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QuEChERS: A Microextraction Technique for Pesticide Residue Analysis in Food Commodities

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Abstract: *Pesticide residues in food commodities has become a major cause of concern all-over the world. Analysis of pesticide residues from vegetable and fruit samples to ensure the safety of consumers is becoming increasingly important. The most important step of any analytical methodologies is sample preparation step because it determines the efficiency of any method. A good microextraction technique reduces the sample and solvent volume, maintaining the high performance, low-cost and improvement of the sampling steps such as extraction, concentration, isolation of analytes, and clean-up. Lots of analytical methods are developed to analysed multiple pesticide residues analysis and contaminantcontroloffoodproducts,feedstuff,andenvironmentalsamples. While in starting, the QuEChERS was introduced for pesticides residues analysis in fruits and vegetables, but over a period of time, it is gaining significant popularity in the analysis of wide spectrum of analytes. QuEChERS method provided high quality results in a fast, easy, an inexpensive approach. The method is very effective and gives recovery for most of the pesticides in the range of 80 -120 percent and the ruggedness of the method is evident from reproducibility, repeatability being within acceptable range in all the tested samples. Liquid-liquid partitioning using acetonitrile and purifying the extract using dispersive solid-phase extraction (d-SPE) is the key point of this method. The objective of this paper is to give an overview of the benefit of QuEChERS and the recent developments in the QuEChERS (quick, easy, cheap, effective, rugged, and safe) approach for sample preparation.*

Keywords: Pesticides, Pesticide Residue Analysis, Food, QuEChERS Method

I. INTRODUCTION

Unapproved and non-judicial use of pesticides has been found to be the cause of presence of harmful level of residues in end user food commodities. The export of food commodities gets negatively affected if pesticide residues are detected above Maximum residues limit (MRL) by the importing country. For these reasons, several countries spend millions of dollars on food contamination monitoring programs and evaluation of data regarding pesticide residues in relation to health risk assessment. The old solvent-based sample preparation methods like liquid-liquid extraction, solid phase extraction, accelerated solvent extraction, matrix solid phase dispersion, needs various matrix pre-treatment steps which are tedious, time consuming, large sample volumes and costly solvents. So, demand of time is to replace these old techniques with some better micro extraction techniques, which are also compatible with the recent advances of highly sensitive analytical instrumentation.A simple, sensitive and rugged method is needed to carry out large scale monitoring of pesticide residues in food commodities. QuEChERS approach first introduced and gained popularity in pesticide residue analysis for its high sample throughput and cost effectiveness(1). The QuEChERS approach using acetonitrile has now become an official method of AOAC International and European Standards Organization (CEN) (2). According to the Web of Science,more than 800 papers have been published till now on QuEChERS methods. The QuEChERS approach was amended and validated so that routine monitoring of pesticide residues in vegetable and fruit commodities can be made quick, cheap, effective and environmentally safe. There have been reports of the evaluation and validation of QuEChERS approach of sample preparation for different commodities such as vegetables and fruits(3-8), baby food (9) olives (10) tobacoo (11), milk, eggs, and avocado (12). Sample preparation by this way has

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been coupled with GC-ECD, NPD (13), GC-MS/MS (14-15) and LC- MS/MS (16-18) for the quantification of pesticide residues. Keeping the essence of this approach intact each laboratory has done some modifications to suit their laboratory conditions and scope of analysis.

Method validation is the process used to confirm that the analytical procedure employed for a specific test is suitable for its intended use. The extent to which a method needs to be validated depends on its application. Selectivity, linearity, accuracy, precision, range, limit of detection and limit of quantitation are the common characteristics that must be measured for validation of any method (19). The most important advantage of the QuEChERS technique is its speed and high sample throughput,abatchof10−30samplescouldbeextractedin30−40min. and it also favours the green chemistry approach due to its low solvent consumption.[20].The method involves an acetonitrile extraction of a solid sample in an aqueous environment followed by dispersive solid phase extraction (d-SPE) to remove matrix interferences [21]. Liquid-liquid extraction (LLE) has an effective method of separating compounds which have different solubilities in two immiscible liquids[23]. High polarity solvents have been investigated for extraction of many analytes that cannot be extracted by conventional LLE solvents. We use acetonitrile as the extracting solvent in place of other non-halogenated solvents such as acetone and ethylacetate because upon the addition of salts, it is separated more easily from water than acetone. The polarity of acetonitrile is higher than that of acetone and ethylacetate, therefore, the medium to high polar pesticides has much better solubility and so higher recoveries obtained. An internal standard is added in multiple steps to minimize the errors. In his own study, Anastassiades explained about the use of different internal standard allow the identification of errors occurs in sample preparation steps during partitioning or clean-up [24].

II. General Procedure

The originally published procedure was a simple method for the determination of pesticide residues in high water content fruits and vegetables, which gives good recoveries and repeatability for a wide range of fortified pesticides [29]. First step is to weigh 10 g of the uniformly homogenized sample into a 50 mL polypropylene centrifuge tube, then addition of 10 mL of acetonitrile and shaking the sample for approximately 1 minute. Next, 4gof anhydrous$MgSO_4$and1gNaCl and an internal standard is added, shaken for30 s and centrifuged. Then a 1 mL aliquot of theupperacetonitrilelayeristransferredintoa15 ml centrifuge tube for cleaned up using Dispersive-SPE. Then supernatant as a final extract can be analyzed by instrumentation like GC and LC-techniques coupled with mass spectrometry detectors. Flowchart for originally developed QuEChERS methods are presentedinFig.1[30,31].

2.1 Modifications in Different QuEChERS Methods Over a Period of Time

Various research papers are published worldwide using the QuEChERS method and modification were done by researchers according to the commodity, conditions and the contaminants. While most pesticides give satisfactory results using these methods, some perform poor extraction efficiency, very polar, acidic or basic analytes might be troublesome, sofor analytes, some improvements should be required. Further, modifications have also be done to confirm the good extraction of pH dependant compounds and to expand the spectrum of matrices covered[33]. Lehotay et al. and Anastassiades et al. realized that use of different buffering salts to improve recoveries of pH-dependant analytes was necessary [34].

Some modified methods are also given below which are implemented and reported.

- Original Unbuffered Method: Fast and Easy Multiresidue Method Employing Acetonitrile Extraction and “Dispersive Solid-Phase Extraction” for the Determination of Pesticide Residues [25]
- European EN 15662 Method: Determination of Pesticide Residues Using GC-MS and/or LC-MS/MS following Acetonitrile Extraction and Clean-up by Dispersive SPE QuEChERSmethod [26]
- Mini-Multiresidue Method: A Mini-Multiresidue Method for the Analysis of Pesticide Residues in Low-Fat Products [27]
- AOAC Official 2007.01 Method: Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate. [28]

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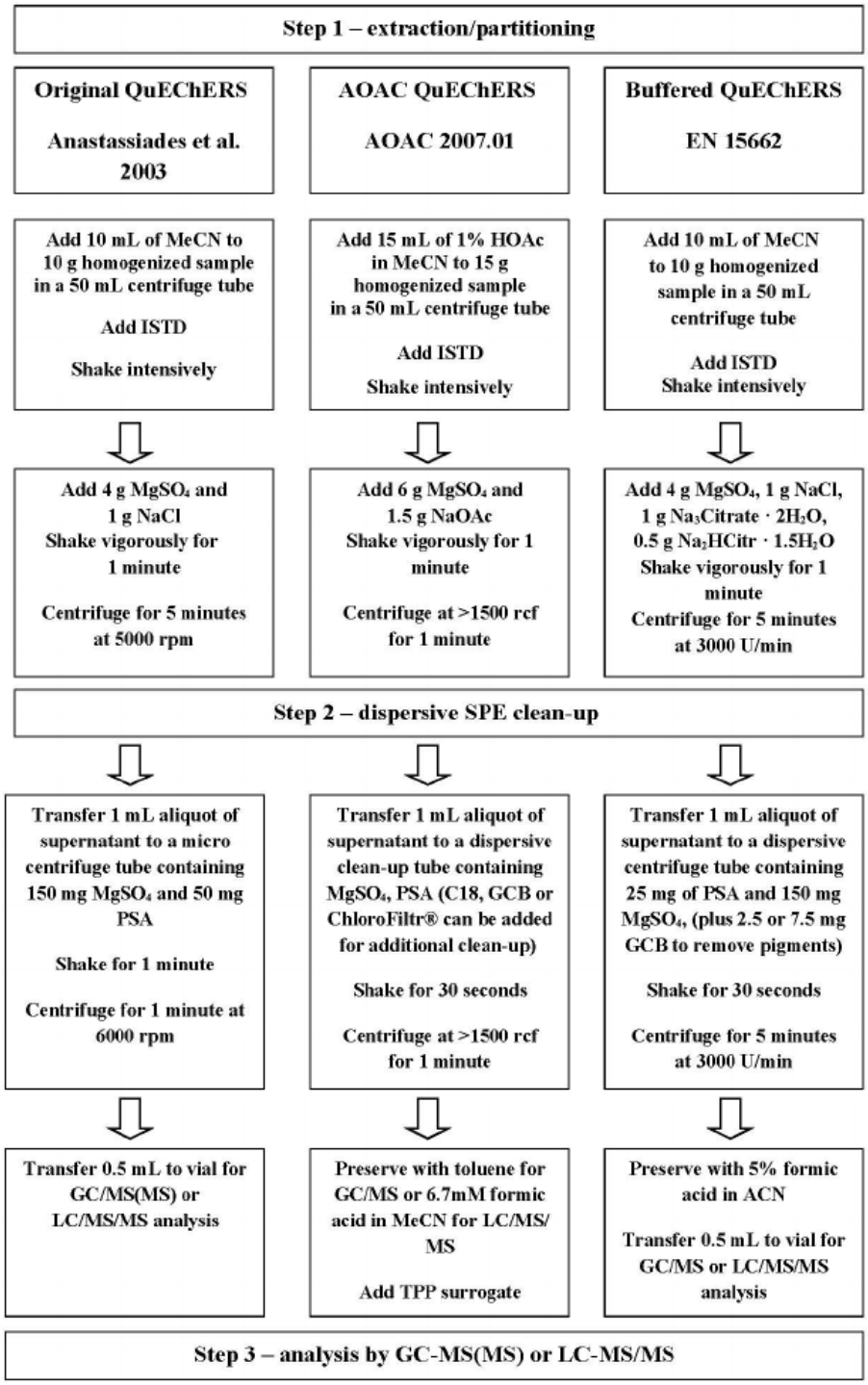

Figure 1: Schematic flow chart for main steps of three primary QuEChERS methods: Original QuEChERS Method [29], AOAC 2007.01 Official Method [30], EN 15662 The European Official Method [31]

III. Conclusion

The QuEChERS method has several advantages in comparison of traditional methods of analysis. It gives good recoveries for a wide range of pesticides. The flexibility of slight modifications of solvents, salts, and sorbents, makes the QuEChERS sample preparation approach adaptable for the analysis of broad spectrum of analytes and matrices. It

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can also be applicable for other analytes like veterinary drugs, mycotoxins, Polycyclic hydrocarbons, dyes analysis, other flame retardants other than pesticides residue analysis and the further scope is still open for the new analysis. The advantages of QuEChERS sample preparation method isits simplicity of operation, fast sampling, less solvent volume, low in cost, high recovery and being environment-friendly.

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