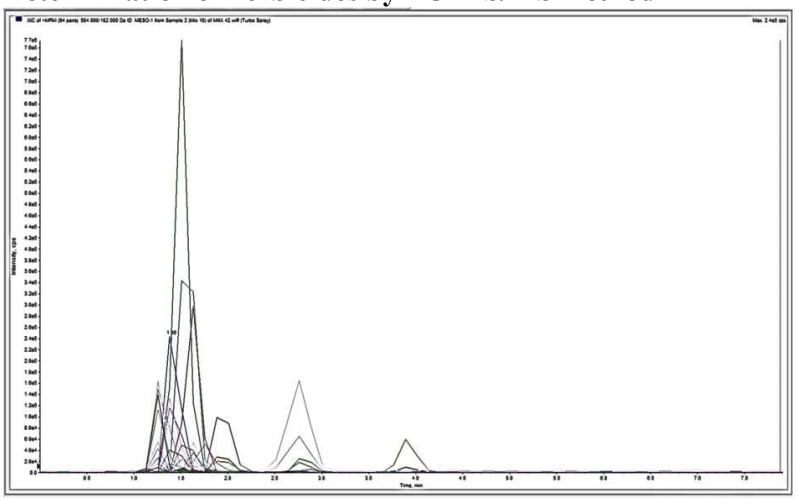
Proforma for submission of proposal for certifying a product/technology

Item		
1.	Name of the product/technology (as defined above):	**A multi-residue LCMS/MS detection for simultaneous determination of 34 herbicides**
2.	Name and address of the Institute:	ICAR-Directorate of Weed Research, Maharajpur, Jabalpur-482002, M.P
3.	Institution(s) responsible for developing/ evaluating/ identifying including collaborators, if any:	ICAR-Directorate of Weed Research, Maharajpur, Jabalpur-482002, M.P
4.	Source of product/technology (Research Project/Student Research/Any other ad-hoc research study):	Research Project : NRMADWR201700100131 Project title: Environmental risk assessment of herbicides under wheat based cropping system and their mitigation measures
5.	Period of development/evaluation/validation	2018-2023
6.	Developers (Lead and Associates)	**Dr Shobha Sondhia (Lead)** **Associates** Dr Sushilkumar Dr V.K. Choudhary
7.	Summary of the product/technology (maximum of 200 words)	A new multi-residue LCMS/MS detection analytical technology is developed for the simultaneous rapid determination of 34 herbicides in environmental samples. This detection provided simultaneous analysis of 34 herbicides in water, soil, plants, grains and fish and increase detection efficiency in comparison to conventional analytical processes. This method is found to be a sensitive, rapid, and reliable method, which facilitate extraction and detection of all 34 herbicides simultaneously at detection limit of 0.001 to 0.01 mg/kg. Furthermore, this technology can be adopted for monitoring of herbicide residue load in environmental samples where several pre and post emergence herbicides are being applied in the same field /crop for control of weeds. This technology associated with a high analytical frequency as 34 herbicides are simultaneously analyzed in a single sample which in conventional analysis by HPLC or UFLC require individual analyses and hence this analytical technology is 18.63 times effective and efficient which save resources as well as time and energy than conventional or single residue analytical techniques.

		This analytical technology provided saving of resources, time, costly organic solvents, energy and provided very high benefit cost ratio.
8.	Is it a new technology? (Yes/No). If no, provide the details of the technology modified	Yes
9.	IPR involved, if any (Patent/Copyright/ Industrial Design Registration/ Variety/ germplasm registration). Provide Filed/Granted number	No yet submitted (Copyright is associated with developers)
10.	Validation procedure followed (within Institute, collaborators, multilocation/ multi-site testing)	Within institute, applicable for multilocation /multisite testing
11.	Brief description of research output/technology: a. Objective of the product/technology	To develop a new multi-residue LC-MS/MS analytical technology for simultaneous rapid determination of 34 herbicides in soil, water, plants, grain, fish and other environmental samples.
	b. Detailed methodology of the proposed product/technology	Application of pre and post-emergence herbicides are being applied all over the world to manage weeds, improve crop yield and quality. Liquid Chromatography attached with mass-mass detector (QTrap) plays an important role for analysis of pesticide in agricultural commodity as a comprehensive technique for the detection and identification of pesticides. Therefore to detect the presence of herbicide residues in crop produce or environmental samples under maximum residue limits fixed by the Joint Meeting on Pesticide Residues (JMPR), a new robust, simultaneously LC-MS/MS analytical technology was developed for the quick detection of 34 herbicides frequently used in agriculture for weed management, namely 2,4-D, alachlor, anilofos, atrazine, bentazone, bispyribac-sodium, butachlor, carfentrazone-ethyl, chlorsulfuron, clodinafop, chlorimuron, cyhalofop, diuron, ethoxysulfuron, fenoxaprop-p-ethyl, fluazifop, haloxyfop, imazethapyr, mesosulfuron, metribuzin, mesulfuron, oxyfluorfen, paraquat, pendimethalin, penoxsulam, propaquizafop, pretilachlor, pyarzosulfuron-ethyl, quizalofop, quizalofop-ethyl, sulfosulfuron, tembotrione, topramezone, tribenuron and triafamone in the soil, water, fish, grain and straw samples.

		After extraction, cleanup, and separation processes, herbicides in organic phase, was concentrated and dissolved in acetonitrile and subjected to newly develop analytical LC-MS/MS detection technology. The detection limit was found to be below <0.001 to 0.01 µg/g, with R^2 (0.760 to 1.0), RSD (<4.59%) and herbicide recovery (89-99%) for all 34 herbicides. This analytical technology makes use of Phenomenex C-18 (ODS) column (3.5 µm particle size, 5×3.5 mm i.d.) and acetonitrile: H_3PO_4 0.01% (70:30 v/v) as mobile phase at a flow rate of 0.38 ml/min with R^2 (0.760 to 1.0).The Rt of all herbicides was in the range of 1.24 to 9.34 minutes in LC/MS/MS. All 34 herbicides are responded well in positive ionization mode in LC-MS/MS, however, two herbicides, iodosulfuron and fomasafen responded well in negative ionization mode.
	c. Yield/productivity gain	The analytical technology provides high productivity gain and saved 12.33 Litres of Acetonitrile that caused money saving of Rs 72587.112 (in comparison to UFLC method) per 100 samples.
	d. Saving of water, labour, time and energy	This analytical technology save the time, solvents, energy in analysis of 34 herbicides in comparison to single herbicide analysis in various commodity and **provides time saving of 508.33 hours, energy saving 43, 18,400 KJ/min, solvent saving (12.33 Litre Acetonitrile costing Rs 45,348) and money saving of Rs 72, 587.112 (in comparison to UFLC method).**
	e. Conservation of soil	This technology worked involves on minimum disturbance and uses of resources under good environment principle and good laboratory practices, hence causing, less environment hazards and less contamination to the soil.
	f. Capacity	This technology enhance the capacity of analyst to analyse maximum number of sample analyses in minimum time in comparison to a single analysis in a short duration of time and 34 herbicides can be analyzed in 15 minutes and therefore in 1500 minutes, 100 numbers of complex samples contained 34 herbicides can be analyzed. Whereas analysis by UFLC, 100 samples contained 34 herbicides will require 34000 minutes or 566.7 hours and therefore this newly developed multi-residue method save 541 hours equal to 22.54 working days and enhance the capacity to analyze more number of environmental samples besides saving time, money and resources tremendously.
	g. Efficiency	**In a developed LC/MS/MS analytical technology, 34 herbicides can be analyzed in 15 minutes and therefore in 25 hours 100 complex samples can be analyzed.** Whereas for similar analysis by UFLC technique requires approximately 566.7 hours. Therefore, this analytical technology saves 541 hours' time equal to 22.54 working days and enhances the efficiency of analysis of

		environmental samples besides saving time, money and resources tremendously. Moreover in these saving hours (541 hrs.) in comparison to UFLC method, another complex 20164 number of more samples for 34 herbicides can be analyzed.
	h. Cost effectiveness including B:C ratio	This analytical technology provides very high cost effectiveness in terms of money saving of Rs 72,587.112 (in comparison to UFLC method), with a very high B: C ratio (24.6) per 100 samples.
	i. Uniqueness of the technology in comparison to existing ones	This LC/MS/MS multi-residue method is a quick detection technology for herbicides residue with low detection limits of 0.001µg/g. In general, analysis by HPLC or UFLC/UPLC where herbicides are being determined and analyzed based on the retention time (Rt) of herbicides and in many cases due to similar retention times; analyses produce ambiguous results besides low sensitivity and poor level of detection limits of herbicide residues. **In this developed LC/MS/MS analytical technology, 34 herbicides in 100 complex samples containing 34 herbicides can be analyzed in 25 hours.** Whereas analysis by UFLC or similar technique will require 566.7 hours for complete analysis of 34 herbicides in individual 100 samples. **Therefore this technology save 22.54 working days and enhance the efficiency and capacity of analysis in environmental samples besides saving time, money and resources tremendously. Moreover in these saving hours (541 hrs.) 20164 number of samples containing 34 herbicides can be analyzed which also enhances the capacity of analytical labs.** Therefore this robust, sensitive and fast unique analytical technology is very useful for herbicides screening and confirmation of presence of herbicide residues in various commodities with low cost input.
	j. Passport data of the product/technology	A new robust, sensitive and fast multi-residue LC-MS/MS detection analytical technology is developed for the simultaneously quick determination and confirmation of 2,4-D, alachlor, anilofos, atrazine, bentazone, bispyribac-sodium, butachlor, carfentrazone-ethyl, chlorsulfuron, clodinafop, chlorimuron, cyhalofop, diuron, ethoxysulfuron, fenoxaprop-p-ethyl, fluazifop, haloxyfop, imazethapyr, mesosulfuron, metribuzin, mesulfuron, oxyfluorfen, paraquat, pendimethalin, penoxsulam, propaquizafop, pretilachlor, pyarzosulfuron-ethyl, quizalofop, quizalofop-ethyl, sulfosulfuron, tembotrione, topramezone, tribenuron and triafamone residues with low detection limits of 0.001 mg/kg in various agricultural/nonagricultural commodity and environment. It is 18.63 times effective and efficient which save resources as well as time and energy than conventional or single residue analytical techniques.

12.	Details of relevant data generated during the development/validation	A new robust, and rapid multi-residue LC-MS/MS detection method is developed for the quick determination and confirmation of herbicides residues in various agricultural/non- agricultural commodity and environment for determination of 34 herbicides in a single run. Validation of detection method was performed with soil, water, fish and plant samples which were collected from herbicide sprayed experimental fields as well as from farmers' field for herbicides residue analysis by developed multi-residues technology. After processing raw samples, final samples were subjected to LC/MS/MS analysis by developed technology that resulted in effective determination of various herbicides in soil, water, fish, plants and other environmental samples successfully with the detection limits of 0.01 to 0.001 µg/g with <6.68% RSD. This analytical technology also validated for analysis of herbicides residue in the soil and crop samples (grain, straw, plants, etc.) from various agricultural fields, under Open Top Chambers (OTC) and Free Air Carbon dioxide Enrichment (FACE) facilities in climate change project under NICRA and prove its uniqueness and effectiveness and benefits in analysis herbicides residues in various commodities.
13.	Proposed stakeholders	National and international analyst, developer, agriculturist, environmentalist, Government, decision and policy makers
14.	Commercial potential, if any	Yes,
15.	Publications/photos/video clipping, if any	**Determination of herbicides by LC-MS/MS method** 

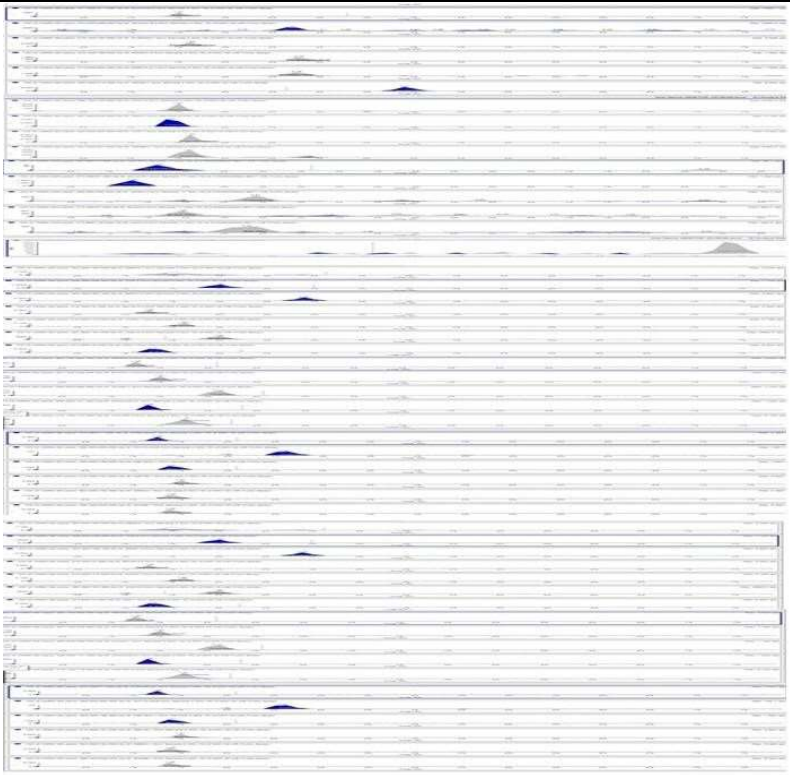
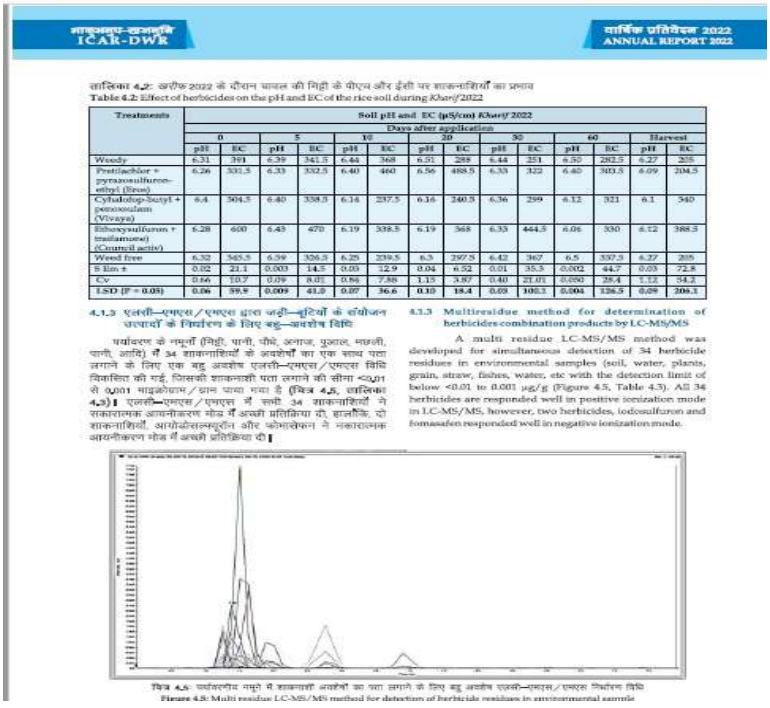


Figure 1. Multi residue LC-MS/MS method for detection of herbicide residues in environmental sample

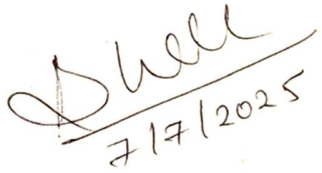


Publication:

- **Sondhia S. (**2021). **A** multi-residue method for the determination of herbicide residues in environmental

		samples by LC-MS/MS. In XV Agricultural Science Congress & ASC Expo' organized by National Academy of Agricultural Sciences and Banaras Hindu University at Institute of Agricultural Sciences, Banaras Hindu University, Varanasi. November 13-16, 2021 abstract 410. • **Sondhia S.** (2022). A multi-residue method for the determination of herbicide residues in environmental samples by LC-MS/MS. In ICAR-DWR. Annual report pg 63-69. • **Sondhia, S.**, Pawar, D.V. & Dasari, S. Degradation dynamics, correlations, and residues of carfentrazone-ethyl, fenoxaprop-p-ethyl, and pinoxaden under the continuous application in the wheat field. **Environmental Geochemistry and Health 45**, 8851–8865 (2023). https://doi.org/10.1007/s10653-023-01487-x (**NAAS 10.90, NAAS Id E092).** • **Sondhia S.** (2022). A multi-residue method for the determination of herbicide residues in environmental samples by LC-MS/MS. In ICAR-DWR Annual report **ICAR Annual report 2022. Pg 99.** • Sharma ·N, Sapehia S, Kaur P, Katwal R, and **Sondhia S. 2023.** Dissipation of in maize and its effecton biochemical attributes of maize under mid-hill sub-humid zone. **Environmental Monitoring and Assessment** (2023) 195:1184 https://doi.org/10.1007/s10661-023-11800-x **NAAS rating 9.31, NAAS Id E100).**
16.	Any other information not covered above	This analytical technology can be used to determine these herbicides in environmental samples as well as in Forensic analysis in biological/non-biological samples or contaminated samples to resolved ambiguity in analytical results.

Declaration: I/We hereby undertake that the above information is correct. All scientists in the development of this research output have been included in the list of Associates. The research output does not involve any third party IPR.



Dr Shobha Sondhia	Dr Suhilkumar	Dr V.K. Choudhary
(Lead developer)	**Associates**	**Associates**

Name and signature of all the developers

Recommendations of the Head of Division

Recommendations of ITMC/PME

Recommendations of Director

Recommendation of SMD

Degíadation dynamics, coíielations, and íesidues of caífentíazone-ethyl, fenoxapíop-p-ethyl, and pinoxaden undeí the continuous application in the wheat field

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Enviíonmental Geochemistíy and Health

Aims and scope

Submit manuscíipt

Shobha Sondhia, Deepak V. Pawaí & Síeekanth Dasaíi

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Weed infestation is a major biotic limitations in wheat cultivation; thus, various herbicides are being applied to control these weeds. Therefore, this study was undertaken for two successive years to assess degradation behaviours, persistence and residue risk imposed by carfentrazone, fenoxaprop-p-ethyl and pinoxaden sprayed as post-emergence herbicides in the wheat crop for management of weeds. Soil and crop samples were collected at periodically

at after two hour of herbicide application till harvest of wheat crop and analysed by a high-performance liquid chromatograph. Degradation of carfentrazone, pinoxaden and fenoxaprop-p-ethyl, in the soil of wheat field occurred rapid to moderately with the mean half-life 9.92, 11.7 and 11.8 days, respectively. Persistence was found to be dependent on the weather parameters as well as physicochemical properties of the soil and herbicides. Half-life of studied herbicides was found to be negatively correlated with persistence (R^2 0.38, $p = 0.05$, $n = 3$) and vapour pressure (R^2 0.99, $p = 0.05$, $n = 3$). Principal component analysis revealed that the first two Principal Components (PCs) had eigenvalues more than 1, and the first and second PCs contributed 77.4 and 22.6% in herbicide residues and different parameters variation, respectively. Terminal residues of carfentrazone, pinoxaden and fenoxaprop-p-ethyl in the wheat straw, grains and soil were found below the maximum residue limits. Owing to the moderate persistence under wheat field conditions, carfentrazone, pinoxaden and fenoxaprop-p-ethyl are supposed to be safe for control of weeds in wheat crop and hence, suspected risk on the human and environment or crop produce under evaluated doses is negligible.

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Cite this aíticle

Sondhia, S., Pawaí, D.V. & Dasaíi, S. Degíadation dynamics, coííelations, and íesidues of caífentíazone-ethyl, fenoxapíop-p-ethyl, and pinoxaden undeí the continuous application in the wheat field. *Environ Geochem Health* 45, 8851–8865 (2023). https://doi.oíg/10.1007/s10653-023-01487-x

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Keywoíds

Degíadation dynamics | Enviíonment contamination | Heíbicide peísistence | Residue detection | HPLC–DAD | Teíminal íesidues

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RESEARCH

Dissipation of tembotrione in maize and its effect on biochemical attributes of maize under mid-hill sub-humid zone

Neelam Sharma · Shaila Sapehia · Pervinder Kaur · Rishu Katwal · Shobha Sondia

Received: 2 August 2023 / Accepted: 30 August 2023

Abstract The present study was undertaken to investigate the dissipation behavior of tembotrione in soil and its effect on the biochemical constituents of maize leaves and grain. The average recovery of tembotrione from soil, maize grain, and stover was in the range of 84.0 to 86.0%, 79.3 to 83.0%, and 81.0 to 84.4%, respectively, with RSD less than 10%. Half-life (DT_{50}) of tembotrione ranged from 9 to 14 days at an application rate of 60 to 240 g ha^{-1}. Terminal residues in soil, maize grain, and stover were below detectable levels (≤ 0.025 µg g^{-1}) at studied application rates. The chemical attributes, i.e., total chlorophyll, total carotenoids, and carbohydrate content, of rice leaves were observed at monthly intervals (zero (2 h), 30, 60 days after the herbicide application) and at harvest for biochemical analysis and grain samples at maturity of the crop for carbohydrate content. The results revealed that total chlorophyll, total carotenoids, and carbohydrate content in maize leaves increased significantly with applied tembotrione treatments, and the maximum increase was noticed in treatment 120 g ha^{-1}. A significant increase in total carbohydrate content in maize grain over the control was noticed in all the herbicide-applied treatments. It can be inferred that the application of tembotrione is safe in the production of food with better quality and food safety.

Keywords Tembotrione · Grain · Maize leaves · Chlorophyll · Carotenoids · Carbohydrates · Soil

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Introduction

Maize (*Zea mays* L.) is an economically important crop worldwide. In India, maize contributes approximately 9% of the national food basket. Maize is the third most important crop both in area and production after rice and wheat in India. Himachal Pradesh is one predominant maize-growing states in India. The Department of Agriculture, Himachal Pradesh reported that the production of maize in the state has gone up from 67.3 kt in 1951–1952 to 644.44 kt in the year 2017–2018. Maize is largely used as a raw material in thousands of industrial products such as alcoholic beverages, cosmetics, food sweeteners,