Trace LC-MS/MS Analysis of Hormones in Tap Water and After Purification to Laboratory Grade

Anastasia Domanov¹, Matias Kopperi², Jevgeni Parshintsev², Patrik Appelblad³, and Stephane Mabic¹.

- 1. Merck, Lab Water, Saint-Quentin-en-Yvelines, France
- 2. University of Helsinki, Department of Chemistry, Laboratory of Analytical Chemistry, Finland
- 3. Merck, Advanced Analytical, Solna, Sweden

Abstract

Three hormones were detected by LC-MS/MS in the tap water of different laboratories. After purification by Milli-Q[®] water purification systems, the hormones were no longer detected in the product ultrapure water.

Key words or phrases

ultrapure water, hormones, trace LC-MS analyses, drinking water, contaminants of emerging concern

Introduction

In recent years, coupling HPLC with mass spectrometry has been used for trace analysis of organic compounds to address environmental health and safety concerns. These methods have very low detection limits, making it critical to avoid, or at least minimize, contamination during the experimental process. Components of the HPLC instrument; the mass spectrometer;¹ sample handling and manipulation;² as well as the reagents and solvents used in the analyses, can all contribute to contamination issues.

Water plays an important role in HPLC, where it is used extensively in the workflow. It is essential that the analytes detected come from the samples, and not from the water used in various steps of the experiment (such as in the preparation of samples, standards, blanks, and eluents; or rinsing/flushing of the HPLC and MS systems).

Results and Discussion

Hormones are examples of contaminants of emerging concern (CEC) that have been detected in environmental and drinking waters around the world in trace amounts.^{2,3} Even at very low concentrations, CECs could potentially exert ecotoxicological effects.³

Table 1 summarizes the results of the LC-MS/MS experiment. Of the three tap water samples analyzed, estradiol and androsterone were detected in tap water in laboratories in France and Spain, while corticosterone was detected in the water sample from the Chinese laboratory. **Figure 1** shows the MRM chromatogram of estradiol.



| Hormone | Concentration (ng/L) | Concentration (ng/L) | |
|------------------------------|----------------------|----------------------|--|
| | Tap water | After purification | |
| Estradiol (France, Spain) | 265.40 | ND | |
| | 297.92 | ND | |
| Androsterone (France, Spain) | 515.33 | ND | |
| | 1635 | ND | |
| Corticosterone (China) | 14.91 | ND | |

Table 1. Hormone concentrations in laboratory tap water and the product ultrapure water.*



Figure 1. MRM chromatogram (ESI+) of estradiol in tap water and after purification using Milli-Q[®] systems.*

The ultrapure water produced in each laboratory was analyzed for the presence of hormones using the same method as the one used for tap water analysis. In all three laboratories, no hormone was detected in the product ultrapure water (**Table 1**).

The extent of organic contamination is important in trace LC-MS/MS analyses. The level of total oxidizable carbon (TOC) provides a general indication of organic contamination. A TOC level below 5 ppb is recommended for LC-MS/MS, which is achieved in Milli-Q[®] systems.

Experimental

Water purification systems

In China and Spain: Elix[®] + Milli-Q[®] Advantage A10 systems

In France: Milli-Q® Integral system

Instrumentation

Agilent 1290 Infinity[®] HPLC coupled to an Agilent[®] 6420 Triple Quadrupole LC-MS system (ESI+, MRM). Gradient elution using a Purospher[®] STAR RP-18 endcapped (2 µm) Hibar[®] HR 50-2.1 column (Merck).

Samples and standards

Quantitation by standard addition method (androstenedione, androsterone, corticosterone, cortisone, estradiol, estrone, progesterone, OH-progesterone, testosterone). Samples: tap water, ultrapure water from Milli-Q[®] water purification systems. 1-liter samples were enriched by SPE prior to LC-MS/MS and analyzed in triplicate.

*All data reported are one-time, one-location data and are not representative of water in the various countries where samples were taken.

Conclusion

Trace levels of hormones were detected in laboratory tap water samples using LC-MS/MS. After the tap water was purified using Milli-Q[®] systems, the hormones were no longer detected. Milli-Q[®] systems produce ultrapure water suitable for trace LC-MS/MS analyses in environmental research.

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