SHIMADZU

TP 297

Determination of Pesticides in Tap Water without Pretreatment by LC-MS/MS

Monique F. Dos Santos[1]; Marilia S. Cardoso[1]; Luis O. Junqueira[1]; Marcos A Pudenzi[1]; Ichiro Hirano[1]
[1]Shimadzu of Brasil, Barueri, Brazil

1. Introduction

- Given the growing concern over the effects of chemical contamination, it has become essential to conduct rigorous monitoring of the substances present in the water consumed by the population. Pesticides, used in agriculture, can infiltrate water sources, jeopardizing human health and the ecosystem[1]. In 1977, the Ministry of Health in Brazil implement water quality control regulations, establishing potability standards[2].
- The Ordinance GM/MS 888 of 2021 established regulations that highlight the analysis of pesticides as a crucial element for the control and monitoring of drinking water quality. In this work, an analytical method using LC-MS/MS was developed, enabling an efficient detection of pesticides mentioned in the regulation without requiring pretreatment.

2,4 – D	Ciproconazole	Molinate
Acephate	Chlorpyrifos	Omethoate
Acrylamide	Chlorpyrifos Oxon	Picloram
Aldicarb	Difenconazole	Profenofos
Sulfone Aldicarb	Dimethoate	Propargite
Sulfoxide Aldicarb	Diuron	Prothioconazole
Ametrine	Epoxiconazole	Prothioconazole desthio
Atrazine	Fipronil	Simazine
Atrazine- 2 - hydroxy	Flutriafol	Tebuconazole
Atrazine-deethyldeisopropyl (DACT)	Imidazolidinone – ETU	Terbufos
Atrazine – desethyl (DEA)	Malathion	Thiamethoxam
Atrazine – desisopropyl (DIA)	Methamidophos	Thiodicarb
Carbendazim	Metolachlor	Thiram
Carbofuran	Metribuzim	

Fig. 1 Analytes monitored by LCMS.

2. Methods

A LCMS-8050 triple-quadrupole was used to achieve the needed sensitivity. The acquisition was performed using MRM in positive and negative modes. Analytical chromatography was performed using two Nexera 40D XR binary pumps. (Nexera XR - LCMS-8050, Shimadzu®, Japan) with the following conditions of HPLC and MS (Table 1 and 2, respectively).

Table 1 Method parameters of HPLC system.

Column	Shim-pack GIST C18-AQ® (4.6 x 150 mm, 3 µm). Shimadzu - PN: 227-30724-07
Mobile Phase	A: Water + 5mM Ammonium acetate + 0.01% Acetic acid B: Methanol + 5mM Ammonium acetate + 0.01% Acetic acid
Flow	0.3 mL/min
Column Temp.	40 °C
Injection Volume	15 µL

Table 2 Method parameters of MS system.

Interface	ESI +/-
Nebulizing Gas Flow	3 L/min
Heating Gas Flow	3 L/min
Interface Temp.	400 °C
Dessolvation Temp.	650 °C
DL Temp.	120 °C
Heat Block Temp.	400 °C
Drying Gas Flow	17 L/min

3. Results

- The optimization of the method was initially carried out by evaluating the analyte intensity. A standards mix at 100 ng/mL was injected with different interface parameters, such as m/z adjust, interface voltage, nebulizing gas flow, drying gas flow and heating gas flow.
- After developing the chromatography parameters, an optimization of mass spectrometry parameters was performed. Based on the results obtained, interface parameters stablished were nebulizing gas flow at 3 L/min, drying gas flow at 17 L/min, heating gas flow at 3 L/min, desolvation temperature at 650 °C and desolvation line temperature at 120 °C.

Fig. 2 Nexera LC-40D XR HPLC coupled to LCMS-8050

- Calibration curves, in tap water, were obtained for 41 pesticides by injecting the fortified samples into the LCMS, without any preparation step.
- Finally, satisfactory results were obtained in the calibration curves (R2>0.99), and chromatographic peaks were achieved at the lower limit of quantification for some analytes using at least six different concentrations as calibrators in filtered water samples.

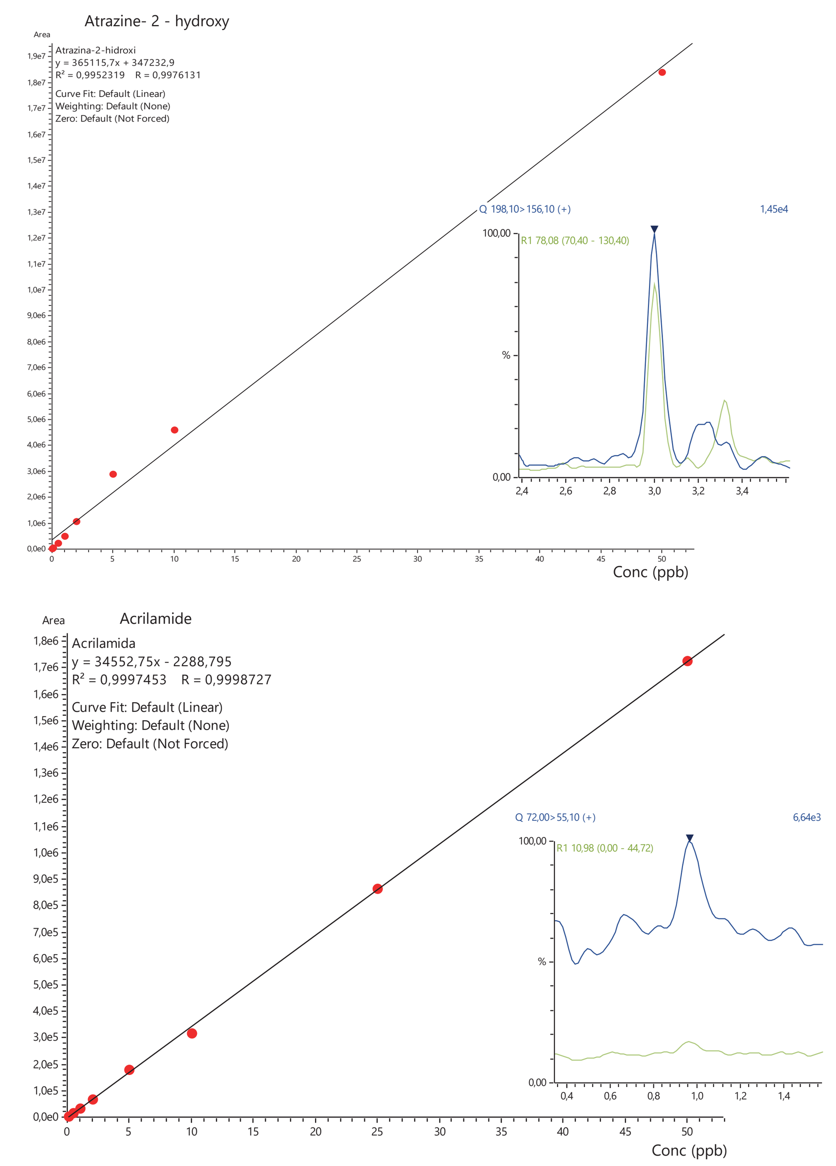

Fig. 3 Calibration curve and chromatographic peaks at limit of quantification of Atrazine – 2 – hydroxy and Acrilamide.

4. Conclusion

- Pesticide method developed to requirements of Ordinance 888/2021, without the need for pretreatment of the samples using LCMS-8050 triple-quadrupole.
- Method development of 41 pesticides required of Ministry of Health by Ordinance 888/2021 (Brazil), without pretreatment using LCMS-8050 triple-quadrupole.

Reference

1) RHEE, J.; AL-ONAZI, W. ALGARNI, T.S. ET AL. Int. J. Environ. Res. Public Health 2021, 18(2),468; https://doi.org/10.3390/ijerph18020468.
2) FORMAGGIA, D. M. E., Uma breve história do Programa de Vigilância da Qualidade da Água para Consumo humano do Estado de São Paulo. Portal Fala SEVISA, Set/2007. Disponível em: http://www.cvs.saude.sp.gov.br/pdf/artigo_sevisa_01.pdf, Acessado em Ago/2021