

COMPARISON OF ANALYTICAL METHODS FOR THE DETERMINATION OF PESTICIDE RESIDUES IN RICE.

Lucía Pareja¹, Verónica Cesio², Horacio Heinzen², Amadeo R. Fernández-Alba¹

¹ Pesticide Residue Research Group. University of Almeria, Almeria, Spain.

² Pharmacognosy and Natural Products. Organic Chemistry Department. Faculty of Chemistry. UdelaR, Montevideo, Uruguay.
e-mail: lpareja@fq.edu.uy

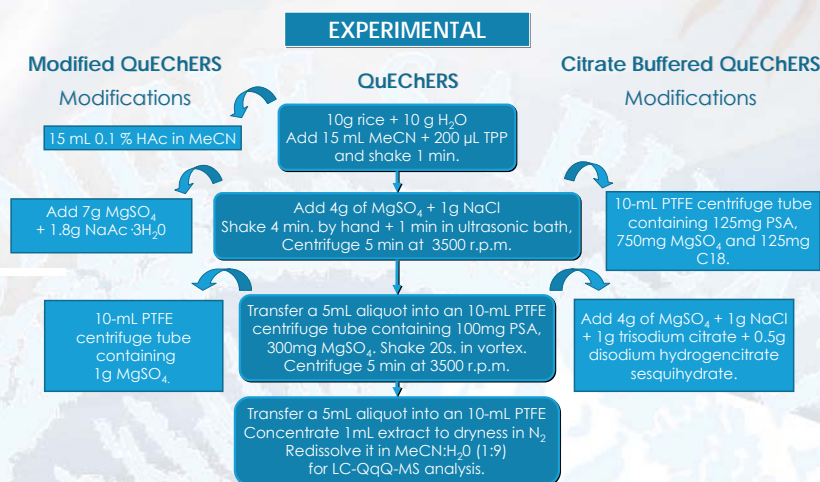
INTRODUCTION

Rice is one of the most important agricultural crops all over the world. Herbicides, insecticides and fungicides are currently employed to enhance crop productivity and can contaminate the final product. Surprisingly, there is not general methodology for pesticide residue analysis reported in the literature, due perhaps to matrix complexity and the wide chemical spectrum of the employed pesticides. Nowadays, only low levels of pesticides are allowed in rice, and therefore, the development of a fast and reliable multi-residue method for pesticide analysis in rice is mandatory. In this communication we report our attempts to develop a multi-residue method for the analysis of 58 pesticides (herbicides, fungicides and insecticides) currently employed in rice production. The scope of pesticides extends from acids to bases and from polar to medium polar pesticides.

The performance of three extraction techniques, using two different spiking processes were compared in polished rice.

The tested methods were compared at two fortification levels: 20 and 100 µg Kg⁻¹ by LC-QqQ/MS. Matrix effects were evaluated with the three methods using LC-TOF/MS.

Linearity, limits of detection and quantification, percentage recovery and repeatability (as relative standard deviation) were assessed.



RESULTS AND DISCUSSIONS

- The Recoveries of the 58 pesticides studied were different for the three methods assayed at both fortification levels. Modified QuEChERS and Citrate buffered QuEChERS showed good recoveries and acceptable relative standard deviations, but the best performance was obtained with citrate buffered QuEChERS at 20 µgKg⁻¹ (Fig. 1).
- For Citrate buffered QuEChERS around 80% of the pesticides under study showed recoveries in the range 70-120% which complies with the DG-Sanco requirements. Some pesticides such as molinate, imazapyr, fluroxipyr, quinclorac, quinoxifen, spiroxamine and temephos showed good precision, but the recoveries did not reach the acceptability requirements.
- 67%, 92% and 43% of the studied pesticides presented a relative standard deviation lower than 20% for the QuEChERS method, the modified QuEChERS and citrate buffered QuEChERS, respectively
- The signal to noise ratio was calculated for 10 µgKg⁻¹ (maximum allowed by European legislation for food) and was higher than 3 for all pesticides, except for: cyhalofop-butyl, iprodione, kresoxim-methyl, tiophanate-ethyl and prochloraz.
- Matrix effect influences the behavior of the base line along the chromatogram, from 0 to 9 min and from 9.5-11min the chromatograms showed almost the same profile, but after 11 min. the differences were significant (Fig. 2).

CONCLUSIONS

- Citrate buffered QuEChERS and modified QuEChERS are suitable for the determination of the selected pesticides in rice.
- Concerning matrix effect the original QuEChERS method is more affected by the matrix.

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LC-QqQ Conditions	
Volume injection	10 µL
Total runtime	ESI (+) 43min
	ESI (-) 15 min
Eluent flow	0.6 mL min ⁻¹
Mobile phase Gradient	A: MeCN, B: 0.1% formic acid in H ₂ O
Column	C8 4.6 x 150 mm, 5µm particle size
Ionization mode	ESI +/-
Gas temperature	325 °C
Gas Flow	12 L min ⁻¹
Nebulizar gas	50psi
Capillary Voltage	5000V
Dwell time	15 ms

Fig.1 Distribution of the recoveries of 58 pesticides for the three methods at 20 µg Kg⁻¹

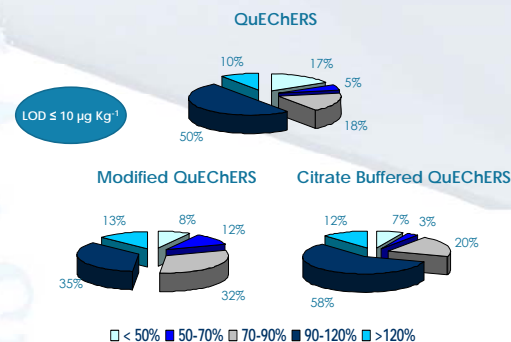


Fig.2. Matrix effect in LC-TOF/MS.

