# QSight-based method for the detection and quantification of polar contaminants in drinking water

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**Abstract**

An analytical method covering various difficult polar contaminats such as chlorate, bromate, bromide, glyphosate and AMPA was successfully developed utilizing direct injection and ion exchange columns. Linearity could be obtained for each compound, with a dynamic range of 2-3 magnitudes and regression coefficients (r2) ≥ 0.995. Furthermore, for some compounds levels as low as 10 ng/L could be reached demonstrating the extreme sensitivity of the QSight UPHLC-MS/MS. Moreover, it could be shown that by simple direct injection of drinking or surface water the sample preparation could be completely eliminated. The present work aims at illustrating the performance of a targeted LC-MS/MS method using a QSight triple quadrupole mass spectrometer for the quantification of several difficult polar contaminants in drinking water and meeting current EU regulatory limits.

**Keywords: Direct injection, Glyphosate, Polar contaminants, Drinking water**

## 1. Introduction

Under the European Union level the Water Framework Directive and subsequent daughter directives (1) indicate environmental quality standards for water (2). These directives have also defined more than 30 priority substances as significant risks to humans. The range of substances is vast comprising of heavy metals, pesticides, herbicides, pharmaceutical and personal care compound (PPCPs), per- and polyfluoroalkyl substances (PFASs) and other industrial pollutants (3). One big challenge for water laboratories are the established limits that range from the lower µg/L (ppb) and below. For this reason, highly sensitive methods are required. One other aspect in addition to the sensitivity, one must consider is the wide variety of compounds and chemical classes these contaminants encompass.

Ultra-High Performance Liquid Chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) has demonstrated to be the gold standard when specificity and sensitivity are needed. Moreover, several standard methods based on LC-MS/MS to assess water contaminants have been established and because of the diversity of compounds, different methods are required.

In this study different methods were demonstrated for the separation, detection and quantitation of difficult polar contaminants by UHPLC-MS/MS in water matrices. Table 1 demonstrates the action levels the EU has set in the new regulations along with what the QSight can achieve. Moreover, an example measuring acrylamide at low ng/L levels will showcase the genuine benefits of having a true dual source technology such as the QSight UHPLC-MS/MS system.

**Table 1.** Action level summary relating to challenging polar contaminants.

| Name | QSight 420 LOQ | % CV (n=3) | EU Action Level |
|---|---|---|---|
| Chlorate | 50 ng/L | 4 | 250 µg/L |
| Bromate | 50 ng/L | 4.6 | 10 µg/L |
| Bromide | 100 ng/L | 6.1 | 10 µg/L |
| AMPA | 10 ng/L | 6.4 | 100 ng/L |
| Glyphosate | 10 ng/L | 3 | 100 ng/L |
| Acrylamide | 10 ng/L | 6 | 100 ng/L |

## 2. Material and Methods

### *2.1. Sample preparation*

Sample preparation was absent as we employed direct injection of both drinking and surface water. Samples were

simply collected, filtered with a 0.2 µm PTFE (hydrophylic) syringe filter and 100 µL directly injected onto the system. Thus, eliminating the need for further sample clean up or enrichment, e.g. SPE.

*2.2 Instrument method*

The instrument parameters for chromatographic separation, MS/MS fragmentation and MRM acquisition were optimized with a mixture of certified reference standards. MS transitions are shown below in table 2. The instruments used were a PerkinElmer QSight 420 Triple quadrupole mass analyzer operated using ESI and/or APCI. The UHPLC was a PerkinElmer LX50, including an autosampler, binary pump and column oven. An Obelisc N 2.1x150 mm, 5 µm (SielcTechnologis, USA) ion exchange column was used for the chromatographic separation. For acrylamide analysis a Hypercarb 5µm, 100x2.1mm(Thermo Scientific, Germany) was employed. All instrument control, analysis and data processing were performed using the Simplicity™ 3Q software platform.

**Table 2.** MRM transitions used in this study.

| Compound | Precursor Ion | Product Ion |
|---|---|---|
| Chlorate* | 82.9 | 67 |
| Chlorate-2 | 84.9 | 69.1 |
| Bromate | 126.8 | 111 |
| Bromate-2 | 126.8 | 94.9 |
| Bromide* | 80.7 | 80.7 |
| Bromide-2 | 78.7 | 78.7 |
| AMPA* | 110 | 63 |
| AMPA-2 | 110 | 79 |
| Glyphosate* | 168 | 63 |
| Glyphosate-2 | 168 | 81 |
| Acrylamide* | 72 | 55 |
| Acrylamide-2 | 72 | 58 |

***Indicates Quantifier fragment**

## 3. Results and Discussion

*3.1 Polar contaminants at PPT levels*

Regulations are frequently calling for lower levels of environmental contaminants, this including the challenging polar compounds that can be very difficult to measure accurately and consistantly. Here we present a method including compounds in Table 1 where we can easily reach EU action level limits. In Figure 1 an overlay of the quantifier for the 5 compounds at 500 ng/L is displayed. This demonstrates the separation capabilities of this technique. Moreover, it shows how using an ion exchange column along with simple direct injection, results in appropriate MRLs being reached.

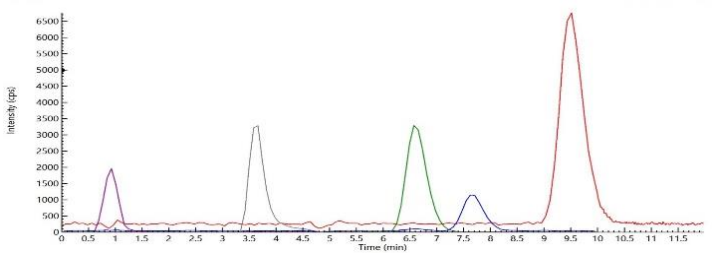


**Figure 1. Chromatogram of MRM transitions for AMPA (purple), glyphosate (grey), bromate (green), bromide (blue) and chlorate (red) at 0.5 µg/L.**

To present which levels can be reached using this method, Table 1 shows the limit of quantification and reproducibility for the 5 compounds. For compounds such as glyphosate and AMPA levels 10x lower (10 ng/L) than EU limits could be detected. Moreover, Figure 3 shows the calibration curves showing dynamic range of 2-3 magnitudes and regression coefficients (r2) ≥ 0.995.

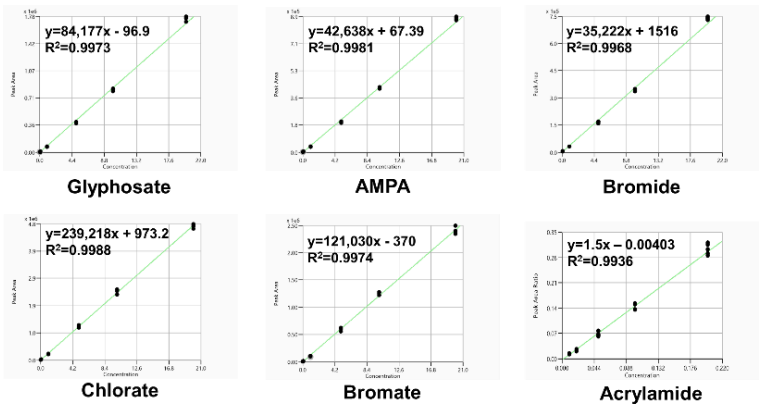


**Figure 2. Calibration curves for chlorate (0.05-20 µg/L), bromate (0.05-20 µg/L), bromide (0.1-20 µg/L), glyphosate (0.01-20 µg/L),AMPA (0.01-20 µg/L) and acrylamide (0.01-0.2 µg/L) .**

*3.2 ESI vs APCI analysis of acrylamide in drinking water*

For the analysis of acrylamide in drinking water two separate runs were setup with ESI and APCI. Because the true dual source design of the QSight allows for the ability to easily switch between ESI and APCI, this allows for different methods to be run without any manual changes to the instrument. As shown in Figure 2 when measuring acrylamide with ESI, there was a very strong matrix effect, but when running the same sample with APCI the effect was drastically reduced. Moreover, the sensitivity was not compromised as lower ppt levels could be achieved.

## 4. Conclusion

The coupling of PerkinElmer's LX50 UHPLC to the QSight 420 proved to be an efficient and effective solution in tackling these tough compounds. Furthermore, this work demonstrated that it is not necessary to use special chromatographic separation techniques, such as ion chromatography, which add additional hardware costs to the system. Owing to the superb sensitivity of the QSight 400 series, it was additionally not required to employ pre-concentration steps like SPE or online-SPE into the methodology, saving further time and cost (4).

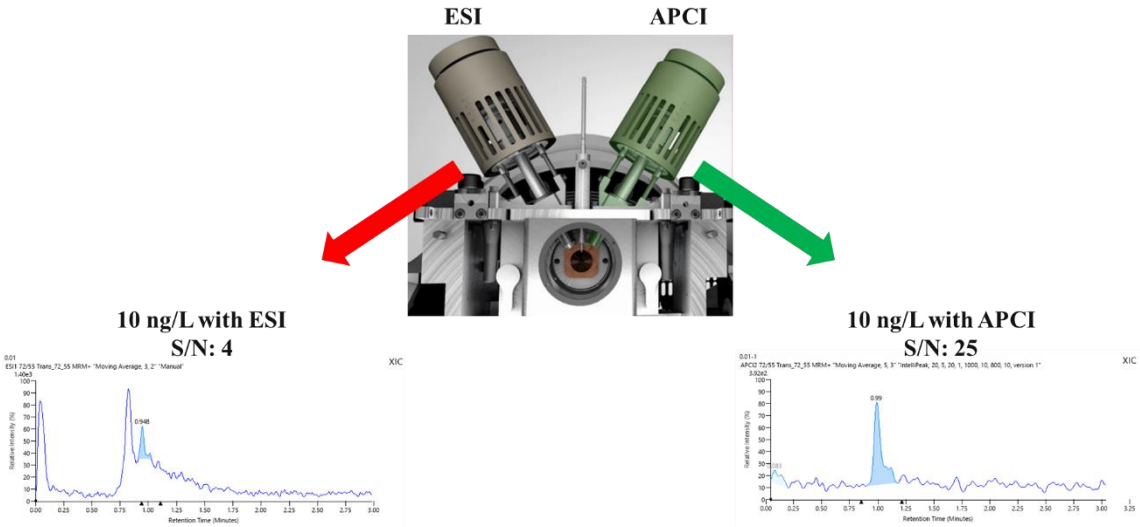


**Figure 3. Comparison of ESI vs APCI at 10 ng/L in a spiked drinking water sample.**

**References**

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