

A rapid procedure for simultaneous determination of glyphosate and AMPA in water at sub $\mu\text{g/L}$ level.

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Glyphosate is the most used pesticide worldwide and its impact on the environment is becoming increasingly significant. Because of its widespread use, glyphosate and its main metabolite AMPA are frequently detected in streams and rivers. The determination of glyphosate and AMPA at sub $\mu\text{g/L}$ level is challenging due to their very polar and ionic character, low volatility, low mass and lack of chemical groups that could facilitate their detection. In this study, an analytical method is presented that combines Ultra-High Performance Liquid Chromatography with mass spectrometry (UHPLC-ESI-MS/MS) for glyphosate and AMPA analysis in water samples. The method was developed starting from an application of Waters Corporation, and involves the use of an alternative derivatizing reagent, the commercially available AccQ•TagTM Ultra Derivatization Kit (Waters Corporation, Milford, MA, USA). The kit was originally designed for amino acid analysis and it contains the derivatizing reagent 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC). This derivatizing reagent reacts with the amino functional group present in glyphosate and its metabolite. Derivatization takes place directly in the injection vial and no sample pre-concentration is needed. The derivatization step is simple, quick and robust, which fits well within the needs of a routine method for the analysis of glyphosate and AMPA. Derivatized glyphosate and AMPA were recorded in positive ion mode. The method demonstrates a good linear relationship in the glyphosate and AMPA concentration range of 0.1-100 $\mu\text{g/L}$ and an accurate recovery. The method LOD and LOQ of 0.05 and 0.1 $\mu\text{g/L}$ respectively were established for the two analytes. The developed method has been successfully applied to the determination of glyphosate and AMPA in 23 runoff water samples collected from a field in the Po Valley (North-East Italy), an important agricultural area where glyphosate is widely used. The method was found to be precise and accurate, with recovery percentages higher than 90% for both molecules in runoff water.