A quick and routine analysis of polar pesticides in water by suppressed ion chromatography and mass spectrometry

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ABSTRACT
Polar pesticides analysis in water and foods has become very hot topic in the past couple of years. A famous representative of this group is glyphosate and its metabolite AMPA. Glyphosate is discovered more than 40 years ago and has become popular due to its low toxicity in comparison with other herbicides. It is used in 100s weeds competing with crops and in the parks and roadsides. In March 2015 the World Health Organization’s (WHO) International Agency for Research on Cancer classified glyphosate as a probable carcinogen1. However in November 2015, the European Food Safety Authority (EFSA) declared glyphosate safe for cancer. There is a big demand to increase the number of methods for the analysis of polar pesticides. Ion chromatography is the preferred method because of the chemical properties it is not possible to analyse these pesticides on the conventional C18 column. There are concerns about their potential adverse effects on detection selectivity when operated in selected reaction monitoring (SRM) mode. The analysis of polar pesticides in surface and drinking water, as well as food and beverages, has become a controversial issue in recent years. The development of genetically modified organisms (GMOs) crops tolerant to glyphosate and glufosinate, for example, promoted the use of these broad-spectrum herbicides. Consequently, polar pesticides are found in foods as residues and in the environment as contaminants of surface waters, soils, etc.

INTRODUCTION
The analysis of polar ionic pesticides in surface and drinking water, as well as food and beverages, has become a controversial issue in recent years. The development of genetically modified organisms (GMOs) crops tolerant to glyphosate and glufosinate, for example, promoted the use of these broad-spectrum herbicides. Consequently, polar pesticides are found in foods as residues and in the environment as contaminants of surface waters, soils, etc.

There are concerns about their potential adverse effects on human health, such as their potential carcinogenicity. Although the latest toxicological assessment does not predict risks for humans under normal conditions or environmental exposure2. Current regulations either maximum residue levels (MRLs) of glyphosate and its metabolite AMPA at 100 ng/l in drinking water. In food and beverage samples, higher MRLs vary widely depending on the commodity. The analysis of glyphosate and other polar compounds presents a difficult analytical challenge. Their polarity does not allow the direct analysis by reversed phase HPLC, so alternative methods need to be applied. Derivatisation of glyphosate prior to analysis or application of specific ion chromatographic columns, such as the Thermo Scientific™ Hypercarb™ columns, are the common approaches3. With both of these approaches poor method robustness and questionable results are often reported in laboratories, because when the IC is applied in routine throughput analysis of samples with rather complex matrixes.

Recent developments in ion chromatography and mass spectrometry offer many advantages for the analysis of very polar substances. Ion chromatography is the preferred separation technique for polar ionic analytes, such as arons, acetates, or small polar analytes (metabolites) and solutes. Mass spectrometry, namely, suppressed ion chromatography (MS/MS) systems, offers very low detection limits and high detection selectivity when operated in selected reaction monitoring (SRM) mode. The system robustness allows the analysis of complex samples of food and environmental matrices. The aim of this work is to develop and validate a (IC-MS/MS) method for direct analysis of polar pesticides and assess its applicability under real conditions.

MATERIALS AND METHODS
Sample Preparation
Samples of tap, bottled and surface water were taken and injected directly into the ion chromatograph. The water samples were filtrated through a syringe disc filter to remove particulates.

METHOD OPTIMISATION
During method optimisation, various analytical parameters including the influence of make-up solvent were assessed. The performance of the method had been evaluated by analyzing fortified drinking water, bottled mineral water and surface water samples. Additional data on accuracy were obtained by analyzing surface water samples provided by Water Laboratory of Pilsen, Czech Republic. The method results are shown in Table 2.

RESULTS
Samples from a survey conducted on the Vitava river in the Czech Republic (CR) were analyzed using the Thermo LC- MS/MS method by the Water Laboratory, Pilsen for concentrations of glyphosate and AMPA. The samples were then run on the newly developed IC-MS/MS for comparison of the two techniques and to determine accuracy of the method. Results are shown in Figure 4 and an example of the SRM chromatogram is shown in Figure 5.

CONCLUSIONS
- The reported IC-MS/MS method enables the quantitative analysis of five polar ionic pesticides with respect to the actual MRL levels.
- The method showed good repeatability, recovery, and linearity and decoupled quantification for drinking, bottled mineral and surface water.
- The developed method has many benefits in comparison with traditionally used LC-MS/MS methods utilizing FIMOC derivatization. Thanks to the direct injection without a long and laborious sample preparation the method is more sensitive, very fast and avoids sample manipulation errors.

REFERENCES

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