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A Selective Spectrophotometric Determination of Metsulfuron Methyl with 4-Amino Azobenzene in Various Environmental Samples

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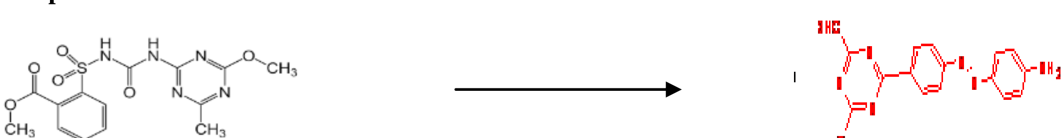
ABSTRACT

A simple and sensitive method for the determination of Metsulfuron methyl, a widely used herbicide is described here which is based on diazotization followed by coupling with 4-animo azobenzene in alkaline medium. The absorbance maxima of the coloured compound formed is measured at 490 nm. Beer's law is obeyed over the concentration range of 0.5-4.0µg in a final solution volume of 25mL.The Standard deviation and relative standard deviations are 0.0030 and 0.0919%. The molar absorptivity and Sandell's sensitivity were found to be 0.0752×10^{6}L mol^{-1} cm^{-1} and 0.0016µgcm^{-2}, respectively. The method has been satisfactorily applied to the determination of Metsulfuron methyl in various environmental samples.

Graphical Abstract



Metsulfuron-methyl Redish orange colour complex

Keywords: Sensitive method, Metsulfuron methyl, 4-animo azobenzene, molar absorptivity.

INTRODUCTION

Pesticides are well known human toxins used in agriculture to protect plants from insects and pests during the production and post-harvest storage of crops to increase agricultural yields. As a result of the widespread and long-term use of pesticides, contamination of both environmental and food samples has occurred [1]. The distribution of pesticide residues in/on treated crops is affected by many factors including, for instance, the type and spatial form of plants, cultivation and application method, and weather conditions during application [2]. From the origin of synthetic organic pesticides (1945) to this day, a remarkable increase in the usage of pesticides has been observed. Recently worldwide consumption of pesticides per annum has exceeded 2 million tons. No doubt during the last few decades the use of synthetic pesticides has offered significant economic benefits and provided a valuable aid to agricultural production by increasing crop protection and yield[3]**.** The use of pesticides is still increasing because of the continued population growth and the resulting increased demand for food. However, pesticides cause different levels of toxicity in various organisms. In addition, according to the World Health Organization (WHO), pesticides are implicated in approximately one million accidental poisonings and two million suicide attempts worldwide per year. They can also be carcinogenic or mutagenic [4]**.** The maximum permissible concentrations of crop protection chemicals in various food and feed commodities are elaborated by the Codex Committee on Pesticide Residues (CCPR) and become voluntary international standards after adoption by the Codex Alimentarius Commission (CAC). The CCPR recommendations are based on the evaluations of the FAO/WHO Joint Meeting on Pesticide Residues [5].

Worldwide pesticide use in crop production has constantly been increasing since the 1950s in total amount and in quantities per unit area. Whereas in developed countries, mostly herbicides are applied and the environmental impacts, for example, fish toxicity and soil damage, are of major concern, in developing countries, the bulk of pesticides used are insecticides and fungicides, and human mortality and morbidity due to exposure to pesticides have become a concern as they significantly affect the livelihood of small farmers [6]. Their excessive use has a deleterious effect on humans and the environment, and their presence in food is particularly dangerous. With their environmental stability, toxicity and ability to bioaccumulate, pesticides may place the human body at greater risk of disease and poisoning. Pesticide residues are frequently found in fruits and vegetables which may damage plant systems too [7]. Although the use of pesticides in agricultural applications. Provides a wide range of beneficial effects, the extensive use of them has been a concern because of their potential harm to the environment and known or suspected toxic effects to human, such as acute neurological toxicity, neurodevelopment impairment, possible dysfunction of the immune, reproductive and endocrine systems, cancer, chronic kidney diseases and other potential diseases [8]. Pesticides are a diverse group of chemical compounds that are generally used to control a variety of pests that can damage crops as well as livestock. From the origin of synthetic organic pesticides 1945 to this day, a remarkable increase in the usage of pesticides has been observed. Recently worldwide consumption of pesticides per annum has exceeded 2 million tons. No doubt during the last few decades the use of synthetic pesticides has offered significant economic benefits and provided a valuable aid to agricultural production by increasing crop protection and yield. But on the other hand the price, which we are paying or will pay in near future in the form of annually up to 200 000 human deaths as well as the contamination of natural resources is certainly very high. Structurally, synthetic organic pesticides can be divided into three main groups i.e., organochlorine, organophosphorus and organonitrogen pesticides [9].

Pesticides are widely used for protecting crops and fruits from insects and diseases, and play a crucial role in agricultural production. However, with increasing variety and amount of pesticides employed in agriculture, the threat of pesticide residue to human health is rising [25-27]. Especially, the non-standard usage of pesticide, such as overusing, misusing or mixing multiple pesticides, adds latent hazard not only to human health but also to environment and ecology. Consequently, the problems of pesticide residues are attracting extensive public attention and merit further investigation [10]. It has a simple chemical structure as shown in the Fig 1.

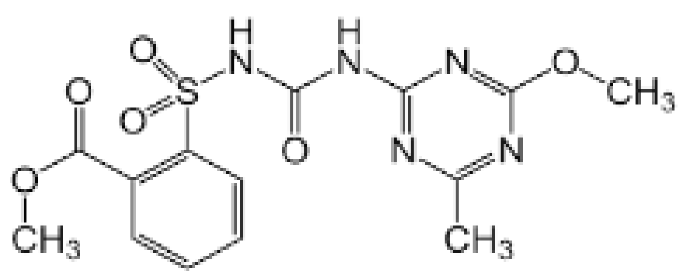
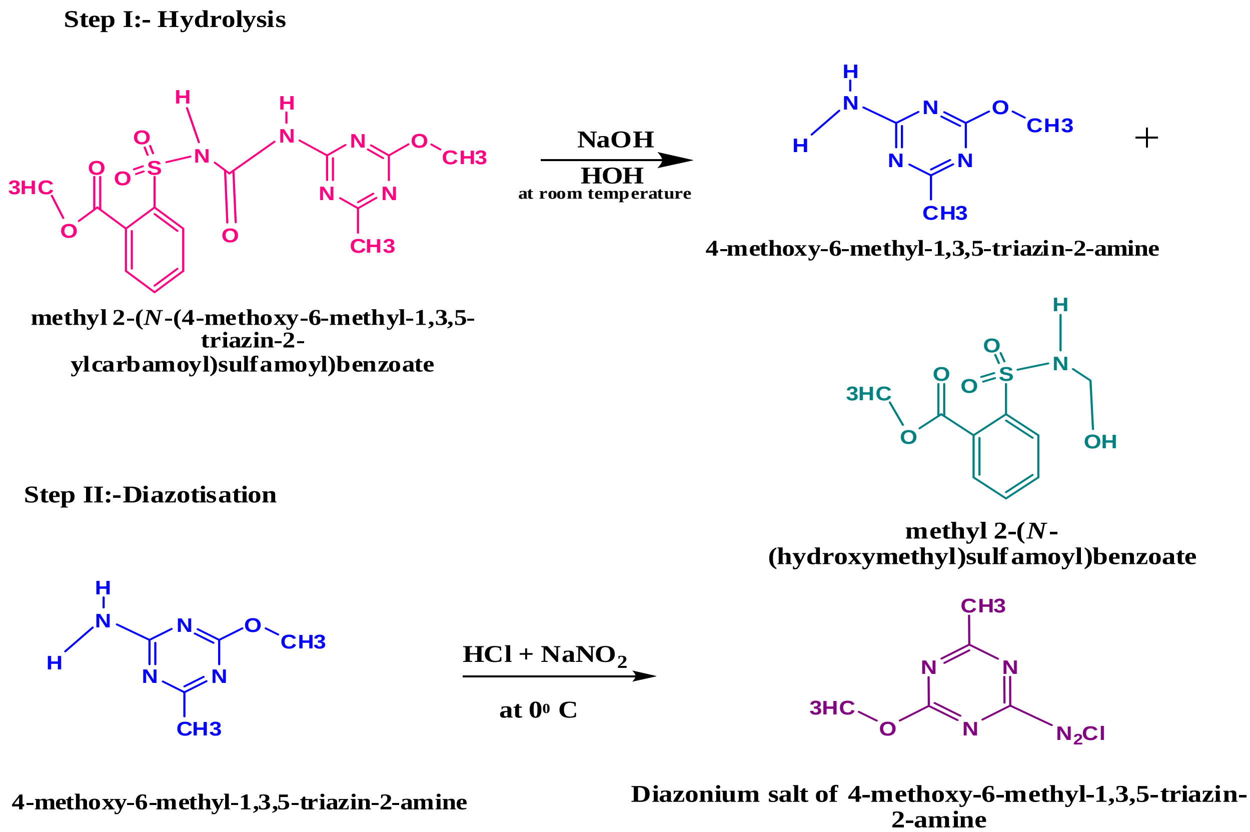
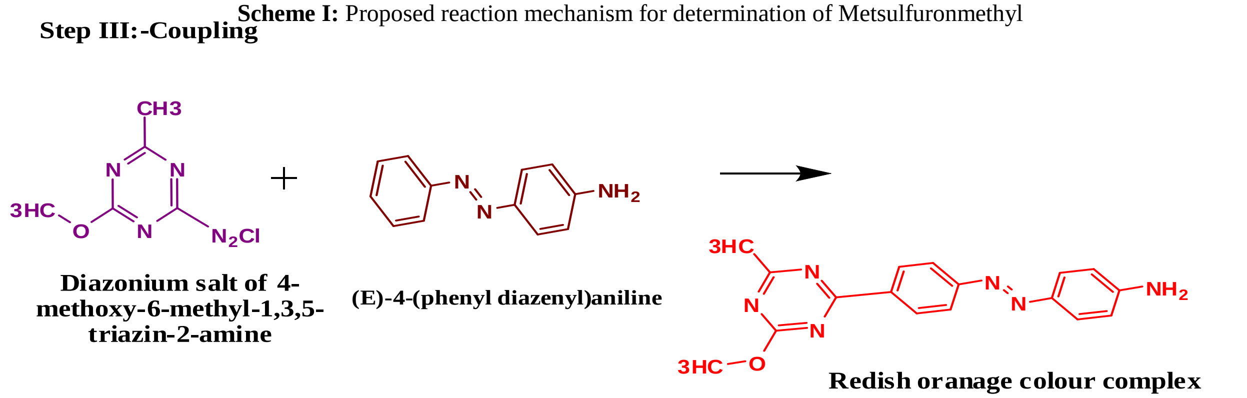


Fig 1. Structure of Metsulfuron-methyl

Trade name	Dupont Algrip
IUPAC Name	2-{[(4-methoxy-6-methyl-1,3,5-triazin-2yl) amino] Oxo methyl]-sulfonyl} benzoic acid methyl ester.
Molecular formula	$C_{14}H_{15}N_5O_6S$
Molecular weight	381.363 g mol^{-1}
LD_{50}	>5000 $mgkg^{-1}$
Half-life	17-69days (soil)



Scheme I: Proposed reaction mechanism for determination of Metsulfuronmethyl



The main aim of the present study is to develop a simple, sensitive and specific method for the accurate determination of Metsulfuron Methyl with 4-Amino Azobenzene. The reaction mechanism is shown in Scheme 1.

Metsulfuron-methyl is a residual sulfonylurea compound used as a selective pre- and post emergence herbicide for broadleaf weeds and some annual grasses. It is a systemic compound with foliar and soil activity and it works rapidly after it is taken up by the plant. Its mode of action is by inhibiting cell division in the shoots and roots of the plant (Pesticide information profile). Other techniques are also used such as liquid chromatography tandem mass spectrometry (QuE ChERS-LC-MS / MS)[11-14], Liquid chromatography mass spectroscopy (LCMS)[15-17], Ultra High Performance Liquid Chromatography with Tandem Mass Spectroscopy UHPLC-TMS)[18-19], UV-Visible Spectrophotometer and Infrared Spectrophotometer, (UV-VIS and IR)[20-22].

MATERIALS AND METHODS

Instruments: A Systronics UV-VIS spectrophotometer model 104 with 1 cm. matched quartz cell is used for all spectral measurement. A Systronics digital pH meter model 335 is used.

Chemicals:

Standard Solution of Metsulfuron methyl: Supplied by GSP Crop. Science Pvt. Limited: A stock solution of 1mg mL^{-1} solution of Metsulfuron methyl is prepared in distilled water. Working standard solution is prepared by appropriate dilution of the stock solution.

Sodium Nitrite Solution:1% standard solution of sodium nitrite was prepared with double distilled water.

Hydrochloric Acid: 1 N HCl solution was prepared with distilled water.

4-Amino azobenzene: A 2% solution of 4-amino azobenzene was prepared with 25% of ethanol.

Procedure: An aliquot of the test solution containing 0.5-4.0µg of Metsulfuron methyl was taken in calibrated test tubes to which 1mL 1N hydrochloric acid and 1mL 1% sodium nitrite solution was added at 0-5^{0}C temperature, respectively and allowed standing in a ice bath for 10 min. with thorough shaking. Then test tubes were removed from ice bath and 2mL of 2% 4-amino azobenzene were added to each test tube. Then the solution was kept for 15 min. for complete colour development and made up to the mark with distilled water. The absorbance of the solution was measured at 490 nm against distilled water.

RESULTS AND DISCUSSION

In this present work, Pesticides can be toxic to a host of other organisms including birds, fish and beneficial insects. However, majority of pesticides are not specifically targeting the pest only and during their application they also affect non-target plants and animals. Many pesticides are not easily degradable, they persist in soil, leach to ground water, surface water, soil, vegetables and contaminate wide environment. Depending on their chemical properties, they can enter the organism, bio-accumulate in food chains and consequently influence the environment [23].

Absorbance Spectra: The absorbance spectra of the colour system showed maximum absorption at 490 nm. The reagent blank had negligible absorbance at this wavelength.

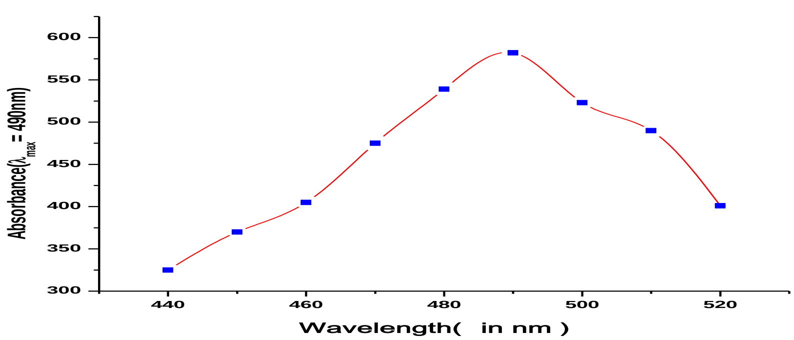


Fig. 1 Absorbance curve of colour compound

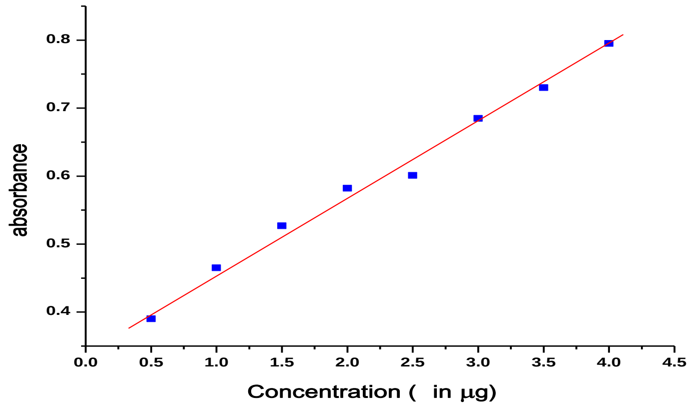


Fig. 2 Calibration curve of the colour compound

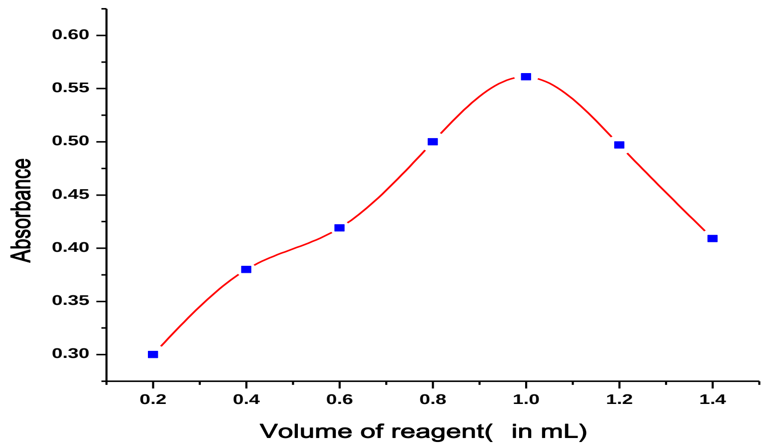


Fig. 3 Effect of Reagent

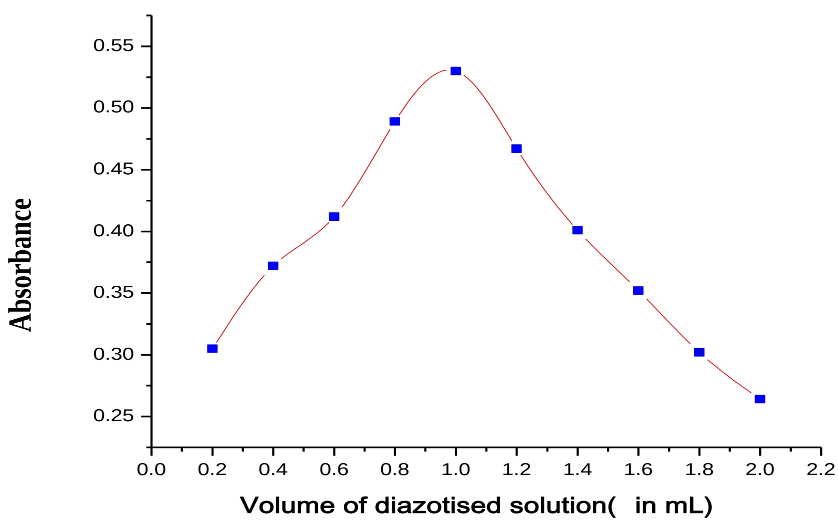


Fig.4 Effect of diazotized solution

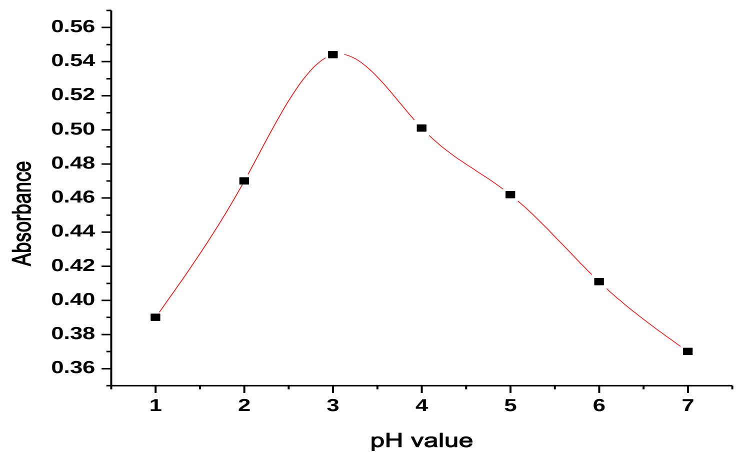


Fig. 5- Effect of pH

Beer's Law and Sensitivity: Beer's law is obeyed over the concentration range of 0.5-5.0µg of Metsulfuron methyl 25mL of the final solution at 490 nm.

Molar Absorptivity: The molar absorptivity of orange color dye was found to be 0.0752×10^{6} L mol^{-1} cm^{-1}.

Sandell's Sensitivity: Sandell's sensitivity of orange colour dye was found to be 0.0016µgcm^{-2}.

Reproducibility: The reproducibility of the method was checked by the replicate analysis of solution containing 10µg 10mL^{-1} of Metsulfuron methyl for a period of 7 days. The Standard deviation and Relative standard deviation are given in Table 1.

Table 1. Reproducibility method

No. of days		Absorbance
1		0.325
2		0.327
3		0.326
4		0.326
5		0.325
6		0.328
7		0.329
Mean	=	0.329
Standard deviation	=	0.0030
Relative standard deviation	=	0.091%

*Concentration of Metsulfuron methyl = 2µg 25mL^{-1}

Condition for Colour Development: Constant and maximum absorbance value was obtained when 1 mL of 4-amino azobenzene was used and it is sufficient for full colour development. Temperature range of 0-5^{o}C was required for 10-15 min.

Effect of pH: The effect of pH on the colour reaction was studied and it was found that pH range of 3. pH is required for the colour development. On increasing pH, the value of absorbance decreases.

Effect of Sodium Nitrite: 1mL 1% solution of sodium nitrite is sufficient for the diazotization. Higher amount of sodium nitrite decreases absorbance value.

Effect of 4-Amino azobenzene: To complete the reaction and full colour development 1mL of 2% 4-aminoazobenzene was sufficient and time required is 15 min. When amount of reagent is increased absorbance value also increases.

Table 2. Effect of foreign species and ions

Species	Tolerance limit in µg L^{-1}
Fanvalrate	250
Monochrotophos	1000
Carbendazim	1000
Acetampride	1100
Deltamethrin	400
Dicofol	750
Na^+	750
K^+	1000
Ca^{2+}	1000
Zn^{2+}	1500
Ba^{2+}	600
Al^{3+}	1000
SO_4^{--}	1000

APPLICATIONS

Determination of Metsulfuron methyl in Water Sample: 50 mL of water sample was taken and fortified with known amount of Metsulfuron methyl and kept for 3 - 4h. Metsulfuron methyl was determined by the proposed method. The recoveries are shown in Table 3.

Table 3. Recovery of Metsulfuron methyl in environmental samples

Sample	Metsulfuron methyl in original found* (X)	Metsulfuron methyl added in µg (Y)	Total Found (Z)	Difference (µg) (Z-X)	Recovery (%) (Z-X) x 100/Y
Water**	1	2	2.9	1.92	96%
Soil***	1.6	2	3.5	1.9	95%
Paddy***	1.2	2	2.4	1.9	95%
Tomato***	0.8	2	2.75	1.95	98%
Potato***	1.3	2	3.24	1.9	95%
Brinjal***	1.2	2	3.15	1.95	98%

*Mean of three replicate Analysis
** Amount of sample 20 mL
*** Amount of sample 5 g

Determination of Metsulfuron methyl in vegetables, grains and soil: Various samples of vegetables, grains, and soil each of 5 g were taken, collected from agricultural fields where Metsulfuron methyl had been sprayed as an insecticide. The samples were crushed and spiked with known amount of Metsulfuron methyl and kept for 3- 4 h. Metsulfuron methyl was analysed by the proposed method. The recoveries are shown in Table 3.

The recoveries range from 92 – 98% by the proposed method.

CONCLUSIONS

This method reports the use of 4-aminoazobenzene as a new reagent for the Spectrophotometric determination of Metsulfuron methyl. It offers sensitivity, selectivity, simplicity and cost effectiveness of the method. The method involves no extraction steps thereby the use of organic solvents, which are generally toxic in nature are avoided. The sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method indicated it to be very reliable for the determination of Metsulfuron methyl in various environmental samples. This method is good alternatives to some reported costly instrumental method. The results showed that the developed method worked satisfactorily.

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