Determination of Sulfonyl Urea Herbicides by Capillary Electrochromatography

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Abstract

Thirteen compounds are investigated using a commercially available CE system and capillary columns packed with 3-µm porous octadecylbonded silica. The detector response is very linear from 1–100 ppm with a correlation coefficient r^2 of 1–0.990 for each compound. This paper is believed to be the first application using CEC for the determination of sulfonyl urea herbicides and the first reported use of hydrodynamic injection in CEC with packed columns and a commercial CE instrument.

Introduction

Sulfonyl ureas, a relatively new class of herbicides, have been determined using either gas chromatography after derivatization of the NH group (1) or high-performance liquid chromatography (HPLC) with mass spectrometry (MS) (2) or photoconductivity detection (3). Capillary zone electrophoresis (CZE) was used by Dinelli et al. (5,6) to detect sulfonyl ureas in tap water and Garcia and Henion (7) used CZE–MS to analyze a mixture of sulfonyl ureas. Capillary micellar electrokinetic chromatography was used in the determination of 5 sulfonyl ureas in grains (wheat, barley, and corn) by Krynitsky and Swineford (4). More recently, Krynitsky (8) reported on a CZE method and an electrospray liquid chromatography–MS confirmatory method for 12 sulfonyl ureas; the CZE separation was achieved at pH 4.5 with 50mM ammonium acetate buffer and acetonitrile.

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Table I. Sulfonyl Urea Herbicides Used in this Study

Compound number	Compound name	Trade name	Molecular weight	Purity (%)	CAS #
Group 1					
1	Sulfometuron methyl	Oust	364	99.2	74222-97-2
2	Bensulfuron methyl	Londax	410	99.4	83055-99-6
3	Thifensulfuron methyl	Harmony	387	99.7	79277-27-3
4	Triflusulfuron methyl	Upbeet	492	98.9	126535-15-7
5	Chlorimuron ethyl	Classic	414	98.8	90982-32-4
6	Metsulfuron methyl	Ally	381	97.4	74233-64-6
7	Chlorsulfuron	Glean	357	99.3	64902-72-3
Group 2					
8	Triasulfuron	Amber	401	95.0	82097-50-5
9	Nicosulfuron	Accent	410	94.5	111991-09-4
10	Prosulfuron	CGA-152005	419	96.0	94125-34-5
11	Sulfosulfuron	Mon 37500	470	99.3	141776-32-1
12	Primisulfuron methyl	Beacon	468	95.0	86209-51-0
13	Halosulfuron methyl	Mon 12000	434	99.5	100784-20-1

Table II. CEC Experimental Conditions

Instrument	Hewlett-Packard CE system
Detector	diode array (scan from 190 to 600 nm; store signals at 200, 240, and 254 nm)
Data system	Hewlett-Packard Chemstation
Column	C_{18}-bonded silica (3-µm particles), 50- or 100-µm i.d. × 25-cm packed length, 8.5-cm unpacked length (from detector to outlet)
Column manufacturer	Unimicro Technologies, Pleasanton, CA
Column temperature	25°C
Polarity	positive
Injection	hydrodynamic (9 bar for 30 s).
Run voltage	25 kV
Current	3.5 µA (for 50-µm i.d. column) and ~7 µA (for 100-µm i.d. column)
Mobile phase	70% acetonitrile–25mM ammonium acetate (pH 3.5)

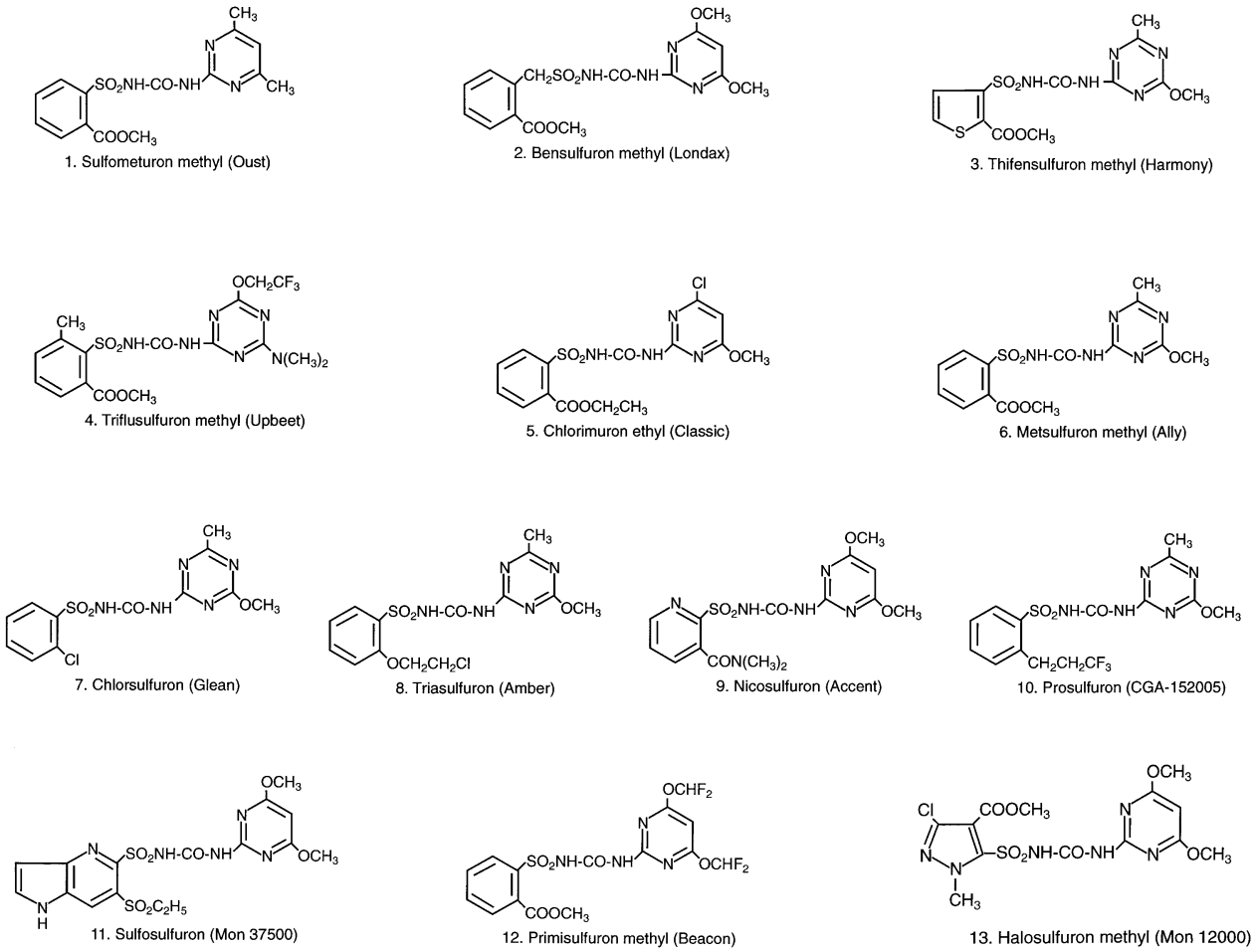

Figure 1. Chemical structures and the corresponding numbers, compound names, and trade names of the sulfonyl urea herbicides investigated in this study.

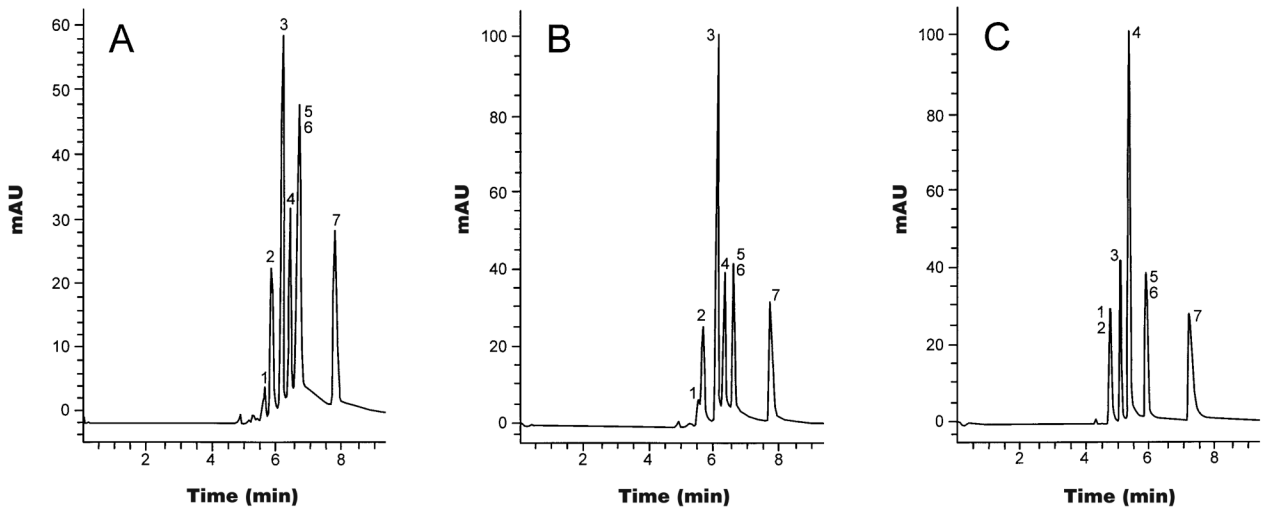

Figure 2. Separation of Group 1 compounds. Mobile phases consisted of 70% acetonitrile–30% 25mM ammonium acetate (pH 3.0) (A), 75% acetonitrile–25% 25mM ammonium acetate (pH 3.5) (B), and 80% acetonitrile–20% 25mM ammonium acetate (pH 3.5) (C). Conditions: column, 50-µm i.d. × 25-cm packed length (3-µm C_{18}-bonded silica); applied voltage, 25 kV; pressure applied to both ends of capillary, 9 bar; temperature, 25°C; detection wavelength, 240 nm. Injection at 9 bar for 60 s; Concentration, 100 ppm.

Capillary electrochromatography (CEC) has the potential to serve as a bridge between micro-HPLC and CZE, thus combining the high efficiency of CZE with the high selectivity of micro-HPLC. Recent applications of CEC reported in the literature include the separation of PAHs (9,10); nitrotoluenes, biphenyls, and thiourea (11); and alkylbenzoates (12) and the chiral separation of chlorthalidone and mianserin enantiomers (13); benzoic and mandelic acid (14); aminoacetophenone and several substituted phenols (15); pharmaceutical compounds (16); and N-, O-, and S-containing PAHs (17).

There are no reports on the CEC of sulfonyl urea herbicides. The present paper is believed to be the first application of the determination of sulfonyl urea herbicides by CEC and the first report on hydrodynamic injection in CEC with packed columns and a commercial CE instrument. Thirteen compounds (see Table I and Figure 1) were investigated using a commercially available CE system and capillary columns packed with 3-µm porous octadecylbonded silica (ODS).

Table III. CEC Migration Times (min) of Target Compounds*

Compound number	Compound name	70% acetonitrile–25mM ammonium acetate (25 kV)	75% acetonitrile–25mM ammonium acetate (25 kV)	80% acetonitrile–25mM ammonium acetate (25 kV)
Group 1 (50-µm-i.d. column)				
1	Oust	5.66	5.19	4.58
2	Londax	5.86	5.31	4.58
3	Harmony	6.17	5.70	4.88
4	Upbeet	6.41	5.94	5.13
5/6	Classic/Ally	6.67	6.19	5.67
7	Glean	7.78	7.27	6.97
Group 1 (100-µm-i.d. column)				
1	Oust	6.04		
2	Londax	6.26		
3	Harmony	6.51		
4	Upbeet	6.78		
5/6	Classic/Ally	6.97		
7	Glean	8.13		
Group 2 (50-µm-i.d. column)				
8	Amber	6.02		
9	Accent	5.78		
10	Prosulfuron	8.17		
11	Mon 37500	8.92		
12	Primisulfuron methyl	10.21		
13	Mon 12000	16.17		
Group 2 (100-µm-i.d. column)				
8	Amber	5.96		
9	Accent	§		
10	Prosulfuron	7.93		
11	Mon 37500	8.19		
12	Primisulfuron methyl	9.67		
13	Mon 12000	14.56		

* Analyzed in a mixture (concentration, 250 ppm).
† The CEC experimental conditions are provided in Table II.
‡ Average migration time from 7 determinations using a composite standard of compounds 8–13 at a concentration of 50 ppm. The compound Accent was not included in this standard.
§ The migration time of this compound was not determined.

Experimental

Chemicals

Individual stock solutions of each of the 13 target compounds at 10 mg/mL in acetonitrile were prepared. Individual working standards at 100 and 500 µg/mL were prepared by diluting 10 and 50 µL of the stock solutions with 990 or 950 µL buffer, respectively. The calibration standards were prepared by the serial dilution of a composite solution containing either 7 (Group 1) or 6 (Group 2) target compounds.

A 25mM aqueous solution of ammonium acetate (pH 3.5) was prepared from neat materials, and the pH was adjusted with 1.5M acetic acid. The mobile phase was prepared by mixing the ammonium acetate solution with the appropriate amount of HPLC-grade acetonitrile (J.T. Baker, Phillipsburg, NJ).

Apparatus

A Hewlett-Packard (Waldbronn, Germany) HP 3D CE system equipped with an Electropak capillary column (Unimicro Technologies, Pleasan-ton, CA) was used for all experiments reported here. The experimental conditions are provided in Table II. The electrokinetic packing of capillary columns was reported by Yan (9), and details of the procedure can be found in the literature. Standards of the target compounds in the elution buffer were injected at a pressure of 9 bar. The injection time varied from 10 to 60 s. The column was conditioned in the CE system at a relatively low voltage (approximately 5 kV) for approximately 15 min prior to the analysis of the target compounds (inlet pressure, 9 bar).

During analysis, the column was pressurized at 9 bar to prevent the formation of gas bubbles in the packed capillary column. A typical current in a 25-cm × 50-µm i.d. column packed with 3-µm C_{18}-bonded silica with 70% acetonitrile–30% 25mM ammonium acetate is approximately 3.5 µA at 25 kV.

Results and Discussion

Figure 2A shows the separation of 7 sulfonyl ureas (Group 1) using a 50-µm i.d. Electropak column and 70% acetonitrile–30% 25mM ammonium acetate eluent (pH 3.5) at 25 kV. Figures 2B and 2C show the separation using 75% and 80% acetonitrile, respectively. The migration times of the target compounds are listed in Table III. Slightly shorter migration times were achieved using 80% acetonitrile–20% 25mM ammonium acetate (pH 3.5), but Oust and Londax coelute under these conditions.

Table IV. Reproducibility of Migration Times and Detector Responses for the Target Compounds*

		%RSD		
			Detector response	
Compound number	Compound name	Migration time	Peak area	Peak height
Group 1				
1	Oust	2.1	2.7	3.1
2	Londax	2.3	4.1	4.5
3	Harmony	2.3	8.8	3.8
4	Upbeet	2.7	4.9	5.1
5	Classic	2.6	9.6	4.0
7	Glean	2.8	5.8	5.5
Group 2				
8	Amber	1.1	8.7	6.1
10	Prosulfuron	1.0	6.6	4.6
11	Mon 37500	1.0	11	5.6
12	Primisulfuron methyl	1.3	9.8	4.6
13	Mon 12000	3.0	8.8	4.3

* The CEC experimental conditions are provided in Table II.
† Number of determinations, $n = 10$; concentration, 100 ppm per compound; column, 50-µm i.d. Reproducibility of detector response is based on peak area measurements.
‡ Number of determinations, $n = 7$; concentration, 50 ppm per compound; column, 100-µm i.d. The reproducibility of detector response is based on peak area measurements.

Attempts to separate Classic and Ally under any of the conditions were unsuccessful. Experiments were also performed with lower concentrations of acetonitrile, but at 50% acetonitrile–50% 25mM ammonium acetate, it was not possible to detect any of the compounds. The efficiencies for the single peaks averaged approximately 35,000 to 40,000 plates on a 25-cm packed capillary column and were comparable with data reported by the column manufacturer for selected polynuclear aromatic hydrocarbons.

Use of a 100-µm i.d. Electropak column and 70% acetonitrile–30% 25mM ammonium acetate eluent (pH 3.5) resulted in slightly longer migration times for the Group 1 compounds (Table III) and a slight tailing, especially for compound 7 (Figure 3). This is not surprising, because these compounds are fairly polar (pK_a ranging from 3.3 to 5.0) and can interact with silanol groups (the particles are not endcapped).

In the case of Group 2 compounds (Figure 4), compounds 8 and 9 (Amber and Accent) could not be resolved, and the data indicate that the migration times are longer when the compounds are analyzed by CEC individually (as compared

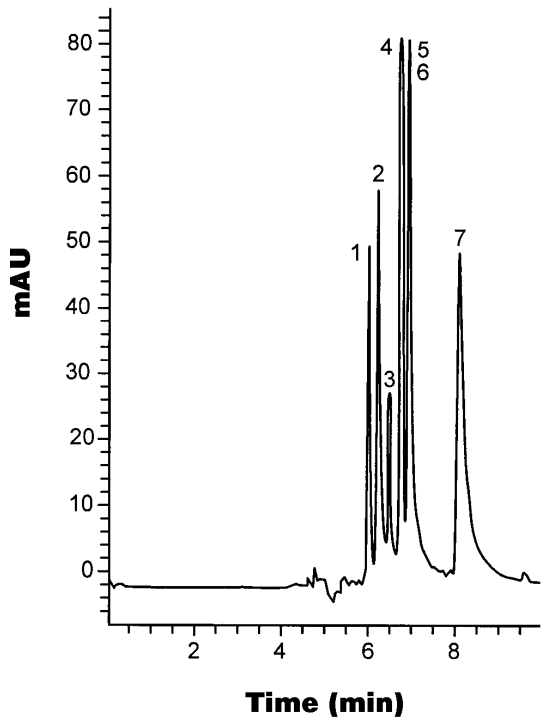

Figure 3. Separation of Group 1 compounds. Conditions: column, 100-µm i.d. × 25-cm packed length (3-µm C_{18}-bonded silica); mobile phase, 70% acetonitrile–30% 25mM ammonium acetate (pH 3.0); applied voltage, 25 kV; pressure applied to both ends of capillary, 9 bar; temperature, 25°C; detection wavelength, 240 nm; injection, 9 bar for 60 s; concentration, 100 ppm.

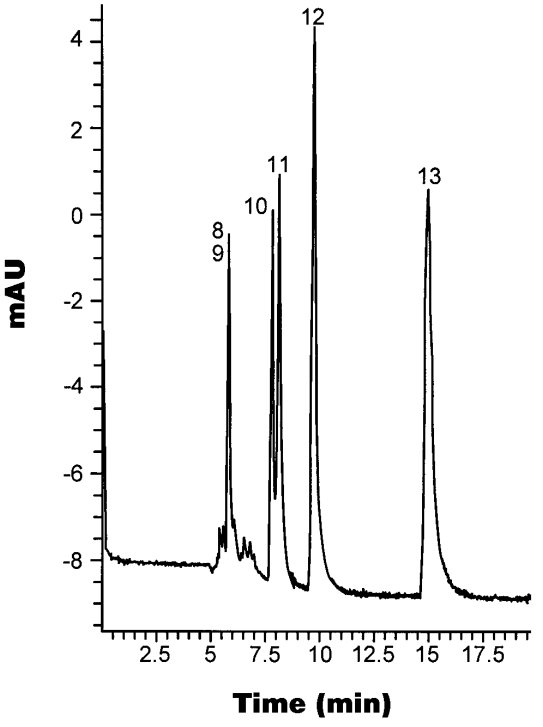

Figure 4. Separation of Group 2 compounds. Conditions: column, 100-µm i.d. × 25-cm packed length (3-µm C_{18}-bonded silica); mobile phase, 70% acetonitrile–30% 25mM ammonium acetate (pH 3.5); applied voltage, 25 kV; pressure applied to both ends of capillary, 9 bar; temperature, 25°C; detection wavelength, 240 nm; injection, 9 bar for 30 sec; concentration, 165 ppm.

Table V. CEC Linearity Data (Slope, Intercept, and Correlation Coefficient) of the Target Compounds*

Compound number	Compound name	Concentration level (µg/mL)	Slope	Intercept	Correlation coefficient r^2
Group 1					
1	Oust	1, 10, 25, 100	1.62	1.57	0.999
2	Londax	1, 10, 25, 100	1.26	2.87	0.999
3	Harmony	1, 10, 25, 100	1.06	0.281	1.000
4	Upbeet	1, 10, 25, 100	1.37	1.76	1.000
5	Classic	1, 10, 25, 100	1.65	5.05	0.997
7	Glean	1, 10, 25, 100	1.67	0.516	1.000
Group 2					
8	Amber	1, 10, 25, 100	1.2	–0.267	0.993
10	Prosulfuron	1, 10, 25, 100	1.52	–0.97	0.997
11	Mon 37500	1, 10, 25, 100	2.89	–7.03	0.990
12	Primisulfuron methyl	1, 10, 25, 100	4.03	–6.86	0.993
13	Mon 12000	1, 10, 25, 100	5.41	–9.07	0.993

* The CEC experimental conditions are provided in Table II.
† Using a 50-µm-i.d. column.
‡ Using a 100-µm-i.d. column.

with composite mixtures). For example, the migration time of Amber was 7.02 min when analyzed alone using CEC in comparison with 5.96 min when analyzed in a mixture with the other Group 2 compounds. Likewise, Mon 12000 had a migration time of 19.08 min when analyzed individually in comparison with 14.56 min when analyzed with the other Group 2 compounds.

The initial experiments were performed using electrokinetic injections. Changing to hydrodynamic injections (pressure at 9 bar), the sensitivity was increased by a factor of 10 for each compound. Despite the fact that hydrodynamic injection provides retention times that are less reproducible than those of electrokinetic injection, it is actually preferred over the electrokinetic injection because it is not biased. The reproducibility of the migration time in percent relative standard deviation (%RSD) was found to be approximately 0.2% for the electrokinetic injection (17) and 10 times higher for the hydrodynamic injection (Table IV). However, the detector responses (peak area or peak height) were comparable between the two injection techniques, and they were also comparable to those achieved by HPLC (%RSDs of 2.7–11 for the detector response). Likewise, CEC linearity data (Table V) were comparable to those achieved by HPLC. The detector response was very linear from 1–100 ppm with a correlation coefficient r^2 of 0.993–1 for each compound. It appears that the elution order is quite similar to the HPLC–MS method reported by Krynitsky (8), with the exception of Oust eluting before Londax.

Conclusion

Thirteen compounds were investigated using a commercially available CE system and capillary columns packed with 3-µm porous ODS. The detector response was very linear from 1–100 ppm (r^2 = 1–0.990) for each compound. This is believed to be the first determination of sulfonyl urea herbicides using CEC and the first report of hydrodynamic injection in CEC with packed columns and a commercial CE instrument. Work is underway in our laboratory to use a high-sensitivity optical cell with a packed capillary column to extend the optical path length and improve the detection capability of this technique.

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