

APPLICATION OF HYBRID LINEAR ION TRAP – ORBITRAP MASS SPECTROMETRY FOR THE QUALITATIVE AND QUANTITATIVE ASSESSMENT OF PESTICIDES IN N.W. GREECE

**NANNOU CH.¹, BOTI V.^{1*}, TSOUTSI C.¹, KONSTANTINOI I.², PATAKIOUTAS G.³,
KARRAS G.³ and ALBANIS T.¹**

¹Dept. of Chemistry, University of Ioannina, 45 110, Ioannina, GREECE

³Dept. of Environmental & Natural Resources Management, University of Patras, 30100, Agrinio, GREECE, ³Dept. of Agricultural Technology, TEI of Epirus, 47100, Kostakioi, Arta, GREECE
E-mail: chnannou@cc.uoi.gr

ABSTRACT

The extended use of pesticides for agricultural and non-agricultural purposes has resulted in their presence in various environmental matrices. Pesticide residues enter surface water mainly through agricultural run-off. Both parent pesticides and metabolites may exert a toxic action in organisms of freshwater systems, whenever the concentration of a compound is sufficient to trigger such effect. The analysis of pesticide residues in a variety of environmental matrices contributes to ensure their safety and quality. Until recently, multi-residue analysis of such compounds at trace levels has been mainly carried out by means of GC and LC coupled to mass spectrometry. Lately, scientific interest has also been shifted to even more accurate and sensitive detectors. In that direction, the use of high-resolution mass spectrometers (LC-HRMS) and especially Orbitrap technologies enables the acquisition of a theoretically unlimited number of species by means of accurate mass measurements in full-scan mode. This allows obtaining the elemental composition of acquired ions, useful for identification of targeted and untargeted compounds, metabolites, or transformation products [1].

In the present study, an SPE sample enrichment procedure was evaluated in order to be applied for the estimation of the pollutant load and its seasonal distribution in natural waters of the Prefecture of Epirus (Aracthos and Louros rivers, Amvrakikos gulf), N.W. Greece. Hybrid LTQ Orbitrap mass spectrometry was employed for the ultra-trace detection and quantification of target pesticides and finally was successfully applied to the analysis of waters. The identification of the positive findings is accomplished with the data from accurate masses of the target ions, based on the full-scan exact mass measurement of $[M+H]^+$ ions, along with retention time data and characteristic on-source fragment ions. The results obtained confirm that high-resolution mass spectrometry is a helpful and reliable tool for the identification and quantitation of pesticide residues, providing at the same time high accuracy.

Keywords: pesticides, surface waters, SPE, LC-MS, Orbitrap

1. Introduction

Widespread use of pesticides is of vital importance in agricultural production, since their residues may pose a risk to non-target organisms and lower the quality of fresh waters. In Greece, and especially in the North Western region, the irrational use of pesticides has raised concern over the years due to possible pollution of aquatic ecosystems, mainly through discharge of runoff from agricultural fields. Hence, the analysis of pesticide residues in a variety of environmental matrices is necessary to ensure their safety and quality about health standards [1].

In that direction, the use of high-resolution mass spectrometers (LC-HRMS), and especially Orbitrap technologies, enables the acquisition of a theoretically unlimited number of species by means of accurate mass measurements in full-scan mode. This allows obtaining the elemental

composition of acquired ions, useful for identification of targeted and untargeted compounds, metabolites, or transformation products [2].

The aim of the present study was to develop a sensitive, reproducible and robust analytical method for the simultaneous determination of various pesticides at trace levels in river and sea waters, taking at the same time advantage of the innovative hybrid technology and versatility of the high resolution- accurate mass LTQ Orbitrap MS platform. Sea water samples from Amvrakikos Gulf were analyzed for selected pesticide residue contamination.

2. Materials and methods

Ultra-high performance liquid chromatography (UHPLC) was employed and chromatographic separation was achieved on a Hypersil Gold column (50 × 2,1 mm, 1,9µm). A Thermo Scientific Orbitrap XL mass spectrometer was operated in full scan mode, (positive ionization for data acquisition). SPE was optimized and evaluated for the isolation and determination of target analytes. The identification of the positive findings is accomplished with the data from accurate masses of the target ions, based on the full-scan exact mass measurement of $[M+H]^+$ ions, along with retention time data and characteristic fragment ions.

Table 1: LC & MS parameters

LC Parameters		MS Parameters	
Mobile phase	A. Water+0.1% formic acid A. Water+0.1% formic acid	Ionization	Positive
Flow rate	300 µL min ⁻¹	Full mass scan positive ion mode (mass range:270-490)	
Column temperature	27°C	Resolution	60.000
Injection volume	10 µL		

3. Results and discussion

An excellent linearity in detector response was observed in the range of 5-500 µg/L, with correlation coefficients close to 0.999 for the majority of analytes. The LOQs, corresponding to a signal-to-noise ratio 10, ranged from 1-25 µg/L for the instrument, while SPE method LOQs were at ppt levels in all cases. Recoveries achieved from spiked water samples were over 70%, exhibiting satisfactory precision for all analytes, expressed as RSD ranged from 6 to 16%. Mass accuracy proved to be <3ppm indicating, overall, the Fourier transform (FT) Orbitrap MS technology reliability & sensitivity for routine analysis of these contaminants at trace levels.

4. Conclusions

In the present work, an analytical methodology using Hybrid LTQ Orbitrap mass spectrometry for the ultra-trace detection and quantification of target pesticides in environmental water samples has been evaluated in order to be applied for the estimation of the pollutant load and its seasonal distribution in Amvrakikos Gulf. The overall performance of the analytical methodology proved accurate and sensitive enough reaching ppt levels, while it confirmed that high-resolution mass spectrometry is a helpful and reliable tool for the identification and quantitation of pesticide residues, providing at the same time high accuracy. Concentrations detected varied seasonally. Therefore, data generated in this study are useful as a baseline in formulation of mitigation measures to protect the affected ecosystem from pesticides residues pollution.

REFERENCES

1. Farré M., Picó Y., Barceló D., 2014. J. Chromatogr. A, 1328: 66-79.
2. Robles-Molina J., Lara-Ortega F.J., Gilbert-López B., García-Reyes J.F., Molina-Díaz A., 2014. J. Chromatogr. A, 1350: 30-43.