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Review

QuEChERS method for the determination of pesticide residues in food commodities- a review

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ABSTRACT

A range of pesticides are applied to crops to control pests and diseases but there are concerns about the persistence of residues in food and processed food products. The quick, easy, cheap, effective, rugged and safe (QuEChERS) method has generally been used for the determination of pesticide residues in different food commodities. QuEChERS principle and the extracts were cleaned up through dispersive solid-phase extraction with primary and secondary amine after salting out with NaCl and $MgSO_4$. This sample preparation approach has emerged as a versatile alternative method for analyte extraction and this technique requires little organic solvent and can also improve the limits of detection. QuEChERS is of increasing interest in the analysis of pesticide residues and is applied in the determination of various classes of pesticides in food commodities.

Keywords: QuEChERS; residues; food commodities

INTRODUCTION

Food safety is an issue of primary importance to human being. Real and perceived concerns about harmful consequences of chemical residues in food and environment have created a strong need for analytical monitoring techniques (Lehotay 2001). It is a regulatory requirement that the analytical methods be developed to determine pesticide residues in crops, feed and food commodities as well as environmental samples. The method may then be adapted or modified to match the requirements and capabilities of the laboratory or the purpose for which the method will be used (Aysal et al 2004). Multi-residue analysis of pesticides in fruits, vegetables and other foods is a primary function of several regulatory, industrial and contract laboratories throughout the world (Fillion et al 2000). Once analytical quality requirements (trueness, precision, sensitivity, selectivity and analytical scope) have been met to suit the need for any particular analysis all purposes for analysis favor practical benefits (high sample throughput, ruggedness, ease-of-use, low cost and labor, minimal solvent usage and waste generation, occupational and

environmental friendliness, small space requirements, and few material and glassware needs).

A number of analytical methods have been designed to determine multiple pesticide residues but very few of these methods can simultaneously achieve high quality results for a wide range of pesticides and the practical benefits desired by all laboratories. A simple, fast and inexpensive method for the determination of pesticide residues in fruits and vegetables has been introduced by Anastassiades et al (2003) which provides high quality results in a fast, easy and an inexpensive approach. We call the novel approach 'QuEChERS' (pronounced as 'catchers') which stands for quick, easy, cheap, effective, rugged, and safe. QuEChERS is of increasing interest in the analysis of pesticide residues and it is applied in the determination of various classes of pesticides in vegetables, fruit, environmental samples (Anastassiades et al 2003, Lehotay et al 2005, Nguyen et al 2008, Brondi et al 2011, Paramasivam and Banerjee 2011, Paramasivam and Chandrasekaran 2013, Paramasivam and Chandrasekaran 2014) and it has been grown in popularity among pesticide residue scientists owing to its inherent advantages such as speed, low cost and wide applicability.

The present article focuses mainly on the QuEChERS method that is currently undergoing an extensive inter-laboratory trial for evaluation and validation by pesticide monitoring programs. There is a need to streamline the final method as much as possible which is meant to avoid excessive sample size, extra glassware, blending, filtration, large volume quantitative transfers, evaporation/concentration steps and solvent exchanges. So minimizing the number of steps in the method not only for reasons of efficiency but also because each step in an analytical method complicates the procedure, increases the potential for analyte losses and adds another potential source of error.

METHODOLOGY

Sample preparation

The methods for extraction of pesticides and clean up of environmental samples are extremely important for their quantitative determination in the matrices of interest. The proper techniques for powerful chopping devices help in achieving good sample homogeneity and to ensure that a 10 g sub-sample is representative for the analysis.

Extraction/partitioning

Homogenized sample (10 g) is taken into 40 ml Teflon centrifuge tube. To it 20 ml acetonitrile (MeCN) is added with the dispenser and tightened with screw cap. It is shaken vigorously for 1 min by using vortex mixer at maximum speed. 4 g anhydrous $MgSO_4$ and 1 g NaCl are added and mixed on a vortex mixer immediately

for 1 min. The action is performed immediately to prevent formation of $MgSO_4$ conglomerates. To it 50 µl standard solution is added, mixed on a vortex mixer for another 30 sec and extract is centrifuged (or batch of extracts) for 10 min at 6000 rpm.

Dispersive SPE clean up

Transfer 4 ml aliquot of upper MeCN layer into 15 ml micro centrifuge vial containing 100 mg PSA sorbent and 600 mg anhydrous $MgSO_4$, cap tightly. Shake by hand or with Vortex mixer for 30 sec. Centrifuge extracts (or batch of extracts) for 5 min at 3000 rpm to separate solids from solution and transfer the resulting cleaned extract of 2.0 ml to a graduated 15 ml borosilicate glass turbovap tube. The extract is evaporated to dryness under a gentle stream of nitrogen in a low volume concentrator by using the Turbovap LV set at 40^{i} C. The residues are then dissolved in 1 ml of hexane and the extract is transferred to an auto sampler vial and an aliquot is analyzed using GC and GC-MS analysis.

QuEChERS analytical methodology

The original QuEChERS method version uses neutral extraction conditions by single phase extraction of multiple analytes with a small volume (10 ml) of acetonitrile followed by liquid-liquid partitioning with the addition of 4 g of anhydrous $MgSO_4$ plus 1 g of NaCl. Removal of residual water and clean up of polar residues are performed simultaneously using a dispersive solid-phase (d-SPE) clean up. The d-SPE clean up carried out by just adding a primary secondary amine sorbent (PSA) and anhydrous $MgSO_4$ are mixed with the sample extract. After quick shaking followed by centrifugation residual water and many polar matrix components such as organic acids, some polar pigments, and sugars are simultaneously removed (Anastassiades et al 2003).

Since the development and publication of the method, QuEChERS has been gaining significant popularity. It is the method of choice for food analysis because it combines several steps and extends the range of pesticides recovered over older and more tedious extraction techniques. The method has undergone various modifications and enhancements over the years since its first introduction. These have been designed to improve recovery for specific types of pesticides or types of food. The traditional methods of determining pesticides in food are usually multi-stage procedures requiring large samples and one or more extract clean up steps. Therefore they are time consuming, labour intensive, complicated, expensive and produce considerable amounts of wastes. Moreover the traditional methods often give poor quantitation and involve a single analyte or analytes from a single class of compounds.

On the other hand QuEChERS method has several advantages over most

traditional methods of analysis: 1) high recoveries (>85%) are achieved for a wide polarity and volatility range of pesticides, including notoriously difficult analytes; 2) very accurate (true and precise) results are achieved because an internal standard (IS) is used to correct for commodity to commodity water content differences and volume fluctuations; 3) high sample throughput of about 10-20 pre-weighed samples in H"30-40 min is possible; 4) solvent usage and waste are very small and no chlorinated solvents are used; 5) a single person can perform the method without much training or technical skill; 6) very little glassware is used; 7) the method is quite rugged because extract clean up is done to remove organic acids; 8) very little bench space is needed thus the method can be done in a small mobile laboratory if needed; 9) the reagent costs in the method are very inexpensive; and 10) few devices are needed to carry out sample preparation.

CONCLUSION

The recent progress in modern sample preparation and extraction techniques for the determination of pesticide residues in different food and environmental matrices was reviewed. It is well known that sample preparation is still one of the most critical steps in the determination of food components and trace pesticide and other residue analysis in different matrices. A lot of progress has been made toward the development of faster, safer and more environmental friendly techniques for sample extraction and extraction clean up prior to instrumental analysis. However their performance should be surpassed by new modern analytical approaches such as QuEChERS (quick, easy, cheap, effective, rugged and safe) and their development should proceed further. Future developments in all areas of analytical sample preparation are expected to continue to be application-driven in a quest for improved recovery, higher sample throughput and reduced consumption of organic solvent with capability to provide accurate results.

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