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Vortex assisted Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) Method Coupled with Gas Chromatography for the Estimation of Pesticide Residue in Orange Matrix

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Abstract—*The Pesticide residue analysis is routinely carried out by means of multi-residue methods based on homogenization of the sample with an appropriate solvent, separation of the liquid portion of the sample from insoluble material and further purification and clean up. In multi residue analysis the representative matrices were analyzed to study the effect of different components of sample on the recovery and stability of pesticides. The content of matrix like water, lipid or sugar is taken into consideration while residue analysis. pH also plays a great role in the stability of pesticides. Some pesticides behave differently in mixture of pesticides because it gets affected by the chemical nature of other pesticides.*

1. INTRODUCTION

High water content of orange makes the estimation of pesticides in this matrix little difficult. In this method the use of analyte protestants simplify the determination of mixture of pesticides and vortex further helps in proper mixting. The effective processing by QuEChERS method at two different temperature conditions gave a proper comparative analysis.

2. MATERIAL AND METHOD:

Treating solution was prepared by dissolving 10 mg of each pesticide separately in minimum amount of solvent acetone in a vial.

Approximately 100 gm of food matrix were weighed in aluminium foils. In case of orange and mango its individual units were cut half into longitudinal sections. The cut surface of unit was then placed on a clean aluminium foil and treating solution was applied carefully on their upper surface. The matrix was kept for 30 min. to allow the absorption of pesticides into the surface.

The treated units were placed in the bowl of chopper and the chopping was carried out for 6-7 minutes at the interval of 1 minute. The matrix was stirred constantly in between the subsequent intervals of chopping. The consistency of the matrix was examined visually by taking the peel size. The peel size was taken by withdrawing 2 gm of sample directly from the chopper and warring blender respectively and diluted it in 1 L water, stirred it and allowed the peels to migrate to the surface. The peels were collected and deposited on filter paper. The chopping was extended till the peel size obtained was more than 2-3 mm. 10 gm of chopped sample were transferred into the centrifuge tubes for the extraction.From the chopper, sampled out 3 replicates each of 10g analytical portion in 100 ml centrifuge tubes.

Extraction of sample was done by the modified QuEChERS method. Initially acetonitrile (10 ml), (1, 2) Disodium hydrogen citrate sesquehydrate (0.5gm), Trisodium citrate dihydrate (1gm) was added and vortexed. Then $MgSO_4$ (4gm) and NaCl (1gm) was added in each analytical portion. Each sample was vortexed for one minute and centrifuged for 5 minute. The extracted supernatant was dried over rotary evaporator.10gm of activated c-florisil was packed in chromatographic column using solvent acetonitrile and a layer of 2 cm magnesium sulphate was added over it. Then the rate of column flow was adjusted at 1 ml per minute. The dried up extract was dissolved in 50 ml acetonitrile and eluted through the packed column. Eluate was dried over rotary evaporator.The dried up extract was redissolved with 5 ml of acetonitrile and was collected in a glass vial. Mixture of analyte protectants was added in each sample. Further this sample was injected into Gas Chromatography with the help of Hamilton`s microinjection syringe for the analysis of the recovery of each pesticide.

In cryogenic processing the chopped unspiked samples (control) and spiked samples were sealed in the polyethylene bags and placed in -20^{o}C refrigerator for overnight (16-18 h). Next day the treated units were placed in the bowl of chopper and samples were grinded along with addition of 100gm of dry ice (in parts of 25gm). The grinding was carried out for 6-7 minutes at the interval of 1 minute. Now the grinded

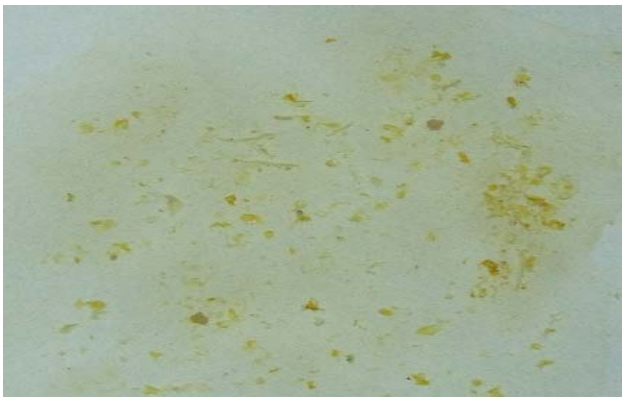
samples were again placed in plastic bags (half sealed) at -20°C for overnight for the evaporation of dry ice from them. Further processing was same as performed in ambient condition.

3. RESULTS AND DISCUSSION:

The orange fruit is one of the most acidic of all seed-bearing plants. The pH level is between 2.5 and 3, depending on the variety. This makes the orange as strong in acid as vinegar. Oranges are one of the largest commercially-grown fruits in the world. The top countries that produce the fruit are Mexico, the United States and Brazil. Many chemical substances including pesticides are applied in order to control undesirable moulds or insects on these fruits. The excess use of pesticides causes contamination of these fruits with their residues.

Efficiency of sample processing:

To determine pesticide residues in orange the proposed method was applied. To check the efficiency of grinding the size of peel was observed. The peel sizes taken from the different experiments are shown in figure- 1 (a) and (b). The peel sizes from all the experiments were around 2-3mm. There was difference in the size of the peel from ambient and low temperature processing. The grinding at lower temperature was more homogeneous. Acetonitrile extracts were heavily pigmented containing large amounts of matrix co-extractants. At this point, acetonitrile extracts are unsuitable for further analysis due to the high levels of endogenous interferences co-extracted with the pesticides during solvent extraction. In this work the orange was spiked and analyzed by two different methodologies. In both methodology the sample was spiked and processed at two different temperature conditions. The metholodoly-I involved two steps processing at ambient temperature using centrifuge. In methodology-II (i.e., cryogenic processing) the samples were initially placed into the fridge and the grinding was performed with dry ice. The dry ice was ued for the homogeneous grinding of the sample.



(a)Ambient Temperature

(b) Lower Temperature

Fig. 1: (a) and (b) representing peel size of orange samples processed at ambient and lower temperature respectively.

4. RECOVERY AND DISCUSSION

The recoveries of each pesticide from the matrix at both the temperature conditions were estimated for each replicate of sub sampled analytical portions. The recovery was calculated from the regression equations obtained from solvent (S), solvent with analyte protectants (SAP), matrix match calibration (MMC), matrix match calibration with analyte protectants (MMCAP) for all the samples. The recovery of analytes with different calibration curves have been shown in figure-2.

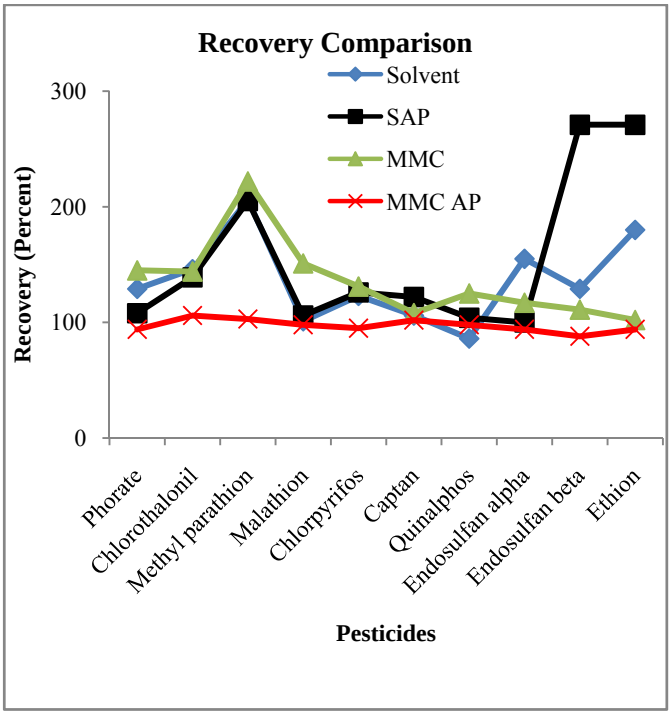


Fig. 2: Comparison of average recoveries of pesticides from mango samples processed at lower temperature condition.

For chlorothalonil the recovery with analyte protectants calibration was 108% and above 144% with calibration without analyte protectants at ambient temperature. At lower temperature condition the recovery of chlorothalonil with analyte protectants calibration was 106% and 144% with calibration without analyte protectants at lower temperature. At ambient temperature methyl parathion was recovered around 111% with analyte protectants calibration and 241% with calibration without analyte protectants. At lower temperature condition the recovery of methyl parathion was 103% with analyte protectants calibration and 222% with calibration without analyte protectants. It indicates that at ambient temperature the matrix effect in recovery with solvent analyte protectants calibration was nullified by analyte protectants.

Matrix enhancement effect (3) increased the recovery of malathion to 151% but with analyte protectant the recovery was controlled at 98% both at ambient temperature and lower temperature condition. At ambient temperature the recovery of chlorpyrifos was 119% with solvent calibration without analyte protectants and 121% with solvent calibration with analyte protectants. When we compared the recovery of matrix match calibration with and without analyte protectants it was better in analyte protectants.

While at lower temperature the recovery of chlorpyrifos was 131% with MMC and 95% with MMCA. Here analyte protectants nullified the matrix effect.

The matrix effect on pesticide recovery was studied for both the methodologies. The matrix resulted in enhancement effect on captan. At lower temperature its recovery with MMCAP was 102% but with MMC it was much higher because of matrix enhancement effect.

The orange matrix resulted both in diminishing and enhancement effect on the recovery of pesticides. Due to the enhancement effect of matrix on the quinalphos, its recovery at ambient and lower temperature conditions enhanced to 129% and 125% with MMC curve respectively. But recovery was balanced with MMCAP and it was 103% and 98% with analyte protectants both at ambient and lower temperature conditions.

The recovery of endosulfan alpha with MMCAP at ambient temperature and lower temperature conditions was 93% and 94% respectively. Its recovery enhanced more or less up to 118% showing the matrix enhancement effect. The reproducibility of endosulfan recovery with MMCAP curve at lower temperature was within the acceptable limit. 88% of Endosulfan beta was recovered at lower temperature with MMCAP curve and the reproducibility within the acceptable limits while 93% recovery was recorded at ambient temperature condition with MMCAP and this time reproducibility was 0.01%. Ethion recovery was 94% with MMCAP curve and the reproducibility was 0.01%, which is within the acceptable limit at lower temperature. Due to matrix enhancement effect its recovery raised at ambient temperature with MMC curve to 100% with 0.01% reproducibility. But with analyte protectants calibration the recovery at ambient was 93% with 0.01% reproducibility.

The processing efficiency of the equipment was determined by the peel sizes of the matrices. The matrix effect (diminishing and enhancement), handling error in chemicals and the improper injection technique are few uncertainty factors which were observed on the recovery of pesticide residues. Four types of calibration curves were constructed to calculate the recovery of pesticides. These were standard with solvent, solvent with analyte protectants, matrix and matrix with analyte protectants to nullify the effect of matrix.

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