According to the requirements of the European Union drinking water directive 98/83/EC pollutants like herbicides have to be monitored in drinking water. The currently demanded limit of detection (LOD) is 25 ng/L (25 ppt). To achieve this limit of detection with an entry level or mid-range triple quadrupole mass spectrometer a larger volume of the water sample has to be enriched on a trapping column. Then, the compounds are eluted to the analytical column. This work describes the method to enrich different trace level herbicides and the separation from each other. The performance of the system is demonstrated by the mass spectrometric detection of a suite of 28 neutral typical herbicides down to a LOD of less than 10 ppt.

Experimental

Instrumentation

Agilent 1200 Infinity Series Online SPE solution system comprising:
- Quadrupole Pump with internal degasser, Standard Autosampler with sample thermostat, Flexible Cube with two 2-position/10-port valves G4232B, Thermostatted Column Compartment. Agilent 6460 Triple Quadrupole LC/MS with Agilent Jet Stream Technology
- LC/MS Method (Table 1): Quadrupole Pump:
  - Solvent A: Water, 5 mM ammonium formate + 0.1% formic acid.
  - Solvent B: ACN + 5% water, 5 mM ammonium formate + 0.1% formic acid.
  - Flow rate: 0.4 mL/min.
  - Gradient: 0 minutes – 5% B, 5 minutes – 10% B, 10 minutes – 100% B. Stop time: 25 minutes. Post time: 10
  - Column: Temperature: 40 °C.
  - Flexible Cube (Figure 1):
    - Valves: 2-position/10-port QuickChange valve heads.
    - 5 minutes – Pump 300 s. Solvent A1
    - 5 minutes – right valve change position
    - 7 minutes – Pump 180 s. Solvent B1
    - 11 minutes – Pump 300 s. Solvent A1
  - Standard Autosampler:
    - Injection volume: 1,800 μL (automated multi draw of 2 times 900 μL).
    - Needle wash in vial (MeOH). Draw and eject speed: 1,000 μL/min. Sample temperature: 10 °C.

Results and Discussion

Table 2: MRM and dynamic MRM MS method, showing the identified optimum fragmentor [v] and collision energy [eV] values for the individual pesticides as well as for the quantifier and qualifier ions. The retention time was used to develop the dynamic MRM method with a window of ±3 times the peak width around the compartment retention time. For some chlorinated compounds, the transitions from both chlorine isotopes to the same fragment were used when other transitions were of lower abundance.

Figure 3: Chromatograms of a calibration standard with a concentration of 100 ppt (ng/L) each for all 28 pesticides measured by the final SPE-LC dynamic MRM method with quantifier and qualifier ion. Calibration curves for each individual compound were obtained by diluting the stock solution containing all 28 pesticides at a concentration of 100 ng/L (100 ppt) in a dilution series down to 0.5 ng/L (0.5 ppt). The pesticides were measured with the developed online-SPE LC method using dynamic MRM. Each calibration standard was injected four times with a volume of 1,800 μL and enriched on the SPE trapping column. The value at a signal-to-noise (S/N) ratio of 3 was used for the LOD and the value at a S/N ratio of 10 was used for LOQ. The calibration curve was calculated from LOD up to 100 ppt (Figure 4).

Figure 4A and 4B show the quantifier transition m/z 207.1 & 72.1 of isoproturon, at a concentration of 5 to 100 ppt B) 1 to 10 ppt C) Calibration curve of Isoproturon at a concentration of 1 ppt–100 ppt (seven levels, seven levels used, 28 points, 28 points used), linear coefficient 0.9986, LOD 1ppt.

Figure 5: Water samples from the Rhine river, tap water, and spring water were spiked with all 28 pesticides to a final concentration of 25 ppt. Analysis of all samples yielded comparable intensities for a large number of the spiked herbicides independent from the source of the water sample (Figure 5). This indicates that residual salt contaminations from the water samples or other contaminants with high ion strength which might cause ion suppression were effectively flushed out of the SPE column. The spiked tap water and river water samples were rich in calcium hydrogen carbonate. The measured concentrations of all pesticides shown in Figure 5 were averaged dependent on the source of water. The calculated concentration precision was between 2.3% and 2.8%. The concentration accuracy was always above 90%.

Conclusions

- This work demonstrates the use of the Online-SPE solution for enrichment, separation, and detection in trace level analysis of pesticide residues in water samples by HPLC with triple quadrupole MS detection.
- It was demonstrated that lowest LOD of 0.5 ppt and LOQ as low as 1 ppt could be achieved. The methodology shows a high sample-to-sample reproducibility with area deviation of less than 7%.
- The efficient online-SPE trapping process allows pesticide detection in real drinking water samples well below the regulatory limits with high precision and accuracy.