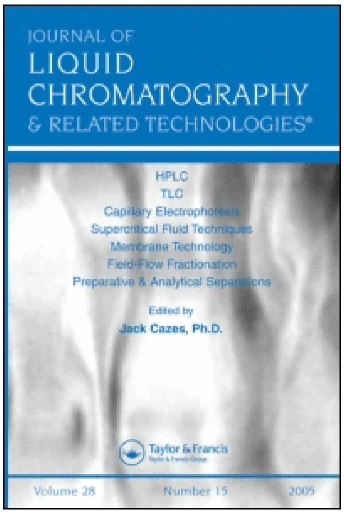

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Simultaneous Determination of Metsulfuron-Methyl, Chlorsulfuron and Bensulfuron-methyl in Various Formulations of Sulfonylurea Herbicides by HPLC-UV Detection

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SIMULTANEOUS DETERMINATION OF METSULFURON-METHYL, CHLORSULFURON AND BENSULFURON-METHYL IN VARIOUS FORMULATIONS OF SULFONYLUREA HERBICIDES BY HPLC-UV DETECTION

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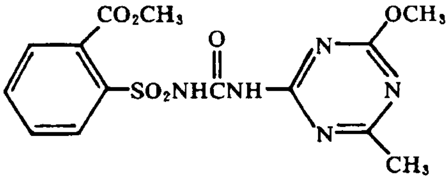
ABSTRACT

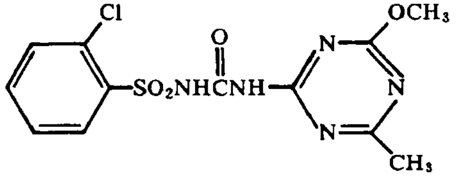
A reliable method is proposed for simultaneous determination of sulfonylureas in various formulation of commercial products by high performance liquid chromatography. HPLC was achieved on a reverse phase C_{18} column by isocratic elution using water (pH 4.3 with acetic acid) / methanol, and detection was by UV absorption at a wavelength of 254nm. This method has been applied for the quality control of sulfonylurea herbicides in the laboratories of agricultural chemical plants.

INTRODUCTION

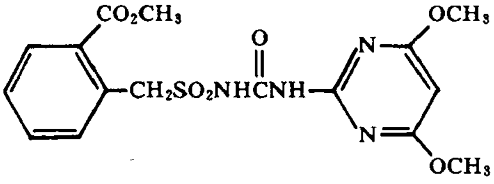
Sulfonylurea herbicides were first introduced by DuPont in 1982, and since then many new sulfonylureas have been developed for controlling broad spectrum broadleaf weeds. Of these herbicides, the most common are metsulfuron-methyl, chlorsulfuron and bensulfuron-methyl, which have the following structural formulae:



metsulfuron—methyl (M)



chlorsulfuron (C)



bensulfuron—methyl (B)

The first two were mainly applied to cereal grain fields, and the last one to rice grain fields. In recent years, these herbicides were widely used for their high herbicidal activity at extremely low application rate.[1-5] Methods developed for sulfonylureas analysis include bioassay,[6,7] enzyme immunoassay,[8,9] gas chromatography with derivatization,[10-15] high performance liquid chromatography-photoconductivity detection[16-20] and UV detection,[21-25] packed capillary liquid chromatography coupled with fast atom bombardment mass spectrometry.[26] But most of these aimed at determination of single sulfonylurea in a herbicide, or residue level of these sulfonylureas and their metabolites in soil, water, plant materials such as grain and straw after application.

These herbicides may exist as sulfonylurea or its sodium salt. The final products from manufacturers can be made into emulsifiable concentrate, wettable powder, or many other formulations. Metsulfuron-methyl, chlorsulfuron and bensulfuron-methyl can not only be used independently but also be used after mixing with each other, or with other kind of herbicides such as chlortoluron, benthiocarb, etc. according to practical needs. In order to control the product quality, therefore, it is essential to develop an efficient and accurate method for separation and quantitative analysis of sulfonylureas in various formulation of products. The results from the determination by high performance liquid chromatography with UV detection are satisfactory.

EXPERIMENTAL

Apparatus

The liquid chromatograph was a Varian LC 5060 with a UV-100 spectrophotometric detector, a VISTA-401 data system (Varian Instrument division, Walnut Creek, CA, U. S. A.), and a Yokogawa Hokuskin Electric Type 3066 pen recorder (Sino-Japanese No. 4 Meter Factory of Sichuan, Chongging, P. R. C.). Chromatograms were recorded by monitoring absorption at 254nm. The analytical column was a stainless steel tube (15cmX4mm I. D.) packed with E. Merck LiChrosorb RP-18, 5μm (Shanghai Institute of Materia Medica, The Chinese Academy of Sciences, Shanghai, P. R. C.). The column temperature was held at 30^0 C to maintain the solubility of sulfonylurea in the mobile phase.

Reagents and Materials

Methanol was HPLC grade (Institute for Fine Chemical Engineering of Huaiyin Plastic Product Factory, Huaiyin, P. R. C., WHO Collaborating Center for Research in Human Reproduction, Tianjing, P. R. C.). Glacical acetic acid was Analytical grade (Nanjing Chemical Reagent Factory, Nanjing, P. R. C.). Water was distilled twice. Methanol and water were purified with the Millipore Milli-Q system (Bedford, MA, U. S. A.). The pH value of aqueous phase was adjusted to 4.3 by using glacical acetic acid. The mobile phase was water (pH 4.3 with acetic acid) -methanol (45/55 V/V) at a flow rate of 1.0mL/min and the injection loop 10μl.

All samples and reference substances of sulfonylurea herbicide were obtained from various manufacturers. A mixture of metsulfuron-methyl, chlorsulfuron and bensulfuron-methyl reference substances was used as a standard solution to optimize the chromatographic separation and to allow the qualitative analysis of the chromatograms of the real samples. The stock solution of individual sulfonylurea was prepared by taking 40mg of each reference substance and dissolving it in 100mL of methanol in a volumetric flask and filtering it on cellulose 0.5μm filter (Millipore) by means of syringe before analysis. Standards at concentrations of 0.02~0.40mg/mL of sulfonylureas were prepared by serial dilutions of these stock solutions with methanol and used for calibration purpose.

Procedure

Technical powder - A 40mg of sample was weighed accurately into a 100mL volumetric flask. After adding methanol to mark and shaking vigorously, the sample solution was filtered through a membrane with 0.5μm micropore. 10μl of the filtered solution was injected to the reverse phase C_{18} column and analyzed under the conditions represented above.

Emulsifiable concentration - An accurately measured volume of liquid sample, equivalent to about 40mg of sulfonylurea, was transferred to a 100mL volumetric flask, diluted to volume with methanol, and mixed. This solution was filtered, injected to the column as described above.

Wettable powder - A 200mg of powder was weighed, transferred to a 100mL volumetric flask, mixed with about 80mL of methanol, and sonicated for about 15min . After bringing to volume with methanol and mixing, the resulting slurry was centrifuged for 10 min and the supernatant liquid was also analyzed as described above.

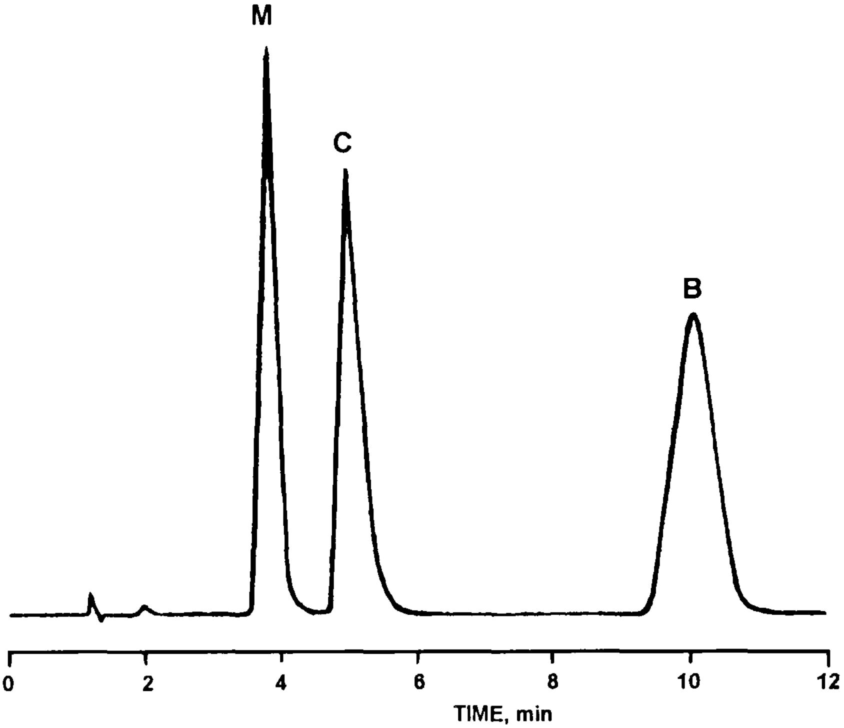


Figure 1. Chromatogram of standard solution containing metsulfuron-methyl (M), chlorsulfuron (C) and bensulfuron-methyl (B).

RESULTS AND DISCUSSION

Chromatogram and Calibration Curve

An HPLC chromatogram demonstrating the separation of three sulfonylureas is shown in Figure 1. As can be seen the order of the retention is metsulfuron-methyl < chlorsulfuron < bensulfuron-methyl, and the resolution is satisfactory for every mixture component. This figure will be the reference chromatogram for the subsequent HPLC analysis of sulfonylurea herbicides produced by various manufacturers.

The quantitation was based on a calibration by series of dilution from primary standard. Linear regression analyses of the relationship between peak area versus amount of standard were carried out within the range 0.20~4.00 μg

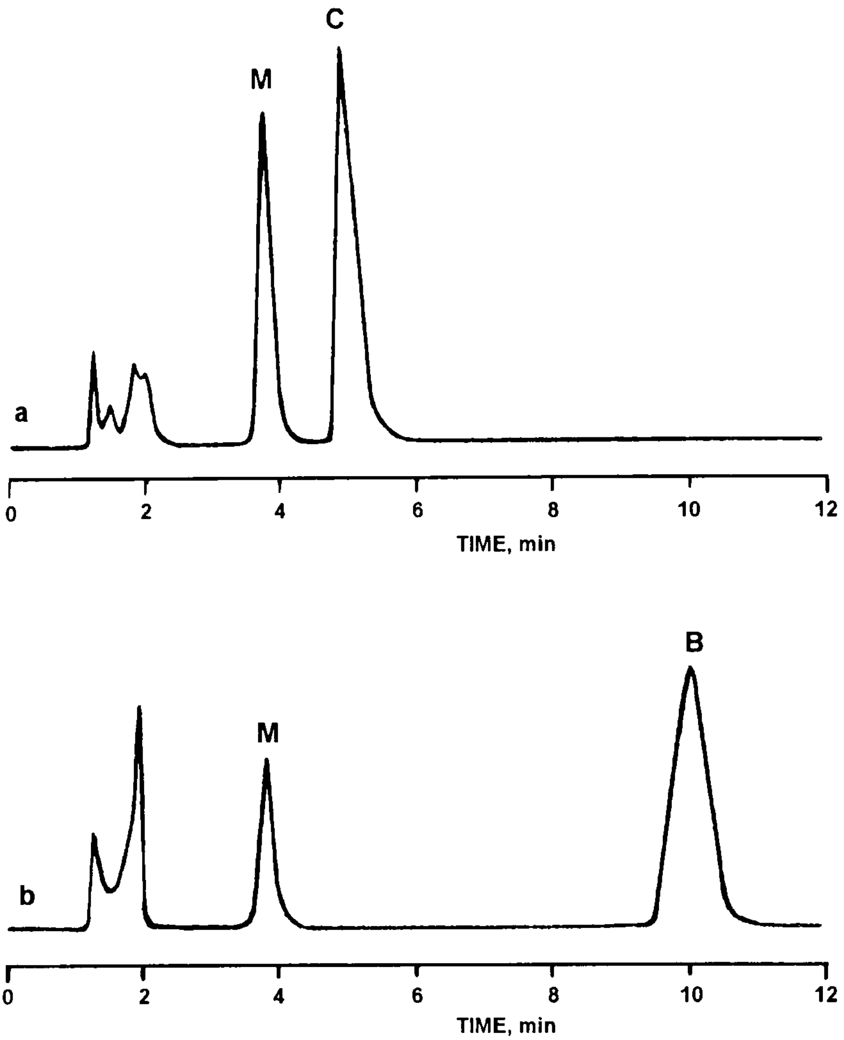


Figure 2. Chromatograms of commercial sulfonylurea herbicide products. a) Maicaoke wettable powder; b) Xindeli wettable powder (for abbreviations see legend to Figure 1).

in 10μl injection volume. The regression equations were y=1760328.30x-593.38 for metsulfuron-methyl, y=1885869.50x+1408.63 for chlorsulfuron, and y=1550125.00x+300.36 for bensulfuron-methyl, with correlation coefficients of 0.9999, 0.9999 and 0.9996 respectively, where y equaled peak area and x equaled final standard concentration (mg/mL). The limits of detection (S/N=2) is 1.2ng, 1.5ng and 2.0ng for metsulfuron-methyl, chlorsulfuron, bensulfuron-methyl respectively.

Analysis of Commercial Samples

Typical chromatograms for metsulfuron-methyl, chlorsulfuron and bensulfuron-methyl in various sulfonylurea herbicides are given in Figure 2. In the present study, 10 random samples of commercial products were analyzed for three sulfonylureas content. The results are summarized in Table 1.

Table 1

Analysis of Sulfonylureas in Products from Several Manufacturers

			------------ $\bar{X}$ ± SD ------------		
Herbicide products	**Form**	**Unit**	**Metsulfuron-methyl**	**Chlorsulfuron**	**Bensulfuron-methyl**
Jiahuanglong	TP	g/100g	95.53±0.47		
Luhuanglong				97.19±0.44	
Jiahuanglong	EC	g/100mL	2.50±0.07		
Luhuanglong				3.53±0.10	
Jiahuanglong	WP	g/100g	10.24±0.21		
Luhuanglong				19.98±0.39	
Luhuanglong (Sodium salt)				70.52±0.58 (Sodium salt)	
Maicaoke			6.32±0.17	8.68±0.17	
Maicaoling			4.47±0.14	15.27±0.32	
Xindeli			1.81±0.12		8.08±0.18

TP - Technical powder
EC - Emulsifiable concentrate
WP - Wettable powder
$\bar{X}$ - Mean value of 6 determinations
SD - Standard deviation

Table 2

Recovery of Sulfonylureas from Emulsifiable Concentrate and Wettable Powder

Form	Unit	Initial account $\overline{X} \pm SD$	Amount added	Amount determined $\overline{X} \pm SD$	Recovery %
			(Metsulfuron-methyl)		
EC	g/100mL	2.50	0.50	3.02±0.09	100.7
			3.00	5.56±0.12	101.1
WP	g/100g	10.24	2.00	12.08±0.17	98.7
			10.00	20.15±0.46	99.6
			(Chlorsulfuron)		
EC	g/100mL	3.53	0.50	4.05±0.11	100.5
			3.00	6.50±0.11	99.5
WP	g/100g	19.98	2.00	21.74±0.48	98.9
			10.00	29.55±0.52	98.6
			(Bensulfuron-methyl)		
WP		8.08	2.00	10.01±0.15	99.3
			10.00	17.85±0.28	98.7

For abbreviations see legend to Table 1

In order to estimate the efficiency of the recovery the samples were spiked with sulfonylureas. The initial amounts of metsulfuron-methyl, chlorsulfuron and bensulfuron-methyl were previously determined using standard curves. Table 2 shows the amounts added of sulfonylureas to these samples and the percentage recoveries.

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