Analysis of pesticides by Paper Spray Ionization and Leaf Spray Mass Spectrometry: an analytical comparison

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Abstract

Qualitative and quantitative analytical performance of PSI and LS-MS were compared by detecting and constructing calibration curves with pesticides atrazine and diuron. Both techniques showed excellent results with similar performance to screening of these two pesticides.

Introduction

Paper Spray Ionization (PSI) and Leaf Spray (LS) are two new ambient ionization techniques for mass spectrometry. In PSI, the sample is deposited on a triangular paper and ions are generated by applying a high voltage on a wetted paper with solvent.[1] The LS technique is a variant of PSI, where the paper is substituted by the matrix itself to be studied, a triangular leaf (in this work, a smooth lettuce leaf).[2] Here, we demonstrated an application comparing PSI and LS-MS to perform qualitative and quantitative screening of pesticides residues (atrazine and diuron). The novelty of the work was not employ a deuterated internal standard (IS) for construction of the calibration curve. Instead of deuterated IS, we use atrazine as IS to diuron and diuron as IS to atrazine.

Results and Discussion

The experiments were performed using the Q Exactive™ Hybrid Quadrupole-Orbitrap with following parameters: positive mode; spray voltage: 3.5 kV; capillary temperature: 275°C; S-lens RF Level: 50%. **Figure 1** ilustrates the mass spectrum of atrazine and diuron by PSI(+) and LS(+)-MS. Atrazine and diuron were detected in low concentrations (10 µg L^{-1}) using both techniques. Calibration curves were constructed with concentrations ranging of 10-1000 µg L^{-1} for the two pesticides **(Figure 2)**. Atrazine and diuron were used as internal standard, no requiring use of deuterated standards. PSI(+) and LS(+)-MS demonstrated similar performance for the two pesticides with R^2>0.99. LOD and LOQ values ranging from 10-16 and 33-54 µg L^{-1} for PSI(+)-MS, and between 5-16 and 16-53 µg L^{-1} for LS(+)-MS. In all cases, these values were lower than the MRL (Maximum Residue Limits) established by Anvisa for atrazine and diuron in some foods, which are 0.25 mg.kg^{-1} for atrazine and 0.1 mg.kg^{-1} for diuron.

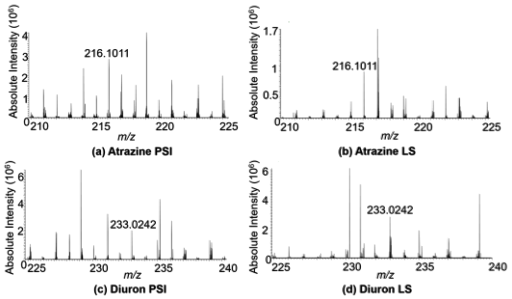

Figure 1. Mass spectrum of atrazine and diuron (10 µg L^{-1}) by PSI(+) and LS(+)-MS.

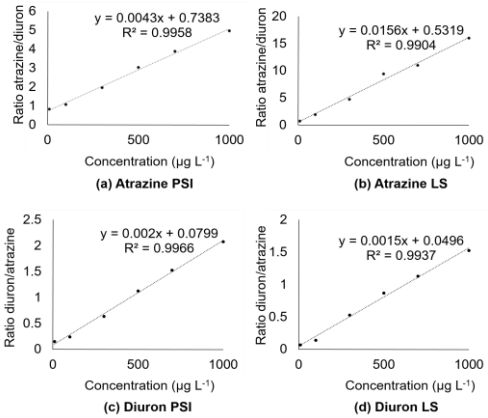

Figure 2. Calibration curves (10-1000 µg L^{-1}) of atrazine and diuron by PSI(+) and LS(+)-MS.

Conclusion

PSI and LS-MS can to be used for detection and quantification of atrazine and diuron in real samples.

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