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Kavindra Singh
Ph.D., Department of Agricultural Engineering Process and Food Engineering, SVP University of Agriculture and Technology, Meerut, Uttar Pradesh, India

Suresh Chandra
Associate Professor, Department of Agricultural Engineering Process and Food Engineering, College of Post-Harvest Technology and Food Processing, SVP University of Agriculture and Technology, Meerut, Uttar Pradesh, India

Akash Tomar
Associate Professor, Department of Recombinant DNA Technology, College of Biotechnology, SVP University of Agriculture and Technology, Meerut, Uttar Pradesh, India

Samsher
Professor and Dean, College of post-harvest Technology and Food Processing, SVP University of Agriculture and Technology, Meerut, Uttar Pradesh, India

Neelash Chouhan
Associate Professor, Department of Agricultural Engineering Process and Food Engineering, College of Post-Harvest Technology and Food Processing, SVP University of Agriculture and Technology, Meerut, Uttar Pradesh, India

MK Yadav
Associate Professor, Department of Agriculture Biotechnology, College of Agriculture, SVP University of Agriculture & Technology, Meerut, Uttar Pradesh, India

Corresponding Author:
Kavindra Singh
Ph.D., Department of Agricultural Engineering Process and Food Engineering, SVP University of Agriculture and Technology, Meerut, Uttar Pradesh, India

Determination of selected pesticide residue in sugarcane (*Saccharum officinarum*) juice by liquid chromatography mass Spectrometry (QuEChERS)

Kavindra Singh, Suresh Chandra, Akash Tomar, Samsher, Neelash Chouhan and MK Yadav

Abstract
The sugarcane (*Saccharum officinarum* L.) cultivation is one of the most important agricultural activities in India, where its main end products are sugarcane juice, white sugar, jaggery, Khandsari and alcohol. Pesticides are used in agricultural crops due to their extensive and effective crop protection, but excessive use of these chemicals has harmful and fatal effects on humans and other organisms. With this in mind pesticide residue analysis was performed in sugarcane juice by QuEChERS. Study carried to analyze eight pesticides (carbofuran, cartap hydrochloride, chlorantraniliprole, chloropyrifos, cypermethrin, fipronil, lambda cyhalothrin & phorate) in sugarcane juice. It was found that only Chlorantraniliprole was present in the juice in traces amount (>LOD), which needs to be used judiciously in sugarcane production system.

Keywords: QuEChERS, pesticide residue, sugarcane juice, mass Spectrometry

Introduction
The sugarcane (*Saccharum officinarum* L.) cultivation is one of the most important agricultural activities in India where its main end products are, white sugar, jaggery, alcohol and derived foods. The demand for food products and fuels has required the use of chemical products, such as pesticides and fertilizers, to guarantee and increase sugarcane production. Pesticide use is important in agriculture to protect crops and improve productivity. However, pesticides have the potential to cause adverse human health or environmental effects, depending on exposure levels.

A pesticide is "any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest" (FIFRA 1947). Pesticides are used in various economic sectors, such as agriculture, forestry, transport (railroads), industrial zones, parks and households (gardens). Among these sectors, however, agriculture is by far the main user (Brouwer *et al*. 1994) [2]. Pesticides are not modern inventions, as they have long been used to control pests and diseases in agriculture (Carson, 1963; Conway and Pretty, 1991; Cremlyn, 1991; Dinham, 1993; van Emden and Peakall, 1996) [3, 5, 6, 10].

Pesticides of agricultural importance can be broadly categorized as: herbicides (for weed control), Insecticides (for insect control), Fungicides (for fungal pathogen control) and others (for nematicides, bactericides and rodenticides). Pesticides are applied to agricultural land to protect crops from probable pests, diseases, and weeds that might decrease productivity. Pesticides are approved according to a precise use and in so far as no secondary damaging effects appear in humans, animals and the environment. Experts come to a conclusion about the approval according to data describing the spectrum of action of these substances and their behaviour in the environment. Maximum concentrations are established for food products. This authorization includes the conditions of use and application techniques (concentration), the time of application and the delay of harvest (time elapsed between treatment and harvest).

Materials and Methods
Modified QuEChERS are used for sample analysis and LC–MS for the simultaneous quantification of 8 pesticides residue was used for sugarcane juice analysis.

Preparation of sample
The sample of the sugar cane juice was prepared from CO-0238 cultivar variety. Juice sample

of sugarcane variety (CO-0238) was picked form the selected farmers of district Meerut and Ghaziabad. Selection of farmers was based on the use of pesticide in sugarcane crop & the maximum productivity of sugarcane. A 10 g weight of sugarcane juice sampled and 10 ml of 1% Acetic acid was added in acetonitrile and done vortex mixture for 5 minutes. Added 6 g magnesium sulphate and 1.5 g sodium acetate and then centrifuged (5 minutes at 4000 RPM) and extracted upper extract. In the obtained upper extract, 1.5 g of $MgSO_4$ and 0.3 gm PSA (Primary Secondary Amine) and 0.2 gm C_{18} added and then again vortex mixing was done for 5 minutes and afterwards centrifuged it for 5 minutes at 4000 RPM. The vials prepared into two categories, in first-one vials sample was concentrated in nitrogen at 40 °C and in second vial sample was diluted with equal amount of acetonitrile and uploaded in LCMS/MS for analysis.

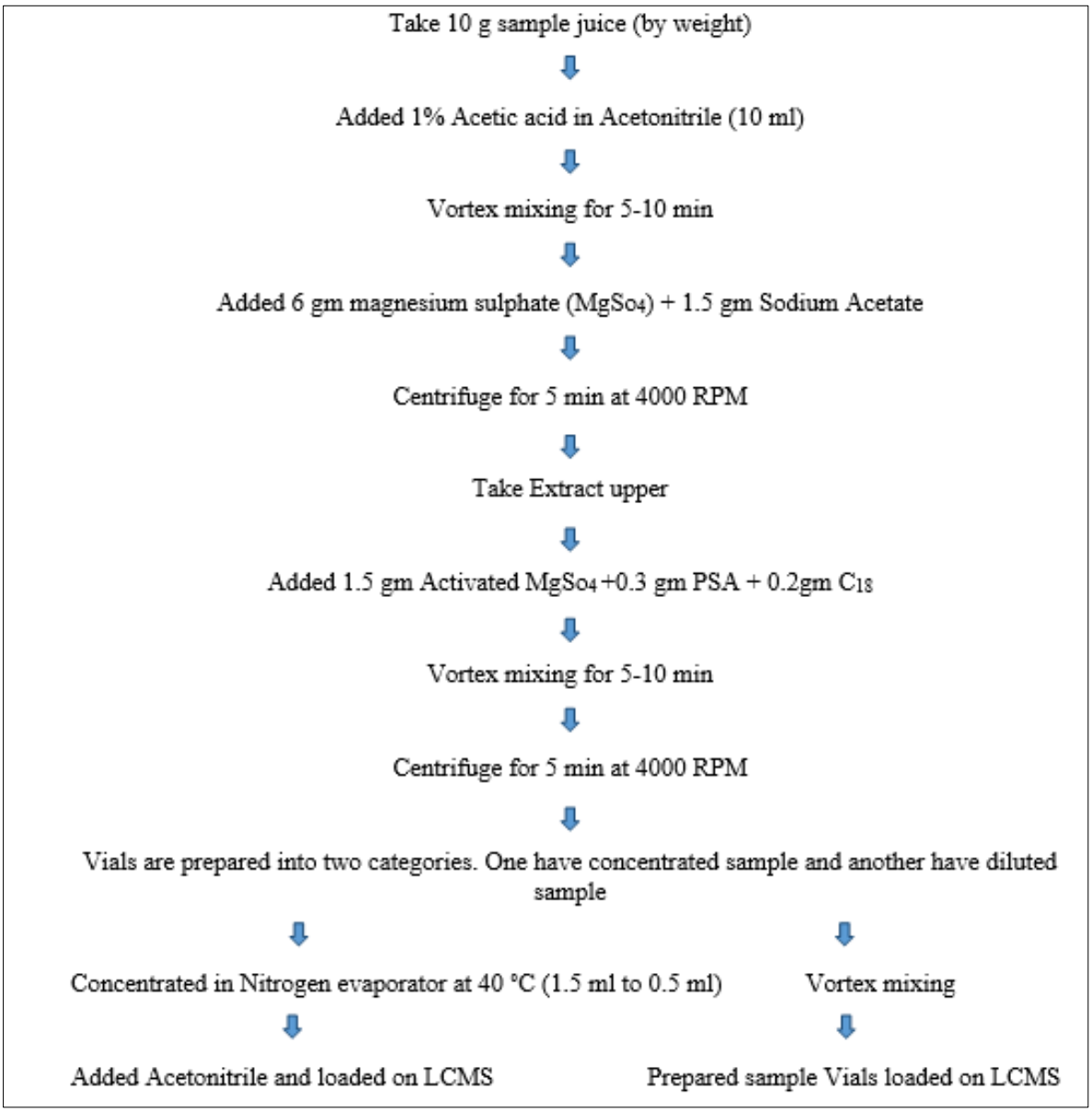

Fig 1: Methods for Analyze the pesticide residue in sugarcane juice

Individual pesticide stock solutions containing 1000 mg/L of the target pesticides were prepared in methanol and stored in deep freezer at −18 °C. Intermediate working standards mixtures in methanol, containing 100 mg/L for each pesticide were prepared and used to prepare the working standard solutions; these ones were used for spiking samples and for preparing the analytical curves in methanol and in the blank matrix extract.

LC-ESI-MS/MS

Liquid chromatography was performed in a Waters Alliance 2695 Separations Module fitted with an auto-sampler, a membrane degasser and a quaternary pump. Mass spectrometry was performed in a Micro-mass Quattro Micro API with an ESI interface. The LC separation was carried out in an XTerra analytical column C_{18} 3.5 µm (50 × 3 mm) (Waters, Milford, MA, USA). Analytical instrument control, data acquisition and treatment were performed by software Masslynx version 4.2, 2018 (Waters, Milford, MA, USA).

Results and Discussion

In all analyzed sample not found any pesticide residue therefore in sample number 03, chlorantraniliprole residue was detected but the amount of detected pesticide was not under prescribe limit. These single chemical only detected in sugarcane variety CO-0238. For this suspect again eight samples was collected only single CO-0238 variety and analyzed again for clear result.

Table 1: First analyzed sample (end of harvesting season, in April months)

Pesticide	Range of testing	Recovery % at (0.05mg/L)	Sample result (mg/L)							
			01	02	03	04	05	06	07	08
Carbofuran	0.01 to 0.5	83.46	ND	ND	ND	ND	ND	ND	ND	ND
Cartap Hydrochloride	0.01 to 0.5	109.73	ND	ND	ND	ND	ND	ND	ND	ND
chlorantraniliprole	0.01 to 0.5	91.85	ND	ND	Traces <LOQ(0.002)	ND	ND	ND	ND	ND
Chloropyrifos	0.05 to 0.5	61.50	ND	ND	ND	ND	ND	ND	ND	ND
Cypermethrin	0.05 to 0.5	57.64	ND	ND	ND	ND	ND	ND	ND	ND
Fipronil	0.01 to 0.5	114.12	ND	ND	ND	ND	ND	ND	ND	ND
Lambda cyhalothrin	0.05 to 0.5	57.49	ND	ND	ND	ND	ND	ND	ND	ND
Phorate	0.01 to 0.5	132.10	ND	ND	ND	ND	ND	ND	ND	ND

(Symbol: ND = Not Detected, LOQ = Limit of Quantification)

The blank sample chromatogram shows the interference peak in the retention time of the target compounds. All pesticides shows the linearity in the concentration range of 0.01- 0.5 ml/ L, with correction coefficient (r) higher than 0.995. There are only few studies that have use of QuEChERS sample preparation, for pesticide analysis using LCMS and a change in the solvent (hexane/acetone) prior to injection in the LCMS Furlani *et al.,* (2010). Research work revealed that, the study made and further used the concentrated and diluted sample. Solvent used for the system injection was acetonitrile & methanol in 12.5:87.5 ratio.

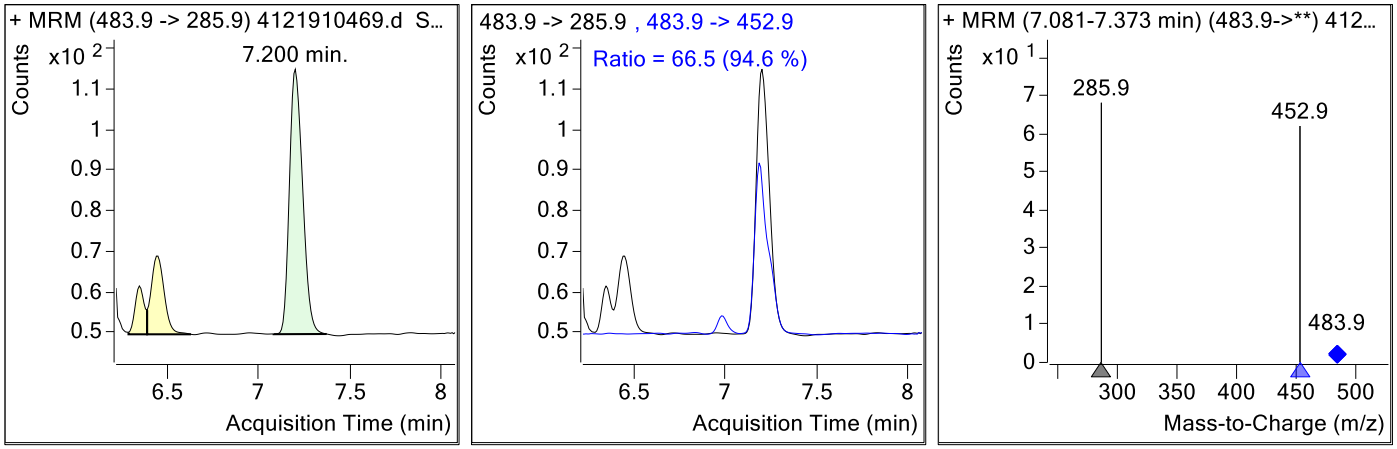

Fig 2: Chromatogram peak of chlorantraniliprole (April month)

The result of the method validation indicate that the QuEChERS sample preparation with the LCMS/MS analysis was suitable for the determination of Carbofuran, Cartap Hydrochloride, chlorantraniliprole, chloropyrifos, Cypermethrin, Fipronil, Lambda cyhalothrin & Phorate in sugarcane juice. In addition, sugarcane juice contains from 14.5% to 23.5% of sucrose (Prati & Camargo, 2008) [9]; these result indicate that the QuEChERS sample preparation was successfully used for analysis pesticide residue in sample with high sugar content (Furlani *et al.*, 2010). Barakat *et al.* (2007) [1] also reported successful use of QuEChERS when analyzing pesticide residue in honey.

Result of present investigation was found similar by Furlani *et al,* (2010), who analyzed 80 samples of sugarcane juice in Brazil. Other similar report for sugarcane juice pesticide residue analysis reported by Zuin *et al.* (2006) [11] revealed that 6 sample of sugarcane juice collected in the city of Sao Carlo, SP, Brazil, for the presence of 17 pesticides using gas chromatography coupled with a mass spectrometry detector. Nothing was founded in all the selected samples, while chlorantraniliprole was traced in one sample of sugarcane juice, variety (Co 0238) samples. However the level of chlorantraniliprole was lower than the LOD established in the present study (0.01 to 0.5 mg/L).

Table 2: Second analyzed sample (starting of harvesting season, in November month)

Analyte name	Range of testing	Recovery% at (0.05mg/kg)	Sample result (mg/kg)							
			01	02	03	04	05	06	07	08
Carbofuran	0.01 to 0.5	86.80	ND	ND	ND	ND	ND	ND	ND	ND
Cartap Hydrochloride	0.01 to 0.5	96.503	ND	ND	ND	ND	ND	ND	ND	ND
Chlorantraniliprole	0.01 to 0.5	85.40	ND	ND	ND	ND	ND	ND	ND	ND
Chloropyrifos	0.05 to 0.5	96.50	ND	ND	ND	ND	ND	ND	ND	ND
Cypermethrin	0.05 to 0.5	113.60	ND	ND	ND	ND	ND	ND	ND	ND
Fipronil	0.01 to 0.5	96.50	ND	ND	ND	ND	ND	ND	ND	ND
Lambda cyhalothrin	0.05 to 0.5	96.50	ND	ND	ND	ND	ND	ND	ND	ND
Phorate	0.01 to 0.5	96.50	ND	ND	ND	ND	ND	ND	ND	ND

(Symbol: ND = Not Detected)

The QuEChERS sample preparation is suitable for determination of 8 selected pesticides residue in sugarcane juice, demonstrating the high versatility of QuEChERS method, which was used for pesticide residue analysis in matrices with high sugar content with LCMS/MS.

During the analysis of all the samples, only one (Chlorantraniliprole) sample was found to contain traces of pesticide, which was much more than the prescribed standards. Therefore results indicate that there is no seasonal or geographical variation in the level of these pesticides. The method (QuEChERS) design for the analysis of pesticide during research will be useful for conducting such research studies in future.

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