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ELECTROCHEMICAL ANALYSIS OF ORGANIC POLLUTANTS

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Electrochemical analysis of organic pollutants

Abstract - The electroanalytical techniques of pulse polarography,
stripping voltammetry and on-line electrochemical detection have been
used for the identification and determination of trace concentrations of
a wide variety of environmentally significant organic molecules, usually
after the application of sample pretreatment procedures, certain
separation techniques and, in some cases, derivatisation. Classes of
molecules that can be determined using these methodologies are carbonyls,
simple aromatics such as nitroaromatics, phenols, polychlorinated
aromatics, carboxylic acids, sulphonates, organophosphorus compounds,
azomethines, thiols, carbamates and amines.

INTRODUCTION

Modern electroanalytical techniques for the identification and determination of trace
concentrations of organic molecules in matrices of environmental significance can be divided
into three classifications of technique (a) pulse polarography, (b) stripping voltammetry
and (c) on-line electrochemical detection generally following high performance liquid
chromatography.

(a) Pulse polarography

Pulse polarography is that variant of the classical polarographic technique invented by
Heyrovsky (refs. 1, 2) that has found most routine acceptance in modern laboratories and
seeks to improve sensitivity by minimising the contribution from the capacitive current due
to the double layer charging of the indicator electrode i.e. the dropping mercury electrode.
Pulse polarography was invented by Barker and co-workers at Harwell in the late 1950's
(ref. 3) and utilises the differing time dependences of faradic and charging currents. The
pulse method imposes a series of pulses of increasing amplitude to successive mercury drops
at a preselected time near the end of each drop lifetime. The initially high charging
current decays away very rapidly and the residual faradic current is sampled during the
final part of the 50-60 ms time pulse. While pulse polarography gives a marked improvement
in sensitivity of approximately two orders of magnitude over the classical technique, it
still gives a similar sigmoidal current-voltage response. A more useful variant for trace
analytical purposes is differential pulse polarography. In this mode, small amplitude (10-
100 mv) pulses of approximately 60 ms duration, superimposed on a conventional linear ramp
voltage, are applied to the dropping mercury indicator electrode near to the end of the
drop's lifetime. The current output is sampled at two time intervals; immediately on the
ramp prior to the imposition of the pulse and then again at the end of the pulse when the
capacitive current has decayed. It is the difference in these two currents that is
displayed on the resulting current-voltage response. As the greatest increase in current for
a given voltage increment will occur at the half-wave potential of the electroactive molecule
then the current-voltage response in differential pulse polarography will have a peak shape.
Because of the favourable signal-to-noise ratio of this polarographic technique, it is
slightly more sensitive than pulse polarography and can determine electroactive molecules
down to concentrations of ca 10^{-7} mol 1^{-1}. The theory of classical and modern polarographic
techniques is adequately dealt with by Bond (ref. 4) and those functional groups in relevant
organic molecules that are electroactive through principally reduction processes at the
dropping mercury electrode are listed in Table I.

(b) Stripping voltammetry

Stripping voltammetry is inherently one of the most sensitive electroanalytical techniques
and has received a great deal of attention in recent years, primarily for environmental
monitoring of very low concentrations ($<10^{-7}$ mol 1^{-1}) of heavy metal ions such as Pb(II),
Cd(II), Cu(II), Zn(II) etc. It is extremely simple in concept, the method consisting of a
two-stage process. The first is a preconcentration step of controlled electrolytic
deposition of the species of interest onto a stationary indicator electrode, usually in a
stirred solution for a time period of several minutes. Mathematical treatment has shown
that the mercury film electrode is capable of more sensitive measurements than the hanging
mercury drop electrode, particularly at concentrations of less than 10^{-7} mol 1^{-1}. This pre-
concentration step is followed by the measurement step which consists of electrolytically
stripping the deposited species back into solution using either a linear or differential
pulse voltage sweep. The latter technique offers a more effective discrimination against
the background charging current and hence offers an increased sensitivity (ref. 5). The

TABLE 1. Electroreducible bonds/groupings

Electroreducible bond/grouping	Reduction mechanism	Comments and examples
(a) Carbon–Carbon Bond		
(i) Double bond	$2e^-$ process resulting in saturation of bond	Occurs at high negative potentials and can give analytically usable waves in tetraalkylammonium supporting electrolytes dissolved in organic solvents. The reduction potential is made less negative if the bond contains electron-withdrawing groups or the degree of conjugation is increased by the presence of say a keto group.
(ii) Triple bond	Reducible if conjugated to an aromatic ring	
(b) Carbon–Halogen Bond	Carbon–halogen bond is cleaved	In general, polyhalogenated compounds give rise to well defined waves/peaks, e.g. hexachlorophane can be determined with a sensitivity of 5×10^{-7} mol l^{-1} (100ng ml^{-1}).
(c) Carbon–Oxygen Bond	$2e^-$ process generally for aldehydes and ketones	Conjugated carbonyl compounds, e.g. quinones and benzophenones reduce at less negative and more analytically usable potentials than non-conjugated ones (e.g. formaldehyde and acetaldehyde). Sugars such as ketoses and aldoses are reduced in kinetically controlled processes at relatively negative potentials and give ill defined peaks on application of differential pulse polarography.
(d) Carbon–Nitrogen Bond		
(i) Single bond	Reductive splitting occurs in quaternary phenyl and alkyl ammonium salts	Reduction occurs at high negative potentials.
(ii) Double bond	$2e^-$ process resulting in saturation of bond	Well defined waves/peaks produced when group is conjugated to aromatic nucleii.
(e) Nitrogen–Nitrogen Bond		
(i) Single bond	Reductive cleavage of bond consuming $2e^-$	
(ii) Double bond	Saturation of bond, in some cases followed by cleavage to form a mixture of amines	The latter process occurs when the group is conjugated to an aromatic one possessing activating substituents, e.g. 4-hydroxyazobenzene.
(f) Nitrogen–Oxygen Bond	Reduction process is dependent on oxidation of nitrogen atom	Aromatic nitro compounds can reduce in $2e^-$, $4e^-$, or $6e^-$ steps depending on the substituents whereas aliphatic counterparts are reduced in $4e^-$ steps to the hydroxylamine. Waves/peaks for the aromatic molecules are well defined. Aliphatic nitroso-containing molecules generally produce ill defined waves/peaks whereas aromatic nitroso ones have been observed to give well defined peaks on application of differential pulse polarography at less negative potentials. Aliphatic N-oxides are reduced at relatively negative potentials. Hydroxylamines are only reduced in the protonated state and generally give ill defined peaks on application of differential pulse polarography. Aryl hydroxylamines have been reported to give well defined waves in alkaline media. Some aliphatic oximes give relatively small reduction peaks on application of differential pulse polarography.
(g) Carbon–Sulphur Bond		
(i) Double bond	Can be reduced in $2e^-$ step	
(h) Sulphur Oxides	Mechanism dependent on oxidation state of sulphur atom	Aromatic S-Oxides give well defined $2e^-$ peaks.
(i) Sulphur–Sulphur Bond	$2e^-$ process resulting in breakage of bond	

technique of cathodic stripping voltammetry refers to electrolytic preconcentration at anodic potentials and electrolytic stripping by imposition of a cathodic voltage scan. It has been primarily used in organic electroanalysis for the trace determination of those molecules which can form insoluble and adsorbable mercury derivatives by electrolysis at anodic potentials such as dithiocarbamate pesticides (refs. 6, 7) and organo-sulphur drugs (ref. 8).

In recent years, an increasing interest has been detected in the literature concerning stripping measurements of organic substances that cannot be preconcentrated by electrolysis. In particular, adsorptive stripping voltammetry refers to an electroanalytical technique in which the analyte is preconcentrated by adsorption onto the indicator electrode followed by voltammetric determination of the concentrated surface molecules. This has resulted in electroanalytical determination of a selection of surface active molecules at concentrations of the order of 10^{-9} mol 1^{-1} e.g. thiourea (ref. 9), nitro- and triazine-containing pesticides (ref. 10) and trichlorobiphenyl (ref. 11).

(c) Electrochemical detection (e.d.) following high performance liquid chromatography

With the aforementioned recent advances in the development of pulse polarographic and stripping voltammetric techniques, analytical methods utilising these electroanalytical "end-steps" now possess a similar, and in some cases better, sensitivity for organic molecules as compared with rival analytical methods employing gas chromatography or spectrofluorimetry. In terms of selectivity, these electroanalytical methods operating in quiescent solution often show a better resolution for structurally related compounds than ultraviolet spectroscopy, but this is rarely sufficient in environmental trace analysis, where there are many naturally occurring molecules and metabolites that can interfer at the concentration levels at which it is required to operate i.e. at concentrations in the range 10^{-7} - 10^{-10} mol 1^{-1} (i.e. nanogram to picogram per ml concentrations). In modern organic trace electroanalysis, therefore, it has been found necessary to incorporate some form of chromatography such as reverse phase high performance liquid chromatography to achieve necessary separations prior to selective voltammetric detection of the eluate. This selectivity is rarely found with stripping techniques which do have the required sensitivity (i.e. 10^{-7} - 10^{-10} mol 1^{-1}) for a limited number of electroactive molecules. The most widely used voltammetric detection systems employed in liquid chromatography are those based on direct current hydrodynamic chronoamperometry where the current arising from the oxidation or reduction of a molecule of interest is measured as a function of time at a fixed electrode whose potential is held constant in the flowing stream of aqueous eluent from the column. Most of the electrochemical cells designed for link-up with high performance liquid chromatography use glassy carbon as the indicator electrode material e.g. "thin layer" and "wall-jet" designs give good sensitivity for molecules which are oxidised in the potential region +0.1 → +1.2V (vs Ag/AgCl). At higher positive potentials, difficulties are encountered due to the high background signal produced by the eluent/ supporting electrolyte. On the reductive side, there have been numerous attempts to develop electrochemical cells for high performance liquid chromatography based on dropping or stationary mercury electrodes and, although much has been achieved to counteract the problems of incorporating mercury electrodes in flowing streams and to overcome the effects of oxygen reduction, the sensitivities for most reducible organic molecules are still inferior as compared to ultraviolet detection.

In those cases where the chromatographic system is unable to separate two compounds of related structure, a certain measure of selectivity in the electrochemical detector can be called into play. This has been well illustrated in the selective determination of the growth promoting hormones dienestrol and diethylstilbestrol (ref. 12) and the carbamate pesticides, barban and captafol (ref. 13). When the oxidation or reduction potentials of two compounds are just separated by the order of 50 - 100 mV, the use of direct current hydrodynamic electrochemical detection may not give the required selectivity and can be improved upon by the use of the differential pulse mode of operation. In some cases, the use of the differential pulse mode may also give improved sensitivity, especially for molecules with high potentials of oxidation or reduction eg., organometallic cations (ref. 14).

In recent years, a major advance in such electrochemical detectors has been the introduction of dual-electrode detection systems (ref. 15) which have been demonstrated to improve both the selectivity and sensitivity of certain determinations. Other advances have also come about through the application of pre- and post- column derivatisation reactions (ref. 16) and future development is seen in the field of scanning electrochemical detection systems to aid further in the identification of unknown peaks.

Table 2 lists those organic molecules that are electrochemically detected following high performance liquid chromatography and are subsequently discussed in the text.

It is the purpose of this paper to comment on the applicability of the aforementioned electroanalytical methods to selected organic molecules (and their metabolites) of environmental significance. Where possible, a critical comparison will be made between them and alternative analytical methods based primarily on chromatographic and spectroscopic techniques.

TABLE 2. Molecules amenable to high performance liquid chromatography - electrochemical detection

Compound	Column/indicator Electrode	Mobile phase	Detector Potential(V)	Notes	Ref.
		(i) Sulphur - containing compounds			
ethylene thiourea (ETU) N-methyl ETU thioimidazole thiohydantoin	Supelco LC-18/DME	0.1M KNO_3, pH 3.0	+0.2	ETU determined in rat urine- e.d. found comparable to u.v.d. for analysis of ETU and related sulphur compounds; e.d. used to confirm the presence of thioimidazole as a metabolite of ETU	17
dithianon	LiChrosorb RP-18/DME	dioxan: acetate buffer (16:9)	-0.05	dithianon determined in fruit down to 10 ng per g of fruit	18
		(ii) Nitrogen - containing compounds			
nitrobenzene	LiChrosorb RP-8/DME	monochloroacetate buffer	-0.70	polarographic detection found comparable to u.v.d.	49
N-nitrosoproline N-nitrosodiethan- olamine	Bondapak Phenyl/SMDE	1% phosphate buffer, pH 3.0	-0.97 (d.p. mode) -1.20 (n.p. and d.c. modes)	limit of detection about 1×10^{-7} mol 1^{-1}	50
2-chloroaniline 3-chloroaniline 4-chloroaniline	LiChrosorb RP-8/ GCE	water: methanol: acetonitrile (75: 20:5) containing 6g 1^{-1} NaH_2PO_4 and 2.5 ml 1^{-1} orthophosphoric acid (85%)	+1.20	simultaneous determination of the three isomers achieved limit of detection about 1 ng (approx 10^{-6} mol^{-1} on injection	62
4,4'-methylenebis (2-chloroaniline) (MOCA) 2-chloroaniline (OCA)	Hypersil ODS/GCE	methanol:phosphate buffer pH 7.5(6:4)	+0.90	MOCA and OCA determined simultaneously in factory air down to 20 and 10 pg respect- ively; detection limits superior to u.v.d.	63
3,4-dichloroani- line 2-chloroaniline 3-chloroaniline	Zorbax ODS/CPE	0.15M phosphate buffer pH 2.1: acetonitrile (6:4)	+1.10	80% recovery of halogenated anilines from urine; limit of detection below 5×10^{-8} mol 1^{-1} (5ng ml^{-1})	64
1-naphthylamine 2-naphthylamine	Dupont SCX/CPE	acetate-citrate buffer pH 5.2	+0.80	limit of detection in the 1-2 pmol range	65
benzidine 3,3'-dichloro- benzidine	RP-2/carbon black/ polyethylene tubular electrode	acetonitrile:0.01M $NaClO_4$ 0.01M acetic acid, pH5 (45:55)	+0.70	compounds determined in waste water at levels 5.10^{-9} mol 1^{-1} (1ng ml^{-1}); sensitivity 50x better than u.v.d.	66
benzidine	Bondapak C-18/CPE	methanol: water (25:75); 0.01M ammonium acetate, pH 6.2	+0.45	benzidine determined in urine in presence of acetylated metabolites	67

TABLE 2.   continued:

Compound	Column/indicator Electrode	Mobile phase	Detector potential(V)	Notes	Ref.
		(iii) Oxygen-containing compounds			
estrogenic and pseudo-estrogenic hormones e.g. estrone, diethyl-stibestrol	Zorbax CN/GCE	Acetonitrile:water (gradient from 30:70 to 42:58), 0.05M in LiClO$_4$	+1.20	9 estrogenic and pseudo-estrogenic hormones simult-aneously determined in meat at pg g^{-1} level.	26
cis- and trans-zearalenone	LiChrosorb RP-8/GCE	acetonitrile: water (45:55); 0.05M in LiClO$_4$	+1.20	isomers of this mycotoxin simultaneously determined in cereal products down to 5ng per g of product	28
Phenol resorcinol	C-18 Kel F-graphite composite electrode	0.05M NaH$_2$PO$_4$: acetonitrile (65:35)	+1.27	phenolic compounds determined in ground water/coal gasifer waste water down to 10^{-8} mol l^{-1}	30
chlorinated phenols	Aminex 50W-X4/ carbon black/polyeth-ylene tubular electrode	acetonitrile: 0.05N H$_2$SO$_4$ (3:7)	+1.20	method applicable to local surface drainage water, waste water and recycled brine waste; more sensitive than u.v.d.	31
2-phenylphenol	Bondapak C-18/CPE	acetate buffer/ ethanol (6:4)	+0.80	amperometric detection more sensitive and selective than u.v.d. for determination of 2- phenylphenol in orange rind	19
carbendazin aminocarb	Bondapak C-18/CPE	phosphate buffer pH6: acetonitrile: methanol (6:3:1)	+1.10	calibration curves rectilinear over 3 orders of magnitude; carbamate pesticides deter-mined down to 3.10^{-8} mol l^{-1} (40 pg/injection of 10µl)	59
barban benomyl propham	LiChrosorb RP-18/GCE	methanol: 0.02M NH$_4$H$_2$PO$_4$ pH3.0 (1:1)	+1.30, -1.37	amperometric detection has more selectivity than u.v.d.; u.v.d. more sensitive	20
Uric acid	Vydax anion exchange column/CPE	0.1M acetate buffer pH5.25	+0.80	uric acid determined in cereal products down to 2 ng per g of product.	21

DISCUSSION

Carbonyl compounds

Although the carbonyl group is electro-reducible, the little work that has been carried out on carbonyl compounds by direct polarographic methods has mainly been confined to aldehydes such as formaldehyde, acetaldehyde, butyraldehyde and furfural. Limits of detection in the 10^{-5} - 10^{-4} mol 1^{-1} region in waste water have been reported (ref. 22). The use of derivatization of the carbonyl group has been exploited by Afgan et al (ref. 23) in a systematic polarographic study of these compounds in various supporting electrolytes using twin cell potential sweep voltammetry. The formation of the semicarbazone was found to be most satisfactory. The formation of the semicarbazone is optimised at pH 4-6 and involves general acid catalysis. Excess of the electro-inactive semicarbazide is added to ensure complete reaction. Using a citrate buffer with EDTA added to complex interfering heavy metals, a limit of detection in the region of 10^{-9} mol 1^{-1} (0.25ng ml^{-1}) was claimed for the determination of some carbonyl compounds present in natural waters and industrial effluents without any separation or preconcentration of the samples. The method was, however, unable to differentiate many aliphatic and aromatic aldehydes and ketones. The peak potentials of representative aldehydes and ketones and their semicarbazone derivatives are given in reference 23. A recent paper (ref. 24) has improved upon the selectivity of this method by the use of reversed-phase high performance liquid chromatography and detection by ultraviolet spectroscopy at 360nm. These authors have achieved resolution and identification of the 2, 4- dinitrophenylhydrazone derivatives of a range of aldehydes and ketones. The combination of photoelectrochemical detection with high performance liquid chromatography has recently been investigated by La Course et al (ref. 25) for the determination of carbonyl compounds. A flow-through, thin layer amperometric cell was modified to irradiate the working electrode surface and so take advantage of new and/or altered electrochemical properties of photogenerated excited states, intermediates or products. The technique has been found responsive to alkyl and aryl aldehydes and ketones i.e. to compounds that undergo n-Π* excitation as opposed to Π-Π* excitation. Detection limits are 2-10ng, comparable to u.v. detection.

Simple aromatic compounds

(i) Nitro compounds. Direct polarographic methods for nitrocompounds in waste water and effluents have been developed. For example, nitrobenzene in industrial wastes has been determined by distillation after separating nitrophenols. The supporting electrolyte consisted of aqueous ethanol containing hydrochloric acid. Nitrochlorobenzenes in water down to 5.10^{-8} mol 1^{-1} (5ng ml^{-1}) have been determined following extraction with activated charcoal and polarography of the eluted acetone solution in a pyridinium hydrochloride supporting electrolyte. These and other relevant publications are collected in reference 22.

(ii) Phenolic compounds. Prior to the development of electrochemical detection in conjunction with high performance liquid chromatography most polarographic methods for the determination of phenolic compounds were based on prior derivatisation procedures eg. phenol in water (ref. 22) has been determined following nitration using pulse polarography with a quoted limit of detection of 10^{-8} mol 1^{-1} (1ng ml^{-1}). Phenols exhibit anodic waves at a variety of solid electrodes at relatively positive potentials (+1.2V → +1.3V) and this can be applied to the analysis of nine estrogenic and pseudo-estrogenic hormones in animal meat (ref. 26) where the use of electrochemical detection permitted the simultaneous determination of eight of these compounds down to pg quantities per g of meat. In addition, this technique was shown to exhibit much less interference from natural constituents in the meat and could selectively determine diethylstilbestrol in the presence of either dienestrol or hexestrol (refs. 12, 26). An alternative procedure has also been described for the determination of diethylstilbestrol in animal tissue using a carbon paste instead of a glassy carbon indicator electrode (ref. 27). In addition, a method has been developed for the determination of the cis- and trans-forms of the phenolic-containing mycotoxin zearalenone in cereal products (ref. 28).

The determination of individual phenols in water is of great environmental importance, and a recent E.E.C. publication (ref. 29) highlights many of the analytical methods currently being investigated for this purpose. The application of high performance liquid chromatography with electrochemical detection for the determination of phenols in ground and waste waters has been reported by several authors (ref. 30-32) and the limits of detection for compounds such as resorcinol, phenol, xylenols and chlorinated phenols quoted to be in the 10^{-8} - 10^{-9} mol 1^{-1} range. The sensitivity is thus much better than corresponding methods employing ultraviolet detection (phenols generally have low extinction coefficients), and should provide a complimentary method to capillary gas chromatography, which is recognised as the forerunner in this area of analysis (ref. 33). Electrochemical detection has also been described for the determination of chlorophenols in urine (ref. 34) and 2-phenyl-phenol in orange rind (ref. 31).

Water/ethanol extracts from plant material are used extensively to analyse a wide range of secondary plant metabolites. These extracts can be used as such or some subfraction can be prepared for analysis with a suitable technique such as high performance liquid chromatography. Such plant extracts are very complex and the chromatograms contain numerous peaks with appreciable peak overlap. Nagels et al (ref. 35) have found single electrode electrochemical detection two to five times more selective than u.v. detection and that dual electrode parallel electrochemical detection can reduce detection limits by a factor up to five for phenolics with high oxidation potentials. Kafil et al (ref. 36) have used a scanning coulostatic electrochemical detector to separate, help identify and determine a mixture of ten phenolic acids at the sub nmol level.

(iii) Polychlorinated compounds. Organochlorine pesticides in aquatic matrices are usually determinated by glass capillary gas chromatography where the electron capture and coulometric detectors offer sensitivity and selectivity not usually obtained by other methods involving spectrophotometry or polarography/voltammetry e.g. Babkina et al (ref. 37) have determined a range of organochlorine pesticides (including dichlorvos, pp^1-DDT, α- and γ-BHC) at concentrations in water samples below 10^{-12} mol l^{-1} (range 5-60 pg l^{-1}). Recently, Farwell (ref. 38) has reported on the use of interrupted sweep voltammetric analysis for the identification of polychlorinated insecticides and other polychlorinated aromatics. The apparatus consisted of a 3-electrode potentiostatically-controlled circuit with a logic-controlled interrupted linear voltage sweep mechanism. Using dimethylsulphoxide/0.1M tetraethylammonium bromide as the supporting electrolyte, voltammograms for many poly-chlorinated aromatics have been obtained. However, at least 9 mg of pure compound are required for positive identification. The technique is therefore of little value in residue analysis but could find more application in the identification of isomeric products formed during the synthesis of polychlorinated agrochemicals. The peak with the most negative potential corresponds to naphthalene and the remaining reduction peaks represent the step-wise removal of Cl atoms.

Carboxylic acids

Materials of the amino polycarboxylic acid type can be determined polarographically, by observing the reduction of a heavy metal-ligand complex, in the presence of excess of metal ion. The reduction potential of this complex occurs at more negative values, and the limiting current of this reduction is used for the quantitative determination of the ligand. Haberman (ref. 39) has demonstrated how nitrilotriacetic acid (NTA), which is a detergent builder with the formula $N(CH_2COOH)_3$, could be determined using In(III). After an excess of In(III) had been added to the NTA in the aqueous solution, the free metal gave a polarographic wave and the limiting current of the complexed In(III) could be found by difference. Studies on metal-NTA complexes have shown that the optimum pH for trivalent metal ion complexation is pH 2 and for divalent metal ions such as Cd(II) and Pb(II), pH 7. Using an anion exchange column to concentrate NTA, Haberman (ref. 39) was able to determine 2.5×10^{-7} mol l^{-1} (25ng ml^{-1}) when In(III) was used as the complexing metal. Afghan et al (ref. 40) has improved the limit of detection of this method to 10^{-7} mol l^{-1} (10ng ml^{-1}) using a Bi complex and has automated the procedure (15 samples h^{-1}).

Alkyl sulphonates and alkyl benzene sulphonates

Polarographic methods such as depression of maxima methods and tensammetry have been developed for anionic, cationic and neutral sufactants (ref. 22) but, in general, they are not specific to surfactant type and an effective separation is a prerequisite to determination in real situations. Ion exchange is the most generally used surfactant separation method, either anionic or cationic type being separated from nonionic by suitable choice of resin. Hart et al (ref. 41) have determined the linear alkyl benzene sulphonate content of sewage and tap water samples by an indirect polarographic method based on nitration of the aromatic ring. The method was proved reliable when concentrations were of the order 2.5×10^{-6} mol l^{-1} (0.5 μg ml^{-1}) or greater and it was found more selective than the colorimetric methylene blue method which gives a measure of total anionic surfactant present in the sample. Reversed-phase high performance liquid chromatography with fluorimetric detection at 295 nm has been used for the resolution and quantitiative determination of sodium alkylbenzenesulphonates (ref. 42). Concentrations down to 5.10^{-7} mol l^{-1} (0.1 μg ml^{-1}) in river water samples could be determined.

Organophosphorus compounds

Gas chromatography with flame photometric or thermionic detection is commonly employed for the determination of organophosphorus compounds in samples of enviromental significance. However, "cold" methods such as high performance liquid chromatography, polarography/ voltammetry are increasingly being investigated as alternative methods due to the instability of these insecticides under the conditions employed in gas chromatographic analysis.

(i) Determination of $\overset{}{\underset{S}{>}P\overset{\diagdown}{\diagdown}}$ and $>P_\checkmark$ - S - containing compounds. Nangniot (ref. 43) has studied the polarographic behaviour of a wide range of organophosphorus pesticides. Although phosphoric acid esters cannot be reduced at the dropping mercury electrode, compounds containing the above functional groups can produce sharp adsorption peaks using

a fast linear sweep voltammetric technique, (250 mV s^{-1}). This can determine concentrations of selected organophosphorus compounds at the 10^{-6} mol l^{-1} level. Cathodic stripping voltammetry, following alkaline hydrolysis of these thiophosphates to release sulphur-containing molecules such as $(RO)_2 - P \lessgtr \frac{S}{O}$ capable of forming insoluble mercury salts, has been applied to the determination of the insecticides, phthalophos and benzophosphate in apples with a detection limit of 0.2 µg per kg of apple sample (ref. 22).

(ii) Determination of NO$_2$-containing organophosphorus compounds. The application of a reductive electrochemical detector for the determination of some nitro-containing pesticides was first demonstrated by Koen and Huber (ref. 44). who were able to selectively determine parathion and methylparathion in lettuce following a liquid chromatographic separation. Since then several other papers have been published dealing with the determination of nitro-containing thiophosphate pesticides using liquid chromatography with polarographic detection (ref. 45-48). In the case of nitro-containing compounds, it has been demonstrated that the sensitivity of high performance liquid chromatographic methods employing a polarographic detector is comparable to such methods employing ultraviolet detection (ref. 49). Such reductive electrochemical detection can also be used for nitroso-containing species (which are reduced at potentials more negative than nitro-containing compounds), where the limit of detection of the method (ca 10^{-7} mol l^{-1}) is similar regardless of whether the analysis is carried out in quiescent solution or in a flowing stream (ref. 50). Improvement in sensitivity may come about with the use of thin film mercury electrodes or gold amalgamated mercury electrodes, as demonstrated in a recent publication (ref. 14). Smyth and Osteryoung (ref. 51) have made a detailed pulse polarographic study of parathion, methyl parathion, paraoxon and other structurally related organophosphorus agrochemicals and their metabolites but were unable to use the differences observed in their behaviour for quantitative purposes. Structurally related nitrophenyl esters should therefore be separated by a chromatographic procedure prior to analysis. More recently, Clark et al (ref. 52) have used high performance liquid chromatography with series u.v. and electrochemical detection at -0.85V (vs Ag/AgCl) for the determination of ethyl- and methyl-parathion residues in vegetable material and surface water samples. Sample preparation techniques were developed which avoided usual preliminary column fractionations and which allowed the parathions to be recovered with an average of 95% at concentrations less than 50 ng g^{-1} for plant material. Concentrations less than 0.7 x 10^{-7} mol l^{-1} (10ng ml^{-1}) were readily measured in water samples using a column concentration procedure. The selectivity of electrochemical detection made it unnecessary to chromatographically resolve the electroactive plant components from the pesticides and allowed rapid analysis. Series detection proved useful in distinguishing various components in the samples from pesticides, in distinguishing various pesticides and in comparing the characteristics of the two detectors. The pesticides, alachlor, atrazine, carbaryl, carbofuran, chloropyrifos, diazinon dyfonate and lannate did not give electrochemical detection under the conditions of the experiment.

(iii) Enzymopolarographic determination. Davidek and Seifert (cited in ref. 22) have developed an enzymopolarographic method for the determination of the organophosphorus pesticide intration. The method was based on the inhibition of anticholinesterase activity by the organophosphorus moiety (a reaction which parallels the in vivo biological activity of these compounds). Unreacted enzyme is then incubated with β-naphthyl acetate and the β-naphthol measured by polarography following nitrosation. The method was applied to the analysis of intration in lettuce, cabbage, cherries and tomatoes. Naturally occurring enzymes which would be capable of hydrolysing β-naphthyl acetate were removed by precipitation with C$_2$H$_5$OH and subsequent centifugation. No interference was observed in the presence of carotenes, xanthophyll, chlorophyll or anthocyanidines and the method was found to be relatively simple and rapid to perform.

(iv) Determination by derivatisation. The herbicide glyphosate (N-phosphonomethylglycine) was found to be more conveniently analysed by polarography than by gas chromatography (ref. 53). For the latter method a lengthy four-stage clean-up and two-stage derivatization procedure was necessary, whereas ion exchange followed by nitrosation only was required for polarography. The eluate from ion exchange was treated with 50% sulphuric acid and potassium bromide and sodium nitrite solutions. After 15 min, ammonium sulphamate was added to destroy excess nitrite and polarography was carried out after de-aerating with nitrogen. The N-nitroso derivative gave a reduction peak at -0.78 V, which could be used to monitor concentrations in the range 2.6 x 10^{-7} - 1.6 x 10^{-6} mol l^{-1} i.e., 35-210 ng ml^{-1} of glyphosate, in natural waters. It was suggested that one analyst could analyse twenty samples a day, using the above procedure.

Compounds containing endocyclic and exocyclic C=N groups

The triazine pesticides, terbutryne, ametryne, and atrazine, which contain reducible endocyclic C = N bonds, have been determined (ref. 54) in pond and canal water down to 4 x 10^{-8} mol l^{-1} (5 ng ml^{-1}) following extraction with dichloromethane, evaporation of the solvent, dissolution of the residue in 50% methanol/0.005M sulphuric acid and polarographic

analysis. The polarographic method matched the gas chromatographic procedure in terms of time of analysis but was inferior with respect to selectivity and sensitivity. Smyth and Osteryoung (ref. 55) have investigated the polarographic behaviour of agrochemicals, cytrolane, cyolane, chlordimeform and drazoxolon, all of which contain exocyclic C = N groups, and recommended optimum conditions for their determination by pulse polarography.

Compounds containing —SH groups

Compounds containing sulphur in the - SH form are particularly amenable to cathodic stripping analysis due to their ability to form partially insoluble complexes with mercury. The application of this technique to the determination of some thiourea-containing agrochemicals has been investigated by Smyth and Osteryoung (ref. 56). Limits of detection at 10^{-7} - 10^{-8} mol 1^{-1} levels were found to be significantly lower than by polarographic methods based on anodic waves observed at the dropping mercury electrode.

Thiourea can also be determined polarographically following complexation with Cu(II) ions (ref. 22) or by liberation of the S atom and subsequent determination of H_2S (ref. 22). This latter procedure has also been used for the determination of other S-containing pesticides, e.g., diazinon, rogor and phenkapton and involved reduction of the pesticide by Al in HCl solutions in the presence of Ni. The H_2S evolved is then determined by monitoring the decrease of Pb(II) concentration in the $Pb(OAc)_2$ trapping solution. The method could determine down to 2 x 10^{-6} mol 1^{-1} (0.25 µg ml^{-1}) in pure solution. This has to be compared with a limit of detection of two orders of magnitude lower using gas chromatography-electron capture detection (for diazinon) (ref. 57).

Brand and Fleet (ref. 58) have investigated the application of cathodic stripping to the determination of the fungicide, tetramethylthiuram disulphide (thiram) in aqueous solutions. They reported that the best results were obtained using a mercury plated platinum electrode in a solution of thiram containing an excess of ascorbic acid. This addition had the effect of chemically reducing the disulphide moiety in thiram to form free - SH groups which were then amenable to cathodic stripping analysis. Using this method, they were able to determine thiram down to 10^{-8} mol 1^{-1} in pure solution.

Carbamates

The reduction of carbamates has been investigated by polarography after derivatisation via nitration or nitrosation (ref. 59) and recently, Anderson and Chesney (ref. 60) have applied their little investigated oxidation reactions to a reverse-phase liquid chromatographic method with thin layer Kel-F-graphite electrochemical detection operation in the constant potential amperometric mode at + 1.1V (vs. Ag/AgCl). Calibration curves were linear over at least three orders of magnitude with relative standard deviations of 1 - 2%. Detection limits in the range 40 - 150pg, which correspond to sample concentrations of the order of 10^{-8} mol 1^{-1} were obtained and the method compared favourably with gas chromatography with electron capture detection following hydrolysis to the corresponding phenols or amines and reaction with halogen rich reagents. The electrochemical detector, in this case, was found more sensitive than both the ultraviolet detector, operated at 190-210 nm, and the fluorimetric detector in which dansyl derivatives were formed prior to injection or post-column derivatisation carried out with o-phthalaldehyde.

Anderson et al (ref. 61) have further investigated the application of high performance liquid chromatography with electrochemical detection for the determination of trace concentrations of carbamates in river water by the use of microarray electrochemical flow detectors operating at high applied potentials. These Kelgraf microarray detectors effectively discriminate between oxidation reactions limited by the rate of mass transport and reactions (including solvent oxidation) limited by the rate of electron transfer or other surface processes and thus can afford improved detection limits at high applied potentials. Sub ng detection limits were obtained for the carbamates, aminocarb, carbendazim and desmedipham.

Halogenated anilines, other aromatic amines and benzidines

The oxidative voltammetric behaviour of aromatic amines in quiescent solution at carbon electrodes is often complicated as was exemplified in a recent study by Hart et al (ref. 62) on 2-, 3- and 4- chloroaniline. However, the use of carbon electrodes in the hydrodynamic chronoamperometric mode often improves the limit of detection for compounds that are easily oxidised (+0.2 → +1.0V) by several orders of magnitude when compared to methods involving reductive electrochemical detection with mercury electrodes. This is exemplified in the case of the chloroanilines where detection limits of the order of 10^{-8} mol 1^{-1} on injection have been quoted for the determination of 2-chloroaniline and 4,4' - methylenebis (2-chloroaniline) in factory atmospheres (ref. 63). A method has also been reported for the detection of chlorinated anilines in urine (ref. 64). In such cases, high performance liquid chromatography-oxidative electrochemical detection offer a great improvement in sensitivity (of up to 50 times) over similar methods employing ultraviolet detection. This is further exemplified in the analysis of aromatic amine carcinogens (refs. 65-74). In the analysis of benzidine, for instance, a variety of different columns (both reverse-phase and ion-exchange) and detection systems (employing carbon paste, carbon black/polyethylene or

reticulated vitreous carbon electrodes) have been used for its determination in waste water in the presence of 3, 3' -dichlorobenzidine (ref. 66), in the presence of its acetylated metabolites in urine (ref. 67), in various effluents (ref. 67), in soil (ref. 72) and in a 1000-fold excess of aniline (ref. 73). In all cases, the methods described were to determine benzidine and other aromatic amines at 10^{-8} mol l^{-1} concentrations on injection with good precision. Other aromatic amines that have been determined in this way include aniline (ref. 68), 1- and 2-naphthylamine (refs. 64-68), hydrazine and its monomethyl-, 1, 1-dimethyl- and 1, 2-dimethyl analogues (ref. 69), anthracene, 2-aminoanthracene and acridine (ref. 74). A further discussion on the use of this technique for the analysis of aromatic amines is given in a recent review (ref. 71).

Miscellaneous compounds

A method has recently been described for the determination of aromatic and aliphatic isocyanates based on a derivatisation reaction with the electrogenic reagent 1-(2-methoxyphenyl) piperazine (ref. 75). The resulting derivatives were all found to give an oxidation wave at +0.75V, and the chromatovoltammetric procedure thus developed was found to be 20 times more sensitive than the corresponding method employing ultraviolet detection. Electrochemical detection methods have also been described for the determination of phenoxy-acid herbicides (ref. 76), 2,4-diisocyanotoluene in air (ref. 77), pesticides in air (ref. 78), and nitro-substituted polynuclear hydrocarbons in diesel soot (ref. 79).

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