

Application of IC-MS/MS for the analysis of cationic pesticides in food

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Introduction

Polar pesticides are usually determined using liquid chromatography (LC) with tandem mass spectrometry (MS/MS). As many highly polar pesticides have ionic character, they can also be separated using ion chromatography (IC) before MS/MS detection. Recently, the options for connecting of IC to MS/MS have improved in terms of robustness and convenience. Here, methods on two IC columns and results of method development and validation are presented.

Method

Sample extracts were obtained following the QuPPE (Quick Polar Pesticides) extraction procedure and its variant for commodities with high protein and/or lipid content (QuPPE-AO) [1,2]. Diquat (DQ) and paraquat (PQ) were extracted using a modified QuPPE procedure with methanol/1M HCl 1/1. For more details on the extraction and quantification of DQ and PQ using LC-MS/MS, see also PD - 45.

IC-MS/MS Instrumentation

IC-System	Thermo Scientific™ Dionex™ Integriion™ HPIC™ system
Column	Thermo Scientific™ Dionex™ IonPac™ CS17, 2x250mm and CS21, 2x150mm
Eluent source	Thermo Scientific™ Dionex™ EGC 500™ MSA eluent generator cartridge
Methanesulfonic acid gradient in mM	CS17: 15 mM (5 min), 15 to 60 mM (1 min), 60 mM (6.5 min), 15 mM (6.5 min). CS21: 4 mM (2 min), 4 to 20 mM (10 min), 20 to 40 mM (1 min), 40 mM (4 min), 1 mM (5 min).
IC flow-rate	CS17: 0.4 mL/min; CS21: 0.3 mL/min
Suppressor	Dionex CDRS® 600; 2mm
Operation temperatures	CS17: 55°C; CS21: 50°C Suppressor: 15°C;
Flow rate of make-up solvent	CS17: 0.2 ml/min acetonitrile (MS-grade); CS21: 0.2 ml/min acetonitrile (MS-grade)

Chromatogram on the CS17 column

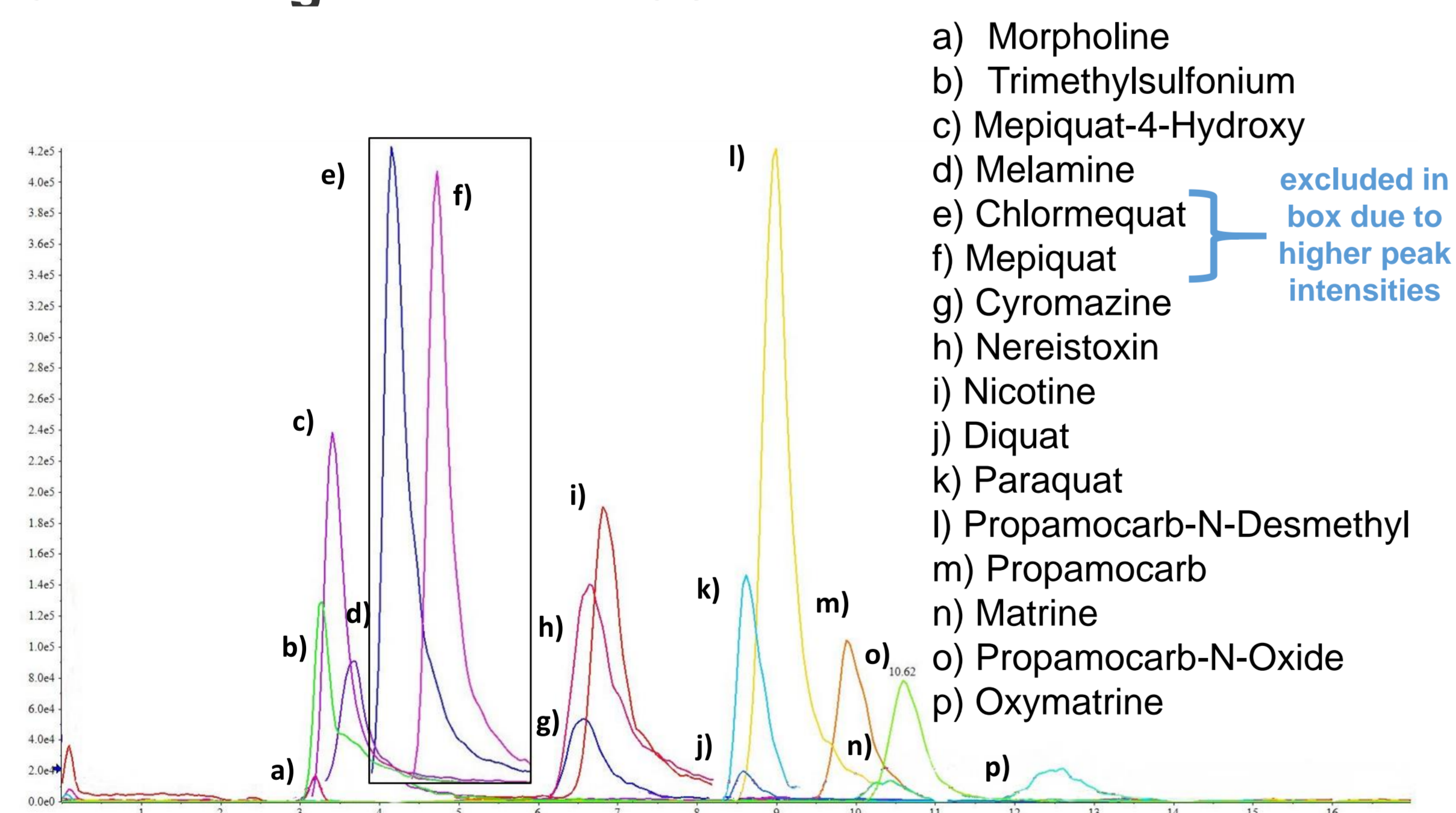


Figure 1: Separation of 16 highly polar pesticides on the CS17 column at 0.01 µg/mL in 5-fold diluted cucumber extract).

Separation of DQ and PQ on different IC columns

DQ and PQ have a similar molecular structure and often co-elute in LC and IC applications. The peaks of PQ and DQ fully overlapped using CS17 (Fig. 1; j) and k), but separated well using CS21 in which they showed a considerably stronger retention (see Fig. 2). Using CS21 reduces the risk of matrix effects and further eliminates the MS-interference caused by diquat on the MRM-transitions having deprotonated paraquat ([M²⁺-H⁺]⁺) as parent ion. On the other hand 5 compounds (l) to p) in Fig. 1) could not be included in the method using the CS21 column.

Using organic solvents to improve sensitivity

Unlike typical LC gradients, IC-gradients are purely aqueous (in this case aqueous methanesulfonic acid). Adding organic („make-up“) solvents to the IC effluates prior to entering the ESI ion-source helps to alter surface tension, improve evaporation and to gain detection sensitivity. This is achieved using an external pump and a T-piece. The signal intensity of most compounds increases when admixing moderate amounts of make-up solvent but drops again at higher rates. Figure 3 shows exemplarily the impact of using methanol and acetonitrile as make-up solvents in the case of chlormequat and nicotine. Overall, acetonitrile seems to be more beneficial than methanol (see Figure 3). Unfortunately, the optimum rates of make-up solvent differ from compound to compound which calls for a compromise solution when analysing multiple compounds.

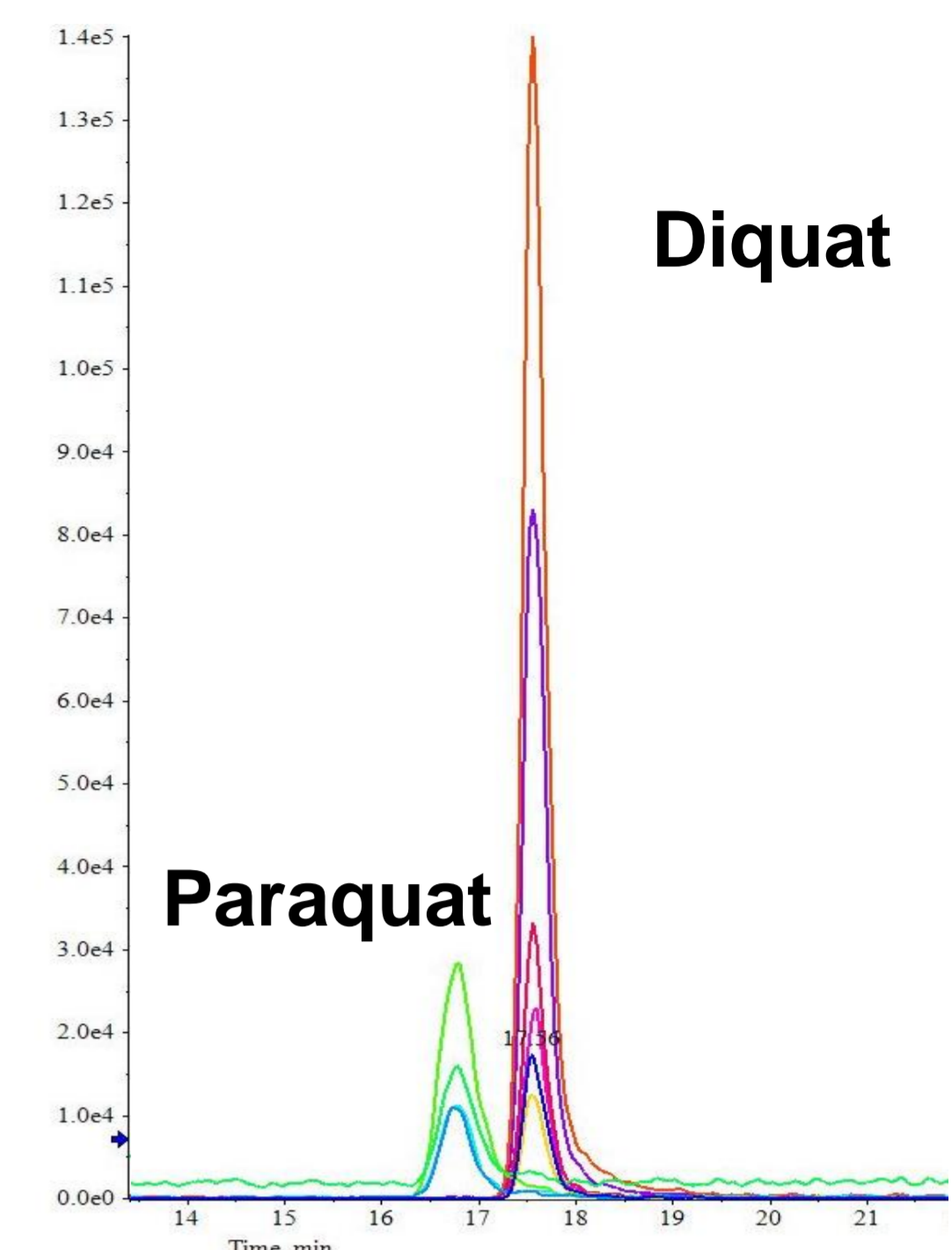


Figure 2: Separation of diquat and paraquat on the CS21.

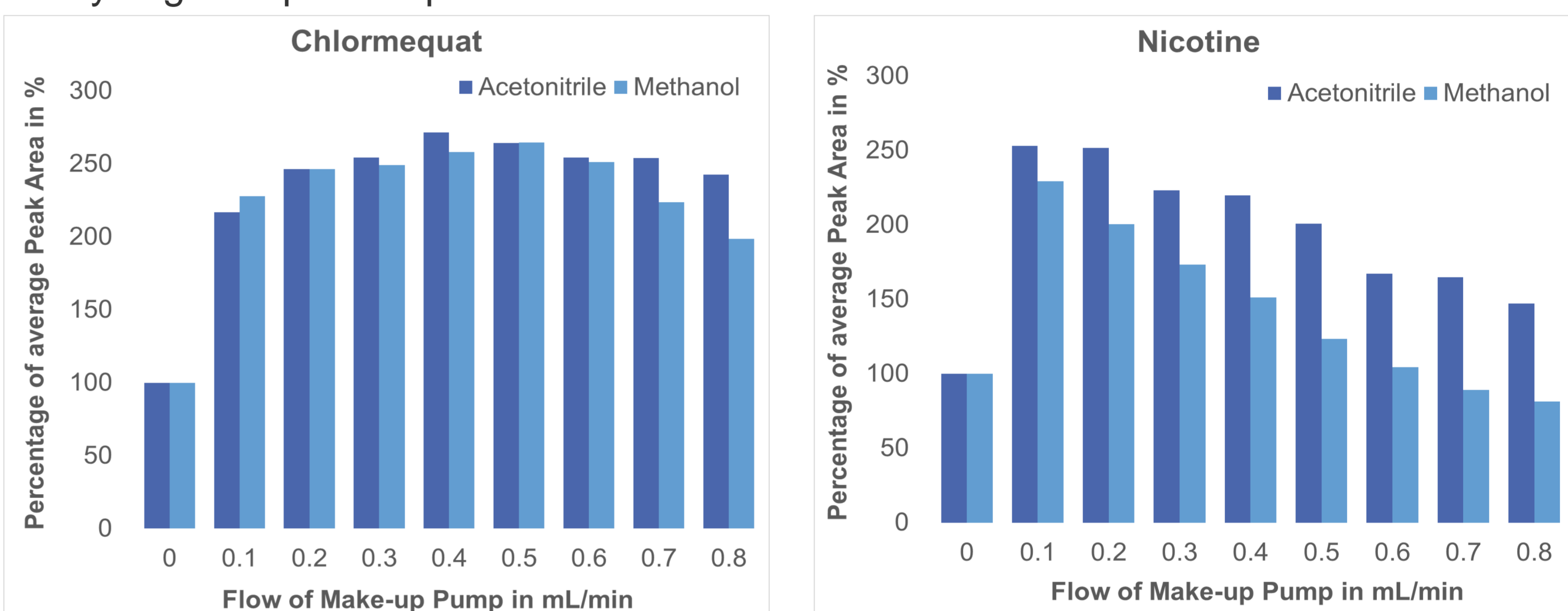


Figure 3: Increasing signal intensities of chlormequat and nicotine by using acetonitrile and methanol as make-up solvents.

Validation

Method validation was conducted at 0.01 mg/kg in raspberry, lemon and milk (analytical portion 10g each) and at 0.02 mg/kg in sesame and rice (5 g each), using ILIS-based matrix-matched calibration (n=5).

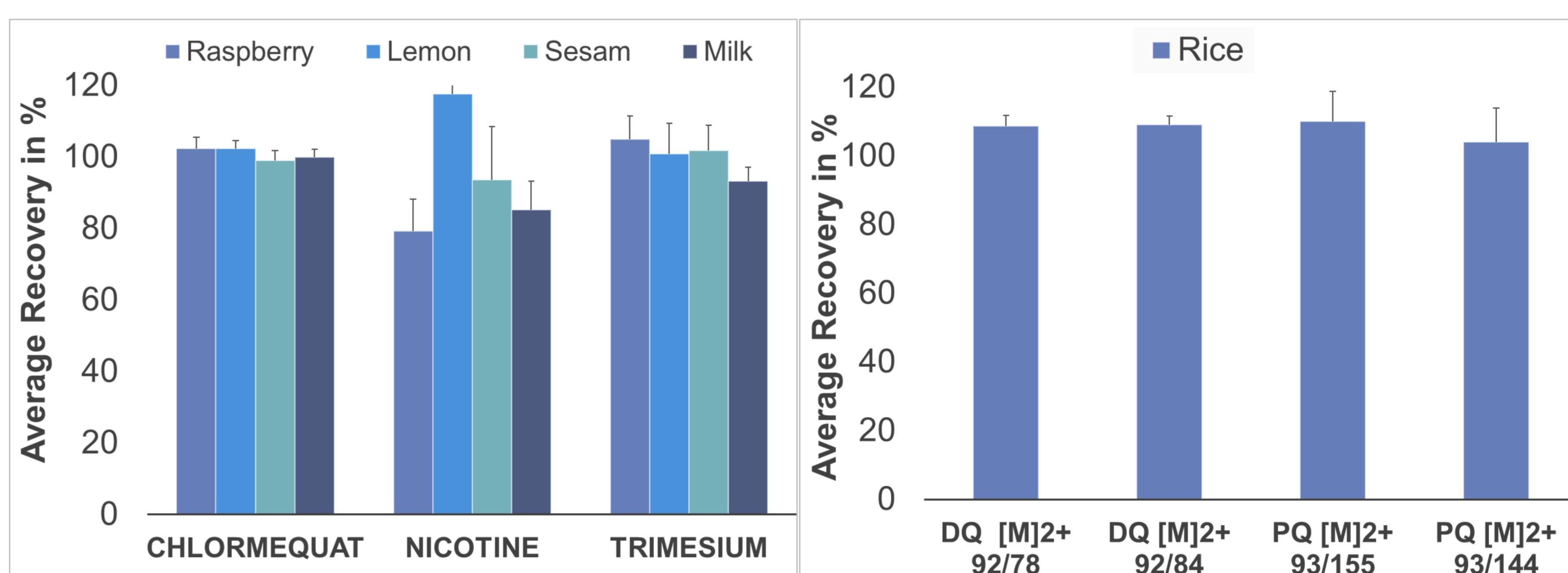


Figure 4: Validation results.

Summary

Two IC methods (using CS17 and CS21 column) for the analysis of polar cationic pesticides in QuPPE extracts were developed. Adding acetonitrile to the IC flow in front of the ion-source improved signal intensity and thus method sensitivity. While DQ and PQ co-eluted on the CS17 column, full separation was achieved on the CS21. Finally, method validation of the QuPPE method was successful on raspberry, milk and lemon at 0.01 mg/kg and in rice and sesame at 0.02 mg/kg.

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