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OXIDATIVE DETECTION OF COULOMETRICALLY REDUCED ORGANONITRO PESTICIDES IN REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

RICHARD T. KRAUSE* and YI WANG*
Division of Contaminants Chemistry, Food and Drug Administration, Washington, DC 20204 (U.S.A.)

SUMMARY

A high-performance liquid chromatographic system is presented for determination of organonitro pesticides, metabolites and industrial chemicals having a variety of chemical structures. The compounds are chromatographed on a C_8 column with an acetonitrile–aqueous ammonium monochloroacetate gradient. The chromatographic responses of the compounds are monitored indirectly by oxidative detection of the coulometrically reduced organonitro functionality by means of a porous-graphite detector. Three nitrophenols (2,4-dinitrophenol, 4,6-dinitro-*o*-cresol and dinoseb), a dinitrophenyl aliphatic ester (binapacryl) and a nitroaniline (dicloran) were detected at low nanogram levels (3–10 ng for 50% recorder full-scale deflection). This technique overcomes the problems of high background currents and oxygen interference, observed in the direct reductive detection of organonitro compounds.

INTRODUCTION

The determination of analytes at residue levels in complex matrices requires a technique which separates the individual analytes and selectively detects the compounds of interest. Such multiresidue analytical approaches have been applied to the gas–liquid chromatographic (GLC) separation and selective detection of volatile organohalogen, organophosphorus and organonitrogen pesticides in food[1]. The electroconductivity detector in the halogen mode and the flame photometric detector in the phosphorus mode are highly selective for detection of organohalogen and organophosphorus pesticides, respectively. Volatile organonitrogen pesticides can be detected with the electroconductivity detector in the nitrogen mode. However, because of the large number of natural and man-made organonitrogen compounds, the practical selectivity is less than that desired. In addition, many toxic organonitrogen contaminants are not amenable to GLC since they are non-volatile and/or heat labile. This problem was solved for the N-methylcarbamate insecticides by using high-performance liquid chromatography (HPLC) to separate the heat-labile compounds; the N-

* Guest Scientist, The Institute of Plant Protection, Beijing, China.

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methylcarbamate moiety was selectively detected by a post-column fluorometric labeling technique[2-4].

The nitro functionality is contained in numerous pesticides, toxic metabolites, and industrial pollutants. A determinative technique was desired which could separate these organonitro compounds (nitrophenols, nitroanilines, nitrophorothioates, nitrodiphenyl ethers and nitrophenyl aliphatic esters) and selectively detect the nitro functionality at residue levels. A few organonitro pesticides and industrial chemicals can be determined by multiresidue methods (*e.g.* binapacryl[5,6], dicloran[1,5], parathion[5-7], dinoseb[6] and 4-nitrocresol[8]). However, the detection techniques (electron-capture, flame-photometric and thermionic detectors) do not selectively detect the nitro functionality, or the detector responds to another functionality in the compound. In addition, nitrophenols require derivatization[6,8] before determination by GLC. The nitrophenols have been chromatographed directly by HPLC, and the eluted compounds were monitored with a UV detector[9,10]. However, because of the multitude of UV-absorbing compounds, the UV detector does not have the selectivity needed for a residue determinative technique.

Organonitro compounds are electrochemically reducible and can therefore be detected by electrochemical detection (ED). Only a few other functionalities (azo, imine, N-oxide, quinone and nitrosamine) undergo electrochemical reduction[11]. Thus ED can provide a fair degree of selectivity for the nitro functionality. The purpose of the work reported here was to determine the feasibility of using HPLC to separate a variety of organonitro pesticides, toxic metabolites, and industrial chemicals, and of detecting the eluted analytes by ED.

EXPERIMENTAL

Chemicals

The organonitro compounds were obtained from the Environmental Protection Agency, Pesticide and Industrial Chemicals Repository (Research Triangle Park, NC, U.S.A.). All organonitro compounds were dissolved and dilutions were made in distilled-in-glass-grade methanol (Burdick & Jackson Labs., Muskegon, MI, U.S.A.). The acetonitrile was Burdick & Jackson distilled-in-glass UV grade. HPLC water was produced by a Milli-Q water system (Millipore, Bedford, MA, U.S.A.), consisting of prefilter, charcoal, ion-exchange and Organex cartridges. Monochloroacetic acid (MCA), Fisher Certified grade (Fisher Scientific, Fairlawn, NJ, U.S.A.), ammonium hydroxide (30%), Baker Analyzed Reagent grade (J.T. Baker, Phillipsburg, NJ, U.S.A.) and Milli-Q-purified water were used to prepare the aqueous 0.5 *M* MCA solution, adjusted to pH 2.70 with ammonium hydroxide.

Apparatus

Initial electrochemical data for the organonitro compounds were obtained with a Model CV-27 cyclic voltammograph (Bioanalytical Systems, West Lafayette, IN, U.S.A.). A glassy-carbon working electrode, palladium reference electrode, and platinum auxiliary electrode were used.

The mobile phase solutions of the HPLC systems were contained in Ultraware HPLC solvent reservoirs (Kontes, Vineland, NJ, U.S.A.) and degassed with helium (99.9955%), purified with in-line Hydro-Purge II and Oxy-Purge traps (Alltech As-

soc./Applied Science Labs., Deerfield, IL, U.S.A.). These solutions were delivered with a Model SP 8700XR pump (Spectra-Physics, San Jose, CA, U.S.A.). Injections were made into the column with a Spectra-Physics Model SP 8780XR autosampler, fitted with a 20-μl loop. The stainless-steel guard column (2 cm × 2 mm I.D.) was packed with 30- to 40-μm Perisorb RP pellicular packing material (Upchurch Scientific, Oak Harbor, WA, U.S.A.). The stainless-steel analytical column (25 cm × 4.6 mm I.D.) was packed with 6-μm spherical Zorbax C_8 packing material (DuPont, Wilmington, DE, U.S.A.). The guard and analytical columns were contained in a Model 2080 HPLC column oven (Varian, Palo Alto, CA, U.S.A.). The effluent from the column was passed through a Model 5020 guard ED cell (ESA, Bedford, MA, U.S.A.) with potential applied by an ESA Model 5100A Coulochem electrochemical controller. All chromatograms were recorded on a Spectra-Physics Model 4200 computing integrator. ESA filters containing 0.2-μm porous-graphite filter elements were placed in-line after the pump and immediately ahead of the guard cell.

HPLC operating parameters

The column oven was operated at 35°C. The mobile phase flow-rate was adjusted to 1.50 ± 0.02 ml/min with water–acetonitrile–aq. 0.5 *M* MCA (4:5:1) (aq. 0.5 *M* MCA, adjusted to pH 2.70 with ammonium hydroxide). The system was equilibrated at 20% acetonitrile (mobile phase components, 7:2:1) for 10 min before injection of the analyte solution. Immediately after injection, a 30-min linear gradient to 90% acetonitrile (mobile phase components, 0:9:1) was begun. The concentration of the aq. 0.5 *M* MCA solution in the mobile phase was kept constant at 10%.

The ED guard cell was set at −1.4 V to reduce the organonitro compounds. Detectors 1 and 2 of the analytical cell were set at −0.20 and +0.70 V, respectively. The multiplier gain switch was set to × 10, and the gain thumbpot switch was set to 10. The computing integrator was set at an attenuation of 8. The time constant was set at 0.4 s.

RESULTS AND DISCUSSION

A variety of organonitro pesticides, metabolites and industrial chemicals are listed in Table I. The electrochemical and liquid chromatographic characteristics of a number of these compounds were examined. The HPLC–ED investigations were conducted with nine organonitro compounds: binapacryl, bifenox, dicloran, dinoseb, 2,4-dinitrophenol, 4,6-dinitro-*o*-cresol (DNOC), 2-nitrophenol, oryzalin and parathion.

Electrochemical characteristics

Cyclic voltammetric data were collected to determine the effect of solution pH, electrolyte, organic solvent concentration and organonitro compound structure on the reduction and oxidation peak potentials. An acetonitrile–aq. 0.2 *M* electrolyte (1:1) solution was used, unless otherwise indicated, to simulate a mobile phase.

The pH of the electrolyte solution (measured before addition of organic solvent) greatly affects the reduction peak potentials of the organonitro compounds. As the pH was decreased from 12 (sodium hydroxide solution) to 2 (phosphoric acid solution), the reduction peak potentials became less negative by 150–400 mV and the

TABLE I

ORGANONITRO COMPOUNDS GROUPED BY STRUCTURE

Dinitroanilines
- Benefin
- Butralin
- Dinitramine
- Fluchloralin
- Isopropalin
- Nitralin
- Oryzalin*
- Pendimethalin
- Penoxalin
- Profluralin
- Trifluralin

Dinitroaromatics
- 2,4-Dinitrotoluene
- 2,6-Dinitrotoluene

Dinitrodiphenyl ethers
- Fluorodifen

Dinitrophenols
- 2,4-Dinitrophenol*
- Dinoseb*
- DNOC*

Dinitrophenylaliphatic esters
- Binapacryl*

Dinitro compounds, miscellaneous
- Dinocap
- Korax

Mononitroanilines
- Dicloran*

Mononitroaromatics
- Nitrobenzene
- Nitrotoluene
- Quintozene (PCNB)

Mononitrodiphenyl ethers
- Acifluorfen
- Bifenox*
- Nitrofen
- Oxyfluorfen

Mononitrophenols
- 2-Nitrophenol*
- 4-Nitrophenol

Mononitroorganophosphates
- O-Ethyl O-*p*-nitrophenyl benzenethiophosphonate (EPN)
- Fenitrothion
- Methyl parathion
- Paraoxon
- Parathion*

* Organonitro compounds used in HPLC–ED studies.

reduction peaks were better defined and showed greater detector response (peak height). Generally, a pH of less than 4 was required to obtain well-defined reduction peaks. Oxidation peak potentials of the reduction products of nitrophenols increased by 50–150 mV as the pH was decreased from 3.5 to 2.

Phosphoric acid and MCA were considered as potential acidic electrolytes because of their buffering capacity around pH 2–3.5. Both acids are good electrolytes; however, MCA is of advantage because its salts (formed on addition of base to adjust the pH) are more readily soluble in acetonitrile. To reduce problems with particulates and to minimize metal impurities, ammonium hydroxide was used to adjust the pH of the aqueous acidic solution before addition of the organic solvent. Cyclic voltammetric data showed that addition of sodium perchlorate to the MCA solution decreased the reduction peak potentials of the nitrophenols by 100–150 mV and increased the detector response by 10–20%.

The organic solvent concentration was found to affect the reduction peak potentials of the organonitro compounds. As the organic solvent concentration was

increased from 20 to 90%, the reduction peak potentials of the organonitro compounds became more negative by 100–300 mV. In the absence of a salt in the 90% acetonitrile–aq. acidic solution, the electrochemical reduction reaction was greatly reduced for bifenox, binapacryl and dicloran.

The location and number of nitro groups and other substituents on the phenyl ring affect reduction peak potentials, as shown by the cyclic voltammograms in Fig. 1. The 2,4- and 4,6-dinitro-substituted compounds (binapacryl, dinocap, dinoseb and 2,4-dinitrophenol) produced two well-defined reduction peaks. The first reduction peak occurs at *ca.* −0.9 V. The second reduction peak is at *ca.* −1.3 V for the dinitrophenols, and at −1.1 V for the two dinitrophenyl aliphatic esters, binapacryl and dinocap. The 2,6-dinitroaniline, oryzalin, did not produce two well-defined reduction peaks, but rather a reduction peak with a slight shoulder at a potential of −1.1 V. The mononitro-substituted compounds had reduction potentials ranging from −1.0 V for bifenox and parathion to −1.2 V for 4-nitrophenol. This range of reduction potentials could be used to advantage in providing added detection selectivity. Also, the data show that a large negative potential is required to monitor all organonitro compounds eluted from a chromatographic column.

Chromatographic characteristics

The organonitro compounds were initially chromatographed on a C_8 column by using an acetonitrile–water gradient. Table II shows the retention times of the

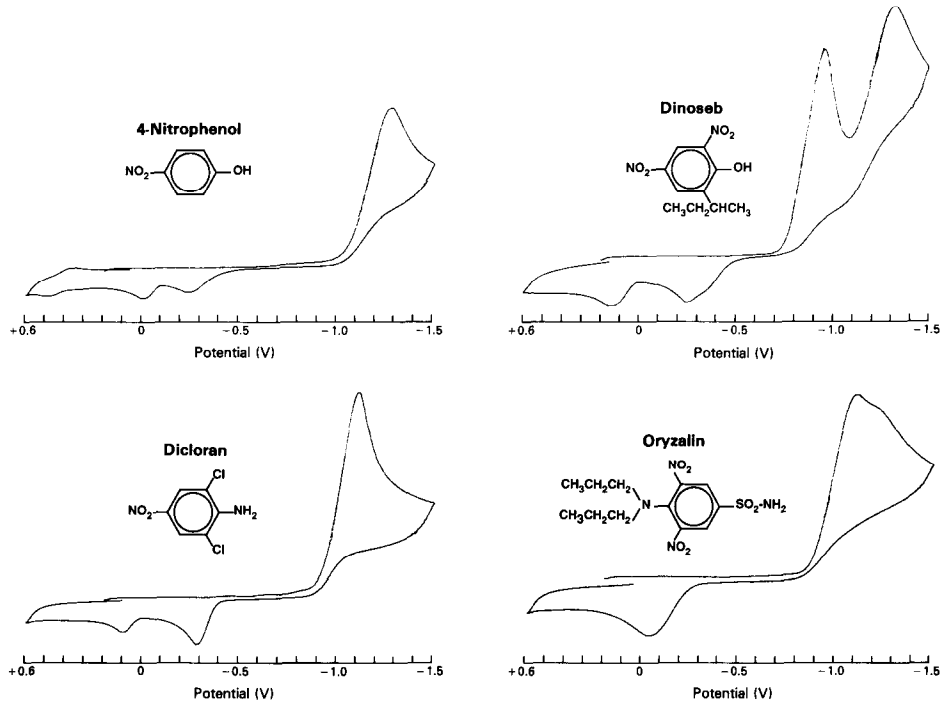

Fig. 1. Cyclic voltammograms of four organonitro compounds. Analyte concentration, 1 m*M*; scan range, +0.6 to −1.5 V; scan rate, 250 mV/s; working electrode, porous graphite; reference electrode, palladium; auxiliary electrode, platinum; electrolyte solution, acetonitrile–aq. 0.2 *M* MCA (pH 2.7, 1:1).

TABLE II

CHROMATOGRAPHIC CHARACTERISTICS OF ORGANONITRO COMPOUNDS ON A C_8 COLUMN WITH NEUTRAL AND ACIDIC MOBILE PHASES

Compound	*Mobile phases*			
	Acetonitrile–water		*Acetonitrile–aq. MCA*	
	Retention time (s)	*RRT**	*Retention time (s)*	*RRT**
2,4-Dinitrophenol	350	0.24	715	0.47
DNOC	598	0.41	971	0.64
4-Nitrophenol	678	0.46	615	0.41
2-Nitrophenol	814	0.56	782	0.52
Paraoxon	982	0.67		
Dicloran	1043	0.71	1039	0.68
Dinoseb	1043	0.72	1384	0.91
Methyl parathion	1214	0.83		
Oryzalin	1270	0.87	1289	0.85
Fenitrothion	1282	0.88		
Parathion	1383	0.95	1434	0.95
Bifenox	1462	1.00	1517	1.00
Nitrofen	1488	1.02		
EPN	1494	1.02		
Fluchloralin	1545	1.06		
Binapacryl	1549	1.06	1634	1.08
PCNB	1550	1.06		
Oxyfluorfen	1578	1.08	1657	1.09
Pendimethalin	1598	1.09		
Trifluralin	1636	1.12		
Benefin	1638	1.12		
Butralin	1646	1.13		
Isopropalin	1741	1.19		
Dinocap**	1746	1.19	1855	1.22
	1764	1.21	1876	1.24

* Retention time relative to bifenox.
** Dinocap contains two major isomers.

compounds (relative to bifenox). Sharp symmetrical peaks were obtained for all compounds except the nitrophenols, which produced broad peaks. Hsu *et al.*[12] and other authors have reported that an organic acid is necessary to diminish any interactions between phenols and residual silanol groups of silica-based reversed-phase packings, as well as to suppress dissociation of the phenols and thereby to improve chromatographic peak shape. In these studies, MCA was used as the organic acid. Its effect on the retention time of the nitrophenols and other organonitro compounds is shown in Table II. The use of MCA at pH 2.7 produced sharp symmetrical peaks for all organonitro compounds, including the nitrophenols. MCA appeared to have little, if any, effect on the relative retention times of the non-phenolic compounds. The relative retention times of 2-nitrophenol and 4-nitrophenol were slightly less with MCA in the mobile phase. However, for 2,4-dinitrophenol, dinoseb and DNOC the relative retention times were considerably longer with MCA in the mobile phase. The reten-

tion times of the phenols in the two mobile phases were found to be related to the pK_a values of the phenols. 2-Nitrophenol and 4-nitrophenol have pK_a values of *ca.* 7.2, whereas 2,4-dinitrophenol, dinoseb and DNOC have pK_a values of 4–4.5. In the acidic mobile phase (pH 2.7) ionization of all the phenols is suppressed, whereas in the acetonitrile–water (pH 6) mobile phase, ionization of the dinitro compounds is increased, resulting in shorter retention times.

HPLC–ED direct detection of nitro functionality

The determination of organonitro compounds by HPLC with direct reductive ED of the nitro functionality was determined to be infeasible. Extremely high background currents were produced at a potential of -1.0 V, which resulted in excessive baseline noise and a large change in the baseline during gradient elution. Also, oxygen in the non-degassed sample produced a large, off-scale, tailing peak, which obscured the responses of numerous organonitro compounds. Attempts to reduce the background current and eliminate oxygen from the sample during injection were unsuccessful.

HPLC–ED indirect detection of nitro functionality

Reduction of organonitro compounds results in formation of such products as anilines and hydroxyanilines. These products are electrochemically active and can be oxidized, as shown in Fig. 1 by the oxidation peaks in the cyclic voltammograms. Thus, it is possible to detect the nitro functionality indirectly.

Nitro polynuclear aromatic hydrocarbons (PAHs) have been reduced in post-column zinc[13] and platinum–rhodium[14] catalyst columns. The reduced nitro-PAHs were reported to be detected fluorometrically. The catalytic reduction of the various organonitro compounds reported here was investigated, using the platinum–rhodium catalyst reported by Tejada *et al.*[14]. Because the reduction takes place in the presence of methanol and not acetonitrile, a methanol–aq. MCA (pH 2.7) mobile phase was used. The ESA coulometric detector was used after the catalytic column to detect the reduction products in the oxidative mode. Although the organonitro compounds were indirectly detected in this manner, after a few hours of use, the electrochemical detector would become "poisoned" and would no longer respond to the reduction products. Although the detector could be reactivated by passing 6 *M* nitric acid through the porous-graphite electrodes, it would soon become "poisoned" when used again.

The design of the ESA coulometric detection cells and electronic controller prompted an investigation of the Model 5020 coulometric guard cell for reduction of the organonitro compounds (post-column) and the Model 5010 analytical cell for detection of the reduction products through electrochemical oxidation. The guard cell has its own potentiostat, which allows a current of 1000 μA to be applied before it becomes overloaded, and this enables operation at high potentials and background currents. Also, because analytes in the total flowing stream are reduced in the porous-graphite cell, no sensitivity is lost at the oxidation electrode. This solves the problem posed by amperometric thin-layer cells of reduced sensitivity at the second electrode due to diffusion of the 2–5% of analyte that has reacted at the surface of the first electrode.

Hydrodynamic voltammetric data were obtained with the HPLC–ED system

for selecting the detector-operating reduction and oxidation potentials. Hydrodynamic voltammograms (HDVs) were first obtained by changing the applied reduction potential on the guard cell while monitoring the response of detector 2 of the analytical cell, maintained at a constant oxidation potential. HDVs were obtained for nine organonitro compounds. Fig. 2 shows the HDVs obtained for five of the compounds. The dinitrophenols (2,4-dinitrophenol, dinoseb and DNOC) were most easily reduced, reaching a maximum detector response between -0.9 and -1.2 V. Binapacryl, bifenox and dicloran approached the maximum response near -1.7 V. 2-Nitrophenol, oryzalin, and parathion appeared to be incompletely reduced, even at a reduction potential of -1.7 V. Sodium perchlorate was added to the mobile phase in an attempt to lessen the reduction potentials of the organonitro compounds, as was observed in cyclic voltammetric studies. However, the reagent-grade sodium perchlorate produced extremely high background currents (possibly due to metal impurities), which negated its use for reducing reduction peak potentials of the organonitro compounds. Because of rapidly increasing background currents above -1.5 V, -1.4 V was selected as the reduction potential for the guard cell.

HDVs were also obtained by changing the oxidation potential of detector 2 and maintaining the guard cell reduction potential at -1.4 V. HDVs for five of the nine compounds are shown in Fig. 3. Near maximum response was obtained at $+0.50$ V for six compounds (bifenox, dicloran, 2,4-dinitrophenol, dinoseb, DNOC and parathion). The detector response for 2-nitrophenol reached a plateau near $+0.6$ V and

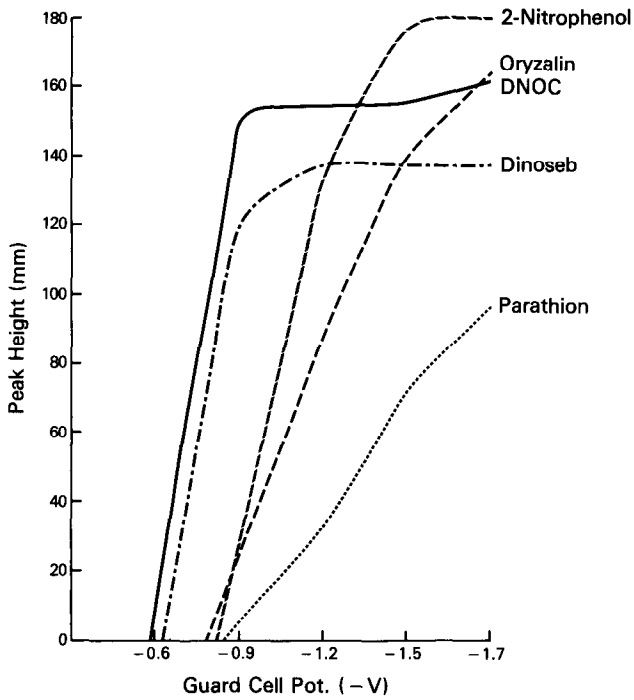

Fig. 2. Hydrodynamic voltammograms with the reductive potential (Pot.) on the guard cell changed. See text for instrument parameters.

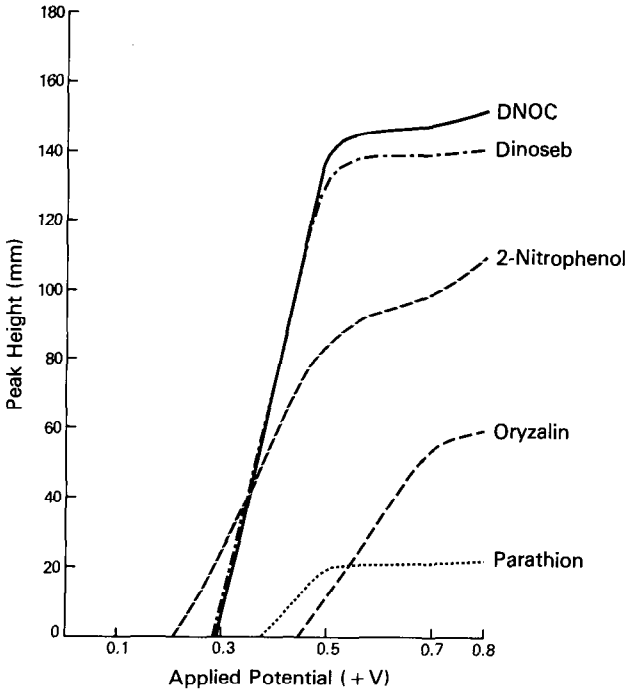

Fig. 3. Hydrodynamic voltammograms with the oxidative potential on the analytical cell changed. See text for instrument parameters.

then increased again, possibly because of the oxidation of the phenol. The maximum detector response for binapacryl and oryzalin was obtained near +0.7 V. An oxidation potential of +0.7 V was selected.

In the HDV oxidation studies, an interesting phenomenon was observed for binapacryl. At potentials of less than +0.3 V, a negative peak was observed; however, binapacryl is not reduced until a potential of *ca.* −0.8 V is applied. Negative peaks were also observed for binapacryl, DNOC and oryzalin at −0.2 V. Baizer[15] has reported that if an amino or hydroxyl group is situated *ortho* or *para* to the nitro group, the intermediate phenylhydroxylamine very rapidly loses water to form the easily reducible quinone, or the mono- or diimine. The loss of water is reported to take place most quickly in acid or alkaline solution. The hydroxyl group in DNOC and the ether group in binapacryl are *ortho* and *para* to the two nitro groups of each compound. Oryzalin contains two nitro groups, which are both *ortho* to the amine functional group. However, it should be noted that the nitro group(s) for the other six compounds are also in the *ortho* and/or *para* position, and for these compounds no change in response was noted when detector 1 was turned off or a potential of −0.20 V was applied. The electrochemical reduction products formed and/or the presence or absence of other functional groups on the phenyl ring may influence the effect on the reduction products of setting detector 1 at −0.2 V. It was observed that by operating detector 1 at −0.2 V, the oxidation response at detector 2 for DNOC, binapacryl and

oryzalin increased by 30, 20 and 10%, respectively, without any change in response for the other six compounds. Therefore, detector 1 was operated at −0.2 V.

A chromatogram obtained at the selected reduction and oxidation potentials is shown in Fig. 4. The sharp chromatographic peaks indicate good flow-through design of the guard and analytical cells. The organonitro peaks in the chromatogram represent 5–20 ng of a specific compound, indicating good detector response. The solvent peak and apparent "oxygen" peak are adequately separated from the peaks of the organonitro compounds. Although the magnitude of the gradient is large (20–90% acetonitrile in water), the change in the baseline has been minimized by maintaining a constant concentration of the electrolyte in the mobile phase. It should also be emphasized that periodic cleaning of the cell required that the cell first be cleaned with dilute nitric acid solution and then dilute sodium hydroxide solution. When the cell was washed with only nitric acid, severe negative peaks were observed immediately after the positive analyte peak. The reason for this phenomenon is unknown.

During our investigations it was necessary to make several injections of the organonitro compounds to obtain stable responses by the detection system. Table III shows the short-term response stability obtained for the nine compounds after the detection system has been "equilibrated". The average coefficient of variation (C.V.)

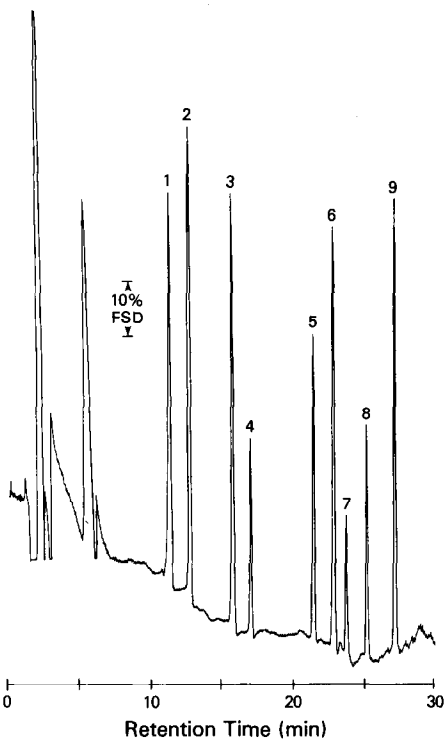

Fig. 4. HPLC–ED chromatogram of nine organonitro compounds. Peaks: 1 = 2,4-dinitrophenol, 5 ng; 2 = 2-nitrophenol, 10 ng; 3 = DNOC, 5 ng; 4 = dicloran, 10 ng; 5 = oryzalin, 20 ng; 6 = dinoseb, 5 ng; 7 = parathion, 20 ng; 8 = bifenox, 20 ng; 9 = binapacryl, 10 ng. See text for instrument parameters.

TABLE III

SHORT-TERM STABILITY OF DETECTOR RESPONSE FOR NINE ORGANONITRO COMPOUNDS

Compound	*Peak height**	*Av. peak height*	*C.V. (%)*
Binapacryl	6885 6789 6904	6859	0.9
Bifenox	3547 3341 3352	3413	3.4
Dicloran	6515 6605 6521	6547	0.8
Dinoseb	6317 6365 6371	6351	0.5
2,4-Dinitrophenol	5895 5870 6002	5922	1.2
DNOC	3004 2959 2967	2977	0.8
2-Nitrophenol	7345 7355 7443	7381	0.7
Oryzalin	4528 4520 4640	4563	1.5
Parathion	2036 2053 1979	2023	1.9

* Peak height units for the Spectra-Physics computing integrator.

in response is 1.3% for the triplicate injections of the nine compounds shown in Table III. Bergens[16] recently reported a similar indirect HPLC–ED system with dual amperometric electrodes for the indirect detection of nitrodiphenylamines.

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