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Journal of Chromatography A, 822 (1998) 253–261

JOURNAL OF  
CHROMATOGRAPHY A

# Gas chromatographic–mass spectrometric determination of alachlor and its degradation products by direct aqueous injection

Song Hong, Ann T. Lemley\*

*Field of Environmental Toxicology, Cornell University, Ithaca, NY 14853-4401, USA*

Received 20 April 1998; received in revised form 28 July 1998; accepted 31 July 1998

## Abstract

A GC–MS method, with direct aqueous injection, has been developed to determine alachlor and its degradation products in water. The method was optimized to give the following conditions: injection with splitless mode, injection port with silanized-glass reverse-cup liner filled with 0.5 cm Carbofrit above the cup; injection temperature of 250°C; and an analytical column with a stationary phase of 5% diphenyl and 95% dimethyl polysiloxane and dimensions of 60 m×0.25 mm×0.25 μm. The minimum detection limit is 0.05 to 1 mg/l in the GC–MS–SIM mode with variation of peak height less than 5% and 5 to 50 mg/l in the GC–MS–Scan mode for alachlor and its degradation products. © 1998 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Direct aqueous injection; Alachlor; Pesticides

## 1. Introduction

Alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)-acetamide] is a widely used herbicide that has been found in groundwater and surface water in many parts of North America [1,2]. It is classified as a B2 carcinogen and has the potential to induce cancer in laboratory animals [2]. It is critical to analyze alachlor and its degradation products when remediating alachlor-contaminated water. The published analytical methods for alachlor using gas chromatography (GC) require the dissolution of alachlor in an organic solvent. Alachlor is transferred from water to the organic solvent by liquid–liquid extraction (LLE) or solid-phase extraction (SPE) [3]. LLE and SPE are simple meth-

ods, but the analytical reproducibility and accuracy are affected by the extraction and condensation.

A simple and accurate method was needed to analyze aqueous samples of alachlor that had been subjected to an advanced oxidation treatment using the Fenton reaction. This treatment involves the electrochemical delivery of ferrous iron and the addition of hydrogen peroxide to an aqueous solution of the pesticide that also contains NaCl to enhance conductivity. GC analysis by direct aqueous injection (DAI) omits the multiple procedures involved in the extraction techniques, thus avoiding or decreasing analytical error. In addition, the analysis is faster [4–7].

In the work reported, injection, column and oven parameters of GC–MS were optimized so that aqueous samples of alachlor and its degradation products (containing NaCl at a few mg/ml, as per the remediation process being studied) could be

\*Corresponding author.

identified and quantified accurately. The scan mode of the GC–MS was used to determine the possible compounds that were present, and the selective ion monitoring (SIM) mode was used to quantify them. The purpose of the research was to understand the mechanisms and kinetics of degradation of alachlor; this analytical method was developed for appropriate concentrations and not refined for detection limits near the drinking water guidelines (20  $\mu\text{g}/\text{l}$ ). However, with some simple refinements (discussed in the paper) a lower detection limit could be achieved.

## 2. Experimental

### 2.1. Chemicals

Alachlor, its possible degradation products (aniline, 2,6-diethylaniline and 2-chloro-2',6'-diethylacetanilide) and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] (internal standard) were analytical standard-grade from ChemService (West Chester, PA, USA) (Fig. 1a). Ammonium bicarbonate and all solvents (Fisher Scientific, Fair Lawn, NJ, USA) were analytical or resi-analysis grade. The helium used for GC–MS was 99.9995% pure.

### 2.2. Accessories

The fillings for the GC injection-port liner were glasswool (Supelco, Bellefonte, PA, USA) and Carbofrit (Restek, Bellefonte, PA, USA). Nylon membrane (0.20  $\mu\text{m}$ ) filters encased in polypropylene cartridges were obtained from Alltech Associates (Deerfield, IL, USA). The pH meter was an Accumet Model 25 (Fisher Scientific, Springfield, NJ, USA).

### 2.3. Sample preparation

Ten to 40  $\mu\text{l}$  of aqueous ammonium bicarbonate (1 *M*) was added to the sample to adjust the pH to a range of 6 to 7. Ammonium bicarbonate was selected because it is a weak base and is volatile with decomposition at 60°C and above [8]. Nylon filters with pore size of 0.2  $\mu\text{m}$  were employed to filter the solution before injecting it into the GC–MS system. All standard solutions were prepared by adding

chemical standards to treated wastewater to match the matrix of the real samples. Since the methods being developed will be used on treated wastewater that will be subjected to advanced oxidation in an electrochemical Fenton system, the standards were added to water containing sodium chloride (to enhance conductivity), ferrous iron (added electrochemically) and hydrogen peroxide, added over time with a syringe pump.

### 2.4. GC–MS operating conditions

Alachlor and its degradation products were analyzed on a Hewlett-Packard (Sunnyvale, CA, USA) 5890 Series II coupled to a HP 5971A MS. Operating conditions were as follows: ionization voltage, 70 eV; interface temperature, 290°C; MS temperature, 170°C; electronic multiplier, 400 V above the autotune for scan mode and 200 V above manual-tune for selective ion monitoring (SIM). The mass spectrometry (MS) system was tuned daily with perfluorotetrabutylamine (PFTBA). The autotune was used for the scan mode. The manual tune was used after the standard autotune for the SIM mode to decrease the discrimination of the MS response on higher mass. The three ions used in the manual tune for alachlor analysis were 69, 219 and 264 charge-to-mass ratio (*m/z*). The threshold for the scan mode was 500, and the scan range was 10 to 300 *m/z*. Metolachlor was used as an internal standard.

The other GC–MS conditions were as follows unless stated elsewhere. The injection conditions were: a silanized-glass, reverse-cup liner (Hewlett-Packard) filled with 0.5 cm Carbofrit (Restek) above the cup, 250°C splitless for 1 min before purging the injection port, and 1  $\mu\text{l}$  of sample solution injected by hand or by HP7673A autosampler (Hewlett-Packard). The types of fused-silica guard column (5  $\text{m} \times 0.25 \text{ mm}$ ) tested were nonpolar (methylpolysiloxane coating, Supelco), intermediate-polar (phenyl/methylpolysiloxane coating, Supelco), and high-temperature silanized (Alltech). Columns were connected with a fused-silica capillary column connector (Supelco), and the junctions were sealed with polyimide resin (Supelco). The guard column with intermediate-polarity (5  $\text{m} \times 0.25 \text{ mm}$ , Supelco) was used to generate the data in the tables and figures listed in this paper.

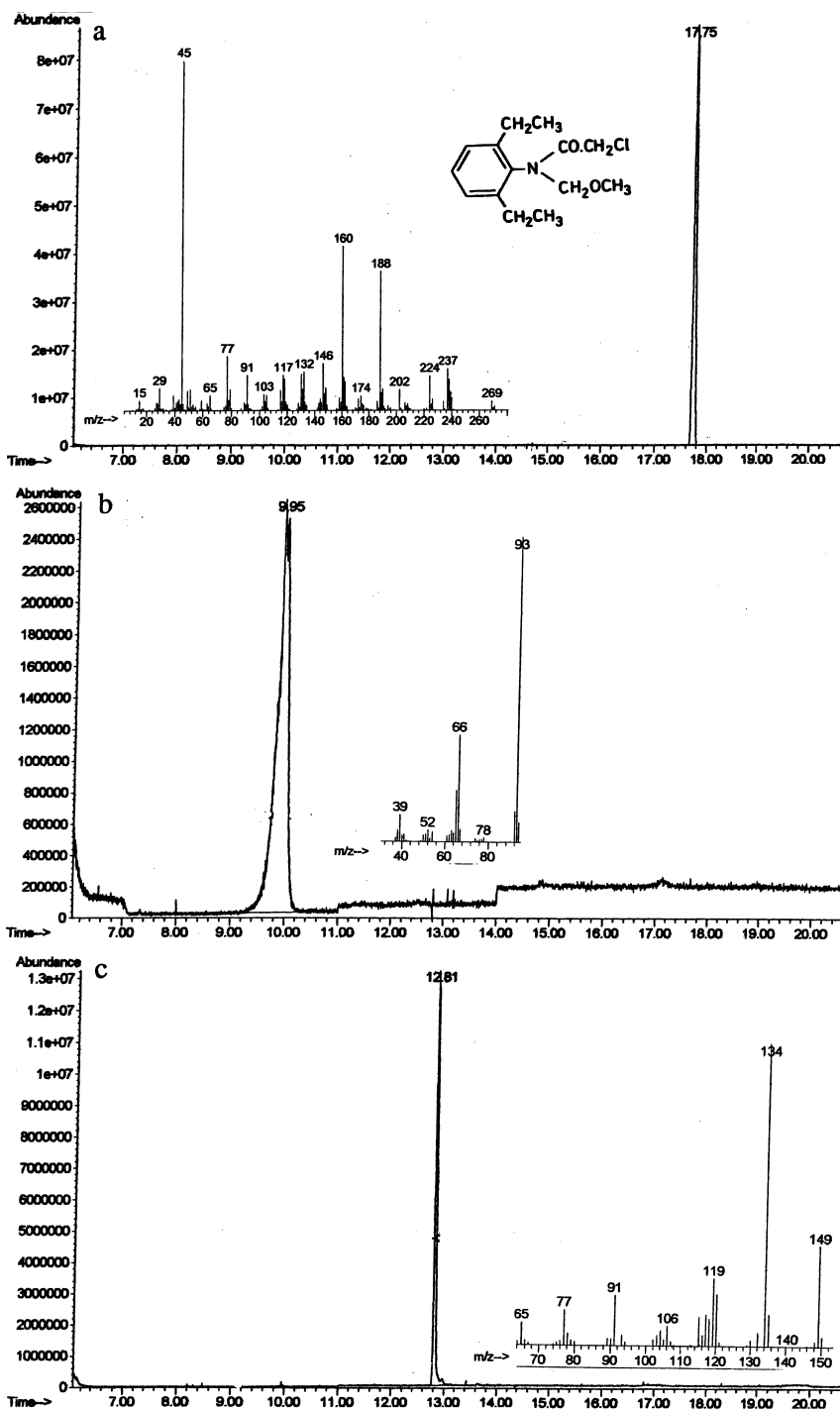


Fig. 1. GC-MS-Scan total ion current chromatograms and mass spectra of alachlor, its degradation products, and metolachlor in aqueous solution on the DB-5 column connected to the PTE-5 column in series: (a) alachlor (500 mg/l); (b) aniline (200 mg/l); (c) 2,6-diethylaniline (200 mg/l); (d) 2-chloro-2',6'-diethylacetanilide (200 mg/l); (e) metolachlor (200 mg/l); (f) aniline (i) (100 mg/l), 2,6-diethylaniline (ii) (100 mg/l), 2-chloro-2',6'-diethylacetanilide (iii) (100 mg/l), alachlor (iv) (200 mg/l) and metolachlor (v) (200 mg/l).

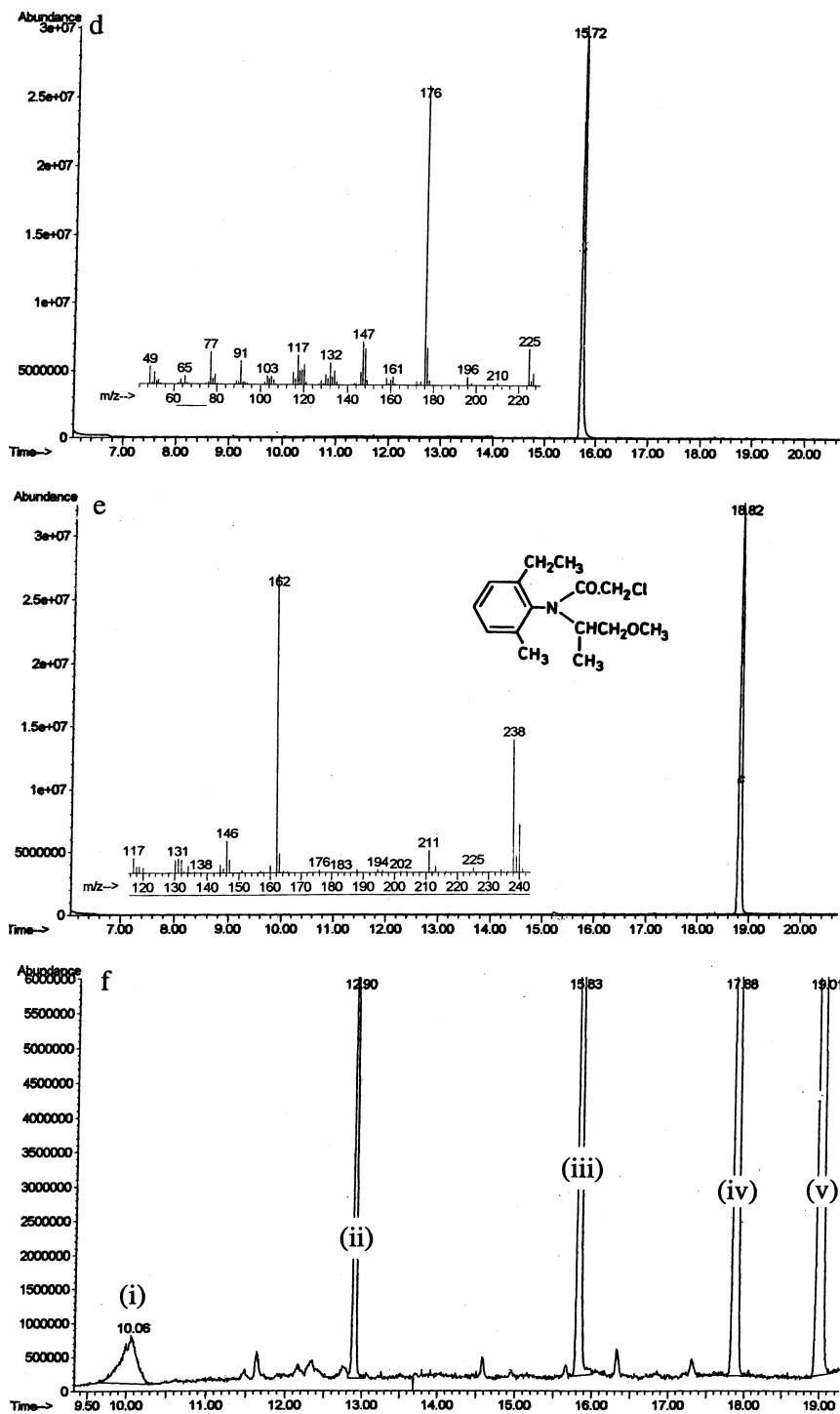


Fig. 1. (continued)

When a DB-5 column (Alltech Associates; stationary phase: 5% diphenyl- and 95% di-methylpolysiloxane; dimensions: 30 m×0.25 mm, 0.25 μm) was used as an analytical column, the conditions were: column head-pressure: 55 kPa; MS vacuum:  $5.3 \cdot 10^{-3}$  Pa; solvent delay: 2.5 min; linear speed of helium in column: 28 cm/s; and oven temperature: holding at 50°C for 1 min, then ramping at 20°C/min to 240°C and held at 240°C for 2 min.

When a DB-5 column and a PTE-5 column (Supelco), which had the same column parameters as the DB-5, were connected in series and used as analytical columns, the conditions were: column head-pressure: 138 kPa; MS vacuum:  $6 \cdot 10^{-3}$  Pa; solvent delay: 6 min; linear speed of helium in column: 30.5 cm/s; and oven temperature: holding at 50°C for 1 min, then ramping at 20°C/min to 240°C and held at 240°C for 10 min.

When an SPB608 column (Supelco; stationary phase: 35% diphenyl- and 65% dimethylpolysiloxane; dimensions: 30 m×0.25 mm, 0.25 μm) was used both for analytical column selection and for confirmation of the analysis, the conditions were: column head-pressure: 55 kPa; MS vacuum:  $5.6 \cdot 10^{-3}$  Pa; solvent delay: 2.65 min; linear speed of helium in the column: 29 cm/s; oven temperature program: same as for a DB-5 column.

### 3. Results and discussion

Since NaCl and other non-volatile components would be present in the aqueous samples to be analyzed, trapping of these non-volatile components in the injection port in order to protect the analytical column was an important aspect of the method development. The split/splitless injection techniques trap non-volatile components in the injection port better as compared with on-column injection [9]. Splitless injection was chosen instead of split injection to increase the sensitivity of the analysis [10]. Various injection port liners and fillings were also investigated in order to optimize trapping of non-volatile components when using direct aqueous injection (DAI).

Table 1 presents the effects of injection-port liners, fillings and initial temperature time (ITT) on the GC-MS-SIM response (peak height) for alachlor and its degradation products. The silanized-glass, reverse-cup liner (SRL) filled with Carbofrit (0.5 cm above the cup) can efficiently trap the non-volatile components from loading to the analytical column, thus allowing alachlor and its degradation products to be analyzed. In fact, the accumulated non-volatile components from samples were visible as solid powder on the Carbofrit when it was replaced for

Table 1

Effects of liners, fillings and initial temperature time (ITT) of oven temperature-programming on GC-MS-SIM response for alachlor and its degradation products<sup>a</sup>

| Liners and fillings                                   | ITT (min) | Peak height ( $\cdot 10^4$ ) |                     |                                   |          |
|---|-----------|------------------------------|---------------------|-----------------------------------|----------|
|   |           | Aniline                      | 2,6-Diethyl-aniline | 2-Chloro-2',6'-diethylacetanilide | Alachlor |
| SRL <sup>b</sup> , no fillings                        | 1         | 4.67                         | 19.2                | 11.6                              | 3.12     |
| 1 cm Carbofrit under SRL cup                          | 1         | 0.923                        | 8.78                | 10.8                              | 2.54     |
| 0.5 cm Carbofrit under SRL cup                        | 1         | 1.02                         | 8.22                | 16.6                              | 3.28     |
| 0.5 cm Carbofrit above SRL cup                        | 1         | 1.21                         | 8.93                | 12.4                              | 3.36     |
| 1 cm silanized glasswool under SRL cup                | 1         | 0.100                        | 2.21                | 5.27                              | 0        |
| 0.5 cm silanized glasswool under SRL cup              | 1         | 0                            | 3.12                | 3.21                              | 0.325    |
| 0.5 cm silanized glasswool above SRL cup              | 1         | 0                            | 2.58                | 6.22                              | 0.143    |
| 0.5 cm silanized glasswool above and under SRL cup    | 1         | 0.112                        | 2.61                | 5.68                              | 0.146    |
| Cylindric silanized-glass liner (inner diameter=4 mm) | 1         | 5.06                         | 21.1                | 13.9                              | 5.24     |
| 0.5 cm Carbofrit above SRL cup                        | 3         | 0.912                        | 8.86                | 16.6                              | 3.28     |
| 0.5 cm Carbofrit above SRL cup                        | 5         | 2.24                         | 11.9                | 10.9                              | 1.00     |

<sup>a</sup> The concentration for each compound was 6 mg/l in aqueous solution (pH 4). The DB-5 column and the PTE-5 column were connected in series and used as the analytical column.

<sup>b</sup> SRL: silanized-glass reverse-cup liner.

every 50 sample injections. Although the SRL with no fillings had a higher GC–MS response than the one with 0.5 cm Carbofrit, one could observe some non-volatiles (most probably NaCl) deposited on the ferrule after about 10 sample injections. There was concern that these could leak to the column. The liner with cylindric silanized-glass and inner diameter of 4 mm was even worse at trapping non-volatile components. The GC–MS response when there was a filling of 0.5 cm Carbofrit above the cup was similar to the response for fillings under the cup, but when it was above the cup it trapped non-volatiles better. The results indicate that the silanized glass wool in the injection-port liner degraded alachlor and its degradation products, but Carbofrit (0.5 cm above the cup) resulted in significantly less degradation.

When the ITT at 50°C was increased to 5 min, the GC–MS response increased for aniline but decreased for alachlor. The longer ITT focused the volatile components better but broadened the chromatographic bands of the less volatile ones. Since the GC–MS responses for the ITT of 1 min were close to those for 3 min, 1 min was chosen as optimal ITT. The GC–MS with DAI requires changing the Carbofrit every fifty samples for the analysis of alachlor and its degradation products in these aqueous samples containing NaCl. Otherwise, the GC–MS response might decrease gradually and finally disappear. Changing the injection temperature from 250 to 350°C and using guard columns of different types did not affect the GC–MS response.

The effects of column type and length on GC–MS chromatograms of alachlor, its degradation products and metolachlor can be seen in Table 2 and Figs.

1–3. When a 30 m PTE-5 column was connected to the 30 m DB-5 column in series, the aniline peak was more symmetric. Its peak on the 30 m DB-5 column is badly tailed. Aniline cannot form a peak on an SPB-608 column. However, the SPB-608 column can be used as a confirmation column for the analysis of alachlor, 2-chloro-2',6'-diethylaniline and 2,6-diethylaniline. Ballinova [11] analyzed alachlor by GC–electron-capture detection (ECD) with an SPB-35 fused-silica capillary column (Supelco; dimensions: 60 m×0.75 mm, 1 µm), which has a stationary phase similar to SPB608.

Fig. 1 presents the GC–MS-Scan total ion current chromatograms and mass spectra of alachlor, its degradation products, and metolachlor (internal standard) in aqueous solutions. The minimum limit of detection by the GC–MS-Scan is 50 mg/l for aniline and 5 mg/l for 2,6-diethyl aniline, 2-chloro-2',6'-diethylacetanilide and alachlor. Fig. 4 presents the GC–MS-SIM total ion current chromatograms of alachlor, its degradation products, and metolachlor in aqueous solutions. The minimum limit of detection (peak height 10-times as high as the noise level of the baseline) by the GC–MS-SIM is 1 mg/l for aniline and 0.05 mg/l for 2,6-diethyl aniline, 2-chloro-2',6'-diethylacetanilide and alachlor. The  $m/z$  of selected ions for GC–MS-SIM of alachlor, its degradation products, and metolachlor are listed in Table 3. The response for the SIM mode, in peak height, was linear for concentrations from 0.05 mg/l to 200 mg/l for alachlor, 2,6-diethylaniline and 2-chloro-2',6'-diethylaniline. The GC–MS-SIM response for aniline is linear for the range from 1 to 200 mg/l. The  $R^2$  values for the linear regression

Table 2

Effects of column type and length on GC–MS-Scan chromatographic capacity factor of alachlor, its degradation products and metolachlor<sup>a</sup>

| Column type<br>(0.25 mm×0.25 µm) | Length (m) | Capacity factor ( <i>k</i> ) |                    |                                   |          |                    |
|----------------------------------|------------|------------------------------|--------------------|-----------------------------------|----------|--------------------|
|                                  |            | Aniline                      | 2,6-Diethylaniline | 2-Chloro-2',6'-diethylacetanilide | Alachlor | Metolachlor (I.S.) |
| DB-5                             | 30         | 0.73 <sup>b</sup>            | 2.13               | 3.55                              | 4.14     | N.D.               |
| DB-5+PTE-5                       | 60         | 1.72                         | 2.51               | 3.33                              | 3.9      | 4.2                |
| SPB608                           | 30         | UD <sup>c</sup>              | 1.21 <sup>b</sup>  | 3.64                              | 6.17     | N.D.               |

Results from duplicate injections.

<sup>a</sup> The concentration for each compound was 60 mg/l in aqueous solution (pH 4).

<sup>b</sup> Peak tailed and distorted.

<sup>c</sup> Unable to detect.

I.S.=Internal standard.

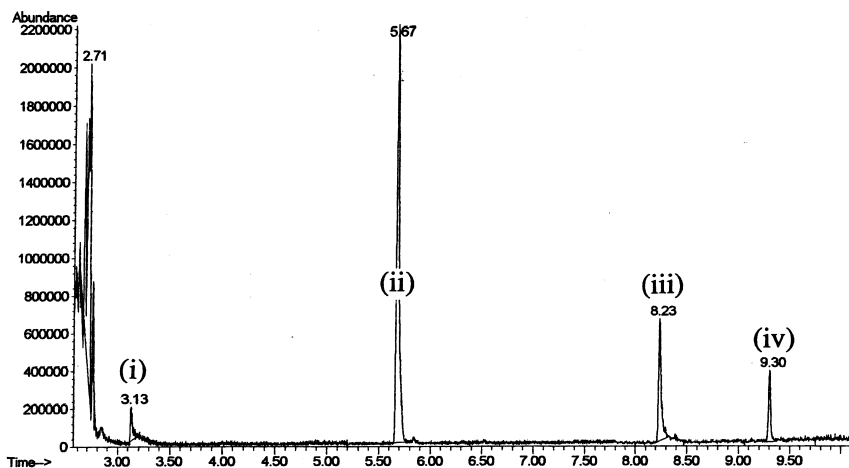


Fig. 2. GC-MS-Scan total ion current chromatograms of alachlor and its degradation products (200 mg/l) in aqueous solution on the DB-5 column: aniline (i), 2,6-diethylaniline (ii), 2-chloro-2',6'-diethylacetanilide (iii) and alachlor (iv).

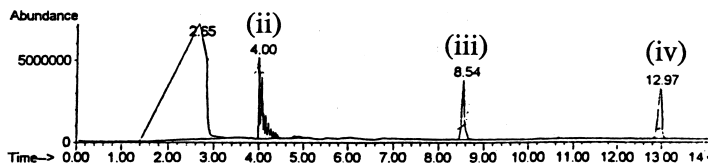


Fig. 3. GC-MS-Scan total ion current chromatograms of alachlor and its degradation products (200 mg/l) in aqueous solution on the SPB-608 column: 2,6-diethylaniline (ii), 2-chloro-2',6'-diethylacetanilide (iii) and alachlor (iv).

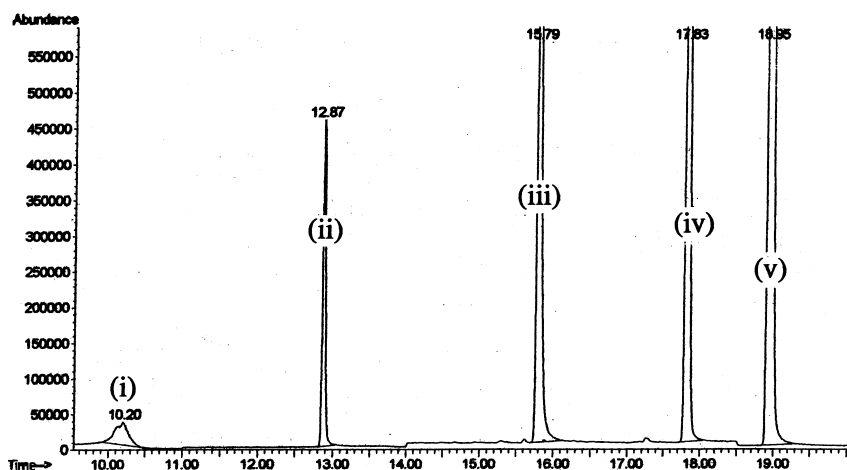


Fig. 4. GC-MS-SIM total ion current chromatograms of alachlor, its degradation products, and metolachlor in aqueous solution on the DB-5 column connected to the PTE-5 column in series: aniline (i) (10 mg/l), 2,6-diethylaniline (ii) (10 mg/l), 2-chloro-2',6'-diethylacetanilide (iii) (10 mg/l), alachlor (iv) (20 mg/l) and metolachlor (v) (20 mg/l).

Table 3

The characteristic ions on GC–MS with electronic ionization for alachlor, its degradation products, and metolachlor

| Compound                          | Molecular ion ( <i>m/z</i> ) | Base peak ( <i>m/z</i> ) | Ions for SIM       |
|-----------------------------------|------------------------------|--------------------------|--------------------|
| Alachlor                          | 269                          | 160                      | 146, 160, 188, 202 |
| 2-Chloro-2',6'-diethylacetanilide | 225                          | 176                      | 132, 147, 148, 176 |
| 2,6-Diethylaniline                | 149                          | 134                      | 134, 149           |
| Aniline                           | 93                           | 66                       | 93                 |
| Metolachlor                       | 283                          | 162                      | 146, 162, 211, 238 |

The concentration for each compound was 60 mg/l in aqueous solution (pH 4). The DB-5 column and the PTE-5 column were connected in series and used as the analytical column.

were greater than 0.99. The slopes of the calibration lines were:  $1.736 \cdot 10^{-4}$  for aniline,  $1.271 \cdot 10^{-5}$  for 2,6-diethylaniline,  $9.925 \cdot 10^{-6}$  for 2-chloro-2',6'-diethyl acetanilide, and  $1.424 \cdot 10^{-5}$  for alachlor. The variations for GC–MS–SIM chromatograms on the DB-5 column connected to the PTE-5 column in series, from eight consecutive repeated injections, were less than 0.2% for retention times, less than 5% for peak height, and less than 7% for peak area. These results suggest that peak height should be used for quantitation rather than peak area.

The aqueous samples requiring analysis will also contain iron salts and have pH values between 2 and 3. The iron salts need to be precipitated and filtered

before GC–MS analysis, and this is accomplished by increasing the pH of the sample. It was necessary to investigate the effect of pH on the GC–MS behavior of the pesticide compounds and determine if alachlor and its degradation products were adsorbed to the precipitates and/or the filter paper at the chosen pH. An experiment was conducted to understand these effects, and the results on the DB-5 column are presented in Table 4. Treated, deionized water samples containing iron salts were adjusted to a pH that caused the iron salts to precipitate. Half these samples were filtered. All were then spiked with analyte standards and adjusted to varying pH levels, with a final filtration before GC–MS analysis. As

Table 4

Effects of sample pH and filtration on GC–MS–SIM response (peak height,  $\cdot 10^5$ ) for alachlor and its degradation products (6 mg/l for each) with the DB-5 column

| Filtration before spiking | Filtration after pH adjustment | pH | 2,6-Diethylaniline | 2-Chloro-2',6'-diethylacetanilide | Alachlor |
|---------------------------|--------------------------------|----|--------------------|-----------------------------------|----------|
| Yes                       | No                             | 11 | 3.11               | 1.65                              | 1.06     |
| Yes                       | Yes                            | 11 | 2.8                | 1.02                              | 0.88     |
| No                        | Yes                            | 11 | 3.02               | 1.06                              | 0.822    |
| No                        | No                             | 11 | 2.78               | 0.968                             | 0.985    |
| Yes                       | Yes                            | 9  | 2.69               | 1.12                              | 1.08     |
| Yes                       | No                             | 9  | 3.13               | 1.21                              | 1.17     |
| No                        | Yes                            | 9  | 3.26               | 0.922                             | 0.819    |
| No                        | No                             | 9  | 2.97               | 1.25                              | 1.01     |
| Yes                       | Yes                            | 7  | 2.97               | 1.03                              | 0.876    |
| Yes                       | No                             | 7  | 3.07               | 1.01                              | 1.05     |
| No                        | Yes                            | 7  | 3.21               | 0.886                             | 0.875    |
| No                        | No                             | 7  | 2.88               | 0.948                             | 0.853    |
| Yes                       | Yes                            | 4  | 4.66               | 2.92                              | 1.44     |
| Yes                       | No                             | 4  | 4.49               | 2.68                              | 1.28     |
| No                        | Yes                            | 4  | 4.57               | 2.51                              | 1.38     |
| No                        | No                             | 4  | 4.63               | 2.73                              | 1.22     |
| Yes                       | Yes                            | 2  | 1.46               | 0.891                             | 0.49     |
| Yes                       | No                             | 2  | 1.27               | 0.8                               | 0.568    |
| No                        | Yes                            | 2  | 1.54               | 0.759                             | 0.479    |
| No                        | No                             | 2  | 1.49               | 0.89                              | 0.59     |



can be observed from the data, filtering before spiking did not affect peak height; thus, adsorption to the iron precipitates is not a concern at any pH. Other samples were prepared with iron salts, spiked with analyte standards, and then adjusted to pH values from 2 to 11. One sample at each pH was filtered. Since adsorption to iron precipitates was already ruled out, any decrease in peak height between filtered and non-filtered samples would be due to adsorption to the filter paper. Filtering after pH adjustment had no effect on peak height at any pH, so adsorption to the filter paper is not a problem.

The GC–MS response for a sample pH of 2 is obviously less than that for the other sample pH values. The compounds are either less stable or less volatile on the GC–MS at this low pH, and samples would need to be adjusted to higher pH before analysis. The GC–MS had the highest response for alachlor and its degradation products at pH of 4, but since the samples need to be adjusted to a pH of 7 to precipitate iron salts, the response at pH 7 is also important. Although the response is not as good at pH 7 as at pH 4, it is sensitive enough for these analyses. One could readjust the pH of samples to 7 after iron salts are precipitated and improve the limit of detection if required.

#### 4. Conclusions

The analytical method developed in this research is accurate, simple, fast and reproducible for analysis of alachlor and its degradation products. The main advantage of this method is the ability to inject aqueous samples directly into the GC–MS. The

minimum detection limit is 0.05 to 1 mg/l in the GC–MS–SIM mode and 5 to 50 mg/l in the GC–MS–Scan mode for alachlor and its degradation products, although it could be refined for lower limits of detection.

#### Acknowledgements

We appreciate the technical support from Michael Ames and additional support from David Saltmiras. We acknowledge and appreciate financial support from the USDA–CSREES Competitive Grant Program 9604166 and USDA Regional Research through Project W-45.

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