MULTI-RESIDUE ANALYSIS OF PESTICIDES IN GRAPES IN BIJAPUR DISTRICT

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ABSTRACT: Fruit samples of grapes were analyzed for pesticide residues, employing multi-residue analysis by gas- liquid chromatography-mass spectrography (GC-MS/ LC-MS/MS). All the fruit samples showed the presence of pesticide residues with one or other group of pesticides. Some of the grape samples contain more than the minimum residue limit. The increasing interest in the study of pesticides in grapes is justified from an enological point of view, since some pesticides can interfere with fermentative microflora used in wine production, as well as affect consumer safety. There were no significant differences between some pesticide levels found in the whole grape (skin and pulp) and in the grape skin. Chlorpyriphos, captan, dichlorovos, oxyfluorfen, fipronoil, 4-bromo-2-chlorophenol and indoxycarb were detected. Nevertheless, consumer intake of pesticides from grapes studied in this work should be decreased as a result of water washing of the grapes. In this paper, multiresidue determination of pesticides using GC-MS/ LC-MS/MS are discussed

Key words- Pesticides, GCMS- LC-MS/MS, Fruits, Residues

INTRODUCTION

Grape is an important fruit crop of northern parts of Karnataka and it is grown over 9000 ha. The area under grape is increasing due to its excellent returns obtained under present agro-climate conditions. One of the major factors responsible for profitable cultivation of grape is the judicious manuring and application of pesticides with proper management practices. The present survey was therefore conducted to assess the pesticide residues in grape fruits. The survey included 10 grape yards which represent entire grape growing areas of Bijapur district.

Grapes, are one of the most widely consumed fruits in the world, are rich in pesticides. Fruits have a pivotal role in the diet for maintenance of health and prevention of disease. A wide range of pesticides are used for the production of fruits and vegetables in India, due to heavy pest infestation throughout the cropping season of horticultural crops (Agnihotri et al. 1999). Pesticides have potentially adverse effects on vegetables, fruits, animal resources and human health (Perez Bendiom; comprehensive Analytical Chemistry). Because of wide spread use of toxic pesticides, their residues have been reported in various environmental matrices (Kumari. B. et al, 1996; Kumari.B et al, Madan,2002; Kumari. B; Singh et al, 2003). Thus the determination of pesticide residues in fruits and other environmental components/ commodities like soil, water and fruits vegetables and total diet has become increasingly essential requirements for consumers, producers and authorities for food quality control. It is hoped that the data will establish a base line for determining changes in residue levels of different pesticides in future.

Organophosphate (OP) and carbamate (C) pesticides are widely used in India for agricultural pest control. The mechanism of these pesticides involves inhibition of enzyme, cholinesterase (AchE), which results in accumulation of the neurotrnsmitter acetylchlorine (Ach) in the nervous system. Supporting this, exposure to OP pesticide in a chemical manufacturing plant was shown to be associated with chronic bronchitis, impairment of respiratory muscles and mild lung hyperinflation in the workers (Kossaman.S et al 1997), Likewise, a greater risk of developing asthamatic symptoms and low respiratory volumes has been reported in farmers chronically exposed to pesticides(Peiris –John et al, 2005).

Currently India is the largest producer of pesticides in Asia and the third largest consumer of pesticides in the world (Kumari.B et al, 2002). Pesticide consumption has increasing steadily in the past few years and there has been a distinct shift from organochlorine (OC) to organophosphates (OP) and carbamate(C) pesticides (Environment, Government of West Bengal : 1999).

However, a number of OC pesticides which have been banned by the government for their toxicity, are still in use in India. People are directly exposed to these pesticides through dermal contact and inhalation and indirectly through the food chain. Although several million people are exposed, the health impact of chronic pesticide exposure in the country is largely unknown.

Presence of OP and SP residue in vegetables and fruits in an indicative change in usage pattern of insecticides in India where shift has been taken place from OC to the easily degradable groups of these insecticides in the last decade. Monitoring studies are imperative to know actual status of contamination due to toxic pesticide residues for future policies as well as to strengthen the confidence of consumer in quality of food. It is therefore, suggested that such studies may be extended to other fruits grown in different agro-climatic regions.

Materials and Methods

Sampling: Ten samples of ripen grapes were collected from grape yards in Bijapur district. Samples of one kg grapes were procured and kept in refrigerator till analysis. All the samples of total fruit (skin and pulp) were crushed and extracted fresh.

Sample extraction and clean up: The extraction of the samples and subsequent clean-up of the extractants were in accordance with the method used for the vegetables which consisted of homogenization, extraction of homogenates, liquid-liquid partitioning with ethyl acetate and clean-up by column chromatography with eluting solvent ethyl acetate:hexane (3:7 V/V) for organochlorines and synthetic pyrethroides (SP) and acetone:hexane (3:7 V/V) for organophosphates (OP). Kumari.B, et al; 2001)

APHA (American Public Health Association 1999) method was followed for analysis. Analysis were carried out by gas liquid chromatography (GLC) on a model 5890A. Hewlett Packard (HP) equipped with ^{63}Ni electron capture detector, capillary column SPB-5 (30mx0.32mm i.d x0.25µm film thickness) of 5% diphenyl 95% dimethyl siloxane for OC and SP. Column temperature:150^{o}C initially for five minute then programmed at 8^{o}C/minute up to 190^{o}C for two minutes and then at 15^{o}C/minute up to 280^{0}C for 10 minutes, injector temperature was 280^{0}C and detector temperature was 300^{0}C, nitrogen flow rate:2 ml/minute through column and make up 60 ml/minute with split ratio 1:10.

For the analysis of OP insecticides, HP gas chromatograph equipped with nitrogen phosphorous detector with mega bore column HP-1 (10m x 0.53 mm i.d. x 2.65µm film thickness) of polysiloxane was used. Column temperature: 100^{o}C initially for one minute then increased at the rate of 10^{0}C/minute to 200^{0}C and was finally increased at the rate of 20^{0}C/minute to 260^{0}C; gas flows:H_2:1.5 ml:N_2 : 18 ml and O_2:135 ml/minute.

In order to ensure quality assurance information before taking up analysis of test samples, the analytical method was standardized by processing spiked samples in triplicate. Control samples were processed along with spiked ones.

RESULT AND DISCUSSIONS

The results of pesticide residues analysis of grape samples of Bijapur district are shown in the Table.1. GC-MS chromatograms of standard mixture and sample no.1 & 2 are shown in Fig.1, 2 and 3 respectively. It should be pointed out that, the present method was tailor-made in view of the previous information about the most prevalent pesticides in the area. From the results it can be seen that chlorpyriphos was detected in the range of 0.004 to 0.01mg/kg. The captan concentration ranged from 0.01 to 0.04 mg/kg. Dichlorovos concentration varied from 0.01 to 0.03 mg/kg. Fipronil concentration ranged from 0.001 to 0.02 mg/kg. 4-bromo-2-chlorophenol concentration varied from 0.01 to 0.02 mg/kg respectively. Residues of some pesticides in some samples, exceeded the MRL values fixed by FAO/WHO 1996, Joint Food standard Programme.

Table.1 Pesticide Residues in Grapes in Bijapur District

Pesticides→ Sample No.↓	Chloro pyriphos mg/kg	Captan mg/kg	Dichlorvos mg/kg	Oxyfluorfen mg/kg	Fipronil mg/kg	4-Bromo-2-chlorophenol mg/kg	Indoxycarb mg/kg
1	0.01	0.02	0.01	0.025	0.005	0.01	0.02
2	0.004	0.01	0.015	0.024	0.004	0.008	0.01
3	0.003	0.03	0.02	0.01	0.001	0.001	0.01
4	0.002	0.01	0.01	0.01	0.001	0.001	0.01
5	0.01	0.04	0.03	0.03	0.002	0.01	0.01
6	0.01	0.01	0.01	0.028	0.01	0.01	0.01
7	0.01	0.01	0.02	0.01	0.01	0.01	0.01
8	0.01	0.01	0.01	0.01	0.01	0.01	0.01
9	0.01	0.02	0.01	0.01	0.02	0.01	0.01
10	0.01	0.01	0.01	0.025	0.01	0.02	0.02

Fig.1 GC-MS Spectra of Pesticides Pesticide: Standard

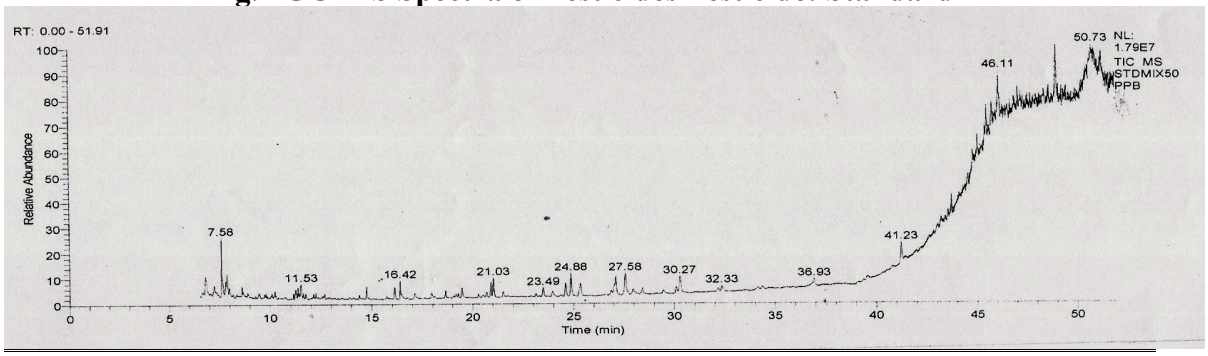


Fig.2 GC-MS Spectra of Pesticides Residue: Sample-1

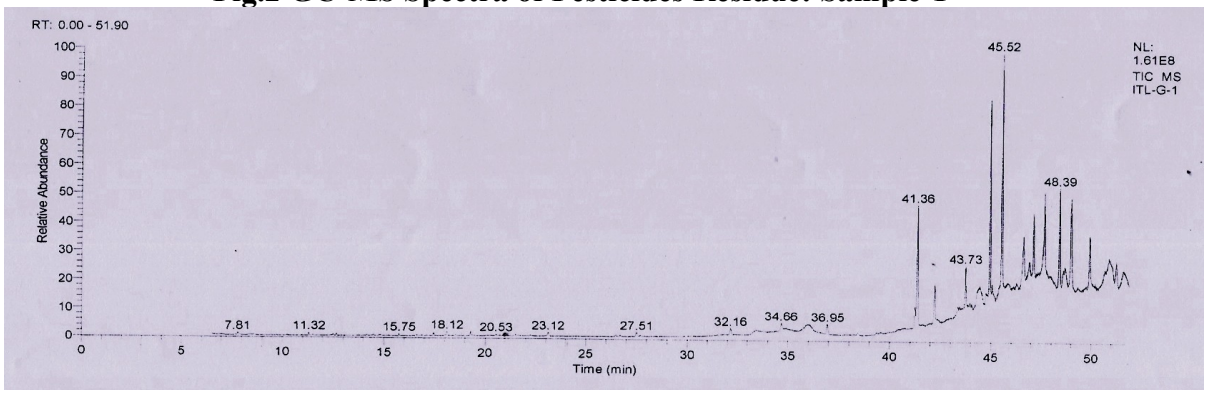
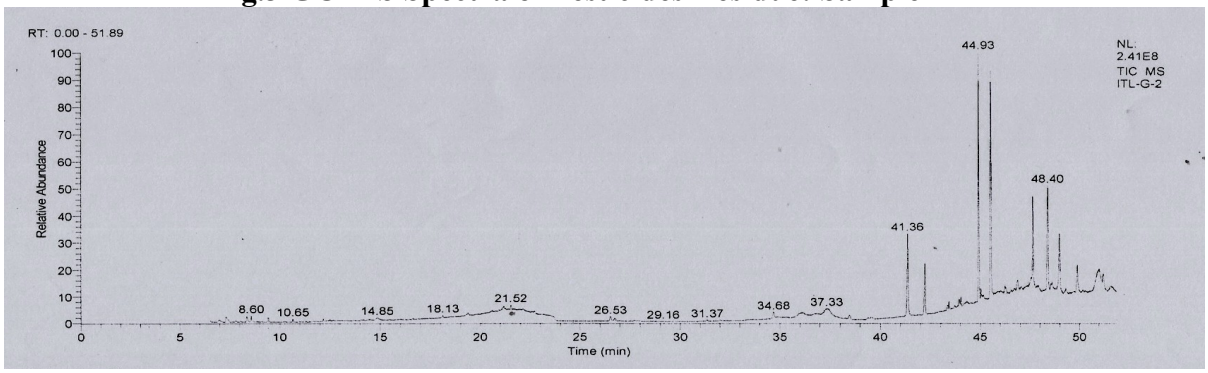


Fig.3 GC-MS Spectra of Pesticides Residue: Sample-2



Presence of pesticide residues in fruits and vegetables has become global phenomenon. Organochlorines and organophosphates were reported in fruits from Ontario, Canada (Frank. R et al, 1987).

Conclusions

It can be concluded that residues of few samples exceeded the maximum residue limits. Processing substantially lowers the residues of pesticides in grapes.

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