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Optimization of electron-capture detector when using packed-column supercritical fluid chromatography with modified carbon dioxide

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Abstract

Response surfaces were obtained for packed-column supercritical fluid chromatography with electron-capture detection (SFC–ECD) under various detector conditions to optimize the ECD for use with modified CO_2. Limits of detection, correlation coefficients and linear dynamic ranges were found to vary with increasing amounts of modifier for several nitrogen-containing and halogenated compounds. Low detection limits (pg) were achieved in the presence of 5% methanol-modified CO_2. Applications of packed-column SFC–ECD to the separation of nitrogen-containing compounds extracted from propellants and phenylurea herbicides are presented.

Keywords: Detectors, SFC; Electron capture detector; Phenylureas; Pesticides; Nitrogen-containing compounds; Propellants

1. Introduction

The advantages of packed-column supercritical fluid chromatography (SFC) are beginning to be realized. Packed-column SFC permits higher sample loadings than open-tubular column SFC, but the activity of the stationary phase may prevent the elution of moderately polar analytes when using 100% CO_2. Fortunately, the stationary phase activity can usually be overcome by adding a modifier to the mobile phase so that the active sites can be covered, thus allowing analytes to elute from the column. The modifier may also facilitate the elution of more polar analytes since the solvating strength of the mobile phase would have been increased. Furthermore, with the advent of variable restrictor technology with packed-column SFC, reproducible flow-rates are possible, which affords in turn reproducible retention times and area counts with relative standard deviations of 2% or less.

Traditionally, packed-column SFC (4.6 and 2.0 mm I.D. columns) has used high-performance liquid chromatographic (HPLC) detectors that employ flow cells before the restrictor [1]. Generally, these detectors, with the exception of fluorescence, lack the detectability (pg detection) required for trace analysis. By employing a postcolumn split, however, part of the packed-column SFC effluent can be diverted to a gas

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chromatographic (GC) detector. Flame ionization detection (FID) has been used in this regard for some applications, but the FID is limited to 100% CO_2 as mobile phase for quantitative results. This prohibits the routine use of organic modifiers, although small amounts of modifier (<1%, v/v) have been used with FID for semi-quantitative results [1].

Another sensitive and selective detection method for SFC is electron-capture detection (ECD) which has one of the lowest minimum analyte detectabilities among all GC detection methods [2]. The first reference to SFC–ECD was a pesticide analysis by Richter and Campbell (cited as personal communication by Later et al. [3]), in which they reported detector linearity over four orders of magnitude for the determination of the pesticide DDT in pork fat with the aid of an open-tubular column and 100% CO_2. Tarver and Hill [4] later compared a pulsed electron-capture detector and a Fourier transform ion mobility detector for open-tubular SFC of pesticides, polyaromatic hydrocarbons and polychlorinated biphenyls. They reported high-picogram detection limits (>100 pg) and found that the baseline rose significantly during pressure programming. Chang and Taylor [5] reported the first optimization of open-tubular column SFC–ECD employing 100% CO_2. They noted the effects of temperature and CO_2 density on the ECD response. They were also able to achieve a detection limit of 0.27 pg for 2,3′,4′-trichlorobiphenyl and 1.50 pg for 3,4-dinitrotoluene at a detector temperature of 350°C.

The first published account of packed-column SFC–ECD was for the determination of a metabolite of triazole by Kennedy and Wall [5]. They reported a detection limit of 35 pg on-column. To prevent baseline rise during pressure programming, they increased the make-up gas (Ar–CH_4) flow-rate to decrease the CO_2 concentration in the detector. Later, Yarita et al. [7] published a packed-column (4.6 mm I.D.) SFC–ECD study in which polychlorinated biphenyls (PCBs) were separated on an octadecylsilyl-silica gel column. All of these papers discussed SFC–ECD with both open-tubular and packed columns using CO_2 without modifier. The first account of SFC–ECD in the presence of a modifier was a preliminary study by Kornfeld [8] for the determination of organochlorines and phenylureas using a silica packed column (25 cm × 4.6 mm I.D.) and 5% (v/v) methanol-modified CO_2. Strode et al. [9] recently reported the determination of felodipine, a drug for the treatment of hypertension, using 6% (v/v) methanol-modified CO_2 and a silica packed column (25 cm × 4.6 mm I.D.) with SFC–UV–ECD. A detection limit of 34 pg at the detector was reported, but the ECD had not been optimized for use with a modifier.

In this work, the optimization of ECD was accomplished with a packed column (4.6 mm I.D.) and modified supercritical CO_2. The commercially available detector was evaluated at various modifier concentrations, detector temperatures, make-up gas flow-rates and modifier types. Detection limits for chlorine-, bromine-, and nitrogen-containing compounds were determined. The separation and detection of propellant components and phenylurea herbicides is also described.

2. Experimental

2.1. Instrumentation

A prototype of the Hewlett-Packard (HP) (Little Falls, DE, USA) Model G1205 SFC system was used for detector evaluation and subsequent separations. The system pressure was maintained electronically by a computer-controlled back-pressure regulator which allowed the flow-rate and pressure to be independently controlled. The mobile phase flow-rate was measured as a liquid at the pump. Organic modifier was added via an auxiliary pump. An internal 5-μl loop was used. A postcolumn split was introduced to divert a small percentage of the column effluent (<1%) through a 100-μm frit restrictor (Dionex, Salt Lake City, UT, USA) to the HP Model 19233 ^{63}Ni electron-capture detector with the remaining effluent (>99%) directed towards a standard HP Model 1050 multi-wave-

length detector (MWD) which employed a 13-μl high-pressure flow cell. For the detector optimization study, a 150 mm × 4.6 mm I.D. Deltabond cyano-derivatized silica (5 μm) column (Keystone Scientific, Bellefonte, PA, USA) was used. A 250 mm × 4.6 mm I.D. Adsorbosphere silica (5 μm) column (Alltech, Deerfield, IL, USA) was used to separate a supercritical fluid extract of a single base propellant. The phenylurea herbicides were separated with a 250 mm × 4.6 mm I.D. Hypersil silica (3 μm) column (Keystone Scientific).

2.2. Chemicals

All solvents (i.e., methanol, acetonitrile and toluene) were of high purity (HPLC grade). Carbon dioxide was of SFE/SFC grade (Air Products and Chemicals, Allentown, PA, USA). 4-Nitrotoluene (99%) and 2,6-dinitrotoluene (99%) were obtained from Aldrich (Milwaukee, WI, USA). 2,4,5-Trichlorophenol, 4-bromophenyl phenyl ether and 4-chlorotoluene were obtained from the Environmental Protection Agency (EPA, Quality Assurance Materials Bank, Research Triangle Park, NC, USA) as solutions. All analyte solutions were dissolved in methanol with concentrations ranging from 1000 to 5000 ppm. Single base propellants were provided by Olin Winchester (St. Marks, FL, USA). Six phenylurea herbicides were obtained from DuPont Agriculture Products Department (Wilmington, DE, USA).

3. Results and discussion

3.1. Detector optimization

Owing to the simple design of the Hewlett-Packard electron-capture detector, only four of the parameters (i.e., modifier concentration, modifier type, detector temperature and make-up gas) could be optimized. Since methanol is the most commonly used modifier in packed-column SFC, it was initially used to determine the optimum detector temperature and optimum make-up gas flow-rate. This was accomplished by mapping the response (peak area unless indicated otherwise) of the detector under various conditions. The detector temperature was varied from 100 to 325°C. Temperatures below 100°C were not used because water would condense and freeze around the restrictor, and temperatures above 325°C were not used owing to detector limitations. The pressure was varied from 100 to 325 bar. Pressures lower than 100 bar were not used owing to the poor chromatographic peak shape, and pressures higher than 325 bar were not used owing to instrument limitations. The make-up gas (Ar–CH_4) flow-rate was varied from 15 to 200 ml/min. Flow-rates below 15 ml/min resulted in large background noise and flow-rates above 200 ml/min were not used owing to instrument limitations. Since the detector responds selectively but to different degrees to compounds with electron-withdrawing groups, a variety of probes containing chlorine, bromine, and nitrogen ($-NO_2$) were chosen. Each response surface was constructed by performing at least 28 experiments. The peak reproducibility for each experiment was found to be <5% relative standard deviation ($n = 3–4$).

The effect of detector temperature on the ECD response at various modifier concentrations was first established. A postcolumn split was used to divert a small flow (7 ml/min of decompressed CO_2) of column effluent to the detector at a constant mobile phase pressure of 200 bar and an oven temperature of 50°C. A make-up gas (Ar–10% CH_4) flow-rate of 200 ml/min was used to ensure a large and consistent stream of thermal electrons at various modifier concentrations. The baseline under these conditions was found to increase slowly with an increase in modifier concentration at a fixed temperature (Fig. 1). The baseline was also found to increase slightly as the detector temperature was raised over the range 100–250°C at a fixed modifier concentration (Fig. 1). At 300°C, the baseline dramatically increased, which suggested that methanol and/or impurities in the methanol were capturing electrons. It was believed that methanol and/or impurities were capturing electrons at all temperatures, but the

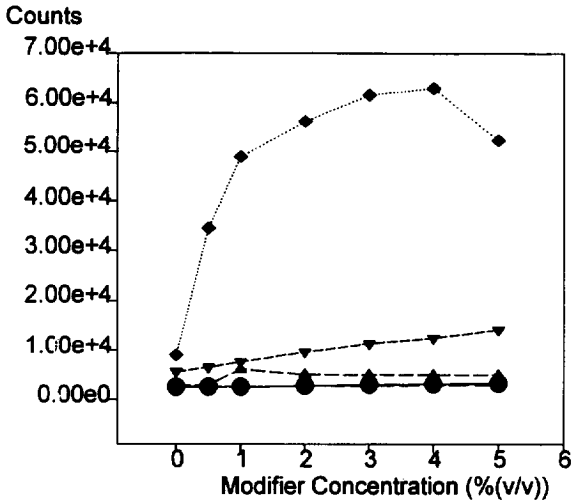

Fig. 1. ECD response surface for baseline level at 0–5% methanol-modified CO_2 and several detector temperatures (100–300°C). Conditions: pressure, 200 bar; oven temperature, 50°C; injection loop, 5 μl; Ar–CH_4 make-up gas flow-rate, 200 ml/min; mobile phase (liquid CO_2) flow-rate, 2 ml/min; Deltabond cyanopropyl-derivatized silica column (250 mm × 4.6 mm I.D., d_p = 5 μm); and 7 ml/min decompressed CO_2 diverted to the detector. Temperature: ● = 100; ■ = 150; ▲ = 200; ▼ = 250; ◆ = 300°C.

higher temperatures enhanced the signal of the methanol and/or impurities.

The effect of temperature on the ECD response is compound specific. The first group of compounds consisted of halogenated compounds such as 2,4,5-trichlorophenol, 4-bromophenyl phenyl ether and 4-chlorotoluene, which yielded the highest response (Fig. 2) at a detector temperature of 250°C regardless of modifier concentration. The second group of compounds consisted of 4-nitrotoluene and 2,6-dinitrotoluene, which gave the highest response (Fig. 3) at a detector temperature of 100°C regardless of the modifier concentration. Even though the second group yielded the highest response at lower detector temperatures, the nitrogen probes still exhibited a strong response at 200°C. Different types of response reflect the fact that electron capture can proceed by two different mechanisms:

$$AB + e^- \rightarrow A + B^- \quad (1a)$$

$$AB + e^- \rightleftharpoons AB^- \quad (1b)$$

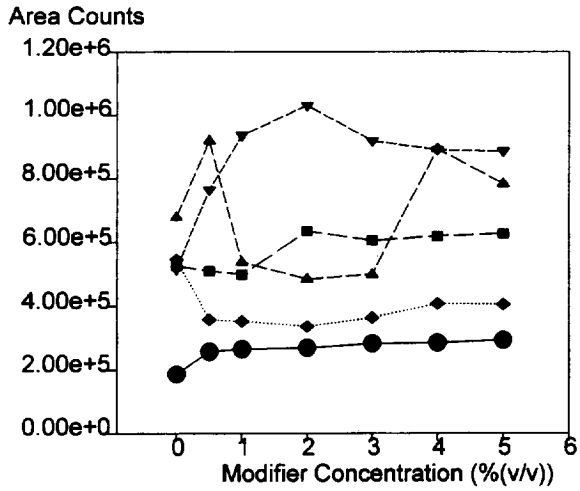

Fig. 2. ECD response surface for 2,4,5-trichlorophenol (1000 ppm solution dissolved in methanol) at 0–5% (v/v) methanol-modified CO_2 and several detector temperatures (100–300°C). Conditions and symbols as in Fig. 1.

The first mechanism (Eq. 1a) is a dissociative electron capture in which the molecule breaks apart upon capturing an electron [2]. This mechanism is favored at higher detector temperatures

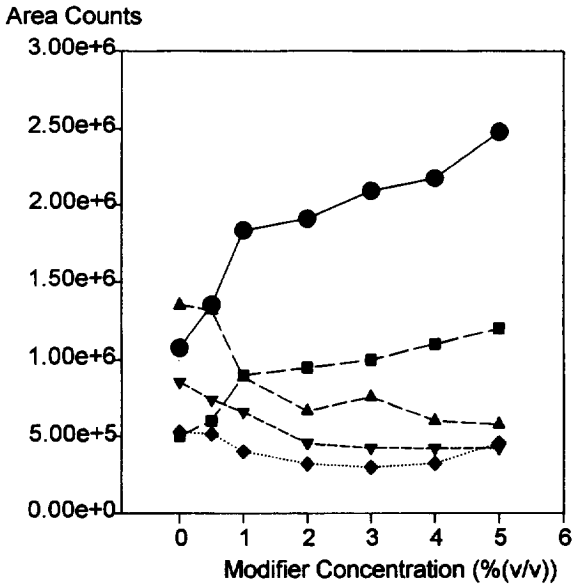

Fig. 3. ECD response surface for 2,6-dinitrotoluene (1000 ppm solution dissolved in methanol) at 0–5% (v/v) methanol-modified CO_2 and several detector temperatures (100–300°C). Conditions and symbols as in Fig. 1.

(>200°C). The higher temperatures enhance the population of the higher excited states required for the dissociative mechanism [2]. The second mechanism (Eq. 1b) is based on a non-dissociative process in which the molecule captures an electron, releases the excess energy and remains intact [2]. This mechanism is favored at lower detector temperatures (<150°C), and in general conjugated molecules capture electrons by this mechanism [2]. At higher temperatures, higher vibrational states would become occupied, thus decreasing the probability of attachment. For our study, a detector temperature of 225°C was deemed appropriate to ensure high responses for compounds capturing electrons by either mechanism.

After fixing the detector temperature at 225°C, the effect of the Ar–CH_4 make-up gas flow-rate at constant modifier concentration on the ECD response was evaluated at 200 bar CO_2, 0–5% (v/v) modified CO_2, detector temperature 225°C, oven temperature 50°C, liquid CO_2 flow-rate 2.0 ml/min and 7.0 ml/min decompressed CO_2 to the detector. Both nitrogen-containing compounds (Fig. 4) and halogenated compounds (Fig. 5) yielded a higher response as the make-up gas flow-rate was decreased. This was not surprising since the ECD response is based on the concentration of the analyte in the detector. If the make-up gas flow-rate was lowered, the ratio of column eluent to make-up gas would increase, resulting in a larger signal.

The effect of different modifier concentrations at constant make-up gas flow-rate can be divided into two groups. The halogenated compounds gave an ECD response which increased with increasing modifier concentration. This was not surprising, since the capacity factor (k') decreased with increasing modifier concentration. As k' decreased, the peaks became sharper and the on-column analyte peak concentration increased. For example, 2,4,5-trichlorophenol had a peakwidth of 0.187 min with a 100% CO_2 mobile phase. As the methanol concentration was increased, the peak width decreased to 0.12

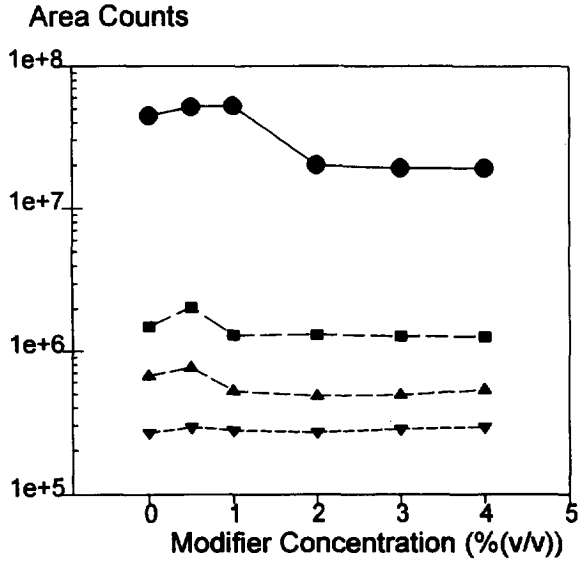

Fig. 4. Effect of make-up gas flow-rate on ECD response for 2,6-dinitrotoluene (1000 ppm solution dissolved in methanol) at 0–4% (v/v) methanol-modified CO_2. Conditions: 200 bar; oven temperature, 50°C; injection loop, 5 μl; detector temperature, 225°C; mobile phase (liquid CO_2) flow-rate, 2 ml/min Deltabond cyanopropyl-derivatized silica column (250 mm × 4.6 mm I.D., d_p = 5 μm); and 7 ml/min decompressed CO_2 diverted to the detector. Marker identity: make-up gas (Ar–CH_4) flow-rate; ● = 15; ■ = 50; ▲ = 100; ▼ = 200 ml/min.

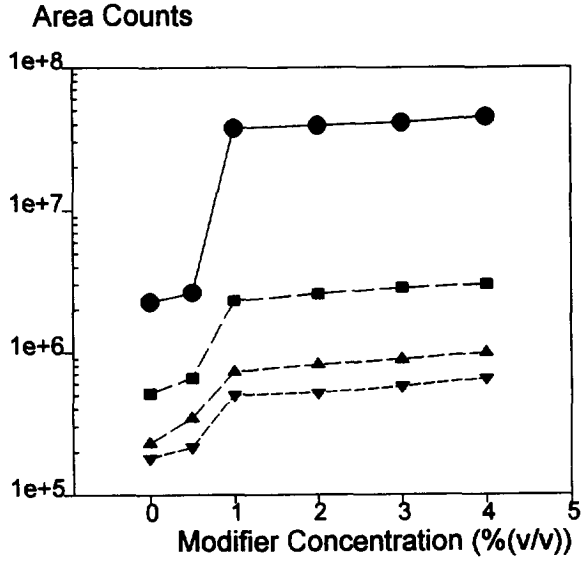

Fig. 5. Effect of make-up gas flow-rate on ECD response for 2,4,5-trichlorophenol (1000 ppm solution dissolved in methanol) at 0–4% (v/v) methanol-modified CO_2. Conditions and symbols as in Fig. 4.

min. The increased analyte concentration resulted in an increased ECD response. The nitrogen-containing compounds, on the other hand, gave an ECD response which decreased as the modifier concentration was increased from 0 to 3%. Since the nitrogen-containing compounds capture electrons based on a reversible non-dissociative mechanism, the number of electrons present affects the signal intensity. It was reasoned that the signal decrease was caused by a decreased number of electrons capable of electron capture. This was further evidence that methanol was capturing electrons. In an attempt to maximize the signal and minimize the increased background noise, an optimum value of 25 ml/min was chosen for the remaining work regardless of modifier concentration.

Once an optimum detector temperature and optimum make-up gas flow-rate had been determined, the effect of modifier type on the ECD response was studied. Two other solvents, acetonitrile and toluene, were studied by measuring the ECD response at 200 bar CO_2, 5% (v/v) modified CO_2, detector temperature 225°C, oven temperature 50°C, liquid CO_2 flow-rate 2.0 ml/min, 7.0 ml/min decompressed CO_2 to the detector and make-up gas flow-rate 25 ml/min. The electron affinity of these solvents is small (acetonitrile 0.5 eV, methanol 0.5 eV, toluene 0.5 eV) (Approximate of electron affinity based on correlation table [2]), which indicates that each should be a poor electron capturer. A *t*-test was performed to determine if the average responses of the analytes with different modifier were statistically different from each other (Table 1) [10].

The highest ECD response was obtained when toluene-modified CO_2 was used. This was expected because toluene should not capture electrons. When acetonitrile-modified CO_2 was used, the average responses, except for 4-nitrotoluene, were statistically lower than those obtained with toluene-modified CO_2. This indicated that acetonitrile was slightly interfering in the detection process, possibly by capturing electrons. Methanol, on the other hand, gave the statistically lowest ECD response for each of the modifiers, which meant that methanol and/or impurities were definitely capturing electrons. Further studies need to be performed to determine how methanol interferes in ECD.

Since CO_2, an electron capturer, and methanol (or an impurity in methanol), an electron capturer, could be introduced into the detector at various pressures, the effect of mobile phase pressure (100–325 bar) at both constant column flow-rate and make-up gas flow-rate was measured at various modifier concentrations. The constant column flow-rate to the detector was produced by preparing a new frit restrictor to deliver 7 ml/min decompressed CO_2 at each pressure from 100 to 325 bar and measuring the ECD response under various modifier concentrations. It was discovered that pressure under these conditions did not have a statistical effect on the ECD response or on the baseline. This result was expected since the amount of mobile phase entering the detector had remained fixed. However, during pressure programming with a fixed restrictor, the baseline rose owing to the increased amount of CO_2 at the detector. There-

Table 1
Effect of modifier on detector response

Probe	Average response (counts)			*t*-Value[a]		
	Acetonitrile	Methanol	Toluene	Acetonitrile vs. methanol	Methanol vs. toluene	Acetonitrile vs. toluene
2,6-Dinitrotoluene	663766	326562	946667	25.2	12.8	16.9
4-Nitrotoluene	750180	74842	723737	52.2	36.0	1.12
2,4,5-Trichlorophenol	767115	621014	775307	7.98	6.13	3.52
4-Bromophenyl phenyl ether	161236	56554	443517	24.0	7.60	6.27

[a] *t*-Critical (one-tailed) is 1.94 ($n = 8$).

fore, the increasing flow-rate of the mobile phase caused the baseline to rise during pressure programming, but the increase was insufficient to prevent the use of pressure programming.

3.2. Detector performance

The limit of detection (LOD) and linear dynamic range (LDR) were determined by SFC–ECD using 1% and 5% methanol-modified CO_2 under the optimized conditions of detector temperature 225°C, AR–CH_4 make-up gas flow-rate 25 ml/min, Deltabond cyanopropyl-derivative silica (5 μm) column (150 mm × 4.6 mm I.D.), flow-rate (liquid CO_2) 2.0 ml/min, 200 bar CO_2, oven temperature 60°C, splitting ratio, 0.0067 and decompressed CO_2 flow-rate diverted to the detector 14 ml/min (Table 2). Methanol was used as the modifier since it has been the most widely used modifier in SFC. Calibration graphs (peak area vs. concentration injected) were based on an average ECD response ($n = 4$) in the concentration range 10–5000 ppm. The LOD was determined by the propagation of errors method [11].

2,6-Dinitrotoluene had a correlation coefficient of 0.997 for both modifier concentrations and an LDR of four orders of magnitude. The detection limit of 2,6-dinitrotoluene was lowered from 100 pg (1% methanol-modified CO_2) to 6 pg (5% methanol-modified CO_2). This enhancement was caused by an improvement in the peak shape and decreasing k', which increased the signal. 2,4,5-Trichlorophenol had a correlation coefficient of 0.9999 for both modifier concentrations and an LDR of four orders of magnitude. The detection limit of 2,4,5-trichlorophenol was raised from 2 pg (1% methanol-modified CO_2) to 20 pg (5% methanol-modified CO_2). This deterioration in the detection limit was attributed to the presence of methanol, which caused more error to be present. Since the propagation of error method took into account the error in both the slope and intercept, more error in the calibration graph would result in a higher detection limit. The LODs determined with 1% methanol-modified CO_2 were 4-nitrotoluene 200 pg, 4-bromophenyl phenyl ether 700 pg and 4-chlorotoluene 500 pg (Table 2). The three compounds had a correlation coefficient of 0.99 and an LDR of three orders of magnitude, but the detection limits were higher than for the compounds with multiple electron-withdrawing groups. At 5% methanol-modified CO_2, the LOD for these three compounds was higher than 1 ng. It was felt that the presence of methanol at both 1% and 5% prevented the sensitive detection of compounds with one electron-withdrawing group. Even though the presence of methanol modifier adversely affected the performance of the detector,

Table 2
Detection limits of probes using 1% and 5% methanol-modified CO_2

Methanol concentration (%)	Probe	Intercept[a] (b)	Slope[a] (m)	Correlation coefficient (R^2)	Linear dynamic range (LDR)	LOD (pg)
1	2,6-Dinitrotoluene	5893 (5)	86.1 (3.0)	0.997	4	100
	4-Nitrotoluene	2679 (2)	18.8 (1.1)	0.994	3	200
	2,4,5--Trichlorophenol	182 (0.2)	182 (0.1)	0.9999	3	2
	4-Bromophenyl phenyl ether	1636 (1)	3.25 (0.6)	0.997	3	700
	4-Chlorotoluene	1762 (1)	6.24 (0.8)	0.97	3	500
5	2,6-Dinitrotoluene	7329 (3)	102 (5)	0.997	4	5
	2,4,5-Trichlorophenol	2031 (1)	182 (0.7)	0.9999	4	20

[a] Standard deviations for the slope and intercept are given in parentheses.

detection of analytes with multi-electronegative groups did occur at low levels (<1 ng) in the presence of the modifier.

3.3. Application

To demonstrate the selectivity and detectability of the SFC–ECD system, the determination of N-nitrosodiphenylamine and diphenylamine from propellants and phenylurea herbicides was undertaken. Several propellant extracts were assayed for N-nitrosodiphenylamine and diphenylamine. Propellant (500 mg) was extracted by supercritical fluid extraction (SFE) at 350 bar, 100% CO_2, 50°C and 2.0 ml/min for 45 min. The extract was collected at 0°C and rinsed off the octadecyl-derivatized silica trap with 1 ml of methanol. Although the analytes were extractable with 100% CO_2, 2% (v/v) methanol-modified CO_2 was required to elute the analytes from a silica column. The extracts were analyzed by SFC–UV–ECD (Fig. 6) using an Adsorbosphere silica packed column with simultaneous UV and ECD. The UV chromatogram showed only diphenylamine and N-nitrosodiphenylamine whereas the ECD chromatogram showed diphenylamine, N-nitrosodiphenylamine and several other unidentified compounds.

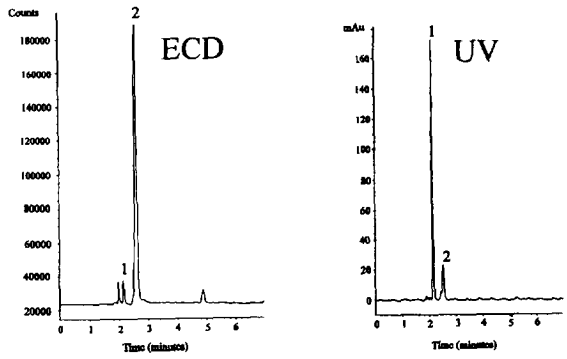

Fig. 6. SFC–UV–ECD separation of propellant extract which was dissolved in methanol. SFC conditions: temperature, 50°C; 2% (v/v) methanol-modified CO_2; liquid CO_2, 2.0 ml/min; 350 bar; injection loop, 5 μl; Adsorbosphere silica column (250 mm × 4.6 mm I.D., d_p = 5 μm); flow-rate make-up gas flow-rate, 25 ml/min; ECD temperature, 225°C; 7 ml/min decompressed CO_2 diverted to ECD; UV detection at 254 nm. Peaks 1 = diphenylamine; 2 = N-nitrosodiphenylamine.

Next, six phenylurea herbicides (each component present at 50 ppm) were assayed using a Hypersil silica packed column with simultaneous UV and ECD. All six phenylureas were detected to varying degrees by ECD (Fig. 7A). Tailing peaks were the main problem in the chromatogam A (Fig. 7). There were three possible explanations for this peak tailing. First, the analytes could have precipitated in the ceramic frit of the restrictor. However, when the frit restrictor was replaced with an integral restrictor (25 μm I.D. fused silica) delivering 10

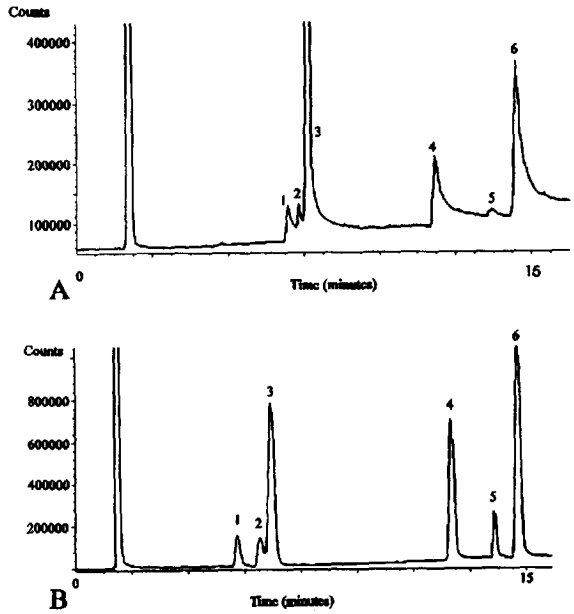

Fig. 7. SFC–ECD separation of phenylurea herbicides (50 ppm concentration dissolved in methylene chloride). SFC conditions: temperature, 60°C; liquid CO_2 flow-rate, 2 ml/min; pressure programming (200 bar, 0.5 min hold; 10 bar/min ramp; 250 bar, 9 min hold); gradeient programming [1.2% (v/v) methanol-modified CO_2, 0.5 min hold; 0.3%/min ramp to 3% (v/v) methanol-modified CO_2, 0 min hold; 1%/min ramp to 10% (v/v) methanol-modified CO_2, 1 min hold); Hypersil silica column (250 mm × 4.6 mm I.D., d_p = 3 μm); 14 ml/min decompressed CO_2 diverted to ECD delivering 3 ng of each component. (A) ECD temperature 225°C and 25 ml/min Ar–CH_4 make-up gas flow-rate; (B) ECD temperature 300°C and 25 ml/min Ar/CH_4 make-up gas flow-rate. Peaks: 1 = metobromuron; 2 = linuron; 3 = chlorobromuron; 4 = fluormeturon; 5 = monuron; 6 = diuron.

ml/min of decompressed CO_2 to the detector, the peak tailing was still observed. Another possible explanation was a loss in solubility when the restrictor was heated inside the detector at reduced pressure of the mobile phase. No peaks were observed by ECD when the temperature of the detector was lowered from 225 to 100°C to eliminate loss of solubility. The last explanation was that the herbicides were not vaporized in the detector, thus precipitating inside the detector. To vaporize the herbicides more adequately, the detector was heated to 300°C, and the peak tailing was eliminated (Fig. 7B). An additional benefit of the increased temperature was the increased signals of all the analytes, especially monuron.

4. Conclusion

Although CO_2 and some modifiers are electron capturers, sensitive detection is still possible in the presence of a modifier. By altering the ECD temperature, the detectability of the electron-capture detector can be enhanced. Packed-column SFC–ECD appears to be a promising technique for assaying environmental and polar samples. It would be especially useful for compounds which (1) lack a chromophore but have an electron-withdrawing group capable of capturing electrons and (2) are problematic with HPLC. Finally, the increased detectability of the electron-capture detector can allow the detection of trace impurities that are missed by other detectors.

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