

Development of a method for monitoring pesticides and metabolites in raw and drinking water in the state of São Paulo

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Highlights:

Brazil updated its water potability legislation, expanding the scope of monitored pesticides. Laboratories had to develop their own methodologies for new parameters. SABESP chose LC-MS/MS for its versatility, sensitivity, selectivity, short analysis time, and low sample preparation cost.

Keywords: LC-MS/MS; Pesticides; Drinking Water

INTRODUCTION

Water is a vital resource for human survival and well-being, as well as for the maintenance of the planet's ecosystems.¹ Therefore, monitoring water quality is crucial to ensure public health and environmental sustainability.

Brazil, being one of the world's largest agricultural producers, faces unique challenges in water quality management. The improper use of pesticides can result in the contamination of groundwater and surface water.¹ In this context, the activity of laboratory analysis becomes essential to ensure water quality.

In May 2021, Brazil updated its legislation on water potability through Ordinance GM/MS 888.² One of the most significant changes was the expansion of the scope of monitored pesticides, including some metabolites, increasing the list in 20 compounds. In addition, the legislation also required the monitoring of raw water used for treatment.

Unlike various other parameters of the legislation, where standardized analysis methods are common to be found, the new parameters required laboratories to develop their own methodologies. At SABESP – Companhia de Saneamento Básico do Estado de São Paulo, liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) and a triple quadrupole analyzer was chosen for the analysis of these new compounds. The choice was made due to the versatility of being able to analyze several substances at the same time, high sensitivity and selectivity, short analysis time, and low sample preparation cost. This work presents the development of an analytical method for the effective monitoring of these contaminants.

METHODOLOGY

An ACQUITY UPLC®I-Class-Xevo TQ-XS system from Waters Corp. was used with the ACQUITY UPLC HSS T3 chromatographic column, 100mm x 2,1mm, 100Å, 1.8 µm. Certified reference materials of the analytes were used and acquired from various suppliers, including Absolute Standards (USA), Accustandard (USA), and Agilent Standard (USA). Solvents, such as methanol, acetonitrile, as well as reagents, for instance, acid formic, were purchased from suppliers, e.g. Supelco (USA) and Merck (USA). Type 1 ultrapure water was obtained by a Milli-Q system.

Intermediate solutions of each of the compounds were infused into the equipment to discover the characteristic transition of each substance. The purpose of the infusion was to optimize some parameters, such as, collision energy, cone voltage and desolvation gas temperature. A solution containing all the compounds was injected into the equipment using a gradient that varies from 100% aqueous to 100% organic. The retention time of each mass transition was adjusted for each substance. The samples, collected in 40 mL amber glass vials with 0.8 mg of ascorbic acid and stored in a refrigerator, are prepared only by filtration and transferring to the vial, being injected directly into the equipment.”

RESULTS AND CONCLUSIONS

The composition of the mobile phase A consists of water/methanol (95:5 v/v) with 0,1% formic acid and ammonium formate 2,5 M. Mobile phase B goes as described: acetonitrile/water/methanol (90:5:5 v/v/v) with 0,1% formic acid. The mobile phase flow is 0,4 mL/min and the oven temperature is 45°C. Run time for each sample is approximately 15 minutes, so, in 24 hour we can analyze almost 96 samples.

With the development of the method, it was possible to monitor 35 compounds in raw and drinking water in the state of São Paulo, being able to achieve lower limits than those required by legislation (Table 1). The implementation of these assays made the LC-MS/MS technique go from 20% to 50% of the total results provided by the laboratory. In absolute numbers, after the application of this new method, the results released per year went from 60.000 to about 225.000 .

Despite the increasing quantity of analytes and samples to be processed, the number of analysts remained the same, demonstrating the high productivity of the technique. Also, this method has shown as an efficient monitor of new pesticides and metabolites in drinking water, providing a safe supply to the population. The company’s strategy proved to be very suitable, allowing for quick compliance with legislation without the need to outsource these tests.

Compound	Quantification Limit (ppb)	Maximum Residue level (ppb)
Hydroxi-Atrazine ^a	2	120
Thiodicarb ^a	2	90
Epoxiconazole ^a	2	60
Picloram ^a	2	60
2,4-D	2	30
Cyproconazol ^a	2	30
Difenoconazole ^a	2	30
Flutriafol ^a	2	30
Metribuzin ^a	2	25
Diuron	2	20
Thiram ^a	2	6
Mancozeb	2	4
Dimethoate ^a	0,2	0,6
Omethoate ^a	0,2	0,6
Atrazine	0,2	0,5
Deethyl-Atrazine ^a	0,2	0,5
Deisopropyl-Atrazine ^a	0,2	0,5
Atrazine-desethyl-desisopropyl ^a	0,2	0,5

Compound	Quantification Limit (ppb)	Maximum Residue level (ppb)
Tebuconazole	0,4	180
Carbendazim	0,4	120
Ametryn ^a	0,4	60
Tiamethoxam ^a	0,4	36
Propargite ^a	0,4	30
Pentachlorophenol	0,4	9
Carbofuran	0,4	7
ETU ^a	0,4	4
Acephate ^a	0,4	3,5
Metamidophos	0,4	3,5
Aldicarb	0,4	3,3
Aldicarb Sulfone	0,4	3,3
Aldicarb Sulfoxide	0,4	3,3
Simazine	0,4	2
Prothioconazole ^a	0,4	1,5
Prothioconazol-desthio ^a	0,4	1,5
Fipronil ^a	0,4	1,2

^a New substances introduced in the GM/MS 888

Table 1 – Pesticides and Metabolites analyzed

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REFERENCES

- 1 - World Health Organization. (2019). Drinking-water. <https://www.who.int/news-room/fact-sheets/detail/drinking-water>
- 2 - Brasil. Ministério da Saúde. (2021). Portaria GM/MS N° 888, de 4 de maio de 2021. https://www.in.gov.br/en/web/dou/-/portaria-gm/ms-n-888-de-4-de-maio-de-2021-*-321540185