Analysis of the Herbicides Chlorsulfuron, Sulfometuron Methyl and Metsulfuron Methyl in Soil and Water

Fei-Wen Mao

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ANALYSIS OF THE HERBICIDES CHLORSULFURON, SULFOMETURON METHYL AND METSULFURON METHYL IN SOIL AND WATER

BY

FEI-WEN MAO

A thesis
submitted in partial fulfillment of the requirements for
the degree Master of Science
Major in Chemistry
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ANALYSIS OF THE HERBICIDES CHLORSULFURON, SULFOMETURON METHYL AND METSULFURON METHYL IN SOIL AND WATER

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Dr. Duane Matthees
Thesis Advisor Date

Dr. David Hilderbrand
Head, Department of Chemistry Date
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INTRODUCTION

Chlorsulfuron, sulfometuron methyl and metsulfuron methyl are new herbicides. They are effective in controlling weeds in different areas. Generally, they are applied at very low levels. Their decomposition rates vary with soil moisture, pH, etc. Since they may be used year after year and their decomposition rates are not very rapid in this climate, the persistence can be a problem with herbicide carryover harming crops in the following years. Therefore, there is a need for a method to measure very low levels of these herbicides in soil and water to ensure that the quantities which might be present are not sufficiently large to be injurious to agricultural crops.

The objective of my thesis research was to develop a method to determine herbicides chlorsulfuron, sulfometuron methyl and metsulfuron methyl in soil and water and estimate the detection limits with the instruments available in this school. Much of my work involved efforts to improve detection levels, and this involved a study of a number of extraction, cleanup and chromatography methods.
Chlorsulfuron, sulfometuron methyl and metsulfuron methyl are sulfonylureas of the following structures:

![Chlorsulfuron](image)

Chlorsulfuron

![Sulfometuron Methyl](image)

Sulfometuron Methyl

![Metsulfuron Methyl](image)

Metsulfuron Methyl

Chlorsulfuron, sulfometuron methyl and metsulfuron methyl are weak acids with pK values 3.8 (Zahnow, 1982), 5.7 (Zahnow, 1985) and 3.3 (Farm Chemicals Handbook, 1986)
respectively. They are soluble in alkaline solution as well as in some organic solvents.

Since 1970, several methods have been reported to determine sulfonylurea drugs in dose form or in serum, blood and urine.

Gas chromatography has been used for sulfonylurea drug analysis. The sulfonylureas must be derivatized to more volatile and stable compounds by reacting the polar NH groups with dimethyl sulfate, methyl iodide, or diazomethane. Derivatization with dimethyl sulfate has been reported by Kleber et al. (1977), Prescott and Redman (1972), Sabih and Sabih (1970) and Simmons et al. (1972). The application of diazomethane was described by Braselton et al. (1975, 1976, 1977), Midha et al. (1976), Taylor (1972), and Taylor et al. (1977). Later, Hartvig et al. (1980) found an extractive methylation method involving methyl iodide in methylene chloride.

The use of liquid chromatography with a normal or reverse-phase system for sulfonylurea drug analysis has been reported by Beyer (1972), Harzer (1980), Molins et al. (1975), Raghaw and Meyer (1981), Reinauer et al. (1980), Robertson et al. (1979), Syed et al. (1976), Uihlein and Sistovaris (1982), Waahlin-Boll and Melander (1979), and Weber (1976). However, It has been reported that it is not necessary to form derivatives in liquid chromatography since
sulfonylureas generally give adequate response with ultraviolet absorbance detectors.

However, the sensitivity requirements for sulfonylurea herbicides chlorsulfuron, sulfometuron methyl and metsulfuron methyl in soil and water are much greater than sulfonylurea drugs in dose form or in serum, blood and urine, and in addition, extraction procedures used for soil and water analyses liberate substantial quantities of impurities which interfere with the determination of these herbicides.

To obtain adequate sensitivity and also eliminate undesirable responses from coextracted materials, Zahnow (1982, 1985) developed a method to determine chlorsulfuron and sulfometuron methyl in soil and water by high-performance liquid chromatography (HPLC) with a photoconductivity detector. However, the photoconductivity detector is new and not yet widely available.
EXPERIMENTAL

Several types of extraction, cleanup and chromatography have been studied in this research to improve the detection limits. Soil used was silt loam from the Southeast Experimental Farm, Beresford, S.D. and water used was tap water.

Extraction Procedure -- Soil
1. Alkaline Solution Extraction

   Since chlorsulfuron, sulfometuron methyl and metsulfuron methyl are weak acids, they could be extracted by alkaline solution from soil. A 100-g sample was weighed into a 300-mL flask in which 100 mL of aqueous 0.1M Na₂CO₃ - 0.1M NaHCO₃ (pH=10.0) was added. The mixture was shaken vigorously by mechanical shaking for one hour. The resulting slurry was centrifuged in an attempt to get a clean separation. The supernatant liquid was decanted into a 100-mL beaker and the volume was measured to calculate the effective sample weight. The solvent recovery was defined as follows:

   \[
   \text{solvent recovery} = \frac{\text{volume of solvent found after filtration}}{\text{total volume of solvent used}}
   \]

   Unfortunately, even though centrifugation was used, it was still very difficult to separate the aqueous solution from soil, and also it was a time-consuming process.

2. Soxhlet Extraction
A 50-gram sample was weighed into a cellulose extraction thimble and refluxed with 200 mL methanol in a Soxhlet apparatus for four hours. Three replicates of chlorsulfuron in soil at a 180.5-ppb level were treated. The recovery and standard deviation are 41.8% and 4.3 respectively. At a 180.5-ppb level, the recovery by Soxhlet extraction was low. Since the recovery will be lower at a lower herbicide concentration, Soxhlet extraction is not a good extraction method for soil analysis.

3. Methanol-Water Extraction

A 100-g sample was weighed into a 300-mL flask in which a mixture of 90 mL methanol and 10 mL distilled water was added. The mixture was shaken briefly at room temperature and left overnight. It was shaken vigorously the next day by mechanical shaking for one hour and filtered through fluted filter paper into a 100-mL beaker. The amount of the filtrate was measured. Three replicates of metsulfuron methyl in soil at a 23.8-ppb level were treated. The recovery and standard deviation are given in Table 1.

4. Acetonitrile-Water Extraction

A solvent system of 80:20 acetonitrile-water could be used to extract chlorsulfuron, sulfometuron methyl and metsulfuron methyl from soil. The procedure for acetonitrile-water extraction was the same as for the methanol-water extraction procedure. Three replicates of
metsulfuron methyl in soil at a 23.8-ppb level were treated. The recovery and standard deviation are given in Table 1.

Acetonitrile-water was a good solvent to extract chlorsulfuron, sulfometuron methyl and metsulfuron methyl from soil since it gave good recoveries and it was easy to separate solvent from soil, so acetonitrile-water was used to extract chlorsulfuron, sulfometuron methyl and metsulfuron methyl from soil.

Table 1. Recoveries and Standard Deviations of Soil Extraction

<table>
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<tr>
<th>extraction</th>
<th>compound</th>
<th>ppb added</th>
<th>% recovery</th>
<th>SD</th>
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<tr>
<td>methanol-water</td>
<td>metsulfuron methyl</td>
<td>23.8</td>
<td>48.5</td>
<td>5.4</td>
</tr>
<tr>
<td>acetonitrile-water</td>
<td>metsulfuron methyl</td>
<td>23.8</td>
<td>90.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Cleanup Procedure -- Soil
1. SEP-PAK C\textsubscript{18} Cartridge

The SEP-PAK C\textsubscript{18} Cartridge (Waters Associates) could be used to eliminate the contaminants with higher or lower polarities than chlorsulfuron, sulfometuron methyl and metsulfuron methyl. The SEP-PAK C\textsubscript{18} cartridge sample preparation strategy includes three steps:
Step 1. Eliminate high polarity compounds by washing the SEP-PAK cartridge with a polar solvent. The polar solvent should be chosen so that the compound(s) of interest is retained on the cartridge.

Step 2. Remove the compound(s) of interest by washing the SEP-PAK cartridge with a less polar solvent. The cartridge eluent collected can now be brought to a known volume for final analysis.

Step 3. The non-polar compounds remaining on the cartridge can be eluted with a non-polar solvent, or discarded along with the spent cartridge.

Since water is more polar than methylene chloride, water and methylene chloride, respectively, were selected as a polar solvent in step 1 and a less polar solvent in step 2. The basic cleanup procedure of using the SEP-PAK C\textsubscript{18} cartridge was as follows:

(1) Evaporate acetonitrile by using a rotary evaporator
(2) Bring aqueous solution to a desired volume by adding distilled water
(3) Adjust pH to 3.0 by adding 3 N hydrochloric acid dropwise while measuring with a pH meter
(4) Put aqueous solution through the SEP-PAK C\textsubscript{18} cartridge and discard the effluent
(5) Add 2 mL methylene chloride to the cartridge and collect the effluent
(6) Evaporate methylene chloride to a desired final volume with a gentle nitrogen stream.

The SEP-PAK C\textsubscript{18} cartridge should be previously washed with 2 mL of methanol and 2 mL of distilled water. Although the SEP-PAK C\textsubscript{18} cartridge was easy and simple to use in this study, the background interference was a problem. The contaminants were not removed very well by using the SEP-PAK C\textsubscript{18} cartridge.

2. SEP-PAK Silica Cartridge

The SEP-PAK silica cartridge (Waters Associates) also can be used to remove the contaminants with higher or lower polarities than the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl. The SEP-PAK silica cartridge sample preparation strategy includes three steps:

Step 1. Eliminate low polarity compounds by washing the SEP-PAK cartridge with a non-polar solvent. The non-polar solvent should be chosen so that the compound(s) of interest is retained on the cartridge.

Step 2. Remove the compound(s) of interest by washing the SEP-PAK cartridge with a more polar solvent. The cartridge eluent collected can now be brought to a known volume for final analysis.

Step 3. The polar compounds remaining on the cartridge can be eluted with a still more polar solvent, or discarded along with the spent cartridge.
Methylene chloride was selected as a non-polar solvent in step 1, and 95:5 methylene chloride-methanol or 90:5:5 methylene chloride-methanol-acetic acid were selected as more polar solvents in step 2. The basic cleanup procedure of using the SEP-PAK silica cartridge was as follows:

1. Evaporate acetonitrile by rotary evaporation
2. Bring aqueous solution to a desired volume by adding distilled water
3. Adjust pH to 3.0 by adding 3 N hydrochloric acid dropwise while measuring with a pH meter
4. Partition aqueous solution with methylene chloride and discard water layers
5. Put methylene chloride through the SEP-PAK silica cartridge and discard the effluent
6. Add 2 mL of 95:5 methylene chloride-methanol or 2 mL of 90:5:5 methylene chloride-methanol-acetic acid to the cartridge and collect the effluent
7. Evaporate the effluent to a desired final volume with a gentle nitrogen stream

The SEP-PAK silica cartridge should be previously washed with 2 mL of hexane. The problem with the SEP-PAK silica cartridge in this study was to find the solvent which could wash the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl off with less background. If 95:5 methylene chloride-methanol was used, chlorsulfuron,
sulfometuron methyl and metsulfuron methyl were retained on the cartridge. Acetic acid is a strong solvent for silica and it can be used to increase the desorption of the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl from the silica. However, 90:5:5 methylene chloride-methanol-acetic acid washed lots of contaminants off, and the background was too much in the HPLC analysis.

3. Sephadex LH-20

Sephadex LH-20 is a type of packing for size-exclusion chromatography. It consists of small polymer particles containing a network of uniform pores into which solute and solvent molecules can diffuse. While in pores, molecules are effectively trapped and removed from the flow of the mobile phase. The average residence time in the pores depends upon the effective size of the analyte molecules. Molecules that are larger than the average pore size of packing are excluded and thus undergo essentially no retention; such species are the first to be eluted. Molecules having diameters that are significantly smaller than the pores can penetrate throughout the pore maze and are thus entrapped for the greatest time; these are last to be eluted. Between these two extremes are intermediate-size molecules whose average penetration into the pores of the packing depends upon their diameters. Within this group, fractionation occurs, which is directly related to the molecular size and to some extent molecular shape.
Size-exclusion chromatography can be used to separate the compounds chlorsulfuron, sulfometuron methyl or metsulfuron methyl and contaminants. The basic procedure of using Sephadex LH-20 to remove some background in this study was as follows:

(1) Evaporate acetonitrile by using a rotary evaporator

(2) Bring aqueous solution to a desired volume by adding distilled water

(3) Adjust pH to 3.0 by adding 3 N hydrochloric acid dropwise while measuring with a pH meter

(4) Partition aqueous solution with methylene chloride and discard water layers

(5) Evaporate methylene chloride to 1 mL

(6) Put methylene chloride solution on the top of the Sephadex LH-20 column

(7) Add methanol on the Sephadex LH-20 column and collect the portion which contains the compounds chlorsulfuron, sulfometuron methyl or metsulfuron methyl

(8) Evaporate methanol to a desired final volume with a gentle nitrogen stream

The Sephadex LH-20 column was 20 cm x 2 cm i.d. Before packing, Sephadex LH-20 should be mixed with methanol and allowed to swell for 10 minutes. The volume of methylene chloride put on the top of the Sephadex LH-20 column must be very small to avoid zone broadening. A standard solution was
run and analyzed by HPLC to decide which portion of methanol would contain the compounds chlorsulfuron, sulfometuron methyl or metsulfuron methyl before the soil extract was treated.

The Sephadex LH-20 column can be used to remove impurities with larger or smaller molecular sizes than the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl. The problem with the Sephadex LH-20 column cleanup was the background interference. Some contaminants were given off by Sephadex LH-20 itself.

4. Bio-Beads S-X8

Bio-Beads S-X8 is another kind of packing for size exclusion. A Bio-Beads S-X8 column was prepared by weighing 20 g Bio-Beads S-X8 and mixing it with tetrahydrofuran. Bio-Beads S-X8 was allowed to swell for 10 minutes in the tetrahydrofuran and was packed in a glass column. The Bio-Beads S-X8 column in this study was 20 cm x 2 cm i.d.

The procedure of using Bio-Beads S-X8 for cleanup was the same as that of using Sephadex LH-20 except that tetrahydrofuran was used instead of methanol.

The problem with the Bio-Beads S-X8 column cleanup was the background interference. A Bio-Beads S-X8 column was also used with chloroform cleanup together in this study, but the background problem still existed.

5. Dowex Macroporous Resin
Dowex macroporous resin is a strongly basic anion resin of ion-exchange. It contains some functional groups \(-N^+(CH_3)_3Cl^-\). Ion-exchange processes are based upon exchange equilibria between ions in solution and ions of like sign on the surface of an essentially insoluble, high-molecular-weight solid which is called resin. It can be used for analytical separation of ions.

When Dowex macroporous resin (stationary phase) is brought in contact with a solvent (mobile phase) containing an anion \(A^-\), an exchange equilibrium set up can be described by

$$\begin{align*} 
-N^+(CH_3)_3Cl^- + A^- \rightleftharpoons -N^+(CH_3)_3A^- + Cl^- 
\end{align*}$$

The equilibrium constant \(K_{ex}\) for the exchange reaction shown above takes the form

$$K_{ex} = \frac{[-N^+(CH_3)_3A^-][Cl^-]}{[-N^+(CH_3)_3Cl^-][A^-]} = \frac{[-N^+(CH_3)_3A^-]}{[A^-]} \frac{[Cl^-]}{[-N^+(CH_3)_3Cl^-]}$$

\(K_{ex}\) represents the affinity of the resin for the ion \(A^-\) relative to ion \(Cl^-\). Where \(K_{ex}\) is large, a strong tendency exists for the stationary phase to retain \(A^-\), where \(K_{ex}\) is small, \(A^-\) is not retained. In other words, \(K_{ex}\) reflects the
selectivity of ion-exchange resin. Different ions with different $K_{ex}$ on ion-exchange resin can be separated.

In general, the mobile phase in ion-exchange chromatography is an aqueous buffer solution, which may contain moderate amount of water miscible organic solvents for macroporous type of resin. The mobile phases of 50:50 water-acetone and water only were used in this study, but they were unsuccessful. By HPLC analysis, chlorsulfuron, sulfometuron methyl and metsulfuron methyl were not found. These compounds may be retained on the column of ion-exchange resin. Based on the report of Nelson (1973) that as the ionic strength of mobile phase is increased, the retention of most of the compounds is progressively reduced, 0.1 M sodium chloride aqueous solution was used. Unfortunately, analyte was not recovered.

6. Amberlite IRA-93 Resin

Amberlite IRA-93 Resin is a macroporous weakly basic anion exchange resin which is in the free base form. It contains some functional groups $-NR_2$.

Because Amberlite IRA-93 Resin is a weakly basic anion exchanger, the number of active sites available depends upon the pH of mobile phase. This is shown by the following equation

$$-NR_2 + H_2O \rightleftharpoons -NR_2H^+ + OH^-$$
The greater the pH, the fewer the active sites on the resin. Therefore, the greater the pH of the mobile phase, the less the compounds are retained. In this study, the solvents 50:50 water-acetone, water, 0.1 M sodium chloride aqueous solution and 0.01 M sodium hydroxide were used, but the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl were not found. They may have been retained on the ion exchange column or they may have decomposed.

7. Countercurrent Extraction

Liquid-liquid partition methods can be extended to the separation of solutes possessing only small differences in their partition coefficients by a method called countercurrent extraction. Countercurrent extraction is a multiple partition process with a large number of stages, entirely discontinuous and stepwise in nature. A fresh portion of solvent (upper phase or lower phase) is added, and the two liquid phases are equilibrated with each other.

In this study, the upper phase was 50 mL 50:50 methanol-water and the lower phase was 50 mL methylene chloride. Six 125 mL separatory funnels were used. From distribution of a standard, it was found that the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl were mainly in No. 6 upper phase, No. 6 lower phase and No.
lower phase. When this method was applied to the soil extract, the background could not be removed.

8. Charcoal

Charcoal is a nonpolar adsorbant in adsorption chromatography, and it retains nonpolar compounds when a polar solvent is used. In the alkaline solution, chlorsulfuron, sulfometuron methyl and metsulfuron methyl are in ionic forms, and it is assumed that they are not retained on charcoal. In this way, charcoal can be expected to separate nonpolar impurities from chlorsulfuron, sulfometuron methyl or metsulfuron methyl to some extent. The cleanup procedure could be as follows:

(1) Evaporate acetonitrile by using a rotary evaporator
(2) Bring aqueous solution to a desired volume by adding distilled water
(3) Adjust pH to 10.0 by adding 1 N sodium hydroxide dropwise while measuring with a pH meter
(4) Run this aqueous solution through a charcoal column
(5) Collect the effluent
(6) Adjust pH to 3.0 by adding 3 N hydrochloric acid dropwise while measuring with a pH meter
(7) Partition aqueous solution with methylene chloride and discard water layers
(8) Evaporate methylene chloride to a desired final volume
When the standards were applied to the column, however, these compounds were not detected by HPLC. These compounds must have been retained on the charcoal column or must have decomposed. The charcoal column used in this study was packed with water and was 15 cm X 1 cm i.d..

9. Chloroform Extraction or Methylene Chloride Extraction Followed by TLC

Since the pK values of chlorsulfuron, sulfometuron methyl and metsulfuron methyl are 3.8, 5.7 and 3.3 respectively, they remain in their ionic forms in the alkaline solution. Therefore, various organic solvents can be used to remove neutral impurities by liquid-liquid partitioning with alkaline solution whereas chlorsulfuron, sulfometuron methyl and metsulfuron methyl still stay in the alkaline solution. Figure 1 which was reported by Slates (1983) shows the effect of pH on the extraction of chlorsulfuron from aqueous solution into chloroform. At pH 10.0, the extraction of chlorsulfuron is nearly negligible. In other words, chlorsulfuron is not lost when the neutral impurities are removed.

However, the background was not sufficiently reduced by chloroform so that it did not interfere with the determination of chlorsulfuron, sulfometuron methyl and metsulfuron methyl. Thin layer chromatography (TLC) was applied to reduce the background further. TLC could separate
Figure 1. Effect of pH on the distribution of chlorsulfuron between equal volumes of chloroform and buffered aqueous phase
the impurities with different $R_f$ values from chlorsulfuron, sulfometuron methyl and metsulfuron methyl. It should be mentioned here that TLC only could not successfully remove the background. The cleanup procedure of chloroform extraction followed by TLC is described below.

The acetonitrile-water filtrate was transferred into a 250-mL round-bottom flask and acetonitrile was removed on a rotary evaporator. The resulting water solution was transferred to a 150-mL beaker using 20 mL of distilled water to rinse the round-bottom flask. The pH was adjusted to 10.0 by adding 1 N sodium hydroxide dropwise while measuring with a pH meter. The aqueous solution was then transferred to a 250-mL separatory funnel. It was washed 3 times with 50 mL portions of chloroform by shaking vigorously for 2 minutes.

The aqueous solution was drained from the separatory funnel into a 150-mL beaker, and pH was adjusted to 3.0 by adding 3 N hydrochloric acid dropwise while measuring with a pH meter. At this pH, the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl exist in the nonionic forms and can be extracted into various organic solvents. Methylene chloride was used in this study. The pH adjustment had to be performed carefully since the pH changed slowly. If the final pH is too low, there is a danger of chemical decomposition of these compounds which was mentioned
by Zahnow (1982), whereas if it is too high, extraction may be incomplete.

The aqueous solution was transferred back to the 250-mL separatory funnel. It was extracted 3 times with 100-mL portions of methylene chloride by shaking vigorously for 2 minutes. The methylene chloride layers were separated from the aqueous phase and were then combined in a 250-mL round-bottom flask. It was taken to dryness on a rotary evaporator. The residue was transferred to a graduated test tube and methylene chloride was evaporated to 0.5 mL with a gentle nitrogen stream. The extract was then taken for further cleanup by TLC. It was spotted on a silica gel plate (Uniplate, Silica Gel GF, 250 microns), and standards dissolved in acetonitrile were spotted on each side of the sample zone. The solvent system of 95:5 chloroform-acetic acid was employed in TLC. The chromatography tank should be washed and dried thoroughly and the volume of chloroform and acetic acid should be measured very carefully. Standards of chlorsulfuron, sulfometuron methyl and metsulfuron methyl appeared as dark spots under short-wave ultraviolet light were marked, and the zone which had the same $R_f$ value as the standards was scraped. It was believed that the scraped silica gel should contain chlorsulfuron, sulfometuron methyl or metsulfuron methyl. Then cotton was put in the tip of a disposable pipet and the scraped silica gel was put in the
pipet. Chlorsulfuron, sulfometuron methyl or metsulfuron methyl were desorbed from the silica gel with 3 mL of 50:50 methanol-methylene chloride, and the solvent was collected in a graduated test tube. The solution was brought to a desired final volume with a gentle nitrogen stream.

This cleanup method was more effective than others mentioned before. If 100 g soil was used and the final volume was brought to 1 mL or even 500 g soil was used and the final volume was brought to 1 mL, the background did not interfere with the determination of chlorsulfuron, sulfometuron methyl and metsulfuron methyl. Nevertheless, if 100 g soil was used and the final volume was brought to 0.1 mL, the background was too much. This was because the concentration of impurities in the 100 g and 0.1 mL case was twice as high as that in the 500 g and 1 mL case. How much soil should be used was dependent upon the concentration of the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl in spiked soil. In this study, 100 g soil and 500 g soil were used for 20-ppb level and 2-ppb level respectively, and the final volumes were 1 mL.

Methylene chloride was another possible solvent to be used to remove the neutral impurities. It showed nearly the same result as chloroform. Since chloroform is known to be a weak animal carcinogen, methylene chloride is a better
choice. Methylene chloride is also more easily evaporated and is less subject to decomposition on storage.

Cleanup Procedure -- Water

By liquid-liquid partitioning with alkaline solution, chloroform could be used to remove the neutral impurities from water. A 500-mL water sample was measured into a 1000-mL beaker and the pH of water was adjusted to 10.0 by adding 1 N sodium hydroxide dropwise while measuring with a pH meter. It was then put into a 1000-mL separatory funnel and washed twice with 100 mL portions of chloroform by shaking vigorously for 2 minutes. The chloroform layers were discarded. The accurate pH measurement is very important in this step to avoid losing compounds chlorosulfuron, sulfometuron methyl or metsulfuron methyl. Figure 1 shows the effect of pH on the extraction of chlorosulfuron from aqueous solution into chloroform. Care of pH control must be taken with this operation.

Based on the same idea as chloroform cleanup, methylene chloride was another possible solvent to remove the neutral impurities from water by partitioning with alkaline solution. The procedure of methylene chloride cleanup was the same as that of chloroform cleanup.

Both chloroform and methylene chloride removed some background so that chlorosulfuron, sulfometuron methyl and
metsulfuron methyl could be determined. However, methylene chloride is a safer solvent than chloroform.

Extraction Procedure -- Water

1. Methylene Chloride Extraction

After cleanup, water was transferred to a 1000-mL beaker. The pH of water was readjusted to 3.0 by adding concentrated sulfuric acid dropwise while measuring with a pH meter. The pH adjustment had to be performed carefully since the pH changed slowly. If the final pH is too low, there is a danger of chemical decomposition of these compounds, whereas if it is too high, extraction may be incomplete. Then water was transferred back to a 1000-mL separatory funnel. It was extracted twice with 100-mL portion of methylene chloride by shaking vigorously for 2 minutes. The methylene chloride layers were separated from the aqueous phase and combined in a 250-mL round-bottom flask. The combined methylene chloride layers were taken to dryness on a rotary evaporator. The residue was transferred to a graduated test tube with methylene chloride and evaporated to 0.2 mL with a gentle nitrogen stream.

2. Ether Extraction

Ether was also used to extract the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl from water. However, the recoveries obtained by using ether
were not as good as those using methylene chloride, as shown in Table 2.

Table 2. Recoveries of chlorsulfuron, sulfometuron methyl and metsulfuron methyl from water and standard deviation

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Compounds</th>
<th>ppb added</th>
<th>% recovery</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Chloride</td>
<td>Chlorsulfuron</td>
<td>1.1</td>
<td>90.6</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>Sulfometuron methyl</td>
<td>1.9</td>
<td>90.6</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>Metsulfuron methyl</td>
<td>2.4</td>
<td>84.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Ether</td>
<td>chlorsulfuron</td>
<td>1.1</td>
<td>69.3</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>Sulfometuron methyl</td>
<td>1.9</td>
<td>54.8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Metsulfuron methyl</td>
<td>2.4</td>
<td>43.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Because methylene chloride gave a better recovery, it was used to extract chlorsulfuron, sulfometuron methyl and metsulfuron methyl from water.

Chromatography

1. HPLC

The equipment used for HPLC in this study consisted of a Milton Roy minipump with Valco CU6 injector and Isco V4 absorbance detector. The relationship between the wavelength
of UV detector and peak height of 53.6 ng chlorsulfuron is shown in Figure 2. The wavelength must be selected to obtain adequate sensitivity and selectivity. The wavelength giving maximal response of 195 nm for chlorsulfuron was not used because of the excessive background interference. The wavelength of 220 nm was employed in this study since it provided reasonable sensitivity and selectivity. The sensitivity of the UV detector was set at 0.005 absorbance.

The mobile phase consisted of 40 parts by volume of acetonitrile and 60 parts of distilled water adjusted to pH 2.5 by adding 85% phosphoric acid. The acidified distilled water must be filtered by a microfilter, and acetonitrile must be HPLC grade. The mobile phase was pumped through the column at 1.1 mL/min.

The column was 25 cm x 4.6 mm i.d. (Alltech Associates, Deerfield, IL) with 5 μm C₈ reversed-phase packing.

A column of 25 cm x 4.6 mm i.d. with 10 μm C₁₈ reversed-phase packing (Alltech Associates, Deerfield, IL) has also been used in this study. Since the particle size of the C₁₈ column was larger than that of C₈ column, the separation by using C₁₈ column was not as good as that by using C₈ column.

Both C₈ and C₁₈ columns are nonpolar stationary phases in partition chromatography. Ion-pairing chromatography has extended the applications of partition separations to ionic
Figure 2. Relationship between wavelength of UV detector and peak height of 53.6 ng chlorsulfuron when the sensitivity of UV detector is set at 0.01 absorbance
compounds. When reversed-phase packings are used, the mobile phase in ion-pairing chromatography consists of an aqueous buffer containing an organic solvent such as methanol or acetonitrile and a counter ion of opposite charge to the analyte. Ion pairing chromatography has also been used in this study. The column in ion-pairing chromatography was C_{18} column, the mobile phase was 40:60 acetonitrile-water which contained counter ion CH$_3$(CH$_2$)$_{15}$(CH$_3$)$_3$N$^+$ at a pH of 6.4 or 40:60 acetonitrile-water which contained counter ion (C$_2$H$_5$)$_3$N$^+$H at a pH of 6.0. However, neither of them gave good results since they gave bad baselines and peaks of chlorsulfuron, sulfometuron methyl and metsulfuron methyl did not show up. The concentration of counter ion in ion-pairing chromatography is important. It may not be right in both cases.

2. GC

Gas chromatography (GC) is another possible method for determination. In GC, the sample is vaporized and injected onto the head of a chromatographic column. Obviously, chlorsulfuron, sulfometuron methyl and metsulfuron methyl must be derivatized to more volatile and stable compounds by reacting the polar NH groups with diazomethane CH$_2$N$_2$ for GC analysis. The resulting compounds contain nitrogen which can be detected by a thermionic detector. The thermionic detector
is selective for organic compounds containing phosphorus and nitrogen.

The working conditions of GC analysis were as follows:

**Instrument:** Varian 3700

**Detector:** Thermionic Detector

**Column 1:** 3% OV-101, 6' x 4 mm i.d.

**Column 2:** 1.5/1.95% OV-17/QF-1, 6'x 2 mm i.d.

**Mobile phase:** Nitrogen gas

**Detector temperature:** 320°C

**Injector temperature:** 230°C

**Oven temperature:** 200°C

However, GC was not as good as HPLC because of the background. There may be too much organic matter in the coextracted materials. A temperature program which gave better separation was used in an attempt to solve this problem. The program was:

**Initial temperature:** 150°C

Time (temperature stays on the initial temperature): 5 min

**Program rate:** 8°C/min

**Final temperature:** 250°C

Time (temperature stays on the final temperature): 0 min

Unfortunately, the background still interfered with the determination.
Standardization

The standard stock solutions of chlorsulfuron, sulfometuron methyl and metsulfuron methyl were prepared by weighing out 1.149 mg, 1.854 mg and 2.374 mg respectively, dissolving them in 10 mL acetonitrile, and diluting them to desired concentration with volumetric pipets. The working standards were used for chromatography as well as for the spiking of recovery samples.

Recovery Experiments

The determination of recovery could be made by comparing the standard and sample. The following formulas show the calculation of recovery.

\[
\text{recovery} = \frac{\text{ppm (found)}}{\text{ppm (added)}} \times 100 \%
\]

\[
\text{ppm (added)} = \frac{C_{\text{std}} \times V_{\text{add}}}{W_{\text{sample}}}
\]

where \( C_{\text{std}} \) = concentration of standard in \( \mu g/\mu L \)
\( V_{\text{add}} \) = volume added of standard in \( \mu L \)
\( W_{\text{sample}} \) = weight of sample in g

\[
\text{ppm (found)} = \frac{V_{\text{final}} \times W_{\text{std}} \times A_{\text{sample}}}{R \times W_{\text{sample}} \times V_{\text{inj}} \times A_{\text{std}}}
\]

Where \( V_{\text{final}} \) = final volume of sample in mL
W std = weight of standard injected in ng
A sample = Area of sample peak
R = solvent recovery after filtration
W sample = weight of sample in g
V inj = volume of sample injected in μL
A std = Area of standard peak

Since the standard could decompose or the solvent could evaporate when the standard was used for several months, the original concentration of standard may change. To avoid this error which would be involved in the calculation of recovery, the following method was used in this study (If appreciable decomposition or evaporation occurs, a new standard should be made). The same volume of old standard was used to spike soil or water and to make a new standard. The new standard was made by dissolving this volume of old standard in the acetonitrile and the total volume of them was brought to the same volume as the final volume of sample. When this new standard was used in chromatography, the recovery could be calculated by the following formula if the same volume of sample and standard were injected.

$$\text{recovery} = \frac{A_{\text{sample}}}{R \times A_{\text{std}}}$$
The height of peak can be used instead of the area of peak if the peaks are narrow and peak widths are the same. In this study, the height of peak was used.

In the recovery experiments, three replicates of each concentration were determined for each compound in soil and water. The extraction solvents used for soil analysis and water analysis were 80:20 acetonitrile-water and methylene chloride respectively. The cleanup methods used for soil analysis and water analysis were methylene chloride partitioning with alkaline solution followed by TLC and methylene chloride partitioning with alkaline solution respectively. Chlorsulfuron, sulfometuron methyl and metsulfuron methyl were detected by HPLC. The recoveries and standard deviations are given in Table 3.
Table 3. Recoveries of chlorsulfuron, sulfometuron methyl and metsulfuron methyl and standard deviations

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Compound</th>
<th>ppb added</th>
<th>% recovery</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Chlorsulfuron</td>
<td>11.5</td>
<td>77.5</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1</td>
<td>70.0</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Sulfometuron methyl</td>
<td>18.5</td>
<td>78.5</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9</td>
<td>76.1</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>Metsulfuron methyl</td>
<td>23.7</td>
<td>90.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>72.8</td>
<td>2.7</td>
</tr>
<tr>
<td>Water</td>
<td>Chlorsulfuron</td>
<td>1.1</td>
<td>90.6</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1</td>
<td>62.9</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Sulfometuron methyl</td>
<td>1.9</td>
<td>90.6</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>74.0</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>Metsulfuron methyl</td>
<td>2.4</td>
<td>84.0</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>60.0</td>
<td>5.9</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Several types of extraction, cleanup and chromatography have been studied in this research. Acetonitrile-water and methylene chloride were the best extraction solvents for soil analysis and water analysis respectively, whereas methylene chloride partitioning with alkaline solution followed by TLC and methylene chloride partitioning with alkaline solution were the best cleanup methods for soil analysis and water analysis respectively. These extraction solvents gave good recoveries and these cleanup methods removed some background so that the compounds chlorsulfuron, sulfometuron methyl and metsulfuron methyl could be determined by HPLC at 2.0-ppb level for soil and 0.2-ppb level for water. HPLC was better suited for analysis than GC, because there was too much background in GC.

As mentioned before, the detection limits for soil analysis and water analysis were 2.0-ppb and 0.2-ppb respectively. The limitations in the determination of chlorsulfuron, sulfometuron methyl and metsulfuron methyl in soil and water were:

1. Detector Sensitivity

The detector response curves of chlorsulfuron, sulfometuron methyl and metsulfuron methyl are shown in Figure 3 when the detector was operated at sensitivity 0.005 absorbance and wavelength 220 nm. The detector response was
Figure 3. UV detector responses for chlorsulfuron, sulfometuron methyl and metsulfuron methyl at sensitivity 0.005 absorbance and wavelength 220 nm.
linear over these particular weight ranges of these compounds. It also can be seen that the minimum detectable quantities of these compounds were about 2 ng and this amount produced a peak around 3 mm in height.

Figures 4, 5 and 6 are the chromatograms of chlorsulfuron, sulfometuron methyl and metsulfuron methyl obtained by injecting 10 μL of 0.0001149 mg/mL, 0.0001854 mg/mL and 0.0002374 mg/mL standards respectively. These chromatographic peaks displayed represent the detection limits of chlorsulfuron, sulfometuron methyl and metsulfuron methyl. Confirmation of the elution of these compounds was obtained by injection of the concentrated standards. Figures 7, 8 and 9 are the chromatograms of chlorsulfuron, sulfometuron methyl and metsulfuron methyl obtained by injecting 10 μL of 0.0011498 mg/mL, 0.001854 mg/mL and 0.002374 mg/mL standards respectively.

Theoretically, the detector sensitivity is not a limitation as long as the amount of soil or water is large enough. But the more soil or water is used, the more impurities will be involved. Because of the background interference, the detector sensitivity is a limitation in the determination of chlorsulfuron, sulfometuron methyl and metsulfuron methyl.
Figure 4. Chromatogram of chlorsulfuron with 0.0001149 mg/mL of concentration and 10 μL injection at sensitivity 0.005 absorbance and wavelength 220 nm

Figure 5. Chromatogram of sulfometuron methyl with 0.0001854 mg/mL of concentration and 10 μL injection at sensitivity 0.005 absorbance and wavelength 220 nm
Figure 6. Chromatogram of metsulfuron methyl with 0.0002374 mg/mL of concentration and 10 μL injection at sensitivity 0.005 absorbance and wavelength 220 nm.

Figure 7. Chromatogram of chlorsulfuron with 0.001149 mg/mL of concentration and 10 μL injection at sensitivity 0.005 absorbance and wavelength 220 nm.
Figure 8. Chromatogram of sulfometuron methyl with 0.001854 mg/mL of concentration and 10 µL injection at sensitivity 0.005 absorbance and wavelength 220 nm

Figure 9. Chromatogram of metsulfuron methyl with 0.002374 mg/mL of concentration and 10 µL injection at sensitivity 0.005 absorbance and wavelength 220 nm
2. Background

It seemed reasonable to use more soil or water or use a smaller final volume to improve the detection limits, but the impurities were concentrated in this way and they interfered with the determination. In this study, a 500 g sample of soil spiked with 1.9-ppb sulfometuron methyl was used. The final volume of sulfometuron methyl dissolved in methylene chloride was 1 ml, and 10 μL of this solution was injected. Since the solvent recovery of filtration and the recovery of extraction were about 50% and 76.1% respectively, the quantity of sulfometuron methyl injected into the column was 3.6 ng which was close to the minimum detectable quantity of sulfometuron methyl.

\[
1.9\text{ng/g} \times 500\text{g} \times 50\% \times 76.1\% \\
\frac{\text{-----------------------------} \times 10\text{μL} \times 10^{-3}\text{mL/μL}}{1 \text{mL}} = 3.6\text{ng}
\]

The detection limit could not be improved to 0.2-ppb level by reducing the final volume to 0.1 ml or using more soil, otherwise the background would be too high.

Since water has less background, sulfometuron methyl in water could be determined at 0.2-ppb level. A 500 g sample of water spiked with 0.2 ppb sulfometuron methyl was used, the final volume of sulfometuron methyl dissolved in methylene chloride was 0.2 ml, and 10 μL of this solution was injected. Since the recovery of extraction was 74.0%, the
quantity of sulfometuron methyl injected into the column was 3.7 ng.

\[ 0.2 \text{ng/g} \times 500 \text{g} \times 74.0\% \times 10 \mu\text{L} \times 10^{-3} \text{mL/\muL} = 3.7 \text{ng} \]

The lower level could not be reached because of the background interference. To improve the detection limits, one would need to develop a better cleanup method.

Also using a better wavelength is another possible choice to improve detection limits. The better wavelengths 195 nm and 205 nm have been tried, but the impurities which did not show up at 220 nm interfered with the determination.

The representative chromatograms for determination of chlorsulfuron, sulfometuron methyl and metsulfuron methyl in soil and water are shown in Figure 10 and 11 respectively, in which the detector was operated at sensitivity 0.005 absorbance and wavelength 220 nm.

Besides the silt loam from the Southeast Experimental Farm, Beresford, S. D., two other kinds of soil have also been used. However, the background was not removed and it interfered with the determination. It seems that different soil or water needs different cleanup method.
Figure 10. Representative chromatograms for determination of clorsulfuron, sulfometuron methyl and metsulfuron methyl in soil (A) Unspiked control (B) Control spiked at 1.149-ppb with clorsulfuron (C) Control spiked at 1.854-ppb with sulfometuron methyl (D) Control spiked at 2.374-ppb with metsulfuron methyl
Figure 11. Representative chromatograms for determination of chlorsulfuron, sulfometuron methyl and metsulfuron methyl in water (A) Unspiked control (B) control spiked at 0.1149-ppb with chlorsulfuron (C) Control spiked at 0.1854-ppb with sulfometuron methyl (D) Control spiked at 0.2374-ppb with metsulfuron methyl
CONCLUSION

The herbicides chlorsulfuron, sulfometuron methyl and metsulfuron methyl can be measured in soil and water. The detection limits are 2.0 ppb for soil and 0.2 ppb for water when a reversed phase HPLC separation is used with a UV detector.

80:20 acetonitrile-water and methylene chloride are the best solvents to extract chlorsulfuron, sulfometuron methyl and metsulfuron methyl from soil and water respectively. The best cleanup method for soil is methylene chloride partitioning with alkaline solution followed by TLC and that for water is methylene chloride partitioning with alkaline solution.

Background is a chief limitation in determination. Since water has less background than soil, the detection limit for water samples is ten times better than that for soil samples.
LITERATURE CITED


Simmons, D. L.; Ranz, R. J.; Picotte, P. J. Chromatogr. 1972, 71, 421.


