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ThP 590

# Determination of Paraquat in Drinking Water by LCMS-2050

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## 1. Introduction

- Paraquat (Fig. 1) is an herbicide widely used in the world and extremely toxic for humans and animals, capable of controlling the weeds growth in crops.[1]
- According with Portaria GM/MS No. 888 (2021) of the Ministry of Health in Brazil, which establish norms and water potability standards, the maximum value allowed of paraquat in drinking water is 13 µg/L.[2] The aim of this work is to develop a method by direct analyses of paraquat in drinking water using a single quadrupole (LCMS-2050).

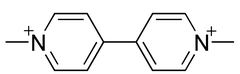


**Fig. 1** Molecular structure of paraquat.

## 2. Methods

Analytical chromatography was performed using an LC-MS (Nexera XSi - LCMS-2050, Shimadzu®, Japan) with the following conditions of HPLC and MS (Table 1 and 2, respectively).

**Table 1** Method parameters of HPLC system.

| | |
|---|---|
| Column | Zic®-Hilic (100 x 2.1mm x 3.5 µm). Merck - PN: 1504410001 |
| Mobile Phase | A: Water + 20mM Ammonium formate + 0.5% Formic acid<br>B: Acetonitrile + 0.3 % formic acid |
| Flow and Column Temp. | 0.4 mL/min - 40 °C |
| Injection Volume | 1 µL |

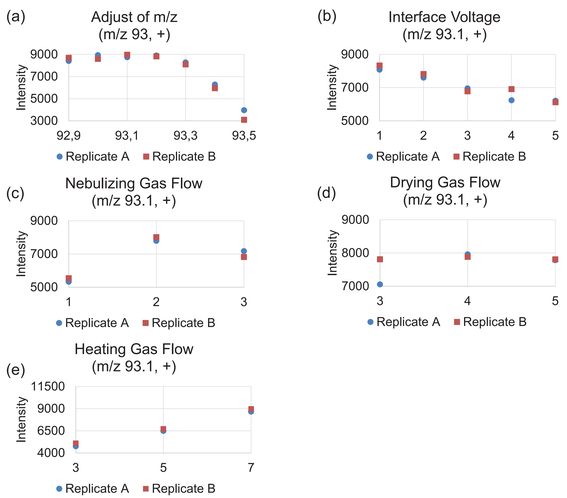
**Fig. 2** LCMS 2050 single quadrupole.

**Table 2** Method parameters of MS system.

| | |
|---|---|
| Interface Voltage | 0.5 kV |
| Interface | ESI + |
| Nebulizing Gas Flow | 2 L/min |
| Heating Gas Flow | 7 L/min |
| Drying Gas Flow | 4 L/min |
| Dessolvation Temp. | 450 °C |
| DL Temp. | 200 °C |

## 3. Results

- Method optimization was performed evaluating the analyte intensity with different mobile phases and interface parameters, such as adjust of m/z, interface voltage, nebulizing gas flow, drying gas flow and heating gas flow, in this order (Graphic 1 a-e).
- Initially, with the aim of increasing the analyte intensity was injected a standard of paraquat at a concentration of 100 ng/mL in different organic mobile phases: acetonitrile versus formic acid (0.3%) in acetonitrile. As a result, a paraquat peak with greater intensity was observed using acetonitrile as mobile phase. Then, a standard of the same concentration was injected in different aqueous mobile phases: ammonium formate (20mM) and formic acid (0.5%), and formic acid (0.5%). As a result, it was observed a better reproducibility using ammonium formate in the phase.
- Following optimizing the chromatography parameters, an optimization of mass spectrometry parameters was performed. According to the results obtained, interface parameters stablished were adjust of m/z was set at 93.1, interface voltage at 0.5 kV, nebulizing gas flow at 2 L/min, drying gas flow at 4 L/min, heating gas flow at 7 L/min, desolvation temperature at 450 °C and desolvation line temperature at 200 °C.




**Graphic.1** Method optimization results using the analyte intensity evaluating interface parameters (adjust of m/z, interface voltage, nebulizing gas flow, drying gas flow and heating gas flow)

- After mass spectrometry optimization, a triplicate linearity range in water was evaluated by SIM (single ion monitoring) mode with the selected m/z. The method demonstrated to be linear through the calibration curve with a $r^2$ of 0,99. The results are presented in Fig. 3, which displays the calibration curve and chromatographic peaks at limit inferior of quantification (LIQ) in ultrapure water samples.
- Finally, a triplicate linearity range in real sample (tap water) was evaluated, resulting in the determination of paraquat in the limit inferior of quantification with a $r^2$ of 0,99 in the calibration curve. In Fig. 4 was presented the chromatographic peaks at LIQ and blank in real samples (tap water).

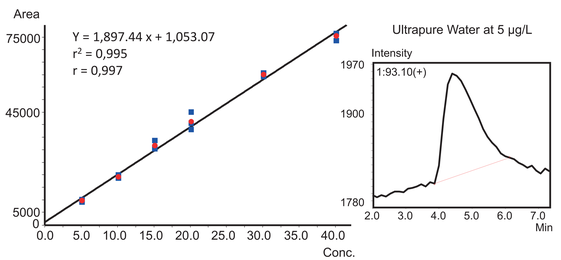



**Fig. 3** Calibration curve and chromatographic peaks at limit inferior of quantification in ultrapure water samples

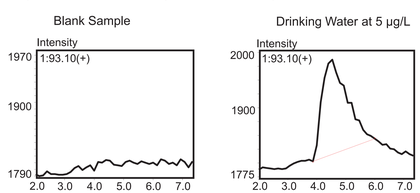



**Fig. 4** Chromatographic peaks at limit of quantification in and blank in real samples (tap water).

## 4. Conclusion

- It was possible to obtain satisfactory results for the determination of Paraquat in tap water using a mass spectrometry single quadrupole, LCMS-2050, which facilitates the work routine and reduces analysis costs. The results obtained reached the limits lower than those recommended in Ordinance GM/MS nº 888 of May 4, 2021, without the need for pre-treatment of the samples.

Reference
1) Martins T. (2013). Semin. Cienc. Biol. Saude. 34(2):175-86.
2) Gabinete do Ministro. Portaria Nº 888, de 04 de maio de 2021.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