, France, and Laboratoire de Chimie Analytique et Appliquée, Faculté des Sciences de Mirande, B.P. 138, 21004 Dijon, France

Electrochemical detection at gold electrodes of flavor-active aldehydes separated by liquid chromatography demonstrates close limits of detection at the 50 ppb level for the three types of molecules studied: saturated, unsaturated, and conjugated. Conversely, UV detection gives worse limits of detection (100 times higher) for saturated aldehydes and better limits of detection (50 times lower) for conjugated ones. Moreover, because the potential of detection of aldehydes allows the simultaneous analysis of alcohols by HPLC-electrochemical detection, a mixture of aldehydes and alcohols, saturated and unsaturated, can be easily studied, while the HPLC-UV analysis gives poor results in this case. This study shows increasing sensitivities of electrochemical detection for aldehydes in the following order: unsaturated > saturated > conjugated. It is concluded that aldehydes seem to have the same behavior as alcohols, i.e. that the addition of double bonds to a saturated alcohol increases its detection ability. Conjugated aldehydes are an exception to this rule, and some hypotheses explaining their lower ability of adsorption at the oxidized electrode compared to nonconjugated aldehydes are proposed.

Keywords: *Electrochemical detection; aldehydes; HPLC; flavor*

INTRODUCTION

While some published findings mentioned that aldehydes separated by high-performance liquid chromatography (HPLC) could be easily detected by electrochemical detection at a gold electrode between ~−0.6 and +0.2 V (Johnson and LaCourse, 1990), we could not find any precise experiment demonstrating it, except for reducing sugars which were extensively studied (LaCourse, 1993; LaCourse and Johnson, 1991, 1993). However, some results have been published on the pulsed electrochemical detection of formaldehyde, acetaldehyde, propionaldehyde or butyraldehyde at platinum electrodes (Weiss, 1986; Rocklin, 1985). The limits of detection found in these conditions were between 1 and 3 ppm. Gold was however proved, using voltammetry, to have, for the oxidation of aldehydes, a better electrocatalytic activity in an alkaline medium compared to platinum (in acidic or alkaline media) (Beden et al., 1987). This is the reason why it seemed necessary to study extensively the pulsed electrochemical detection of aldehydes at gold electrodes in an alkaline medium.

The compounds studied were chosen both for their structure and their olfactive properties. We chose saturated aliphatic aldehydes whose UV detection is not very sensitive. We also chose unsaturated aliphatic aldehydes, conjugated or nonconjugated, to make a comparison with the results obtained recently on alcohols: the addition of double bonds to a saturated alcohol improved the sensitivity of its detection by a better adsorption at the electrode surface (Le Fur et al., 1994).

MATERIALS AND METHODS

Solvents and Reagents Used. Standard flavor-active aldehydes were obtained from Aldrich. Acetonitrile was an HPLC grade solvent from Carlo Erba. Sodium hydroxide was a Baker analysed reagent from J. T. Baker, Holland. Acetic acid was a Chromanorm reagent for HPLC from Prolabo, France. The relative proportions of neral and geranial in citral were determined by gas chromatography to be 37.46 % and 62.54% respectively.

Chromatographic Separation. The eluent (a mixture 1:1 of water and acetonitrile containing 0.1% acetic acid) was degassed with helium using an Eluent Degas module from Dionex. The column was connected to an advanced gradient pump from Dionex (Sunnyvale, CA) via a Rheodyne 9126 injector equipped with a 25 μL peek (polyether ether ketone) loop. Detection was made with a pulsed electrochemical detector (PED, Dionex). The postcolumn addition of an electrolyte (NaOH 0.3 M for detection at gold electrodes) was necessary to ensure the conductivity of the solution. Sodium hydroxide has been chosen because it gives particular properties to the gold electrode surface: the electrode is covered by an hydrous oxide film that improves the adsorption of aldehydes. The addition of an electrolyte was made possible by a reagent delivery module (RDM, Dionex) at 1 mL/min. The RDM module was connected after the analytical column by a mixing tee. Nitrogen was used to pressurize the RDM to avoid formation of sodium hydrogen carbonate when NaOH was used. A 124 cm × 500 μL beaded reaction coil was placed after the mixing tee to facilitate the mixing of the sodium hydroxide and eluent streams with minimal band broadening. An UV spectrophotometric detector (SPD 6A from Shimadzu) was also used to detect aldehydes. The UV and electrochemical detectors can be set in line to allow double detection. In this case, the UV detector was placed between the analytical column and the mixing tee. Because of the respective flows coming from the column and from the alkali container, PED detection was consequently made in a water/acetonitrile mixture 3:1 containing NaOH 0.15 M while UV detection was made in a water/acetonitrile mixture 1:1.

A Lichrospher 60 RP 8 Select B, 5 μm, 250 × 4 mm (Merck) column was chosen for the chromatographic separation of a mixture of aldehydes. This column, less apolar than a C_{18} one, was found to strongly improve the separation compared to a C_{18} column. However, the peaks of saturated aldehydes remained too wide with an isocratic elution with CH_3CN/H_2O

[†] INRA.
[‡] Faculté des Sciences de Mirande.

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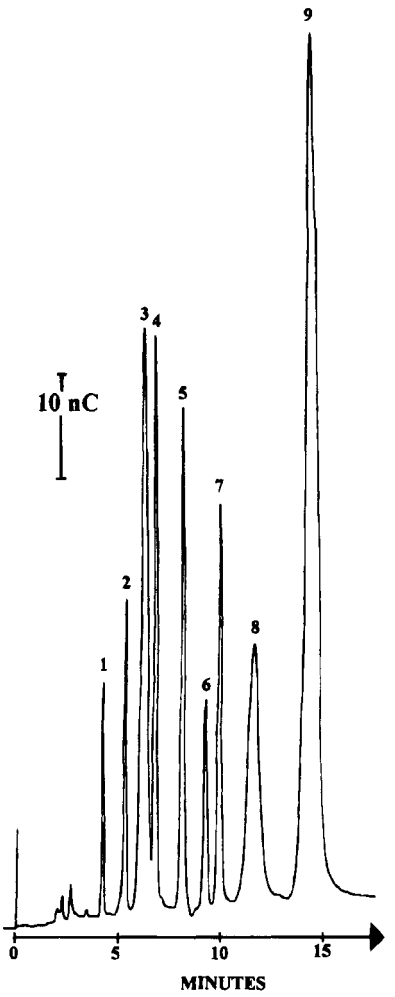

Figure 1. HPLC-PED Au analysis of a mixture of aldehydes and alcohols. Column, Lichrospher 60 RP Select B 5 μm Merck; CH_3CN:H_2O (v:v) + 0.1% CH_3COOH eluent at 1ml/min; NaOH 0.3 M postcolumn reagent at 1 mL/min; 25 μL loop; E_{det} = 0.05 V (0–0.5 s), E_{ox} = 0.7 V (0.51–0.63 s), E_{red} = −0.9 V (0.64–0.9 s), integration 0.3–0.5 s. Reference: Ag/AgCl. Peaks: (1) *cis*-3-hexenol, 4.55 ppm, (2) *trans*-2-hexenal, 47 ppm, (3) hexanal, 47 ppm, (4) 1-octen-3-ol, 19 ppm, (5) geraniol, 12.4 ppm, (6) neral, 38 ppm, (7) geranial, 63.5 ppm, (8) octanal, 47.7 ppm, (9) citronellal, 47.9 ppm.

(1:1). The addition of 0.1% acetic acid to the eluent overcame this problem and the chromatogram obtained was satisfactory (Figure 1).

Amperometric Detector Cell. A thin layer cell was used with a silver/silver chloride reference electrode and the stainless steel body of the cell as counter electrode. The working electrode was a round gold electrode (1.4 mm diameter) included into a block of inert teflon material. The thickness of the cell was set up to 50 μm corresponding to 1.25 μL internal volume. To avoid the accumulation of adsorbed species at the electrode surface, a multistep potential waveform was applied: after the potential of detection (E_{det}) where the current was recorded, adsorbed species were oxidatively desorbed by the application of a large positive potential step (E_{ox}) which causes the formation of surface oxides (AuO). These oxides must then be cathodically dissolved by a negative potential step (E_{red}) to regenerate the electrode activity (Figure 2).

Pulsed amperometric detection is appropriate to the detection of molecules which have their oxidation potential in the region of oxide free surface. The detection potential (E_{det}) of aldehydes was determined in relation to the oxidation potential and in order to optimize the signal to noise ratio.

Determination of the Detection Potential. The best detection potential was estimated by two different methods. First, by cyclic voltammetry using an external system with a

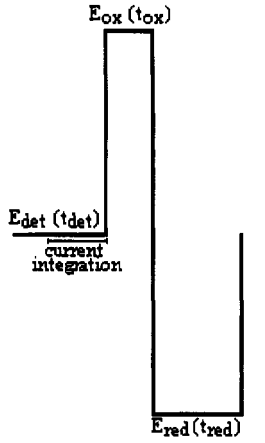

Figure 2. Potential-time waveform for pulsed amperometry: E_{det}, anodic detection; E_{ox}, oxidative cleaning; E_{red}, cathodic reactivation. The integration period is 200 ms.

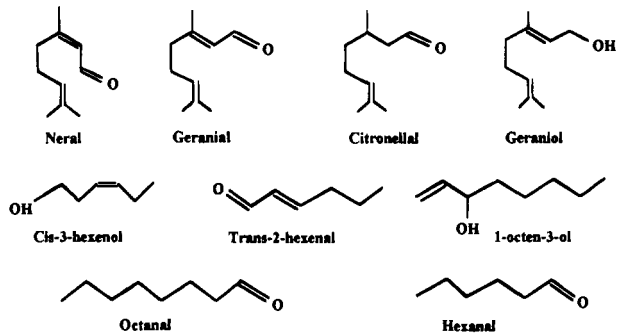

Figure 3. Developed formulas of flavor-active molecules studied.

gold rotating disk electrode (Au RDE: d = 2 mm; 1000 rpm; 200 mV/s) connected to a PRT potentiostat and a UAP4 unit (both from Tacussel) with a calomel reference electrode and a platinum counter electrode. Second, with repetitive injections in HPLC-PED by measuring the effects of changing the working potential on peak height. The potential sequence applied to the gold working electrode was the following: E_{det} (t_{det} = 500 ms); E_{ox} = 0.7 V (t_{ox} = 120 ms); E_{red} = −0.9 V (t_{red} = 260 ms). The oxidation current was integrated from 300 to 500 ms at E_{det}.

RESULTS AND DISCUSSION

The developed formulas of the molecules studied are shown in Figure 3.

Potential of Detection. *Voltammetry at a Rotating Disk Gold Electrode (Au RDE).* The cyclic voltammograms obtained (Figure 4) show the behavior of the three types of aldehydes: saturated (octanal), unsaturated (citronellal), and conjugated (*trans*-2-hexenal). From these i-E curves it can be concluded that aldehydes have a very wide detection potential range located between +0.2 and −0.5 V/calomel. However, these curves clearly show that nonconjugated aldehydes (octanal, citronellal) compared to conjugated ones (*trans*-2-hexenal) have a different behavior mainly because they produce a larger anodic current.

All the compounds studied seemed to present two oxidation potentials at −0.2/−0.3 and +0.1/+0.2 V. According to Anastasijevic et al. (1993), the first oxidation potential is related to the formation of hydrogen during the oxidation of the aldehyde. The second wave may be due to the increase in faradaic efficiency for oxidation at potentials where hydrogen is no longer formed. Van Effen and Evans (1980) also observed these two oxidation waves in rotating disc gold elec-

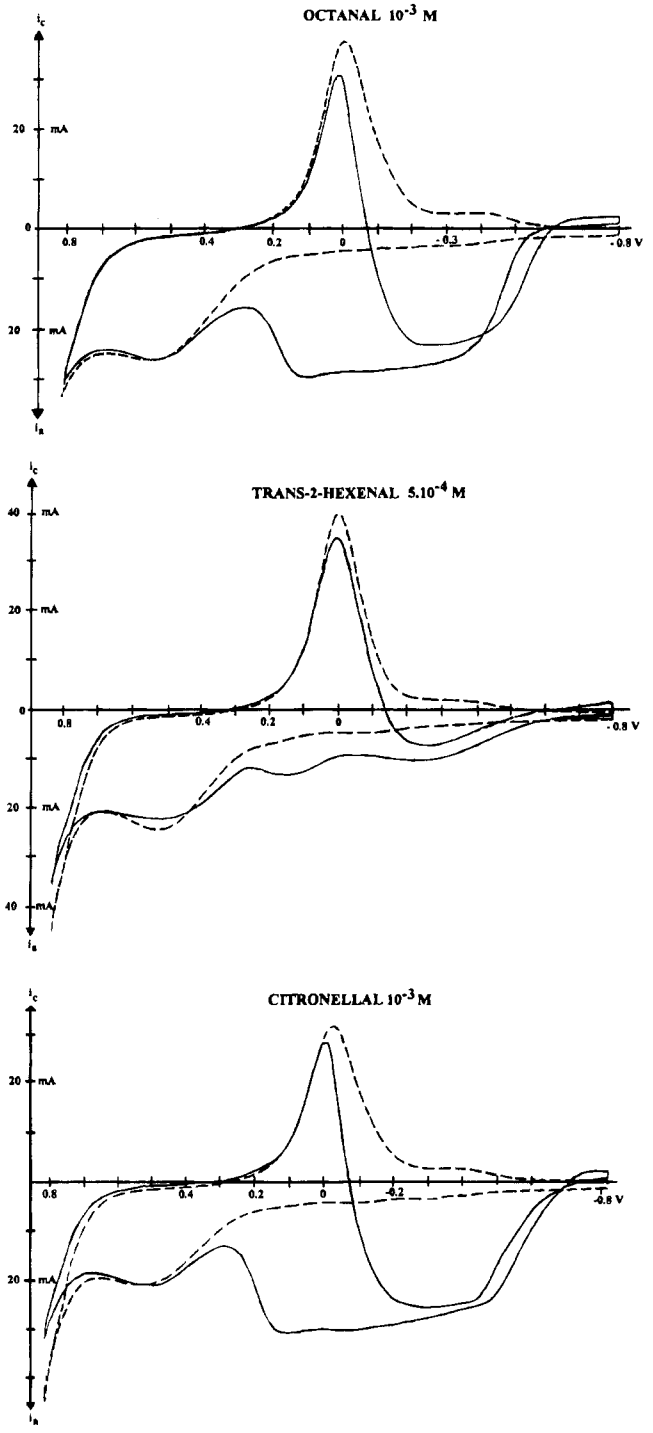

Figure 4. Voltammetric responses of octanal, *trans*-2-hexenal, and citronellal at a gold electrode. Au RDE 1000 rev min^{-1}; scan rate, 200 mV s^{-1}; reference, calomel; counter electrode, platinum; solutions were degassed by N_2; (- - -) blank, NaOH 0.2 M:CH_3CN 30% (v:v); (—) sample, blank + aldehyde.

trodes voltammograms of aldehydes and showed that linear sweep voltammograms gave only one oxidation wave (corresponding to the more negative peak).

Hydrodynamic Voltammograms Using the HPLC-PED Apparatus. The hydrodynamic voltammograms were established via successive injections of the same sample (a mixture of aldehydes) while the potential of detection was incremented as already described (Le Fur et al., 1994). Figure 5 gives the results of these analyses for different aldehydes. It shows that all aldehydes are very well detected in the range −0.1/+0.1 V/Ag/AgCl. The detection potential chosen to determine limits of detection will be −0.1 V. This potential is the optimum potential of oxidation for three of the six aldehydes studied. For citronellal and octanal, this potential is on the oxidation plateau and for hexanal the best potential could be chosen between 0 and 0.1 V.

No oxidation potential was found in the −0.2 V region for conjugated aldehydes despite the voltammetric results.

The detection potential of aldehydes at a gold electrode is in the same range as is determined for the detection of flavor-active alcohols in the same chromatographic and detection conditions (Le Fur et al., 1994). Therefore, molecules of these two chemical classes can be simultaneously detected. This is demonstrated with the chromatogram given in Figure 1.

Absorption Wavelengths for Aldehydes. Absorption wavelengths for saturated aldehydes are located at 285 nm and at 200 nm. For *trans*-2-hexenal, we determined a maximum absorption wavelength at 225 nm while that of neral and geranial is at 240 nm. An HPLC-UV analysis was carried out on the same mixture of aldehydes and alcohols (Figure 6), with the UV detector set in line with the PED. At 200 nm, all the compounds, except hexanal and 1-octen-3-ol, can be detected, but the sensitivity of the response is far from the maximum. Also the background signal is not negligible because the eluent contains acetonitrile. Indeed, it can be seen, when looking to the chromatograms obtained at 225 nm for instance, that *trans*-2-hexenal can be detected with a sensitivity at least 4 times higher. However, a 225 nm wavelength of detection is very selective since it allows only a good detection for conjugated aldehydes (*trans*-2-hexenal, neral, geranial). Similar observations can be done for the chromatograms obtained at 240 and 285 nm.

Thus, unlike the electrochemical detection at a gold electrode, UV detection does not allow a simultaneous analysis of saturated and unsaturated aldehydes in the optimum conditions for all the compounds.

Sensitivity and Limits of Detection of Aldehydes Using UV and Electrochemical Detections. The results obtained from UV and electrochemical detection of six aldehydes are given in Tables 1 and 2.

They show that UV detection is very sensitive for unsaturated aldehydes and particularly for the conjugated ones such as *trans*-2-hexenal, neral, and geranial. These can be detected at low concentrations (around 1 ppb). However, saturated aldehydes were poorly detected with limits of detection 1000 times higher (in the 1−10 ppm range). The sensitivity of the electrochemical detector toward aldehydes is completely different because the aldehydes studied are detected in a very narrow range of detection limits (30−100 ppb). Compared to UV detector, PED is therefore less sensitive towards unsaturated aldehydes while it is more sensitive toward saturated ones.

For both detections, peak heights were chosen to determine limits of detection. The values obtained with PED do not show clear differences between the different types of aldehydes. Because saturated aldehydes produce wider chromatographic peaks than unsaturated ones, peak areas were also measured for actual sensitivity. This comparison (Figure 7) reveals a better sensitivity in the detection of nonconjugated aldehydes, and particularly of citronellal, than of conjugated ones. Magnitudes of detection sensitivity are in the following order: citronellal > hexanal, octanal > geranial, neral,

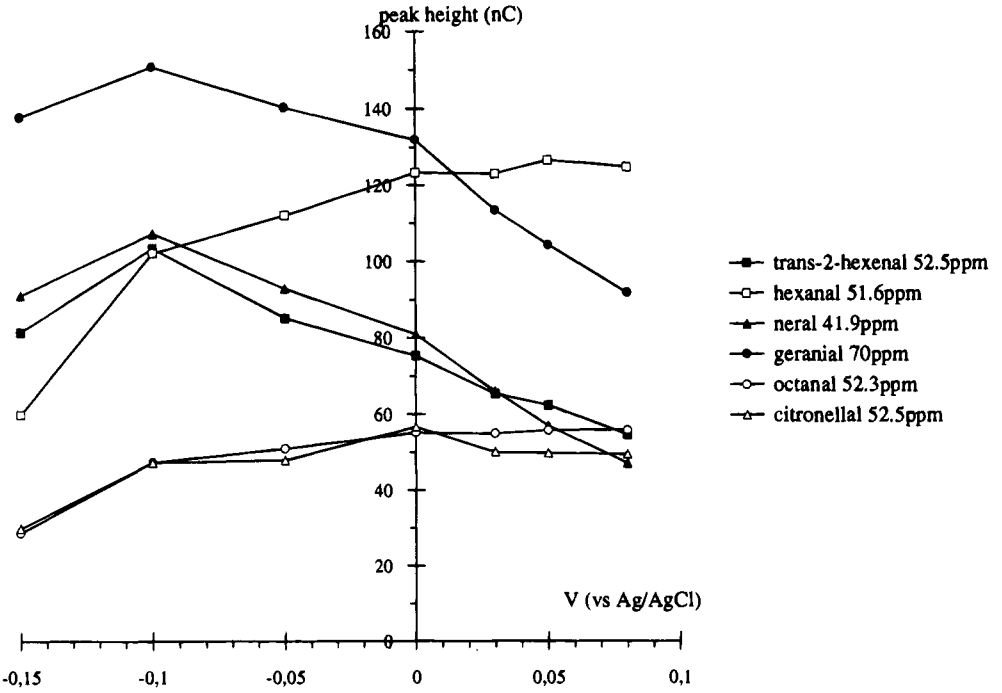

Figure 5. Hydrodynamic voltammograms of aldehydes. Working electrode, Au 1.4 mm diameter; column, Lichrospher 60 RP Select B, 5 μm (Merck); eluent CH_3CN:H_2O (v:v) + 0.1% CH_3COOH at 1 mL/min; postcolumn reagent, NaOH 0.3 M at 1 mL/min; loop, 25 μL; E_{det} (0–0.5 s), E_{ox} 0.7V (0.51–0.63 s), E_{red} −0.9V (0.64–0.9 s), integration 0.3–0.5 s.

Table 1. Detection of Aldehydes by UV[a]

		absorbance: AU = $a + b \times$ concn (ppm)					
compound	λ (nm)	a	b	n	r^2	noise (AU)	limit of detection (ppm)
trans-2-hexenal	225	2.6×10^{-5}	3.4×10^{-2}	4	0.99991	1.9×10^{-5}	0.001
hexanal	285	-1.3×10^{-6}	6.6×10^{-6}	5	0.99934	1.5×10^{-5}	4
neral	240	5.1×10^{-4}	1.2×10^{-2}	6	0.99998	1.2×10^{-5}	0.0019
geranial	240	3.6×10^{-4}	1.0×10^{-2}	6	0.99992	1.2×10^{-5}	0.0029
octanal	285	-8.2×10^{-6}	5.8×10^{-6}	3	0.99933	9.8×10^{-6}	6.5
citronellal	200	-4.2×10^{-4}	1.4×10^{-3}	5	0.99974	6.1×10^{-5}	0.17

[a] Parameters of analysis: column, Lichrospher 60 RP Select B, 5 μm, 244 × 4 mm (Merck); eluent, CH_3CN;H_2O (50/50) + 0.1% CH_3COOH at 1 mL/min; loop, 25 μL. Limits of detection were determined for a signal-to-noise ratio of 3.

Table 2. Detection of Aldehydes by Electrochemical Detection at Gold Electrode[a]

		linear regression: $nC = a + b \times$ concn (ppm)					
compound	E_{det} (V)	a	b	n	r^2	noise (nC)	limit of detection (ppm)
trans-2-hexenal	−0.1	−0.1	1.4	7	0.99999	0.024	0.1
hexanal	−0.1	-3.5×10^{-2}	2.4	7	0.99999	0.024	0.03
neral	−0.1	1.6×10^{-2}	1.5	7	0.99998	0.024	0.03
geranial	−0.1	-3.8×10^{-2}	1.6	7	0.99999	0.024	0.04
octanal	−0.1	-2.2×10^{-2}	1	7	0.99999	0.024	0.05
citronellal	−0.1	−0.2	0.9	7	0.99984	0.024	0.06

[a] Parameters of analysis: column, Lichrospher 60 RP Select B, 5 μm, 244 × 4 mm (Merck); eluent CH_3CN/H_2O (50/50) + 0.1% CH_3COOH at 1 mL/min; loop, 25 μL; postcolumn reagent, NaOH 0.3 M at 1 mL/min; working electrode, Au 1.4 mm diameter; reference electrode, Ag/AgCl; detection program, E_{det} (0–0.5 s), E_{ox} = 0.7 V (0.51–0.63 s), E_{red} = −0.9 V (0.64–0.9 s); integration, 0.3–0.5 s. Limits of detection were determined for a signal-to-noise ratio of 3.

trans-2-hexenal. This result is in agreement with the i-E curves obtained by voltammetry.

From previous studies carried out on alcohols (Le Fur et al., 1994), it was concluded that the addition of double bonds to a saturated alcohol improved the electrochemical detection at gold electrode by a better adsorption at the electrode surface. Aldehydes seem to follow the same behavior that alcohols, i.e. citronellal which gave a ~3 times greater peak area response than hexanal or octanal (Figure 7). Conversely, the response was decreased by a factor of ~3, compared to the saturated molecules, when the unsaturation was conjugated with the aldehyde group. This is well demonstrated by the comparison between hexanal and *trans*-2-hexenal sensitivities. Conversely, there are no obvious differences in sensitivity between citral (with a terminal double bond) and *trans*-2-hexenal, while the presence of a double bond in citronellal contributes to an increase of detection sensitivity compared to octanal or hexanal.

To explain these results, one can refer to the literature. The field of oxidation mechanisms at gold electrodes in alkaline medium, therefore at an hydrous oxide film, was much less studied than the phenomenon occurring directly at the surface of electrodes. However, some authors studied these mechanisms mainly on carbohydrates or on small organic molecules (formaldehyde, short saturated alcohols). These studies were mainly directed toward the development of analytical sensors and hydrocarbon fuel cells.

The differences observed between conjugated and

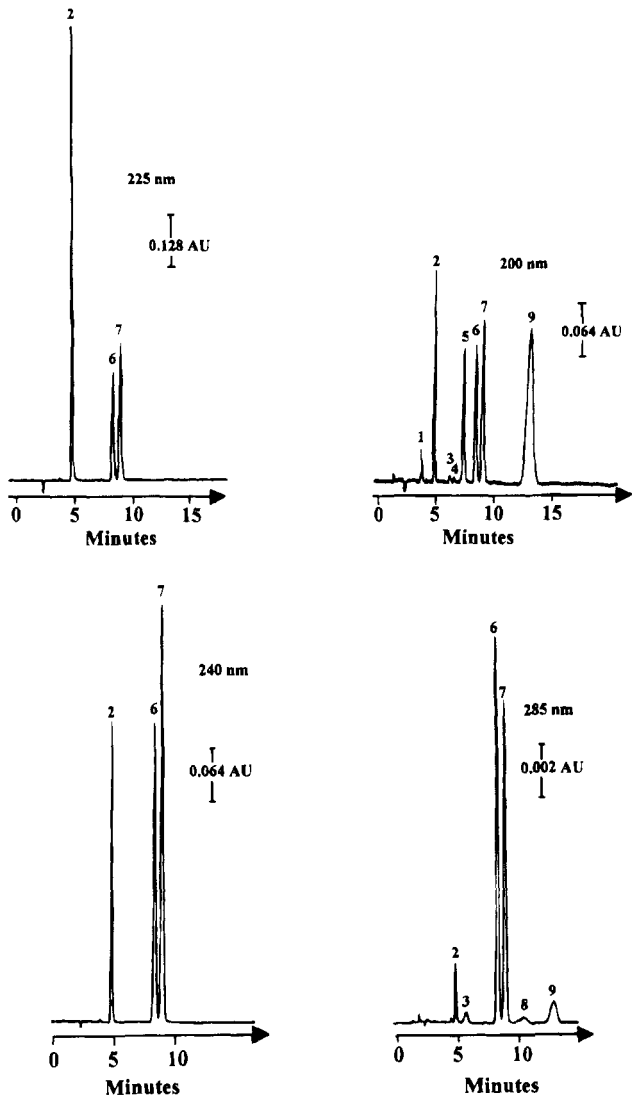

Figure 6. HPLC-UV analysis of the mixture of aldehydes and alcohols at 200, 225, 240, and 285 nm. Column, Lichrospher 60 RP Select B 5 μm Merck; CH_3CN:H_2O (1:1) + 0.1% CH_3COOH eluent at 1 mL/min; 25 μL loop. Refer to Figure 1 for peak identification.

nonconjugated aldehydes may be explained from this literature by the particular ability of nonconjugated aldehydes to be in the *gem*-diolate form in alkaline medium (Anastasijevic et al., 1993). This structure allows the aldehyde to adsorb onto the electrode exactly in the same way than alcohols do, via hydrogen bridges between hydrous gold oxide and the radical alcohol (Van Effen and Evans, 1980; Ocón et al., 1986). Other authors (March, 1985) demonstrated that a +I inductive group, such as methyl, decreases the hydrate formation, and while formaldehyde is 99.99% in the *gem*-diol form, for acetaldehyde the proportion is only 58%. So, we could predict a lower proportion of the hydrated form for citronellal or hexanal. However, in the case of cyclohexanecarboxaldehyde, Van Effen and Evans (1980) also proposed a mechanism of adsorption proceeding via the radical *gem*-diolate form. This hydrated form is not favored for conjugated aldehydes because the aldehyde carbon is less positively charged and due to the particular stability of the conjugated form.

Another characteristic of aldehydes in alkaline medium is the ability of the proton located on the α carbon to be abstracted. The resulting anionic molecule is therefore in equilibrium with the enolate form which

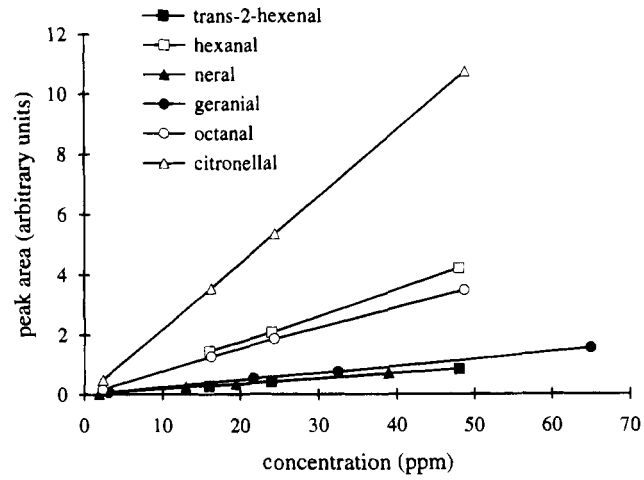

Figure 7. Peak area vs concentration calibration of aldehydes by HPLC-PED Au analysis; column, Lichrospher 60 RP Select B 5 μm (Merck); eluent CH_3CN:H_2O (v:v) + 0.1% CH_3COOH at 1 mL/min; postcolumn reagent, NaOH 0.3 M at 1 mL/min; $E_{det} = -0.1$ V (0–0.5 s), $E_{ox} = 0.7$ V (0.51–0.63 s), $E_{red} = -0.9$ V (0.64–0.9 s), integration 0.3–0.5 s.

can adsorb onto the catalytic AuOH. In conjugated aldehydes, this proton is less acidic, so the anionic form is not favored. These are two reasons which could explain why conjugated aldehydes are detected with less sensitivity than nonconjugated ones.

A third explanation can also be proposed. According to Larew and Johnson (1989), glucose (c > 30 mM) adsorbs onto the gold hydroxide film, by the pairing of surface –OH species, via hydrogen bridges with the aldehyde, leading to the formation of an acid. This adsorption mechanism is not favored for conjugated aldehydes because the aldehydic carbon is less positively charged than in a nonconjugated molecule. Therefore, the relatively small gap between the detection sensitivities of nonconjugated and conjugated aldehydes may proceed through a difference in adsorption rates.

In any case, it is important to consider the kinetics of equilibriums between the aldehyde and its different forms in an alkaline medium. The electroactive species do not have to be predominant in a solution if the equilibrium with the aldehyde form is fast.

CONCLUSION

This study shows the interest of electrochemical detection as compared with UV detection in the analysis of aldehydes:

Saturated, nonconjugated, and conjugated aldehydes can be simultaneously detected at gold electrodes at −0.1/+0.1V/Ag/AgCl while their optimum absorption wavelengths in UV radiations are very different and do not allow the simultaneous detection of a mixture of different types of aldehydes at a fixed wavelength.

The detection potentials of aldehydes and alcohols at gold electrodes are in the same range. Therefore, molecules of these two chemical classes can be simultaneously analyzed by HPLC-PED. This is of particular interest since these two classes of molecules are generally biochemically connected.

The sensitivity of electrochemical detection for aldehydes is at the 50 ppb level (12 pmol injected).

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