Optodes based on a calixarene ester for the determination of aldehydes *via in situ* generation of the Girard's reagent P derivative

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Optode membranes for the general determination of aldehydes by visible spectroscopy were developed. A plasticized poly(vinyl chloride) membrane containing a calixarene ester which is used as a host molecule, a hydrogen ion-selective chromo-ionophore (ETH5294) and potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB) responds reversibly to a guest molecule which is generated *in situ* from an aldehyde and a Girard's reagent P. The sensitivity of the optode can be modulated by changing the concentration of the calixarene ionophore in the membranes and the pH of the measuring solution. The proposed method shows a good correlation with the theoretically derived equation in the range 4×10^{-5}–0.2 mol l^{-1} butyraldehyde with an error of $< 6\%$ and with a detection limit of 5×10^{-7} mol l^{-1}. Typical response times (t_{95}) for the samples are 5 min.

Introduction

During the last 20 years, considerable interest in the development and construction of chemical sensors with optical transduction has been documented.[1,2] However, optodes specifically designed for organic substances have received less attention in spite of the fact that they are being found almost everywhere. Aldehydes are a class of organic compounds widely used in a variety of manufacturing industries.[3,4] Analyses of aldehydes are mainly performed with GC,[5] HPLC[6–8] spectrophotometric,[9,10] and electroanalytical methods.[11] However, these methods suffer from various disadvantages, such as a time-consuming procedure, poor sensitivity and high running costs. There is still ample room to develop new and simple methods for the determination of aldehydes. We have developed aldehyde-selective polymeric membrane electrodes based on a calixarene ionophore.[11] It displayed excellent sensitivity and selectivity for aldehydes owing to the highly specific host–guest interaction between the calixarene ionophore and pyridinium acetohydrazone derivatized from an aldehyde and Girards reagent P.

In this paper, we propose a new and general optode analytical method for the determination of aldehydes based on the same host–guest interaction as exemplified by the determination of acetaldehyde, butyraldehyde and heptaldehyde. The optode membrane contains a neutral calixarene ionophore (C) as the host selective for the ionic derivative of aldehydes, a chromo-ionophore, ETH 5294 (IND), selective for the hydrogen ion and a lipophilic salt, potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB), as the anionic site (R^-). The pyridinium acetohydrazone ion derived from an aldehyde and Girard's reagent P was extracted into the bulk of the membrane by the host–guest interaction, triggering a change in the optical absorption properties of the sensing layer.

The relatively bulky hydrazone cation derived from the aldehyde, like many organic cations, consists of both a lipophilic hydrocarbon chain and a hydrophilic pyridinium moiety. Hence a strong complex between the sensing material and the analyte comprising both hydrophobic and hydrophilic interactions will be formed. This results in a distinctly different optode response behaviour to that for inorganic cations. This paper addresses the sensitivity, selectivity, reproducibility and response time of the proposed method.

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Experimental

Reagents

For optode membrane preparation, the following compounds were purchased from Fluka (Buchs, Switzerland) and used as received: high relative molecular mass PVC, bis(2-ethylhexyl) sebacate (BOS), 1,2-benzo-7-(diethylamino)-3-(octadecanoylimino)phenoxazine (ETH5294) and potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB). For the synthesis of calix[*n*]arene esters, a previously described procedure was used.[12,13] Calix[6]arene, calix[4]arene, ethyl bromoacetate, *p-tert*-butylpyridine and *p*-ethylpyridine were obtained from Aldrich (Milwaukee, WI, USA). *P*-Ethyl-Girard's reagent and *tert*-butyl-Girards reagent P were prepared as described elsewhere.[14] Girards reagent P was purchased from Merck (Darmstadt, Germany). TRIS, for the preparation of buffer solutions, was purchased from Sigma (St. Louis, MO, USA).

All solutions were prepared with distilled water. Inorganic and organic chemicals were of analytical-reagent grade and used without further purification. For recording the response of the optode membrane, 0.05 mol l^{-1} TRIS–HCl buffer solutions of appropriate pH were used.

Optode membrane

Unless stated otherwise, the optode membranes were prepared from a mixture of 80 mg of PVC, 160 mg of plasticizer (BOS), 4.8 mg (4.12 μmol) of calix[6]arene hexaester or 4.1 mg (4.12 μmol) of *tert*-butylcalix[4]arene tetraester, 1.0 mg (2.06 μmol) of borate (KT*p*ClPB) and 1.2 mg (2.06 μmol) of ETH 5294. The membrane components were dissolved in 1.0 ml of tetrahydrofuran (THF). By using a spin-on device, two identical membranes of approximately 4 μm thickness were cast on two

quartz-glass plates that were subsequently mounted on the measuring cell.

Apparatus

The measuring cell containing the two optode membranes was placed in a conventional UV/VIS spectrophotometer (Model 150-20, Hitachi, Tokyo, Japan). All measurements were made in the transmission mode. ^{1}H NMR spectra were measured on a JEOL JNM-EX270 Fourier transform NMR spectrometer (^{1}H, 270 MHz).

Measurement procedure

About 3.4 ml of a sample solution were injected into the laboratory-made measuring cell. Absorbance measurements were taken under batch conditions. The limiting absorbance values A_1 and A_0 were determined with the optode membrane in contact with 0.1 mol l^{-1} HCl and 0.1 mol l^{-1} KOH, respectively.

Synthesis of Girard's reagent P and aldehyde adduct

A 0.1 mol amount of Girard's reagent P was dissolved in 100 ml of absolute ethanol in a 250 ml round-bottomed flask and 0.15 mol of acetaldehyde (or butanyraldehyde heptaldehyde) and 6 drops of glacial acetic acid were added successively. The reaction mixture was stirred and heated at 50 °C in a water-bath for 3 h. The solution was then concentrated in a Rotavapor to give an oily liquid. The oily liquid was washed three times with 25 ml of dry diethyl ether, then dried under vacuum. The product was obtained as a pale yellow solid and its structure was confirmed by ^{1}H NMR spectroscopy.

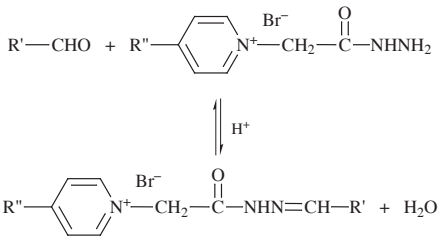
Standard solution

A 0.1 mol l^{-1} stock standard solution was prepared by dissolving 5.00 mmol of the pure Girards P adduct in TRIS–HCl buffer and diluting to 50.0 ml. A series of working standard solutions with concentrations range from 1.00×10^{-6} to 0.05 mol l^{-1} in TRIS–HCl buffer were obtained by appropriate dilution of the 0.1 mol l^{-1} stock standard solution with the supporting buffer standard solution. Calibration curves were constructed by plotting α (see below) against the logarithm of the concentration of the standard solutions.

Results and discussion

Derivatization of aldehyde

In this work, in the presence of an acid catalyst, an aldehyde was converted into its ionic hydrazone derivative by reaction with commercially available Girard's reagent P and the synthetic ethyl-Girard's reagent and *tert*-butyl-Girards reagent P:



where R′ = –CH_3, –$CH_2CH_2CH_3$ or –$CH_2(CH_2)_2CH_3$ and R″ = –H, –CH_2CH_3 or –$C(CH_3)_3$. Table 1 summarizes the structures and abbreviations of the adducts between the three types of Girard's reagent P and various aldehydes. The optode membrane responses to these nine adducts were investigated.

Principle of operation

The proposed optical device works on the basis of a cation-exchange system as described by Morf *et al.*[15] In this device, the optode membranes contain the neutral calix[6]arene hexaester or calix[4]arene tetraester (C) as the selective host for R″-PGA, R″-PGB or R″-PGH ion (M^+), a chromo-ionophore ETH5294 (IND) selective for the hydrogen ion and a lipophilic salt, KT*p*ClPB, as the anionic site (R^-). Fig. 1 shows the absorption spectra of the membrane M4 (see below), which were obtained after 6 min of equilibration with pH 9.5 TRIS–HCl buffer solution containing different concentrations of *tert*-butyl-Girard's P acetylhydrazone of butyraldehyde ion (*t*-butyl-PGB). A reduction in the absorption band of $INDH^+$ at 614 and 660 nm and an increase in the absorption band of IND at 535 nm were evidenced, which are due to the facile complex formation between the calix[4]arene host and *t*-butyl-PGB adduct. Assuming that a 1 : 1 calix[*n*]arene ionophore–R″-PGA or –R″-PGB or –R″-PGH ion complex is formed, the overall equilibrium between the polymeric membrane phase (m) and the aqueous

Table 1 R″-Girard's reagent P–aldehyde adducts studied

R″	Acetaldehyde	Butyraldehyde	Heptaldehyde
–H	PGA	PGB	PGH
–CH_2CH_3	Et-PGA	Et-PGB	Et-PGH
–$C(CH_3)_3$	*t*-Butyl-PGA	*t*-Butyl-PGB	*t*-Butyl-PGH

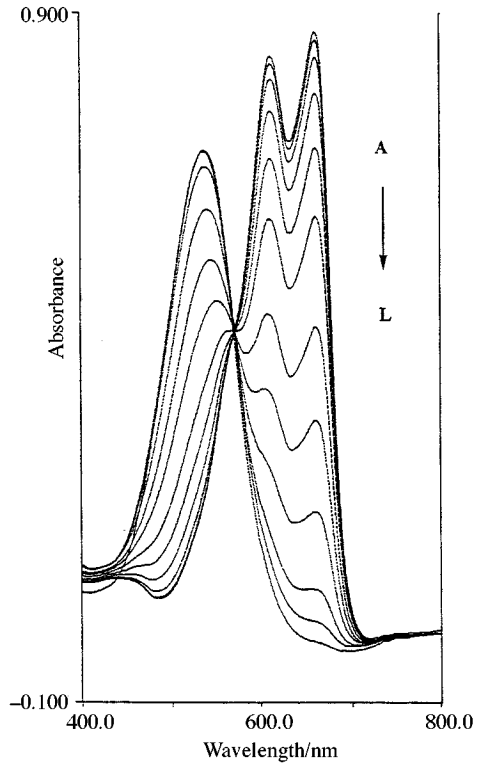


Fig. 1 Absorption spectra of optode membrane M4 after equilibration with pH 9.5 TRIS–HCl buffer solutions containing different concentrations of *tert*-butyl-PGB: A, buffer; B, 1.00×10^{-6}; C, 5.00×10^{-6}; D, 1.00×10^{-5}; E, 5.00×10^{-5}; F, 1.00×10^{-4}; G, 3.00×10^{-4}; H, 5.00×10^{-4}; I, 1.00×10^{-3}; J, 3.00×10^{-3}; K, 5.00×10^{-3}; and L, 0.1 mol l^{-1} KOH solution.

sample solution (aq), governed by the equilibrium constant K_{exch}, can be described as

$$M^{+}_{(aq)} + INDH^{+}_{(m)} + C_{(m)} \overset{K_{exch}}{\rightleftharpoons} M^{+}\cdot C_{(m)} + IND_{(m)} + H^{+}_{(aq)} \quad (1)$$

According to the derivation reported elsewhere, the response function for R″-PGA, or R″-PGB or R″-PGH ion is:

$$\frac{[M^+]}{[H^+]} K_{exch} = \frac{\left\{[R^-]_T - (1-\alpha)[IND]_T\right\}}{\left\{[C]_T - [R^-]_T + (1-\alpha)[IND]_T\right\}} \frac{\alpha}{1-\alpha} \quad (2)$$

where $[C]_T$, $[R^-]_T$ and $[IND]_T$ are the respective total concentrations of the calixarene ionophore, KT*p*ClPB and ETH 5294 in the membrane preparation, and α is defined as the ratio of the concentration of unprotonated chromo-ionophore to that of the total chromo-ionophore present in the membrane phase:

$$\alpha = \frac{[IND]}{[IND] + [INDH^+]} = \frac{[IND]}{[IND]_T} \quad (3)$$

If the optode membrane follow Beer's law:

$$\alpha = \frac{A_1 - A}{A_1 - A_0} \quad (4)$$

where A_1 and A_0 are the limiting absorbance values for fully protonated (α = 0) and deprotonated (α = 1) chromo-ionoophore, respectively.

Response behaviour of different membrane formulations

As revealed by eqn. (2), the response of the optode membrane is highly dependent on its composition. To study the composition effect, membranes M1–M5 of different formulations as shown in Table 2 were fabricated. For specific membrane compostions M1, M2, M3, M4 and M5 satisfying the conditions provided by the equation

$$m[R^-]_T = m[IND]_T = [C]_T \quad (5)$$

the response function denoted by eqn. (2) can be simplified to:

$$\frac{[M^+]}{[H^+]} K_{exch} = \frac{\alpha^2}{(1-\alpha)(m-\alpha)} \quad (6)$$

where for M1 $m = 1$, for M2 $m = 2$, for M3 $m = 5$, for M4 $m = 8$ and for M5 m = 2.

The theoretical prediction curves for M1, M2, M3, M4 and M5 were constructed based on eqn. (6) with a value of 1.2×10^{-8} assigned to K_{exch} for the host–guest complex between the calix[4]arene and PGB. Direct comparisons of the theoretical curves with the corresponding experimental data are made in Fig. 2–4. Good agreement between the calculated curves and experimental results was found for all five membrane systems. Therefore, the 1 : 1 relationship between the calix[*n*]arene ionophore and the R″-PGB ion in the complex was confirmed.

It is noteworthy that the response slope, dynamic working range and detection limit of the membrane can be modulated by controlling the relative amount of calix[4]arene in the membrane preparation (Table 3). This flexibility allows us to formulate a unique ion-selective membrane 'cocktail' that fits the particular requirement of the analytical method. The response behavior of the optode membrane is pH dependent over a certain pH range, as shown in Fig. 3. By controlling the pH of the solution, different detection concentration ranges of the analyte may be defined. At pH 9.0, the best detection range ($0.05 \leq a \leq 0.9$) of the optode membrane for *t*-butyl-PGB is from 5×10^{-3} to 5×10^{-5} mol l^{-1}. At pH 9.5, a highly sensitive optical method for the determination of *t*-butyl-PGB has been realized with a detection limit of 5×10^{-7} mol l^{-1}.

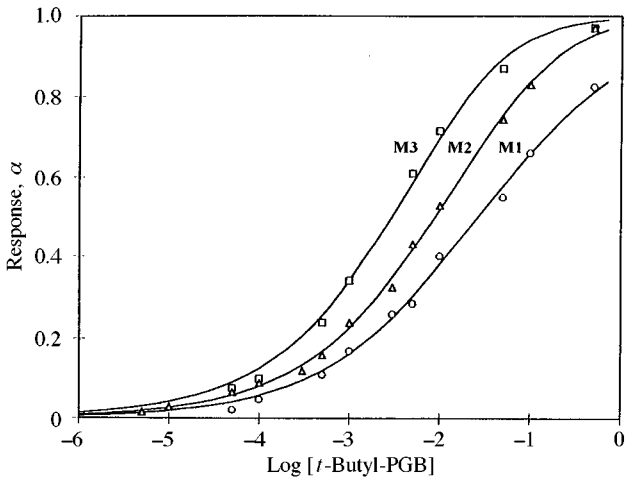


Fig. 2 Membrane responses of different optode membranes at 660 nm as a function of log[PGB] at pH 9.5. Symbols represent experimental findings and the lines represent theoretical predictions.

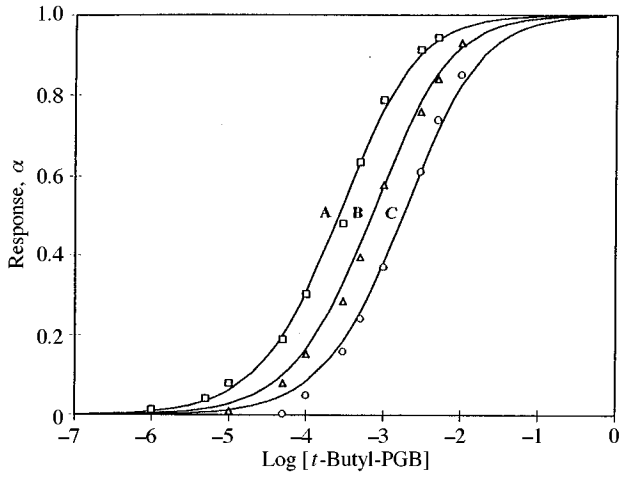


Fig. 3 Membrane responses of optode membrane M4 at: pH (A) 9.5, (B) 9.0 and (C) 8.5.

Table 2 Compositions of optode membrane casting solutions

	ETH5294		KTpClB		Calix[4]arene		Calix[6]arene	
Entry	μmol	Ratio	μmol	Ratio	μmol	Ratio	μmol	Ratio
M1	2.06	1	2.06	1	2.06	1	—	—
M2	2.06	1	2.06	1	4.12	2	—	—
M3	2.06	1	6.06	3	10.3	5	—	—
M4	2.06	1	2.06	1	16.5	8	—	—
M5	2.06	1	2.06	1	—	—	4.12	2

Interaction between the host and the guest analyte

The chemical recognition of the optode membrane towards R″-Girard's reagent P–aldehyde conceivably arose from the specific complexation between the calixarene ionophore and the analyte. The complexation of the *tert*-butylcalix[4]arene tetraester and PGB was studied by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum of a $CDCl_3$ solution of the calixarene ionophore and PGB, a significant downfield shift of the *para*-proton of the pyridinium ring of the guest was observed (from δ 8.60 to δ 9.50), indicating that the pyridinium ring of the guest is situated in the deshielding zone of the host molecule. Hence, the host–guest interaction is evident for the calixarene ionophore and the analyte. In order to study the effects of the host in relation to the sensory capability of the optode membrane, three sets of optode membranes having the same composition, but containing different ionophores (*i.e.*, calix[4]arene tetraester, calix[6]arene hexaester and calix[6]arene) were prepared. Fig. 4 shows that the optode membranes containing the calix[6]arene hexaester and the calix[4]arene teraester (*i.e.*, membranes M2 and M5) both exhibit a good response to PGB. This means that both the calix[4]arene teraester and calix[6]arene hexaester ionophore interact with PGB to form a host–guest complex but with different overall K_{exch}. The complex of the calix[6]arene hexaester ionophore and PGB is more stable. In contrast, the response of the membrane containing calix[6]arene was much smaller than that of the calix[4]arene tetraester. In addition, the response of a membane containing no calixarene was shown to be insentive to concentration changes of the analyte. Obviously, the presence of the calixarene ionophore is essential for the sensory characteristics of the optode membranes.

Fig. 5 shows the response curves of the optode membrane incorporating the calix[4]arene ionophore towards PGA, PGB and PGH. The result shows that the response sensitivity of the membrane increases with increase in the chain length of the aldehyde moiety. Conceivably, the greater hydrophobic interaction arising from the longer carbon chain of the Girards reagent P adducts and the aromatic sheath of the ionophore favors the formation of a stronger host–guest complex.

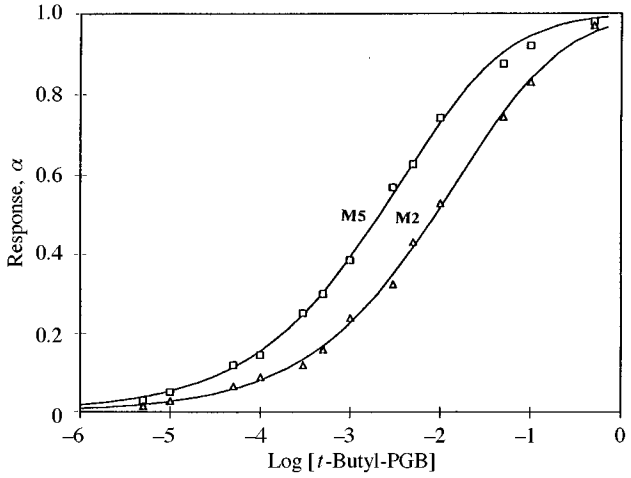


Fig. 4 Membrane response of optode membranes containing different host molecules at pH 9.5: M2, the calix[4]arene ionophore; and M5, the calix[6]arene ionophore.

Table 3 Response behavior of optode membranes with different concentrations of the calix[4]arene ionophore towards PGB at pH 9.5

Membrane	Response slope (α = 0.5) (Δα/Δlog *C*)	Dynamic range/ (mol l^{-1}) (0.05 ≤ α ≤ 0.9)	Detection limit/ (mol l^{-1}) (α = 0.01)
M1	0.288	7×10^{-5}–0.8	3×10^{-6}
M2	0.346	4×10^{-5}–0.2	1.5×10^{-3}
M3	0.370	1×10^{-5}–0.06	5×10^{-7}

Effect of derivatization reagent

The reaction between the Girard's reagent P and aldehydes is the basis of the present indirect optode method for aldehyde determination. Girard's reagent P reacts with an aldehyde to give the acetohydrazone derivative under weak acidic conditions (pH ≈ 5). In our experiments, three types of Girard's reagent P were used, namely Girard's reagent P, ethyl-Girard's reagent P and *tert*-butyl-Girard's reagent P. As indicated in Fig. 6, the optode membrane incorporating the calix[4]arene ionophore is highly sensitive and selective for adducts of the three kinds of Girard's reagent P and butyraldehyde. For the determination of butyraldehyde, the sensitivity of the method increases in the order Girard's reagent P < ethyl-Girard's reagent P < *tert*-butyl-Girard's reagent P. However, the derivatization agent, being an ionic organic species, may also interact with the host molecule as well. Hence, the interference responses of the three kinds of Girard's reagent P were studied and the results are given in Table 4. No appreciable interference response was observed from 1×10^{-5} to 0.1 mol l^{-1} Girard's reagent P. Understandably, the interference response increases with increase in the number of carbon atoms in the derivatiza-

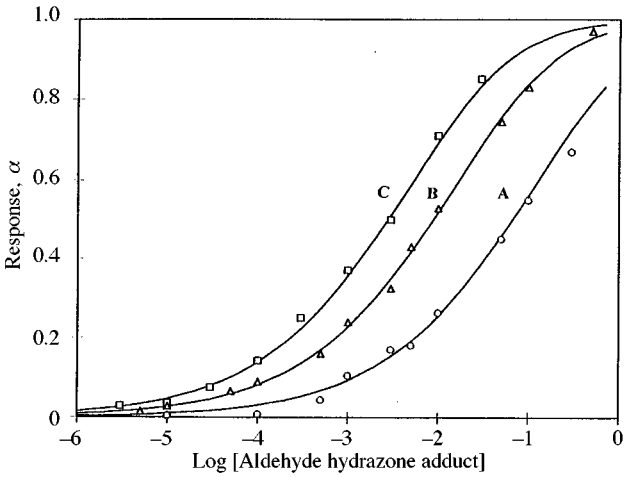


Fig. 5 Membrane response of optode membrane M2 at pH 9.5 as a function of concentration of Girard's P adducts derived from (A) acetaldehyde, (B) butyraldehyde and (C) heptaldehyde.

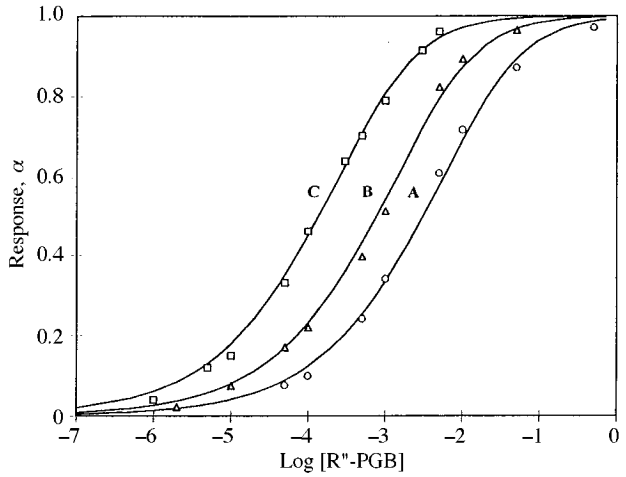


Fig. 6 Membrane response of optode membrane M3 at pH 9.5 as a function of concentration of different butyraldehyde adducts derived from (A) Girard's reagent P, (B) ethyl-Girard's reagent P and (C) *tert*-butyl Girard's reagent P.

tion agent and decreases with its hydrophilicity. For instance, the membrane responded more sensitively to *tert*-butyl-Girard's reagent P. Therefore, when using the pure Girards adduct for optode measurements, the higher sensitivity *tert*-butyl-Girards reagent P derivative should be used. However, for *in situ* determination of aldehydes, Girard's reagent P was used instead because the excessive amount of derivatization agent left after the derivatization showed much lower interference.

Response time, reproducibility and stability

The optode membrane exhibited a fast response time: less than 4 min were required to attain the t_{95} value after the solution step change from the buffer to 0.001 mol l^{-1}, 0.003 mol l^{-1} and 0.01 mol l^{-1} PGB, and less than 5 min were required if a backward step change was applied (Fig. 7). To study the stability of the optode membrane, the response value of the membrane in contact with 3.00×10^{-4} mol l^{-1} PGB in pH 9.5 TRIS–HCl buffer was recorded over a period of 2 h. From the absorbance values taken every 15 min, the mean absorbance was 0.3998 with a standard deviation of 1.4×10^{-3} (relative standard deviation, $S_T = 0.35\%$, $n = 9$).

Lifetime

The A_1 absorbance values of the M2 optode membrane at 660 nm decreased by only 0.017 (from 0.877 to 0.860) for the measurement of the sample solution of PGB repeatedly 39 times. However, during prolonged use (*i.e.*, over 20 h), the sensitivity of the membrane decreased fairly rapidly and therefore regular calibration would be required.

Interferences

The selectivity of the optode membranes containing either the calix[4]arene or calix[6]arene ionophore for R″-Girard's reagent P–aldehyde adducts is shown in Table 4. The results clearly show that the presence of the excess Girard's reagent used for the *in situ* derivatization did not interfere with the aldehyde determination. Since sodium and potassium ions interact strongly with the calix[4]arene and calix[6]arene ionophores, respectively, it is not surprising that their presence would seriously interfere with the determination of aldehydes. Common organic substance, such as alkanes, ethers, alcohols, esters and organic acids, showed no response to the optode membrane. Because of the much slower derivatization reaction taking place between ketones and Girard's type reagents, the interference of ketonic compounds in the determination of aldehydes would be unimportant.

In situ derivatization reaction

For a real determination of an aldehyde, we must seek conditions for its complete derivatization. The *in situ* determination was performed in two parts, as exemplified by butyraldehyde. The purpose of the first part was to study the degree of conversion of butyraldehyde to its adduct in the presence of different amount of Girards reagent P. Two butyraldehyde solutions with concentrations of 0.01 and 0.1 mol l^{-1} in 95% ethanol was prepared. A set of seven and nine samples, respectively, each containing 5.00 ml of the above stock standard solution, were derivatized with different amounts of Girard's reagent P for a period of 50 min and then diluted to 50.0 ml with pH 9.5 TRIS–HCl buffer. As indicated by the constant optical properties of the resulting solution, the derivatization reaction was complete within the given time for 0.01 mol l^{-1} butyaldehyde using a fivefold amount of Girard's reagent P and for 0.1 mol l^{-1} butyaldehyde using a threefold amount of Girard's reagent P. In addition, the presence of excess of Girard's reagent P did not significantly affect the optode measurement.

The purpose of the second part was to study the accuracy and reliability of the concentration range for the proposed method. The response curves for 1.00×10^{-5} and 0.01 mol l^{-1} butyraldehyde solutions derivatized *in situ* with 500–3-fold excesses of Girard's reagent P was obtained in duplicate. The derivatization conditions were the same as the first part

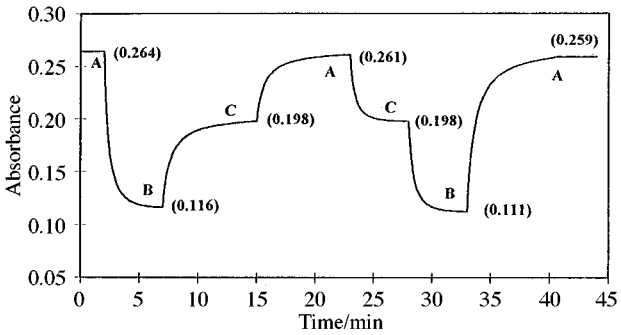


Fig. 7 Absorbance of optode membrane M3 *versus* time for two 4 μm thick membranes at 660 nm after concentration changes between (from left to right) A, 1.00×10^{-3} and B, 1.00×10^{-2}; B and C, 3.00×10^{-3} mol l^{-1} PGB; C and A; A and C; C and B; and B and A.

Table 4 Optical selectivity for R″-Girard's reagent P, R″-Girard's reagent P–aldehyde adducts and common inorganic cations determined by the separate solution method at pH 9.5 and $\alpha \approx 0.5$

	Guest					
Parameter[a]	*t*-Bu-PGB	GSP[b]	Et-GSP[b]	*t*-Bu-GSP[b]	PGA	PGB
$K^{opt[4]}_{t\text{-Bu-PGB},j}$	1.0	$\sim 1 \times 10^{-6}$	$\sim 2 \times 10^{-4}$	$\sim 4 \times 10^{-3}$	5.9×10^{-3}	4.4×10^{-2}
$K^{opt[6]}_{t\text{-Bu-PGB},j}$	1.0	—	—	$\sim 3 \times 10^{-2}$	—	5.4×10^{-2}

	Et-PGB	PGH	Li^+	Na^+	K^+
$K^{opt[4]}_{t\text{-Bu-PGB},j}$	1.8×10^{-1}	1.5×10^{-1}	2.4×10^{-2}	37	2.6×10^{-1}
$K^{opt[6]}_{t\text{-Bu-PGB},j}$	—	—	8.7×10^{-4}	5.2×10^{-2}	16

[a] $K^{opt[4]}_{t\text{-Bu-PGB},j}$ was determined using *tert*-butylcalix[4]arene tetraester as the ionophore and $K^{opt[6]}_{t\text{-Bu-PGB},j}$ was determined using calix[6]arene hexaester. [b] Tested at $\alpha \approx 0.1$.

described above. The results were compared with a calibration curve for authentic synthesized pure PGB (Fig. 8). The experimental results agreed very well with the theoretical response derived from the proposed method and indicated that the derivatization reaction offers a very clean, simple, accurate and efficient method for the indirect assay of aldehydes.

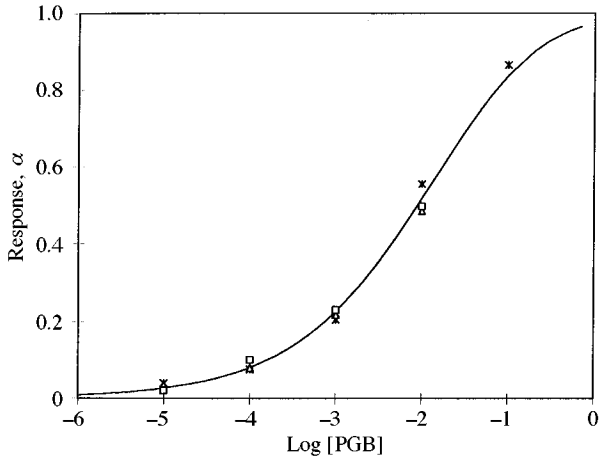


Fig. 8 Response of optode membrane M2 at 660 nm and pH 9.5 as a function of PGB generated from (✳) standard PGB solution and (△) and (□) two sets of *in situ* derivatizations between butyraldehyde and Girard's reagent P.

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