Advantages of Ultra Performance Liquid Chromatography–High Resolution Mass Spectrometer for the Analysis of Cyanotoxins in Water for Human Consumption

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INTRODUCTION

The presence of cyanobacteria in water intended for human consumption may represent a risk to human health due to the possible production of secondary metabolites, called cyanotoxins, toxic for animals and humans. This work presents the comparison between two different mass spectrometric techniques (UPLC-HRMS/M5 and LC-MS/MS) that allow the simultaneous detection of 21 cyanotoxins, of different classes (including 12 Microcystins, 5 Microginins, 2 Cyanopeptolins, and 2 Anabaenopeptins).

EXPERIMENTAL METHOD

Drinking water samples were extracted and analyzed using a triple quadrupole and a High Resolution Q-TOF mass spectrometer and the results were compared.

METHOD

EXTRACTION ON SPE CARBOGRAPH 4 CARTRIDGES:

50 µl sample
Injected on Black Ribbon filters.

LC-MS/MS METHOD

- API 3000 (Atmospheric Pressure Ionization)
- Source TIS Turbo Ion Spray
- TIS 5500 V (positive ionization mode)
- Temperature: 450 °C
- Curtain gas flow: 10 u.a.
- Nebulizer gas flow: 12 u.a.
- Turbo gas flow: 7 u.a.
- Altisima C18 column
- 50 µl injected

UPLC-HRMS METHOD

- Xevo G2 (Oros)
- Ion Mass: 50 to 1200 Da
- Polarity: ESI+
- Analyser Mode: Sensitivity
- Source Temperature (°C): 130
- Desolvation Temperature (°C): 500
- Desolvation Gas Flow (L/Hr): 1000.0
- Column Temperature (°C): 40
- Column: BEH C18 1.7 µm
- 10 µl injected

RESULTS AND DISCUSSION

- LC-MS/MS method: reproducibility better than 17% and LODs were in the range of 0.003–0.03 µg/L for all the analytes; a good linearity was achieved, with correlation coefficients in the range 0.9925 ≤ R2 ≤ 0.9998.
- UPLC-Q-TOF method: recovery percentages above 85%, with relative standard deviations ≤16% and LODs between 0.001 and 0.047 µg/L for the intended purposes at the concentrations of interest; a good linearity was achieved, with correlation coefficients in the range 0.9902 ≤ R2 ≤ 0.9999.

CONCLUSIONS

Both methods have been proven to be robust, precise and accurate with recovery percentages above 85% and with relative standard deviations ≤17%, fit for the intended purposes at the concentrations of interest; a good resolution has been obtained with both methods.

The performance and reliability of the method was proven to raw, treated and distributed water samples, with LODs 0.001 to 0.047 µg/L, at least 20-fold lower than the guideline value proposed by the WHO for drinking water (1.0 µg/L for microcystin-LR).

The advantages obtained by UPLC-HRMS method are the shorter analysis times (16 minutes vs 27 minutes) and a lower injection volume (10 µl vs 50 µl). Furthermore, this method allows the simultaneous identification of target and non-target compounds, allowing to detect the presence of other compounds potentially harmful to human health.