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MEMBRANE SYSTEMS FOR PIEZOELECTRIC AND ELECTROCHEMICAL SENSING IN ENVIRONMENTAL CHEMISTRY

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This paper illustrates work at the University of Wales College of Cardiff (formerly UWIST) relating to the development and applications of membrane systems in various modes for possible use in environmental analysis. Three main types are illustrated, namely, membranes coated on quartz crystals for piezoelectric monitoring of gases and vapours, membranes used as the sensing components of potentiometric ion sensors, and catalytic enzyme membranes used for converting analyte components into suitable forms for electrochemical sensing.

The piezoelectric type membranes are illustrated by modified cyclodextrins for detecting benzene, epoxyoctacosahydro[12]cyclacene derivatives for detecting nitrobenzene and other aromatic vapours, and pyridoxine hydrochloride for ammonia detection. Potentiometric ion-sensing, that is, ISE membranes, are illustrated by selected crown ethers as ionophores with tetraphenylborate for detecting the herbicides, diquat and paraquat. Finally, catalytic type membranes are illustrated by catalase and peroxidase-based membranes as modifiers for producing species in hydrogen peroxide monitoring that can avoid the interferences involved in the direct electrochemical detection of hydrogen peroxide.

KEY WORDS: Piezoelectric crystal detection, ion-selective electrodes, enzyme electrodes, gas and vapour analysis, herbicide analysis, hydrogen peroxide analysis.

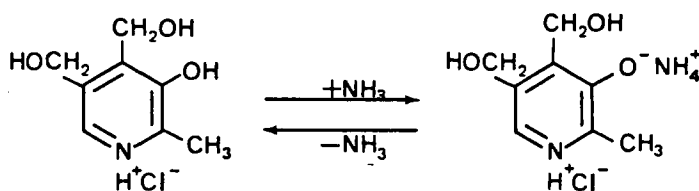
INTRODUCTION

There is an ever-increasing demand for analytical methods for monitoring purposes in environmental chemistry. Among the available methods are the approaches of piezoelectric crystal detection of gases and vapours^{1,2} and electrochemical sensing.³ While the piezoelectric crystal detection approach is essentially dependent on the decrease in oscillating frequency of a quartz crystal caused by sorption of a component from the surrounding gas/vapour phase by a coating on the quartz crystal, the electrochemical approaches are much more diverse. Thus, these can be essentially based on potentiometric, voltammetric, and other electrochemical principles. It is the purpose of this paper to briefly describe recent work of relevance to environmental chemistry in the author's laboratories on membrane systems which have been studied for use in the piezoelectric quartz crystal detection of gases and vapours as potentiometric ion-selective electrode (ISE) type

sensors for diquat and paraquat, and as catalytic membrane oxidation systems for the electrochemical analysis of hydrogen peroxide.

PIEZOELECTRIC QUARTZ CRYSTAL MEMBRANES FOR INORGANIC GASES

Sensor membranes have been described for the piezoelectric quartz crystal detection of many inorganic gases and vapours, such as sulphur dioxide, hydrogen sulphide, hydrogen chloride, ammonia and water vapour. The sensing components can be of many different types. Thus, *Capsicum annum* pods, ascorbic acid, ascorbic acid with silver nitrate, L-glutamic acid hydrochloride and pyridoxine hydrochloride (vitamin B6 hydrochloride) have been described for ammonia.^{1,2} Of these, pyridoxine hydrochloride has been found to be of good reversibility and selectivity, and exceptional sensitivity:⁴



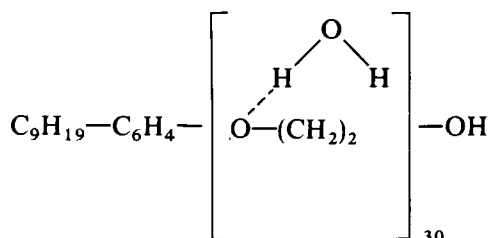
Further studies on pyridoxine hydrochloride have shown that the use of a polymer-type support matrix for the sensor coating on the quartz crystal helps to considerably extend the useful lifetime of the piezoelectric detector.^{5,6} In this way, it was found that the system functioned well for up to 60 days, whilst without the polymer support the lifetime was only ≈ 10 days.^{5,6}

The sensor/polymer cocktail for application to the quartz crystal consisted of mixtures (1 + 1 v/v) of a 0.2% m/v solution of pyridoxine hydrochloride in ethanol and water (1 + 1 v/v) and a 0.2% m/v solution of Antarox CO-880 in acetone,⁶ and could be applied by either the capillary or brush coating approaches, with the latter being the more reproducible.⁶ The Antarox CO-880 is a nonylphenoxy-polyethoxylate with 30 ethoxylate units, and study of this system gave the opportunity for assessing a range of parameters, including an extended range of interferences and the effectiveness of the syringe dilution method for obtaining lower concentrations of gas/vapour standards.⁶

As a result of the above studies, various recommendations have been made, including procedural changes in the approach to syringe dilution in order to minimize errors arising from the volumes of syringe needles and connections.⁶ Thus, the slopes of less than 1 obtained for plots of the log form of $\Delta F = KC$ (where ΔF is the decrease of frequency brought about by the sorbed analyte of concentration, C , in the gas phase passing over the crystal, and K is a constant)

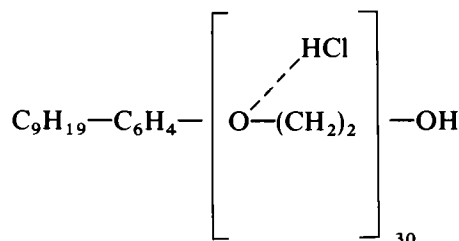
are significantly increased by modifying the syringe dilution procedure.⁶ However, other factors are also involved, for the log-log slopes still fall short of 1.

The Antarox CO-880 support matrix used for stabilizing the membrane of sensor is a humectant wherein water is readily held by hydrogen bonding:



Alternative polymers, such as PVC are impractical, so that water vapour has to be removed from the carrier and sample streams passing over the coated quartz crystal. Also, the matrix system incurs possible interference from hydrogen chloride gas (which would hardly be expected to occur with ammonia in a gas stream) although, except for triethylamine, other gases studied at high levels (sulphur dioxide, nitrogen dioxide, carbon dioxide and hydrogen sulphide) give only a small piezoelectric signal.⁶

The hydrogen chloride interference can be ascribed to the formation of hydrogen bonds between the oxygen from the ethoxylate groups and the hydrogen from hydrogen chloride:



The extent of this interference yields the basis of a hydrogen chloride piezoelectric sensor, although the concave nature of the $\log \Delta F$ versus $\log [\text{HCl}]$ calibration is a disappointing feature.⁷

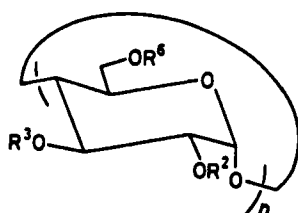
PIEZOELECTRIC QUARTZ CRYSTAL SENSORS FOR ORGANIC GASES AND VAPOURS

Among organic vapours, much attention has been devoted to aromatic hydrocarbons. Thus, a mixture of nujol with *trans*-chlorocarbonyl bis(triphenylphosphine)iridium(I) is an early example of such a sensor.⁸ Toluene in ambient air has been monitored using Carbowax 550 coated crystal,⁹ while Carbowax 1000 has been investigated for 2-nitrotoluene.¹⁰

Edmunds and West¹¹ have examined the behaviour of various coatings on a

9 MHz AT-cut quartz crystal (most piezoelectric crystal detection studies have use of such a vehicle and these quartz crystals are obtainable from Webster Electronics Ltd., Rosemills, Hartbridge, Ilminster, Somerset, TA19 9AQ, UK) to toluene and chloroform, and favour Pluronics 64 (a g.l.c. stationary phase material) as the most sensitive coating for ethylbenzene, 2-methyltoluene, and hexane.

More recently, interesting studies have been made of the role of some chemically-modified cyclodextrins,



	n	R^2	R^3	R^6
α CD	6	H	H	H
DS α CD	6	TBDMS	H	TBDMS
DA α CD	6	CH ₂ CH=CH ₂	H	CH ₂ CH=CH ₂
DM β CD	7	Me	H	Me
DM β CD-B ₇	7	Me	PhCO	Me

as piezoelectric crystal coating sensors for benzene vapour.¹² Three such compounds were examined (shown underlined) on the basis of their predicted selectivity¹³ for benzene vapour, wherein it was said¹³ that the interaction was the cumulative effect of many noncovalent interactions, rather than by the usual method of making or breaking one or two covalent bonds. The cyclodextrin receptor molecules are usually concave in shape, having specific electronic characteristics that enable them to provide a number of reactive sites on their surfaces. Such sites will interact via the weak interactions mentioned, with matching sites on the usually convex surface of a guest molecule, e.g., benzene.

The modified cyclodextrins examined¹² were 2,6-per-*O*-(*t*-butyldimethylsilyl)- α -cyclodextrin (DS α CD), 2,6-per-*O*-allyl- α -cyclodextrin (DA α CD), and 2,6-per-*O*-methyl- β -cyclodextrin-3-per-*O*-benzoate (DM β CD-B₇). DS α CD was found to be the best sensor for the range of ≈ 80 to 4×10^5 mg m⁻³ benzene vapour in air, while DA α CD is a possible alternative. Both sensors are selective towards benzene vapour over methane, propane, butane, pentane, ethyne, ammonia, and nitrobenzene. Toluene is the most serious interferent which, for the preferred DS α CD sensor, leads to only <20% of the decrease in piezoelectric frequency observed with the corresponding amount of benzene. However, the interference is slightly greater for the DA α CD sensor.¹²

The toxicity of nitrobenzene (the maximum allowable concentration is 5 mg m⁻³) presents a need for sensitive detectors. Against this, charcoal, PEG-750, PEG-400 and other materials have been assessed as piezoelectric quartz crystal coatings for nitrobenzene detection.¹⁴ They were tested to full equilibration for 35 mg m⁻³ nitrobenzene.¹⁴ A further prospect is offered by the recently synthesized^{15,16} hexaepoxyoctacoahydro[12]cyclacene derivative [1].

This was tested¹⁷ for the range 1840 to 22 mg m⁻³ nitrobenzene, when the lifetime of the piezoelectric detectors system was >60 days, even after many exposures to possible interferents, such as 2- and 3-nitrotoluenes, chlorobenzene, bromobenzene, benzene and ammonia.¹⁷ Interferences (Table 1) arose chiefly with ammonia and 2- and 3-nitrotoluenes.¹⁷

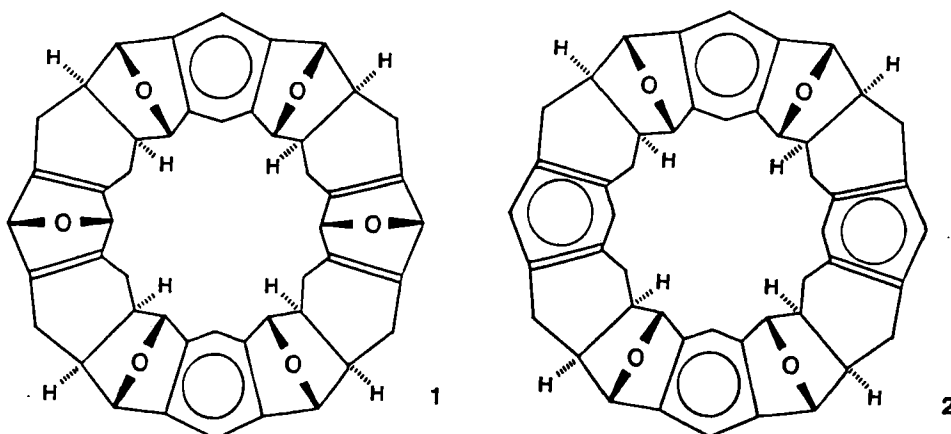


Table 1 The response of a piezoelectric quartz crystal (gold electrode) to various vapours for coatings of compounds [1] and [2] and to a triallylmacrocycle

Vapour	Concentration ^a (10 ³ mg m ⁻³)	Compound [1]		Compound [2]	Triallyl macrocycle
		Response ΔF/Hz coatings		Response ΔF/Hz coating	Response ΔF/Hz coating
		1st	2nd	1st	1st
Toluene	30.0	19	10	86	128
	6.6	13	13	-	-
	1.5	9	10	-	-
2-Nitrotoluene	1.40	48	46	136	111
	0.31	25	23	-	-
	0.07	16	15	-	-
3-Nitrotoluene	1.50	38	37	85	72
	0.33	19	20	-	-
	0.07	10	11	-	-
Chlorobenzene	15.4	16	18	81	100
	3.37	11	12	-	-
	0.74	8	9	-	-
Bromobenzene	4.18	30	31	75	86
	0.92	17	18	-	-
	0.20	10	12	-	-
Benzene	19.2	10	12	125	130
	4.2	8	9	-	-
	0.9	6	7	-	-
Ammonia	3.90	40	42	-	-
	0.48	19	19	-	-
	0.06	10	11	-	-
Nitrobenzene	1.84	111	109	121	98

^aCalculated from vapour pressure data, except for ammonia, analysed as previously discussed.⁶

Also examined¹⁷ was the tetraepoxy analogue [2] of compound [1]. This does not show the degree of selectivity shown by the hexaepoxy compound [1] towards nitrobenzene for any of the compounds studied (Table 1) and ranks as a more universal type of sensor. However, the response towards 2-nitrotoluene equals, and even slightly excels, that towards nitrobenzene.¹⁷ A further compound offering promise as a selective system towards toluene¹⁸ is a triallylmacrocyclic and is similarly rather universal¹⁹ (Table 1).

ISE MEMBRANES BASED ON CROWN ETHERS AND TETRAPHENYLBORATES FOR HERBICIDES

ISEs based on neutral carrier ligand molecules have become well established,²⁰ helped by the wide use of valinomycin as an ISE sensor for potassium. Thus, synthetic neutral carriers, such as the cyclic polyethers (crown ethers)²¹ have been produced. Of these, dodecylmethyl-14-crown-4 has yielded an interesting lithium ISE,²² and bis(crown ether) derivatives of 15-crown-5 and 18-crown-6 have yielded potassium and caesium ISEs.²³

The way by which the selection of suitable neutral carriers for ion-sensing can be helped by structural studies on interactions between carriers and ions have been well demonstrated by Stoddart and co-workers (for a list of relevant references, see Reference 24 of this paper) who have shown interesting features on the interactions between macrocyclic polyethers and molecules and cations according to three main types of bonding:

- i) coordination via [N—H...O] hydrogen bonds as in complexation between polyether and ammonium ions,^{25,26}
- ii) coordination through [C—H...O] linkages to the diquat [DQT] dication,²⁷ etc.; and
- iii) metal ion coordination to oxygen atoms of the crown ether compound.

The structural information obtained by Stoddart and co-workers has been directed to the development of ISE sensors for diquat (DQT) and paraquat (PQT) dications in the way recently reviewed.²⁸ This is an important application in view of the use of DQT and PQT as contact herbicides. This focus of interest arose from structural studies relating to the complexation of DQT and PQT with dibenzo-30-crown-10 (DB30C10) which led to studies of the crown ether as an ISE sensor.²⁴

The maximum stability for DB30C_n complexes with DQT occurs when $n=10$ ²⁹⁻³² (Table 2) while the X-ray structure shows the plane of the DQT molecule to be enclosed in a U-shaped cavity formed by DB30C10.^{28,29} The complexation involves three kinds of DB30C10-(host)-DQT(guest) interactions:

- i) DB30C10 catechol-oxygen electrostatic interaction with the positively charged nitrogen atoms in DQT. For this, the crown ether catechol O—O separation (2.6 Å) and N—N separation in DQT (2.8 Å) are similar (Figure

Table 2 Stability constants (K_a) and free energies of formation (ΔG_f) of [DQT.DB3n-crown-n] complexes in acetone^a (from Reference 33)

Crown ether	$K_a (M^{-1})$	$\Delta G_f / kJ mol^{-1}$
DB27C9	4.1×10^2	15.0
DB30C10	1.8×10^4	24.3
DB33C11	1.1×10^4	23.1
DB36C12	2.0×10^3	18.9
DB30C10($-OCH_2$) ₂ Ph	–	31.0

^aData from References 29, 30 and 32.

- 1) so that the catechol oxygens are nearly directed above and below the DQT nitrogens in the [DQT.DB30C10]²⁺ complex.
- ii) DB30C10 benzene ring π -electron charge transfer to the electron deficient DQT²⁺.
- iii) Hydrogen bonding between H⁶ and H^{6'} (Figure 1) with oxygen atoms in the DB30C10 framework, and as mentioned above.

A wide ranging study has been undertaken^{24,33} during which various crown ethers, namely, dibenzo-30-crown-10 (DB30C10), bis-metaphenylene-32-crown-10 (BMP32C10), bis-metaphenylene-34-crown-10 (BMP34C10), bis-paraphenylene-37-crown-11 (BPP37C11), and dinaphthalene-36-crown-10 (DN36C10) have been tested for their efficacy as sensor for DQT and PQT and related to conformational phenomena in their complexation with the two dications and with the related 4,4'-dipyridinium (4,4'-DPy). Also studied³⁴ have been the use of ion-pairing reagents in ISEs for the dications, these being related also to searches for the best type of anion excluder for use in PVC ISE type membranes with the crown ether neutral ligand.

The best electrodes for DQT are based^{24,33} on DB30C10 plus DQT.2TPB (TPB=tetraphenylborate) with either 2-nitrophenyl phenyl ether (NPPE) or 2-nitrophenyl octyl ether (NPOE) as solvent mediator (Figure 2, top) but good electrodes were also obtained with just DQT.2TPB and the solvent mediators (Figure 2, bottom). The other crown ethers studied gave³³ good ISE properties for 4,4'-DPy of calibration slope between 33 and 41 mV decade⁻¹, extending down to 1.7 to 6 μ M. However, the expectation in this study³³ was to discover a PQT ISE based on BPP34C10 since a complex exists¹³ (of stability constant 730 dm³ mol⁻¹) arising from the O—O separation (5.5 Å) in this host being not too far removed from the N—N separation of 7.0 Å in PQT (Figure 1(b)). The expectation was not realised,³³ probably because the [PQT.BPP34C10]²⁺ complex is less stable than [DQT.DB30C10]²⁺ (stability constant 18000) and too weak to exhibit a potentiometric function.

A wide range of anion systems, namely, phosphorus hexafluoride (PF₆), anthraquinone-2-sulphonate (AS), octyl sulphate (OS), picrate (PIC), dipicrylaminate (DPA), Diamine Green B (DGB), tetraphenylborate (TPB) and tetrakis-4-chlorophenylborate (T4CIPB) have been studied as possible ion-pairing agents for use in ISE membrane for PQT, DQT and 4,4'-DPy, but only PF₆, TPB and

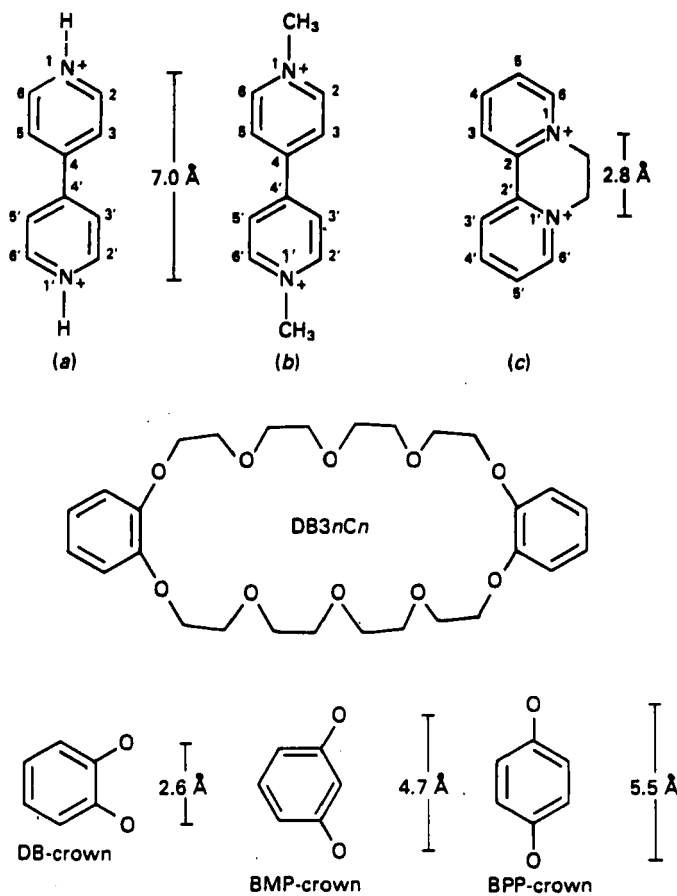


Figure 1 Chemical structures (top) of (a) 4,4'-dipyridinium, (b) paraquat, and (c) diquat, showing some dimensions, and structure (bottom) of dibenzo type 3n-crown-n crown ethers, showing the positions of the benzene O,O-disubstitution in dibenzo (DB), bis-metaphenylene (BMP) and bis-paraphenylene (BPP) crown ether derivatives (from Reference 33).

T4CIPB gave good electrodes,³⁴ and the PF_6 ones were not selective, leaving just the TPB and T4CIPB systems as suitable for exploitation. In this respect, electrodes based entirely on DQT.2TPB or PQT.2TPB had already been found²⁴ to give excellent ISEs with appropriate solvent mediators.

The calibration response of a DQT.2T4CIPB based ISE for DQT during an appraisal study³⁵ was found to be stable for 55 days with a near-Nernstian slope and detection limit in the μM range. The electrode was of fast response (3 s at 1 mM and 25 s at $1 \mu\text{M}$) and was usable at pH 2 to 12 over a sample temperature range of 2 to 50°C . Samples could be determined by the standard addition method with about a -5% error and a precision of 7 to 8%. For comparison, DQT was also determined by titration with sodium tetraphenylborate using DQT.2TPB and TBA.TPB ISEs as sensors. Here, the errors were 12 to 20% for DQT analysis in deionized water, sodium chloride solution or simulated serum.³⁵

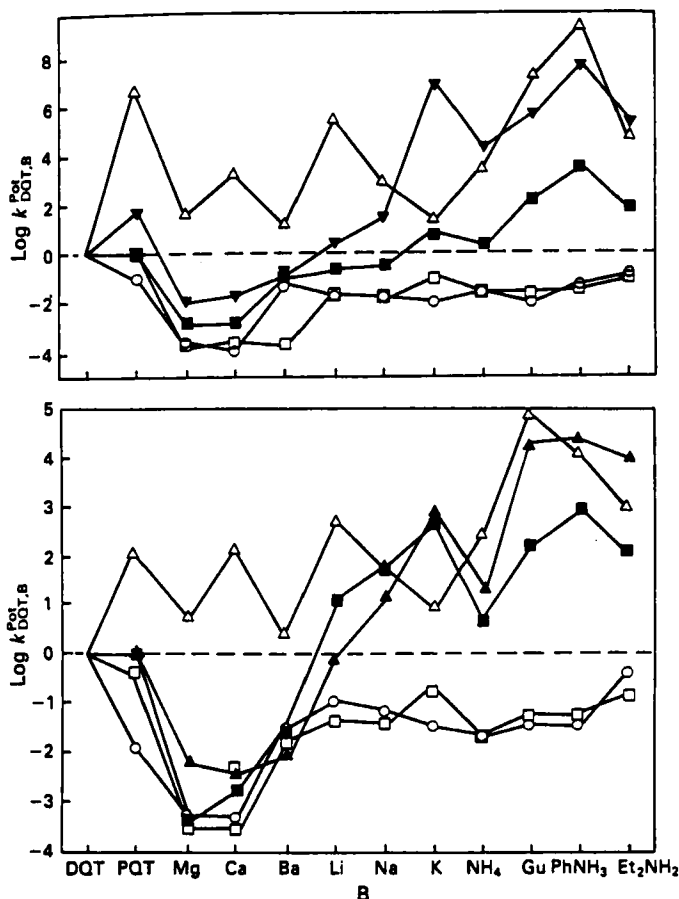


Figure 2 Effect (top) of plasticising solvent mediator on selectivity of diquat ISEs based on DB30C10 plus DQT.2TPB. Key: ○, NPOE; □, NPPE; △, DOPP; ▲, DNP; and ■, DBP. Effect (bottom) of plasticising solvent mediator on selectivity of diquat ISEs based on DQT.2TPB without crown ether. Key: ○, NPOE; □, NPPE; △, DOPP; ▲, DNP; and ■, DBP. Lines joining points connect the various solvent mediator types (from Reference 34).

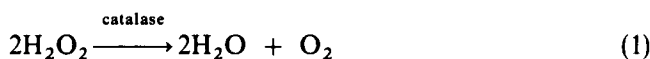
CATALYTIC MEMBRANES FOR THE ELECTROCHEMICAL ANALYSIS OF HYDROGEN PEROXIDE

Although hydrogen peroxide is essentially an industrial material, it is highly important in the environmental sense, being used for waste water treatment, sterilization, and as a source of oxygen. The methods of analysis generally used are titrimetric,³⁶ colorimetric,^{37,38} and chemiluminescent.³⁷ Such methods can suffer various interferences, and can also be time-consuming, with many requiring expensive reagents.

Electrochemical methods offer alternative approaches to analysing hydrogen peroxide, for example, an amperometric oxidative method with a platinum electrode has been used for determining hydrogen peroxide products of enzyme

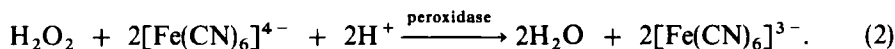
reactions.³⁹ This has been adapted for the flow injection analysis (FIA) at a platinum electrode of enzymically produced hydrogen peroxide.⁴⁰ Such an electrode is normally set at +600 mV *versus* a silver/silver chloride reference electrode, but at such high potentials other electroactive species, e.g., ascorbic acid may also be oxidised. This is a problem with biological and food-based samples unless there is appropriate sample pre-treatment.

In order to overcome interferences, other analytical procedures have been suggested, e.g., a carbon electrode sputtered with platinum and gold^{41,42} permits anodic oxidations at lower potentials. Certain interferences can also be overcome by catalytical decomposition of hydrogen peroxide. Thus, metal oxide membranes^{43,44} and catalase immobilized onto collagen gel,⁴⁵ and cellulose acetate⁴⁶ or catalase-rich bovine liver slices⁴⁷ have been employed. The catalyzed decomposition approach through the agency of appropriate membrane based catalysts has been further studied in the author's laboratories. For example, the membrane systems employed include the immobilization of catalase on nylon net by the agency of glutaraldehyde.⁴⁸ This is placed over a Teflon membrane of an oxygen electrode.⁴⁸ Such an arrangement can be used in a dip mode⁴⁸ for analyzing hydrogen peroxide, measured electrochemically by the increasing oxygen produced as a result of its enzyme catalyzed decomposition:



This system, used with a Yellow Springs Instruments type 5739 oxygen electrode is appropriate for the analysis of hydrogen peroxide in waste streams under alkaline conditions,⁴⁸ and can be calibrated between $<10^{-5}$ and $>10^{-3}$ M hydrogen peroxide.⁴⁸

An alternative catalytic membrane approach for avoiding interferences in the electrochemical determination of hydrogen peroxide is the immobilization of peroxidase over the platinum tip of a modified Stelte cell, as has been used in the bienzyme electrode determination of glucose and hypoxanthine.⁴⁹ This is a low potential approach to the analysis of hydrogen peroxide by the agency of a soluble mediator, e.g., hexacyanoferrate(II):



The hexacyanoferrate(III) generated is then reduced at the platinum electrode at -100 mV *versus* a silver/silver chloride reference electrode:



A typical recorder output for hydrogen peroxide detection by the peroxidase electrode in the FIA mode is shown in Figure 3.

Neither the catalase nor the peroxidase electrode systems suffer interference from many components in conditions where hydrogen peroxide is employed, nor in waste water type samples.⁴⁸ Hypochlorite, sulphide and cyanide are natural

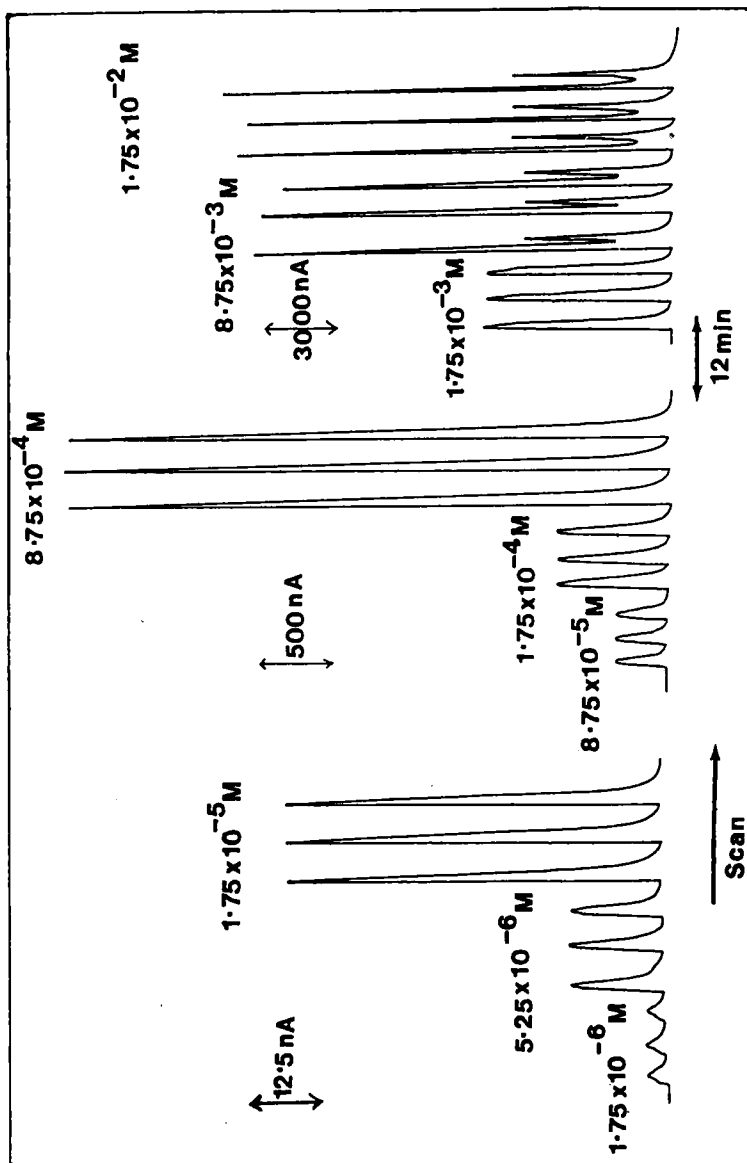


Figure 3 A typical chart recorder output for the FIA detection of hydrogen peroxide by a peroxidase electrode (from Reference 48).

interferents by being oxidized by hydrogen peroxide. Sulphite, thiocyanate and formaldehyde show slight enzyme interference.⁴⁸

The electrodes were tested on food type samples, and where hydrogen peroxide is employed, and found to be effective.⁴⁸

CONCLUSION

Membrane type systems have a potentially important role in environmental analysis. Thus, studies have illustrated that they can be used as primary sensors as in piezoelectric crystal detection of gases and vapours, or as sensing membranes in potentiometric ion sensing, or as modifying intermediates for producing species that can be sensed by alternative approaches and illustrated here for catalytic enzyme membranes for decomposing hydrogen peroxide to provide species that can be electrochemically sensed. In each case, the systems can be set up for FIA which is a convenient means of screening large numbers of samples as is frequently required in environmental analysis.

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