

Extractability of Incurred Residues using QuEChERS

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INTRODUCTION

Recoveries obtained in typical method validation experiments, where pesticides are spiked to sample homogenates in the lab, do not necessarily reflect the extractability rates achieved for incurred residues (resulting from the application of pesticides during crop production). Incurred residues are not always easily accessible as they may be enclosed in cells, vacuoles or wax particles or may have even undergone strong non-covalent interactions with matrix sites. To achieve quantitative extraction, sample preparation should ensure that all residues are accessible and transferable to the extraction solvent. Good comminution of the sample and small particles are thus essential in assisting extraction.

QuEChERS employs acetonitrile for extraction which is miscible with water thus ensuring a one-phase extraction system, but at the same time acetonitrile, even more when mixed with water, is quite weak in dissolving lipids and penetrating waxes. The method foresees a 1 min extraction after the addition of acetonitrile as the standard procedure. Extended extraction times are foreseen for special cases.

EXPERIMENTAL

Various types of shaking and homogenization devices were checked to determine the minimum extraction times required to quantitatively extract incurred residues (see results). Furthermore it was tested how the extension of the extraction times affects the recoveries of spiked residues at extreme pH values within the physiological range. The impact of extraction on the amount of co-extracted matrix components as well as on the "matrix effects" in determinative analysis were also studied. Commodities with incurred residues were checked for sufficient homogeneity before starting any comparison experiments. In comparison experiments each setting was typically checked in triplicate.

RESULTS

1 min shaking, foreseen in QuEChERS, was shown to be in many cases not sufficient to quantitatively extract incurred residues. For practical reasons the use of automated shakers is thus considered as necessary.

In some commodities extended extraction times resulted in deeper coloured extracts and higher dry residue. The impact on matrix-effects was tested using blank samples and was shown to be insignificant suggesting that the compounds responsible for matrix effects are rather quickly extracted.

Where the yields of incurred residues were at least 15% lower at 1 min extractions compared to the plateau (typically reached at 10-15 min depending on matrix and pesticides) the effect was considered as significant. Significant effects were observed in ca. 50% of the tested cases of incurred residues. In ca. 15% of the cases the recoveries were even lower than 75%. In total more than 80% of the tested samples (fruits, vegetables and cereals) showed a significant effect for at least one of the pesticides contained.

Shakers: The shaking intensity seemed to play a less important role than the extraction times which indicates that soaking effects may be very important. The use of ceramic homogenizers or metal balls did not reduce extraction times of incurred residues. Employing samples at room temperature rather than frozen, notably accelerated the extractions.

Ultra-Turrax dispenser and **ultrasound probe** were shown to significantly accelerate extraction but were considered as impractical for routine applications. They are recommended where sample particles need further comminution to improve residue accessibility (e.g. for insufficiently comminuted cereals, pulses).

Pesticides: No clear link between pesticide polarity (logP) and extraction yields could be made.

Matrix: extraction retardation seems to be more pronounced in certain commodities (e.g. grapes) than in others. Natural surface-wax that is only slowly penetrated by the extractant may play a role.

Impact of extended extraction times on recoveries: In total ca. 430 pesticides were tested whether they degrade during prolonged extraction times using commodities representing the lower and upper end of the physiological pH range. Only very few pesticides showed a degradation effect e.g. captan, folpet, dichlofluanid, chlorothalonil in the higher pH-range.

**Place for two flip-chards
(see additional files)**

SUMMARY

Experiments with real samples have shown the need for prolonged extraction times (e.g. 10-20 min) to increase the recoveries of incurred residues. The use of mechanical shakers is thus indicated.

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