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LIQUID AND GAS CHROMATOGRAPHY DETERMINATION OF SULFONYLUREA HERBICIDES METSULFURON METHYL AND ETHAMETSULFURON METHYL IN WATER AND SOIL SAMPLES.

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Liquid and Gas Chromatographic Determination of Sulfonylurea Herbicides Metsulfuron Methyl and Ethametsulfuron Methyl in Water and Soil Samples

by

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MANAGEMENT PERSPECTIVE

The use of sulfonylurea herbicides to control target weeds is increasing in recent years. Because of their persistence and high phytotoxicity, transport of these herbicides by air and water may have adverse effects to non-target plants, such as impairment in crop production or causing death of plants. Metsulfuron methyl and ethametsulfuron methyl are two of these herbicides registered for use in the prairies and other parts of Canada. Analytical methods are developed in this work to measure residues of these compounds in water and sediment samples collected in spraying experiments. This study is part of a collaborative research project with the National Wildlife Research Centre of the Canadian Wildlife Service.

SOMMAIRE À L'INTENTION DE LA DIRECTION

L'utilisation d'herbicides à base de sulfonylurée pour éliminer certaines mauvaises herbes est en progression ces dernières années. Vu leur persistance et leur phytotoxicité élevée, le transport de ces herbicides par l'air et l'eau peut avoir des effets nocifs sur des plantes non ciblées, et notamment entraîner des baisses de production chez les plantes cultivées ou l'élimination d'autres plantes. Le metsulfuron-méthyle et l'éthametsulfuron-méthyle sont deux de ces herbicides homologués pour utilisation dans les Prairies et dans d'autres régions du Canada. On a mis au point ici des méthodes analytiques pour déterminer la quantité de résidus de ces composés dans les échantillons d'eau et de sédiments, prélevés lors d'expériences de pulvérisation. La présente étude fait partie d'un projet de recherche conjoint avec le Centre national de la recherche faunique du Service canadien de la faune.

ABSTRACT

Methods for the determination of sulfonylurea herbicides such as metsulfuron methyl (MM) and ethametsulfuron methyl (EM) in water and soil samples are described. For water samples, a solid phase extraction (SPE) technique using Empore-C_{18} disks was adopted for the preconcentration of the herbicides. The extracts were analyzed by HPLC using a diode array detector (DAD). With the detector operating at 225 nm (signal) and 450 nm (reference), a detection limit of 0.1 μg/L was achieved. Recoveries at the detection limit were 92 ± 4 % and 94 ± 5 % for MM and EM, respectively. Alternatively, the herbicide extracts could be analyzed by GC/MS after derivatization with pentafluoropropionic anhydride. For soil samples, the herbicides were first extracted by a $KHCO_3$ solution, then the acidified extract was processed by the same SPE procedure. At the detection limit of 0.1 μg/g using HPLC and DAD, the recoveries were 88 ± 6 % and 105 ± 7 % for MM and EM, respectively. Direct extraction of the ureas from soil with methanol-modified supercritical carbon dioxide produced lower recoveries than the base extraction procedure, particularly for EM.

RÉSUMÉ

On décrit les méthodes pour le dosage d'herbicides à base de sulfonylurée, comme le metsulfuron-méthyle (MM) et l'éthametsulfuron-méthyle (EM) dans des échantillons d'eau et de sol. Dans le cas des échantillons d'eau, une technique d'extraction en phase solide (EPS) utilisant des disques Empore-C_{18} a été adoptée pour la préconcentration des herbicides. Les extraits ont été analysés par CLHP avec un détecteur à réseau de diodes (DRD). Le détecteur étant réglé à 225 nm (signal) et à 450 nm (référence), on a obtenu un seuil de détection de 0,1 mg/L. À ce seuil, les taux de récupération étaient de 92 ± 4 % et 94 ± 5 % respectivement pour MM et EM. On a également analysé les extraits d'herbicide par CG/SM après obtention d'un dérivé avec l'anhydride pentafluoropropionique. Dans le cas des échantillons de sol, les herbicides ont d'abord été extraits à l'aide d'une solution de $KHCO_3$, les extraits étant ensuite acidifiés par la même méthode (SPE). Au seuil de détection de 0,1 mg/g, avec CLHP et DRD, les taux de récupération étaient de 88 ± 6 % et 105 ± 7 % respectivement pour MM et EM. L'extraction directe des urées à partir du sol à l'aide de dioxyde de carbone supercritique modifié au méthanol a donné des taux de récupération inférieurs à ceux de la méthode d'extraction de base, particulièrement pour EM.

INTRODUCTION

Metsulfuron methyl (MM, 2-(((4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl)aminosulfonyl)benzoic acid methyl ester, Ally, Escort) and ethametsulfuron methyl (EM, 2-(((4-ethoxy-6-methylamino-1,3,5-triazin-2-yl)aminocarbonyl)aminosulfonyl)benzoic acid methyl ester, Muster) are sulfonylureas that are also known as acetolactase synthase (ALS) inhibitor herbicides. They restrict the growth of susceptible plant species by inhibiting the ALS (also known as AHAS or acetohydroxacid synthase) which initiates the synthesis of some essential amino acids [1]. These herbicides are very efficient in weed control at low application rates, selective to plants and are relatively non-toxic to mammals. A brief description of their properties is given in Table 1 and their chemical structures are depicted in Figure 1. In 1990, 3931 kg (active ingredient, ai) of Ally had been applied to western Canada as a post-emergent herbicide to control target weeds for several plant species such as wheat and barley. At an application rate of 4.5 g-ai/ha, an estimated 900,000 ha of farmland were sprayed. Muster has been used on canola. These two sulfonylureas have recently become of environmental concern since they are persistent. Transport of these ALS inhibitors both atmospherically and by surface water may have an adverse effect on non-target plants because of their high phytotoxicity [2,3].

Several analytical methods have been developed for MM and a few other sulfonylurea herbicides. For water samples, preconcentration was usually carried out by solid phase extraction (SPE) with C_{18} disks or columns [4-9], although solvent extraction [10,11] and liquid membrane extraction [9] have also been reported. Because of their high

water solubility at neutral and higher pHs, sulfonylureas in soil samples were first extracted by an aqueous base, followed by SPE or solvent partitioning of the acidified extract [6,7,12-14]. Recently, successful supercritical fluid extraction (SFE) of MM and chlorsulfuron in soil has also been demonstrated [15].

Analysis of the parent herbicides can be conveniently done by high performance liquid chromatography (HPLC) [4,9] or capillary electrophoresis (CE) [8] using a variable wavelength ultraviolet detector. Enhanced selectivity and sensitivity can be achieved when a mass spectrometer is used for detection in the above cases [14,16]. Alternatively, gas chromatographic methods employing electron capture, nitrogen specific, and mass spectrometric detectors developed for the analysis of the thermal or hydrolytic degradation products, or the derivatives of these herbicides could also be used [5-7,10,11]. With the exceptions of the mono- and di-methyl derivatives of chlorsulfuron and MM [10,17], chemical derivatization often resulted in cleavage of the herbicide molecule [5,6,11]. In that case, method specificity was lost as different sulfonylureas with the same triazine moiety (or sulfonamide moiety, depending on the derivatization procedure) would not be distinguishable after derivatization. As of late 1996, no method had been reported for the determination of EM in either water or soil sample.

In this report, a method using solid phase extraction with HPLC and GC/MS analysis for the determination of MM and EM in water is described. For soil samples, aqueous base extraction and supercritical fluid extraction methods for the isolation of these herbicides are also evaluated..

EXPERIMENTAL

Chemicals and reagents

Analytical grade standards of MM (purity 99.0%) and EM (purity 97.4%) were obtained as gifts from E.I. DuPont de Nemours & Company, Experimental Station, Wilmington, Delaware 19880-0402, USA. Pentafluoropropionic acid anhydride (PFPA) was purchased either from Pierce or Aldrich. Anhydrous potassium bicarbonate was a product of Fisher Scientific. All solvents were in distilled-in-glass grade available from Burdick and Jackson. SFE grade carbon dioxide without a helium head pressure was obtained from Air Products (Nepean, Canada). Empore solid phase extraction disks, 47 mm diameter with Bakerbond octadecyl (C_{18})-bonded silica, were distributed by J.T. Baker.

Solid Phase Extraction (SPE) of MM and EM from water samples

Extraction of water samples was carried out with 47 mm diameter C_{18} Empore disks. Prior to extraction, the disk was soaked in ethyl acetate in a covered Petri dish for at least 15 min. After the disk was thoroughly wetted, it was then placed in the extractor for further conditioning. Under partial vacuum, 15 mL of ethyl acetate, in three aliquots, was slowly passed before the disk was dried for 2 min. Conditioning of the C_{18} disk was continued by slow passage of 10 mL of methanol followed by 10 mL of pH 2 water (twice). Care was taken not to dry the disk at this stage. The acidified water sample (1 L, pH 2) was passed through the Empore disk at a flow rate of ca. 50 mL/min by adjusting the vacuum. The sample container was rinsed twice with 5 mL of pH 2 water, and the rinsing was also extracted by the disk. Strong vacuum was then applied to

the extraction system, for two min, to remove any water trapped in the disk holder. The herbicides on the disk were removed by first soaking the disk with 5 mL of ethyl acetate without vacuum and then by slow elution of the solvent with a gentle vacuum. This elution process was repeated once. The combined ethyl acetate eluate was dried over an anhydrous sodium sulfate column prepared in a Pasteur pipet.

Extraction of MM and EM from soil samples

A suspension of 100 mL of 0.1 M $KHCO_3$ and 10 g (dry weight) of a soil sample in an Erlenmeyer flask was vigorously mixed for 15 min in a sonicator bath at 30°C. The supernatant was decanted into another container and the extraction was repeated twice with 100 mL aliquots of the base. After filtration through a layer of Celite, the combined extract was acidified to pH 2 with HCl. MM and EM in this aqueous sample were then extracted by the above procedure using an Empore disk.

Supercritical carbon dioxide extraction of MM and EM from soil samples

All SFE was carried out with a Hewlett-Packard 7680T extraction module. To prepare for extraction, the bottom end of a thimble was closed with a cap. A piece of filter paper previously cut to the diameter of the thimble was placed on top of the cap. Then 200 mg of Celite followed by 1.0 g of the soil sample were weighed into the thimble. 500 μL of a modifier such as methanol was spiked to the sample as a static modifier. After the void volume was filled with a piece of glass rod of a suitable length and diameter, the thimble was sealed tightly with another cap. Extraction was carried out at 60°C with a CO_2 density of 0.86 g/mL (ca. 5000 psi) for 25 min (10 min static and 15 min

dynamic) at a flow rate of 2 mL/min. The nozzle temperature was kept at 50°C throughout the extraction and the ODS trap was set at 10°C during extraction and 50°C during elution. The herbicides adsorbed on the ODS trap was eluted with two 1.5 mL aliquots of acetonitrile. The combined extract was analyzed by HPLC.

HPLC analysis

Sample extracts of MM and EM for HPLC analysis were evaporated just to dryness and the residue redissolved in one mL of acetonitrile. The concentrated extracts were analyzed by a Hewlett-Packard 1100 series HPLC system consisted of a quaternary pump, an autosampler, a thermostatted column compartment, a diode-array detector, and a workstation with dedicated software. A 3.5 μm Zorbax SB-Phenyl column, 4.6 mm ID x 15 cm, and a column temperature of 40°C were used. The mobile phase was 35% acetonitrile (A) and 65% water (B, with 10 mM KH_2PO_4 and adjusted to pH 3 with phosphoric acid). The flow rate was 2.0 mL/min and 10 μL injections were made. The diode-array detector was set at 225 nm (signal) and 450 nm (reference).

Derivatization of MM and EM with PFPA

For GC/MS analysis of MM and EM, the ethyl acetate extract above was concentrated to ca. 50 μL in a screw-cap conical centrifuge tube. To this extract, 50 μL of PFPA and 500 μL of iso-octane were added. A piece of Teflon-lined disk was installed under the cap to ensure a tight seal before the mixture was heated at 85°C in a tube heater for 90 min. After the reaction mixture was cooled, the internal standard, 25 μL of a 10

μg/mL anthracene-d_{10} solution, was added and the volume was adjusted to 1.0 mL prior to GC/MS analysis.

GC/MS analysis

Mass spectra for the PFPA derivatives of MM and EM were obtained by full scan GC/MS from m/z 40 to 500 using a Hewlett-Packard (HP) 5890 Series II gas chromatograph and a HP 5972A Mass Selective Detector. A 30 m x 0.25 mm i.d. x 0.25 μm HP-5-MS column was used and 1 μL sample injection was made by a HP 7673 autosampler. The GC oven temperature program was 70°C initial (held for 1 min), increased to 160°C at a rate of 30°C/min, and then to 275°C at a rate of 10°C/min. Injection port and detector interface temperatures were 250 and 280°C, respectively. Carrier gas (helium) linear velocity was held constant at 38.4 cm/sec by means of an electronic pressure controller. The electron energy and electron multiplier voltage were 70 eV and 400 V above autotune value, respectively.

For the quantification of the herbicides in sample extracts, the detector was operated in selected ion monitoring (SIM) mode. Characteristic ions of m/z 286, 256, 119 (for MM-PFP derivative), m/z 286, 270 (for EM-PFP derivative), and m/z 188 (for anthracene-d_{10} internal standard), were monitored.

RESULTS AND DISCUSSION

SPE of MM and EM in water samples

As reported by other workers on sulfonylureas [7], conditioning of the Empore disks played an important role in the recovery of these herbicides from water samples. In our earlier work, it was found that, in addition to regular conditioning, the recoveries of MM and EM could be improved by 10 to 30% by soaking the disks thoroughly in ethyl acetate for at least 15 minutes. Because of the high water solubility of MM and EM at pH higher than 5 (Table 1), water samples were acidified to pH 2 before extraction in order to reduce their solubility. While further reduction of the sample pH to 1 did not produce higher recovery of MM and EM, extraction at pH higher than 2 generated lower results for the herbicides, especially MM. Sample flow rates from 15 to 70 mL/min during extraction had no observable impact on the recoveries. Therefore, a flow rate of 50 mL/min was chosen for shorter extraction time. Elution of the herbicides was conveniently carried out by 10 mL of ethyl acetate; incomplete desorption of MM and EM would occur if a smaller volume of solvent was used.

HPLC analysis of sulfonylurea herbicides

Several reports for the HPLC analysis of sulfonylurea herbicides such as MM and chlorsulfuron have been published [4,9]. In those cases, reversed phase columns with either C_{18} or C_8 packing materials were used. Earlier, the separation of five sulfonylurea herbicides (nicosulfuron, thifensulfuron methyl, MM, chlorsulfuron , and rimriduron) using a 5 μm Zorbax SB-Phenyl column in less than five minutes has been demonstrated [18]. With the same column, MM and EM were efficiently resolved in four minutes.

Since the two herbicides have maximum uv absorbance in the range from 220 to 230 nm and nearly no absorbance at 450 nm, the diode array detector was set at 225 nm for signal and 450 nm for reference. With the detector operating at these wavelengths, an injection of 0.25 ng of each herbicide standard produced a peak with a signal-to-noise ratio better than 10:1.

Formation of pentafluoropropionyl (PFP) derivatives of MM and EM

In a heated injection port of a gas chromatograph, chlorsulfuron, a sulfonylurea herbicide, decomposed thermally to form 2-amino-4-methoxy-6-methyl-1,3,5-triazine and 2-chlorobenzenesulfonamide [19]. The formation of the sulfonamides and the accompanying triazine by the hydrolytic cleavage of chlorsulfuron and MM at elevated temperatures and in the presence of an aqueous acid has also been reported [11].

At elevated temperatures, MM and EM reacted with PFPA to produce a single derivative for each herbicide. Prior to the formation of the PFP derivatives, MM and EM underwent an acid-catalyzed hydrolysis to form the sulfonamide and the triazines as proposed in Figure 1. The primary amino groups of the triazines reacted readily with PFPA to yield the respective PFP derivatives. Since EM has a secondary amino group on the triazine moiety, this active hydrogen was further replaced by a second PFP group. Under the reaction conditions used in this work, only the di-PFP substituted derivative of EM was produced as the final product. No reaction between the sulfonamide and PFPA was observed. As the present derivatization scheme would produce the same derivative for sulfonylureas with the same triazine moiety, this approach would not be applicable to the simultaneous determination of herbicides such as chlorsulfuron and MM.

GC/MS properties of PFP derivatives of MM and EM

The electron-impact mass spectra for the PFP derivatives of MM and EM are shown in Figure 2 and 3, respectively. In the case of MM, intense molecular ion (M^+) at m/z 286 was observed, confirming the formation of a pentafluoropropionyl derivative. Other characteristic ions at m/z 256 (base peak), corresponding to $[M\text{-}OCH_3+H]^+$ and at m/z 167, corresponding to $[M\text{-}C_2F_5]^+$, were also observed. While the molecular ion for the EM derivative (m/z 461) was much weaker, it confirmed the formation of a di-PFP substituted molecule. The EM derivative also exhibited characteristic ions at m/z 417 $[M\text{-}OC_2H_5+H]^+$, 342 $[M\text{-}C_2F_5]^+$, 314 $[M\text{-}COC_2F_5]^+$, 286 $[M\text{-}C_2H_5\text{-}COC_2F_5+H]^+$, as well as 270 $[M\text{-}OC_2H_5\text{-}COC_2F_5+H]^+$. In addition, intense ions at m/z 119 and 69 corresponding to $C_2F_5^+$ and CF_3^+, respectively, were also observed for both herbicide derivatives.

The PFP derivatives of MM and EM are relatively volatile, as indicated by the fact that they both have shorter retention times than the internal standard anthracene-d_{10}. Using SIM, an injection of 20 pg of each derivative produced a signal-to-noise ratio of 10:1.

Optimization of derivatization conditions

While the perfluoroacylation of MM and EM proceeded readily, the derivatization procedure must be carefully optimized in order to obtain the best results. First, in order to ensure complete reaction, the derivatization was carried out at a relatively high temperature (85°C in this case). Reactions at 60 and 75°C would result in either lower yields for both derivatives; these results were consistent with the previous

observation that acid hydrolysis of MM was facilitated at higher temperatures [11]. Lower yields for both derivatives were also observed from reactions at temperatures much higher than 85°C due to losses of the reagent PFPA (b.p. 69°C) and the relatively volatile products.

The dependence of yields of the PFP derivatives on reaction time was studied. At a temperature of 85°C, MM reacted readily with PFPA. The reaction was nearly complete for this urea after 30 min and there was no significant increase in yield after 60, 90 and 120 min of reaction. On the other hand, a longer reaction time was required for EM to form the disubstituted product. The derivatization was only 72 and 89% complete after 30 and 60 min of reaction time, respectively. However, similar yields of the EM-PFP derivative were observed at 90 and 120 min. From these results, a 90-min reaction time was chosen for the derivatization of MM and EM.

Stability of the PFP derivatives

The PFP derivatives of MM and EM were stable for at least two weeks at -20°C. However, the detector response for these derivatives progressively diminished after a day or two, even if the extract was stored at -20°C. Later, it was observed that the response and chromatography could be restored by the addition of a small amount (e.g. 5 μL per mL of extract) of PFPA to the sample. It was therefore concluded that the drop in response was due to the gradual loss of the volatile PFPA in the derivatized sample extracts or standard solutions rather than the decomposition of the derivatives. Presumably, adsorption of these derivatives on active sites in the chromatographic system occurred in the absence of PFPA, causing tailing peaks and eventually complete

disappearance of the derivatives in the chromatogram. For the same reason, a base wash step originally designed for the removal of excess PFPA reagent after derivatization was eliminated.

Recovery of MM and EM from spiked water and soil samples

In order to evaluate the performance of the analytical methods, spiked water samples were extracted by Empore disks and the extracts were either analyzed by HPLC for the parent compounds or by GC/MS after derivatization. As shown in Table 2, the precision and accuracy of the HPLC procedure were excellent at spiking levels of 1 and 0.1 μg/L. The recoveries of MM and EM were all above 90% and the relative standard deviations were less than 6%. However, the precision for the GC procedure was worse at a spiking level of 0.1 μg/L because of the extra derivatization steps.

This SPE technique was also applied to the determination of MM and EM in soil samples after they were first extracted by an aqueous base. At spiking levels of 1 and 0.1 μg/g, results with good precision and accuracy were obtained (Table 3). Due to the interference arising from the coextractives in soil, application of this method to samples at spiking levels below 0.1 μg/g was unsuccessful. Attempts of direct and more selective extraction of these herbicides from soil with supercritical carbon dioxide have also been made. Modifiers such as water, methanol, trifluoroacetic acid and combinations of them have been used in these extractions with various degrees of success. At a spiking level of 1 μg/g, the recoveries (ranging from 27 to 86% and from 16 to 61% for MM and EM, respectively) were in general lower than those obtained by the aqueous base

extraction technique. The modifier producing the highest recoveries of these herbicides was methanol.

Applications and conclusions

A solid phase extraction procedure has been validated for the isolation of the sulfonylurea herbicides MM and EM from water at sub μg/L levels. Using a diode array detector and a HPLC system, a detection limit of 0.1 μg/L was achieved for the herbicides. This detection limit was similar to those reported in the GC methods previously developed for MM in water samples. While the estimated detection limit for our GC method was lower (0.02 μg/L), the procedure was more tedious and the overall precision was lower. As the herbicide molecules were cleaved after derivatization, some specificity was lost. Bearing in mind these limitations, the GC/MS procedure should only be applied when LC/MS instrumentation is unavailable and the detection of MM and EM at less than 0.1 μg/L is required.

The same procedure could also be used for soil samples after the ureas were first extracted by an aqueous base. This base extraction technique was chosen since it produced higher recoveries of MM and EM than supercritical carbon dioxide extraction. Again, a detection limit of 0.1μg/g was achieved by the HPLC/DAD procedure. For lower detection limits, LC/MS is recommended.

The HPLC procedure has been applied to the direct analysis of MM in tank mixtures in greenhouse spraying experiments and the results were very close to the designed values. The base extraction and derivatization GC procedure has also been applied to the determination of MM on deposition cards in spraying experiments.

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Table 1. Selected properties of metsulfuron methyl (MM) and ethametsulfuron methyl (EM).

	MM	EM
CAS No.	74223-64-6	97780-06-08
Molecular formula	$C_{14}H_{15}N_5O_6S$	$C_{15}H_{18}N_6O_6S$
Molecular weight	381.37	410.40
pK_a	3.5	4.64
Solubility in water	270 mg/L at pH 5 9500 mg/L at pH 7	1.7 mg/L at pH 5 50 mg/L at pH 7 410 mg/L at pH 9
Trade names	Ally, Escort	Muster
Label application rate (g-ai/ha)	4.5	22.5

Table 2. % Recoveries and relative standard deviations (in parentheses) of MM and EM from 1 L of spiked water samples by HPLC/diode array detector and GC/MS methods.

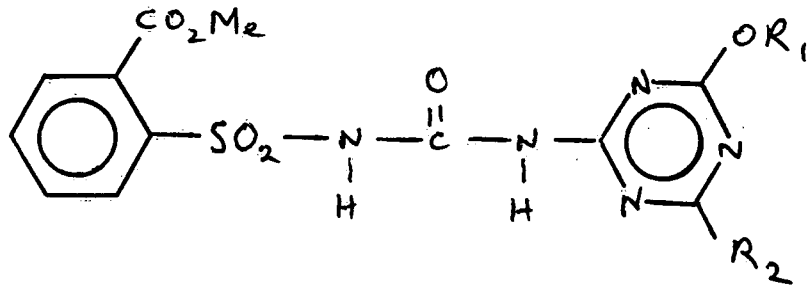
	HPLC	HPLC	GC
Spiking level, µg/L	1.0	0.1	0.1
No. of replicates	6	7	6
MM	90 (6)	92 (4)	88 (12)
EM	91 (4)	94 (5)	105 (9)

Table 3. % Recoveries and relative standard deviations (in parentheses) of MM and EM from spiked soil samples by base extarction/SPE and HPLC method.

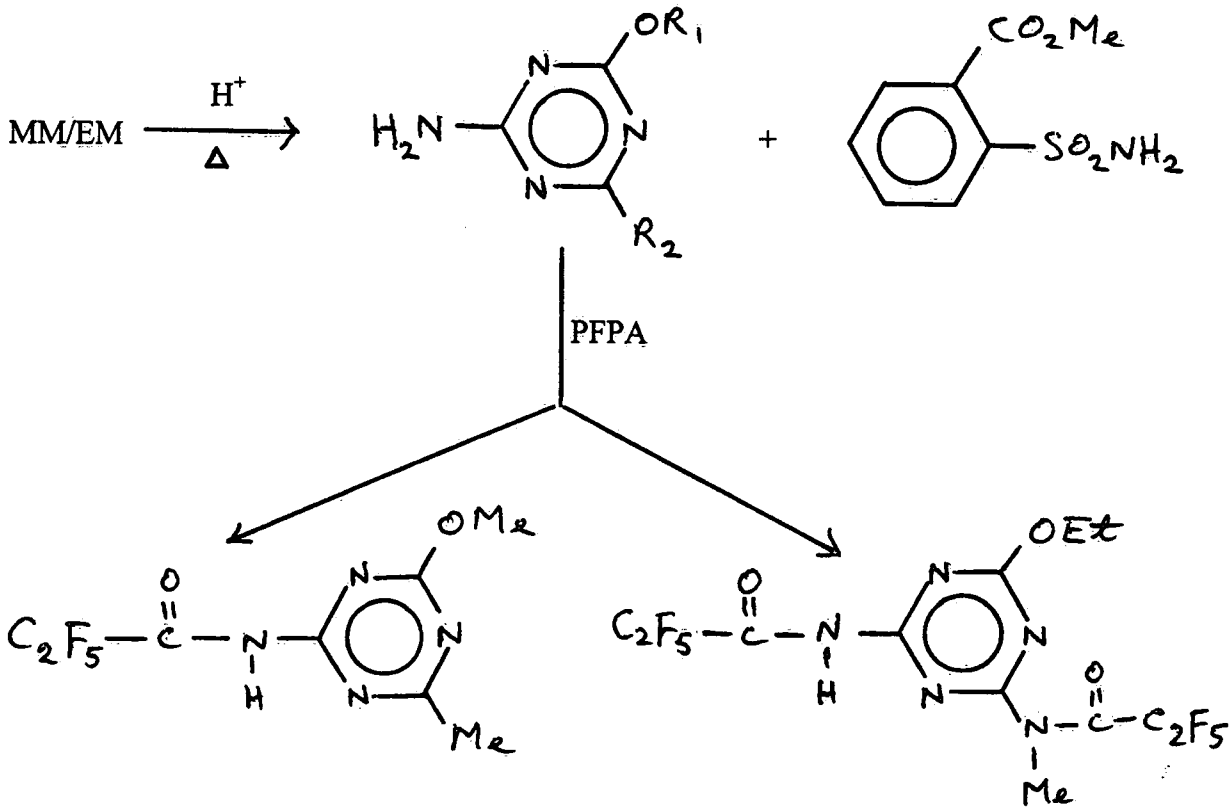
Spiking level, µg/g	1.0	0.1
No. of replicates	4	4
MM	96 (5)	99 (6)
EM	93 (5)	103 (7)

List of Figures:

Figure 1



MM : R_1=R_2=Me
EM : R_1=Et, R_2=NHMe



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EM-PFP
MW=461

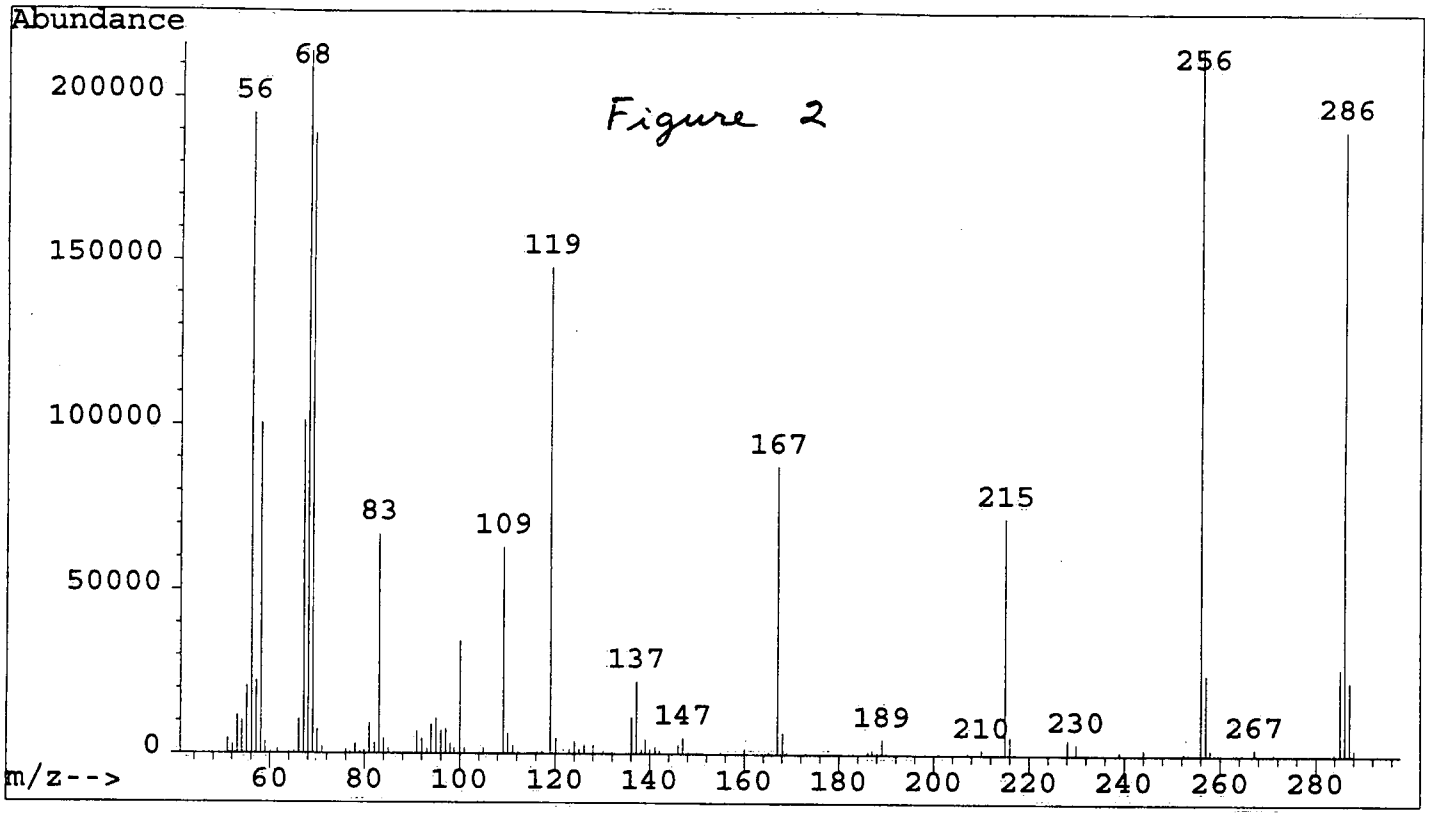

Figure 2

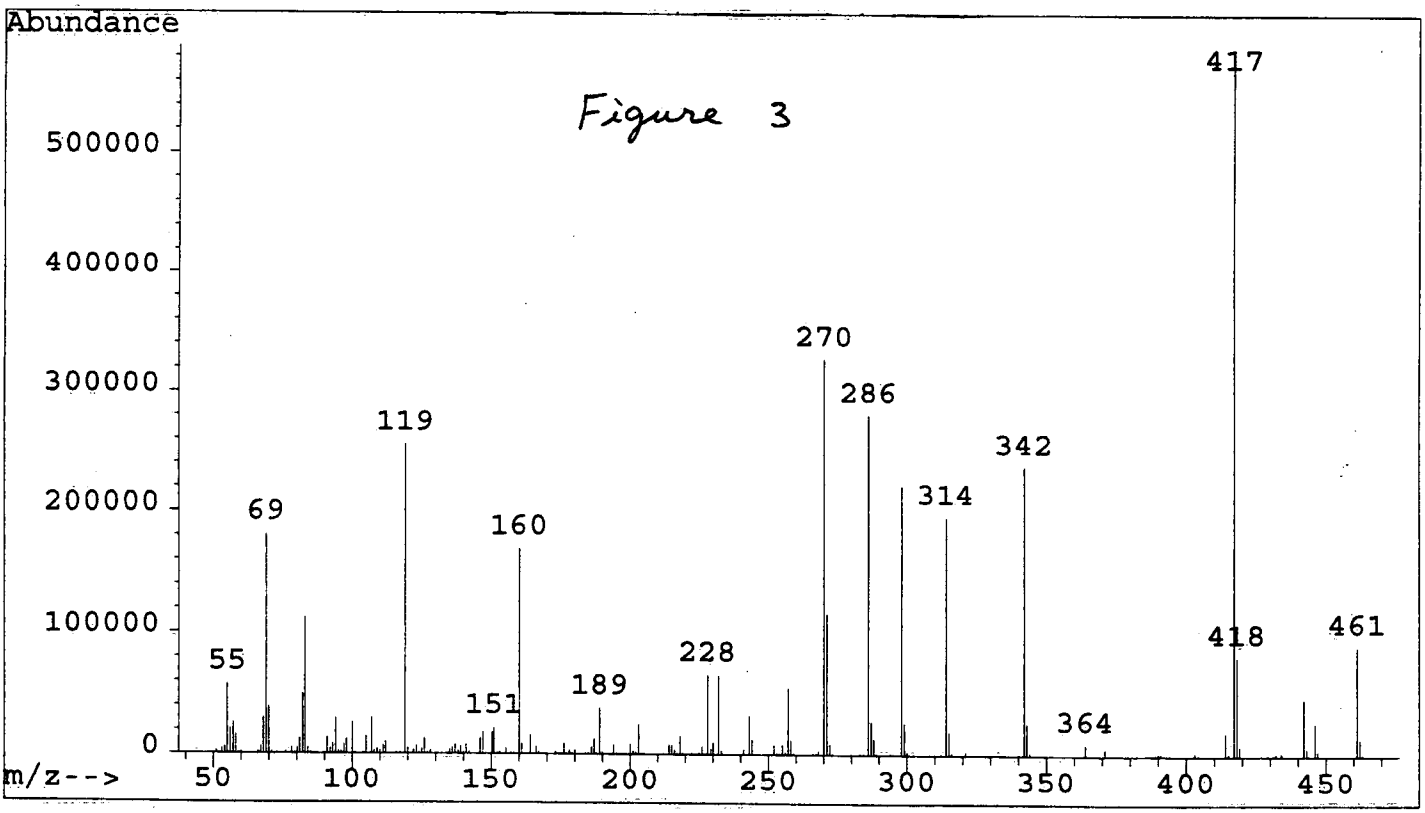

Figure 3

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