



Review article

The role of derivatization techniques in the analysis of glyphosate and aminomethyl-phosphonic acid by chromatography



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ABSTRACT

Derivatization, prior to the chromatographic analysis of the particularly polar herbicide – *N*-(phosphonomethyl) glycine (glyphosate, GLYP) and its main metabolite aminomethylphosphonic acid (AMPA)] – proved to be a key step: also in cases applying liquid chromatographic techniques.

In this paper the analytical proposals for GLYP and AMPA are reviewed: performing analyses by chromatography. First sorting was based on the chromatographic separation method. Within the same chromatographic techniques, like gas chromatography (GC) and liquid chromatography (LC), distinction was made between GLYP and AMPA separations in their initial forms (without derivatization) and as various derivatives. The examined matrix, enrichment, derivatization, acquisition protocols, limit of detection (LOD), limit of quantitation (LOQ) data were listed; additional herbicide(s), analyzed in a single run, were also shown. Special attention was paid to the selectivity and sensitivity properties of methods. Analytical performance characteristics were documented and commented in details.

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1. Introduction

The relevancy and continued interest towards chromatographic analyses of GLYP and its main metabolite, AMPA can be explained by the foreseeable exponential production and use of GLYP taking into consideration its application forecasts up to 2020: global glyphosate demand was over 700 kt in 2013, which is expected to exceed 1000 kt by 2020 [1].

The role of derivatization for GLYP and AMPA analyses can be best characterized by the fact that independent on the chromatographic techniques used, (published in the last two decades, summed up on Science Direct basis, according to our selection), in 99% of contributions, expressed in the total of representative papers, was performed with derivatized species.

Thus, the utility of an overview from the points of view comparing methodologies, sensitivity, selectivity, reliability and reproducibility of proposals applying underivatized and derivatized GLYP and AMPA, contrasting suitability for their simultaneous identification and quantification in different matrices, (environmental waters, soils/sewages, fruits/

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vegetables, serum/plasma/urines, derivatization/standard impurity, or adsorption/degradation/antibody studies) is not questionable.

Literature reviews, published in the last thirteen years [2–16], were related primarily on method and matrix selection [2–14]. In this contexts gas chromatography (GC: [2,3,5,7]), liquid chromatography (LC: [4–9,11,14]) and capillary electrophoresis (CE: [7,10,12,13,16]) techniques were compiled. Focusing, all, on sample preparation strategy [2–16] and herbicide residues analysis: in foods [3–5,8,11,13], in environmental waters [2,3,6–8,11,13], in soil [9] and in sediment [13]. Reviews, on bioanalytical approaches are worth mentioning [15,16] such as discussing GLYP's phytotoxicity [15] and developing method for the comparative analysis of metabolic profiles from transgenic soybean, distinguishing its glyphosate resistant alternative [16].

In this review those relevant papers were compiled – without completeness – in which for GLYP and AMPA analysis – GC [17–46], LC [47–70], CEC [71,72], ion chromatography (IC) [73–75], spectrophotometry [76,77] and neutron magnetic resonance (NMR) [78–80] protocols were used. Further classifications were listed according to the matrix they had to be extracted from and/or to the detailed process they were subjected to, prior to their identification and quantitation analysis.

1.1. Sample and method selection

The aim of this compilation was to assess the involvement of GLYP and AMPA, these, freely water soluble herbicides, emerging in various matrices we are faced by. Distribution of polluted matrices reveals that the most frequently analyzed sample types vary from 35.1% (environmental waters) to 5.9% (adsorption/degradation/antibody studies), expressed in the total of our selection (Fig. 1).

In favor of unambiguous transparency and easy traceability, all the expressions used together with their abbreviated forms are compiled in Table 1A, the structure and physical/chemical properties of the target analytes (GLYP, AMPA) in Table 1B.

From methodological point of view, regarding selected papers [17–80] – we examined in details the GC based, simultaneous acylation and esterification (Table 2), the various alkylsilylation techniques (Table 3) and the different liquid chromatographic (Table 4) proposals. Evaluation is also based on our earlier experiences being deeply involved in the analysis of organics even as environmental pollutants [81–85].

In general, it is worth mentioning that derivatization does have a particular importance in the chromatographic protocols. This time consuming and tedious process, by research and application chemists, equally, was and it is still regarded as the main disadvantage of sample preparation, needed primarily, prior to GC analyses, only. However, this so called 'disadvantage' is dwarfed in comparison to several advantages associated with the analysis of derivatized compounds (increased selectivity, sensitivity and the possible identification and quantification of species in question, in a single column, simultaneously). In the present case – meaning the polar herbicide analysis – derivatization does have a particular importance, it is a key issue, even prior to LC separations; the preliminary derivatization step proved to be unavoidable necessary. Out of the reviewed LC selections [47–70], in three, author declared their method as direct derivatization [62,67,68]: however, having a look inside the method, it turns out that this statement – in two proposals [62,67] – is questionable.

2. GC of GLYP and AMPA

2.1. Quantitation of GLYP without derivatization

Recently, two trials were found [39,44]: in one of them authors confirmed that "... The method developed... for 32 pesticide residues in vegetables... was only incapable of adequately determining four of the pesticides from Regulation MS 518/2004: glyphosate... was not... suitable for direct GC determination" [39]. Similarly, a "...method for the rapid simultaneous screening and identification of multiple pesticide residues in vegetables was established using a novel database and gas chromatography in combination with hybrid quadrupole time-of-flight mass spectrometry (GC-QTOF MS). A total of 187 pesticides with different chemical species were measured" ...including... "glyphosate herbicide"... which could not be detected at all [44]. It means there is no method in the literature suitable for GLYP and AMPA analysis, without derivatization, by GC.

2.1.1. Simultaneous acylation and esterification

Papers were sorted in line of their appearances representing all matrices of interest (Table 2). Enrichment protocols – were cation or anion exchange cleanings, including, filtering, centrifugation, evaporation. Solid samples were mainly water extracted. Except a

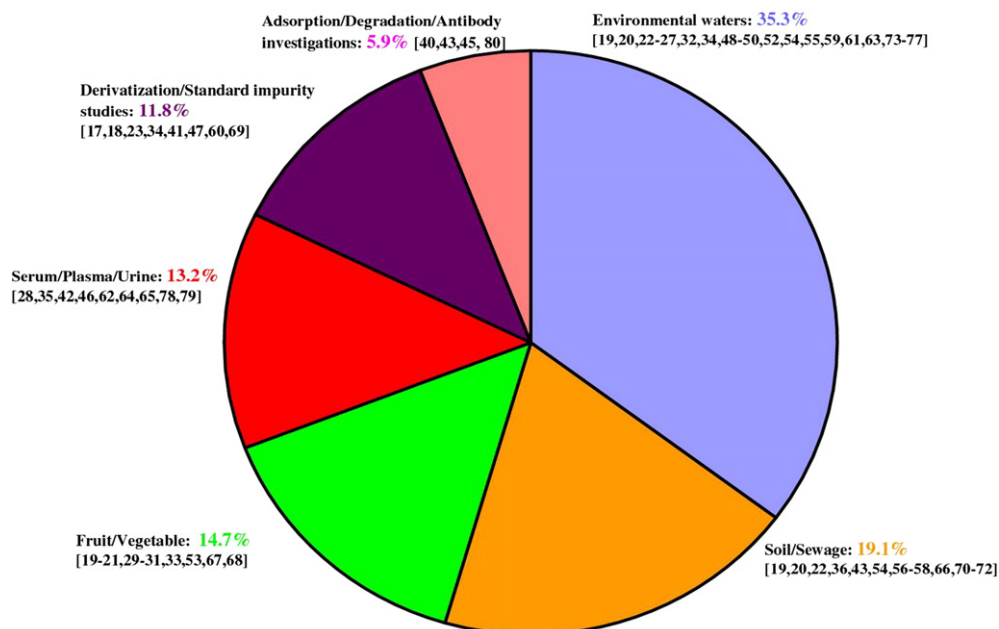


Fig 1. Distribution of the most frequently analyzed sample types to identify and quantify GLYP and AMPA residues in various matrices, by chromatography.

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