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Liquid Chromatographic Determination of Imazosulfuron in Food Commodity, Water and Soil Using Photo Diode Array Detector

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An analytical procedure for detecting residues of a new herbicide imazosulfuron 1-(2-chloroimidazo[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,6-dimethoxy-2-pyrimidinyl)urea in soil, water, rice grains and straw by reversed-phase liquid chromatography method using various solvents and extraction methods was standardized. The best results were obtained when imazosulfuron fortified at 0.50 and 0.10 μg g^{-1} was extracted with acetonitrile:dichloromethane:ammonium hydroxide; ethyl acetate and acetonitrile:water solvent systems for soil, water and plant samples, respectively. The method makes use of Phenomenex C-18 (ODS) column (250 × 4.6 mm i.d.) and acetonitrile:water (70:30 v/v) as mobile phase and diode array detection at 230 nm. Recovery of imazosulfuron from water at 0.10 to 0.50 μg mL^{-1} was 80-94 %. Whereas it was 30-98 %, 70-90 % from soil and plant samples respectively. The retention time of imazosulfuron was found approximately 3.72 min.

Keywords: Soil, Rice grains, Straw, Water, Imazosulfuron, Analysis.

INTRODUCTION

Presently about 20 sulfonylureas have been successfully marketed in the world due to low application rates, high selectivity and very low mammalian toxicity [1]. Imazosulfuron,1-(2-chloroimidazo[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4-dimethoxypyrimidin-2-yl)urea (Fig. 1), is a new post-emergence sulfonylurea herbicide applied once per-growing season. It is highly active at low application levels and used to control most annual and perennial broad-leaf weeds and sedges in rice (75-95 g a.i ha^{-1}) and turf (500-1000 g a.i. ha^{-1}) [2-5]. Chemical cleavage of the sulfonylurea bond gives 2-amino-4,6-dimethoxypyrimidine (ADPM) and 2-chloroimidazo[1,2-*a*]pyridin-3-sulfonamide (IPSN) and 1-(2-chloroimidazo[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4-hydroxy-6-methoxypyrimidin-2-yl)urea (HMS) which are the main degradation pathway of imazosulfuron in aerobic and anaerobic conditions [4-7].

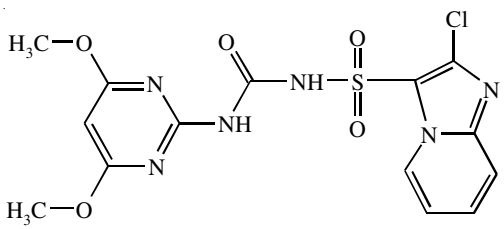

Fig. 1. Structure of imazosulfuron 1-(2-chloroimidazo[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,dimethoxypyrimidin-2-yl)urea

Ventriglia *et al.* [8] used liquid chromatography (LC) to determine imazosulfuron in drinking water. In this method imazosulfuron was extracted from water using solid-phase extraction on C18 bonded silica. The elutes were evaporated to dryness and residue dissolved in acetonitrile and analyzed by liquid chromatography with UV detection with 90-95 % recoveries. Mikata *et al.* [9] found ^{14}C imazosulfuron in the upper 30 cm soil layer and no ^{14}C imazosulfuron was detected below a depth of 50 cm and concluded that imazosulfuron and its degradation products can only slightly translocated in soils and groundwater [4,8]. Literature survey suggests that imazosulfuron adsorbs poorly on soil and can leach deeper in the soil horizon where anaerobic like conditions may occur [5,6,9].

Excessive use of pesticides can harm environment. The sources of pesticide contamination are manufactures, transport, handling and application to crops. Extraction and isolation are important steps in the process of determination of pesticides. Although liquid-liquid extraction method [4,10-14] and more recently solid phase extraction have been used for isolation of pesticides from soil, water and crop samples [15-22]. There remains a need for reliable methods to measure their concentration in soil, water and crop produce. Although there are several reports on the efficacy of imazosulfuron against various weeds in rice [3-5] but few reports are available in literature on the methods of analysis of imazosulfuron from crop produce, soil and water. The method described in this paper presents a

rapid and simple procedure for analyzing imazosulfuron in soil, water as well as in crop produce.

EXPERIMENTAL

The reference grade imazosulfuron was obtained from ACCU standard, USA and commercial grade imazosulfuron was from Sumitomo, Japan. All the solvents were HPLC grade and reagent were analytical grade obtained from E Merck, Germany.

Preparation of standard: A stock solution of imazosulfuron (1000 μg mL^{-1}) was prepared by dissolving 25 mg in 25 mL of acetonitrile. Other imazosulfuron solutions (5, 0.5, 0.05, 0.005, 0.0005 μg mL^{-1}) were prepared from the stock solution by dilution with acetonitrile.

The HPLC system consisted of a Shimadzu instrument equipped with degasser, LC-10 ATVP pump, SPD-M10 AVP diode array detector (DAD) and Rheodyne injection system. The column was a Phenomenex Luna RP-18 stainless steel column (5 μm particle size, 250 mm × 4 mm i.d.). The instrument was connected to a computer detector response having software able to compute detector response in terms of peak area. The injection volume of each standard and fortified samples was 20 μL and flow was set at 1 mL min^{-1}. The quantification was carried out at 230 nm at ambient temperature using a gradient of acetonitrile:water (70:30) as mobile phase. Quantification of imazosulfuron was accomplished by comparing the peak response for samples with peak area of the standards.

Extraction from soil: A soil containing 0.80 % organic carbon with a pH of 7.2 and a sandy clay loam soil texture consisting of 35.47 % clay, 12.45 % silt and 52.09 % sand was used. Soil samples (25 g) were fortified with imazosulfuron with different concentrations (0.10 and 0.50 μg g^{-1}) of imazosulfuron and extracted with 100 mL of five combinations of solvent system *viz.*, i) acetonitrile: water: 1 M ammonium hydroxide (30: 8: 2 mL); ii) acetonitrile: dichloromethane: 1 M ammonium hydroxide (30: 8: 2 mL); iii) acetonitrile: ethyl acetate: ammonium hydroxide (30: 8: 2 mL),); iv) methanol: ethyl acetate: 1 M ammonium hydroxide (30: 8: 2 mL); and v) acetonitrile: ethyl acetate: water (30: 8: 2),) using horizontal shaker for 1 h. The contents were filtered through a buchner funnel. The extraction was repeated twice (50 + 25 mL). The filtrates were combined and concentrated on rotary vacuum evaporators to about 2 mL.

Extraction from water: Water samples (25 mL) were fortified with imazosulfuron at 0.10 and 0.50 μg mL^{-1}. Dichloromethane and ethyl acetate were tested for the efficiency of extraction of imazosulfuron from water. 25 mL water samples were extracted with 50 mL of dichloromethane and ethyl acetate in a separatory funnel. Organic layers were collected and passed through anhydrous sodium sulfate which then concentrated on rotary vacuum evaporator to approximately 10 mL.

Extraction from rice grains and straw: Powdered rice grains and straw samples (25 g) spiked with 0.01, 0.10 and 0.50 μg g^{-1} amount of imazosulfuron were extracted twice with acetonitrile:water (80 mL) on horizontal shaker for 2 h. The contents were filtered, collected and solvent was evaporated to approximately 5 mL in a rotary vacuum evaporator.

Cleanup: No cleanup was required for soil and water samples. The concentrated extract was filtered through Pall Nylon 0.45 μm filter paper prior to hplc injection.

Rice grains and straw samples were subjected to glass column cleanup. A glass column (10 cm × 2 cm i.d.) was packed with celite (1 g) between anhydrous sodium sulfate (2 g) at each end. The concentrated extract was added at the top after pre-washing with acetonitrile and eluted with acetonitrile and water (70:30). Elutes were collected and solvent was evaporated on a rotary vacuum evaporator and dissolved in 2 mL acetonitrile prior to analysis.

RESULTS AND DISCUSSION

The extraction efficiency of imazosulfuron from soil, water, rice grains and straw samples fortified with imazosulfuron at 0.01, 0.1 and 0.5 μg g^{-1} levels and untreated samples (control) are presented in Table 2-4. Imazosulfuron was resolved as a

TABLE-1
CALIBRATION OF IMAZOSULFURON BY HPLC METHOD

Concentration (μg mL^{-1})	Area (three injections)			Average	Standard deviation
5.0	66442009	72472009	60695287	66536435	± 5888929
0.5	7616617	7068291	7002080	7228996	± 337218
0.05	682758	896746	786925	788809.7	± 107006
0.005	116766	153269	103697	124577.3	± 25693
0.0005	56933	60789	48346	55356	± 25693

TABLE-2
RECOVERY OF IMAZOSULFURON FROM FORTIFIED SOIL BY VARIOUS SOLVENT SYSTEMS

S. No.	Solvents used for extraction	Amount added (μg g^{-1})	Amount recovered (μg g^{-1})	Recovery (%)
1.	Acetonitrile:water:ammonium hydroxide	0.50	0.40	80
		0.10	0.07	70
2.	Acetonitrile:dichloromethane:ammonium hydroxide	0.50	0.48	98
		0.10	0.09	90
3.	Acetonitrile:ethyl acetate:ammonium hydroxide	0.50	0.17	34
		0.10	0.03	30
4.	Methanol:ethyl acetate:ammonium hydroxide	0.50	0.45	90
		0.10	0.08	80
5.	Acetonitrile:ethyl acetate:water	0.50	0.26	52
		0.10	0.05	50

single peak by HPLC and had a retention time (R_t) approximately of 3.72 min. The method showed linearity over a range from 0.0005 to 5 μg mL^{-1} (Fig. 2). The limit of detection of the techniques was 5 ng g^{-1} of imazosulfuron.

TABLE-3
RECOVERY OF IMAZOSULFURON FROM RICE GRAINS AND STRAW

Matrix	Amount added (μg g^{-1})	Amount recovered* (μg g^{-1})	Recovery (%)
Rice grains	0.50	0.39	77
	0.10	0.07	70
	0.01	0.002	20
Rice straw	0.50	0.45	90
	0.10	0.09	90
	0.01	0.003	30

*Average of three replications.

TABLE-4
RECOVERY OF IMAZOSULFURON FROM WATER

Solvents used for extraction	Amount added (μg mL^{-1})	Amount recovered* (μg mL^{-1})	Recovery (%)
Dichloromethane	0.50	0.44	88
	0.10	0.08	80
Ethyl acetate	0.50	0.46	94
	0.10	0.09	90

*Average of three replications.

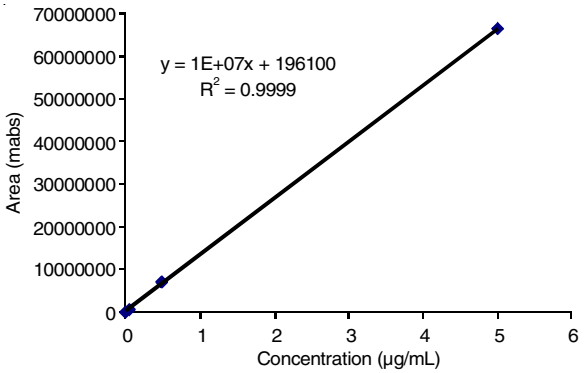

Fig. 2. Calibration of imazosulfuron at 0.0005 to 5.0 μg mL^{-1} level

Three-fold injection of imazosulfuron was used to determine standard deviation. It was observed that triplicate injections of each samples were optimum for operating 95 % confidence interval.

Following optimization of instrument operation conditions was extended to the analysis of soil, water, rice grains and straw samples. Extraction of imazosulfuron from soil was best performed by acetonitrile:dichloromethane: ammonium hydroxide followed by methanol:ethyl acetate: ammonium hydroxide and acetonitrile:water:ammonium hydroxide solvent system as the co-extractives were not interfering in this solvent system. Extraction efficiency of the herbicide from soil in acetonitrile:ethyl acetate: water: (51 %) and acetonitrile: ethyl acetate: ammonium hydroxide (32 %) was rather low as compared to acetonitrile: dichloromethane: ammonium hydroxide (average 94 %) followed by methanol: ethyl acetate: ammonium hydroxide ((average 85 %) and acetonitrile:water: ammonium hydroxide (average 75 %) (Table-2).

Although there was no interference in any extract in HPLC chromatogram, the extraction efficiency of the herbicide from water in ethyl acetate (average 92 %) was high as compared to dichloromethane (average 84 %) (Table-4).

The equations of analytical calibration graphs, obtained by plotting peak areas in 'y' axis against concentrations of imazosulfuron in 'x' axis within the range of 5 to 0.0005 μg mL^{-1} was, y = 1E + 07x + 196100, showed good linearity and the value correlation coefficient was 0.99.

The imazosulfuron recovery varied from 20-90 % for rice grains and straw samples fortified with 0.01, 0.1 and 0.5 μg g^{-1} of imazosulfuron. Recovery was acceptable upto fortification level of 0.1 μg g^{-1}. Low recoveries (20-32 %) of imazosulfuron at 0.01 μg g^{-1} was obtained hence could not consider. Due to the short retention time of the herbicide (< 4 min) and the absence of interfering peaks in the area of herbicides for the matrix analyzed each sample injection should be completed within 5-8 min and it was possible to analyze a large number of samples in a short time. This may be concluded that the described extraction and detection method is simple and gives good recoveries for the various fortified samples. The HPLC is thus sensitive, specific, quick and can be successfully used to quantitatively estimate the residues of imazosulfuron in soil, water as well as in crop samples.

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REFERENCES

1. H.M. Brown and J.C. Cotterman, in eds.: J. Stetter and W. Eding, Chemistry of Plant Protection-herbicides Inhibiting Branched Chain Amino Acid Biosynthesis, Springer-Verleg, Berlin, Germany, pp. 47-81 (1994).
2. T.R. Roberts, Metabolic Pathway of Agrochemicals, Part 1, Royal Society of Chemistry, Cambride, UK (1998).
3. C.D.S. Tomlin, The Pesticide Manual, British Crop Council, Surrey, UK, edn 12 (2000).
4. S. Sondhia, *Environ. Monit. Assess.*, **137**, 205 (2008).
5. S. Sondhia, B. Singhai, V.P. Singh and P. Verma, International Rice Research Congress, New Delhi, p. 555 (2006).
6. Y. Akiyama, N. Yoshioka and M. Tsuji, *Shokuhin Eiseigaku Zasshi*, **43**, 99 (2002).
7. P. Morrica, F. Barbato, A. Giordano, S. Seccia and F. Ungaro, *J. Agric. Food Chem.*, **48**, 6132 (2000).
8. M. Ventriglia, P. Restani, P. Morrica, P. David, L. De Angelis and C.L. Galli, *J. Chromatogr. A*, **857**, 327 (1999).
9. K. Mikata, F. Schnöder, C. Braunwarth, K. Ohta and S.I. Tashiro, *J. Agric. Food Chem.*, **51**, 177 (2003).
10. P. Morrica, F. Barbato, S. Seccia and F. Ungaro, *J. Agric. Food Chem.*, **49**, 3816 (2001).
11. A.G.S. Prado, E.M. Vieira and M.O.O. Rezende, *J. Braz. Chem. Soc.*, **12**, 485 (2001).
12. S. Hyun and L.S. Lee, *J. Environ. Qual.*, **33**, 1354 (2004).
13. J. Rouchaud, O. Neus and K. Cools, *Bull. Environ. Contam. Toxicol.*, **64**, 651 (2000).
14. S. Sondhia, *Geobios*, **28**, 140 (2001).
15. E. Oleszewska, *Acta Chromatogr.*, **4**, 231 (2004).
16. G. Ozhan, S. Ozden and B. Alpertunga, *J. Environ. Health B*, **40**, 827 (2005).
17. T.S. Thompson and R.G. Treble, *Bull. Environ. Contam. Toxicol.*, **57**, 525 (1996).
18. S. Sondhia, *Toxicol. Environ. Chem.*, **91**, 425 (2009).
19. S. Winrow, S. Hird and P. Brown, *Food Addit. Contam.*, **20**, 1064 (2003).
20. S. Sondhia, U. Waseem and R.K. Varma, *Chemosphere*, **93**, 2140 (2013).
21. S. Sondhia, *Bull. Environ. Contam. Toxicol.*, **89**, 1032 (2012).
22. S. Sondhia, *Pesticide Res. J.*, **19**, 248 (2007).