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Glyphosate detection with ammonium nitrate and humic acids as potential interfering substances by pulsed voltammetry technique

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ABSTRACT

Pulsed voltammetry has been used to detect and quantify glyphosate on buffered water in presence of ammonium nitrate and humic substances. Glyphosate is the most widely used herbicide active ingredient in the world. It is a non-selective broad spectrum herbicide but some of its health and environmental effects are still being discussed. Nowadays, glyphosate pollution in water is being monitored but quantification techniques are slow and expensive. Glyphosate wastes are often detected in countryside water bodies where organic substances and fertilizers (commonly based on ammonium nitrate) may also be present. Glyphosate also forms complexes with humic acids so these compounds have also been taken into consideration. The objective of this research is to study the interference of these common pollutants in glyphosate measurements by pulsed voltammetry. The statistical treatment of the voltammetric data obtained lets us discriminate glyphosate from the other studied compounds and a mathematical model has been built to quantify glyphosate concentrations in a buffer despite the presence of humic substances and ammonium nitrate. In this model, the coefficient of determination (R^2) is 0.977 and the RMSEP value is 2.96×10^{-5} so the model is considered statistically valid.

1. Introduction

Glyphosate is the most widely used herbicide active ingredient in the world [1]. This is due mainly to the widespread use of glyphoresistant seeds [2], which inhibits the growth of competitive weeds in combination with glyphosate [3,4] allowing crops to be very productive and efficient at low cost [5,6]. Glyphoresistant seeds are genetically modified organisms, mainly soya, corn, canola, wheat, sugar beet, and cotton [7].

Glyphosate is a non-selective wide spectrum herbicide. It works by inhibiting the enzyme EPSPS from plants, which is essential for the development of certain amino acids. In the environment, it has a half-life between 7 and 174 days [8,9] and metabolizes into AMPA, methylamine, ammonia, and carbon dioxide [10]. Extensive and recurrent uses, as well as an inappropriate product application, cause its presence in unwanted areas and glyphosate can be found in soil [11], water [12,13], crops [14], plants [2], animals [15], and human inhabited areas [16], with a significant toxicological and environmental potential damage [17].

Despite the lack of control and legislation of this herbicide in many countries [18], the USEPA is the worldwide legal reference in terms of limit concentrations for glyphosate in water bodies [19–21], setting a maximum concentration of 0.7 mg/l. In addition, the Health Canada Drinking Water Guidelines set 0.28 mg/l as its maximum acceptable concentration in drinking waters [22,23]. There are directives and regulations based on these organizations guidelines in most of the developed countries, such as the Water Framework Directive 2006/60 CE in European Union [24].

Nowadays, glyphosate is mainly detected and quantified by high performance liquid chromatography combined with mass spectrometry (HPLC-MS) [17,25] but there are other applied techniques such as fluorescence, colorimetry [26], caplillary electrophoresis [27], and electrochemiluminescence [28]. These techniques are slow and expensive and must be developed in a laboratory, so pulsed voltammetry may become a feasible alternative.

In fact, voltammetric techniques are showing good results in various research areas like pollutants detection in air [13], water [10], and food [29]. In addition, they are starting to be considered as promissory alternatives to the traditional analytical methods in several fields by developing an appropriate selection of metals and coatings. Some examples of this success can be seen in published papers such as the one presented by Aquino [30], or using an appropriate combination of diverse metals as silver and

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platinum [31], copper [32], enzymes [33], and double-layer hydroxides [34] as working electrodes and coatings.

The main goal of this paper is to build and validate a mathematical model to quantify glyphosate in a buffer solution despite the presence of different concentrations of some common pollutants in natural water bodies that can be possible interfering substances. Several assays have been carried out with different concentrations of glyphosate, ammonium nitrate and liquid humus dissolved in 0.1 M sodium dihydrogen phosphate.

2. Materials and methods

2.1. Chemicals

Voltammetry measurements have been done to different dissolutions combining five glyphosate concentrations (96%, Molekula) ranging from 5 · 10–5 M to 5 · 10–4 M, three different concentrations of ammonium nitrate (ACS reagent, 98%, Sigma-Aldrich) ranging from 10 ppm to 100 ppm, and other three ones of a commercial liquid humus (C/N = 12.5, pH = 4.5, density = 124 kg/l, 2.2%, nitrogen. Commercial product from MasoGarden) from 5 ppm to 50 ppm, all of them dissolved in 0.1 M sodium dihydrogen phosphate (ACS reagent, Sharlau).

2.2. Electrochemical measurement

All measurements have been carried out with an electronic device designed and developed by the Institute of Molecular Recognition and Technological Development (IDM) called FraPlusMini [35–37] that is capable to run tests of pulsed voltammetry, cyclic voltammetry and impedance spectroscopy. This electronic device and measurement system has been described in detail in previous papers working with glyphosate [18,29] and has been successfully used in food [38–40], water analyses [41] and the determination of environmental parameters [42].

As in the previous works with glyphosate [18,29], pulsed voltammetry technique was used to apply an electric voltage to the utilized electrodes (working electrodes) when submerged in glyphosate dissolutions. Then the electric current that circulates through each electrode could be measured. This is because the flow of the current through the dissolution is a function of the applied voltage and the chemical concentration in the dissolution.

2.3. Electrochemical sensors (electrodes)

In order to carry out the analyses, two different arrays of metal sensors have been developed. Each array has been confined in a stainless steel tube as shown in Fig. 1. The first one containing four different noble metals (Ir, Rh, Pt, and Au) and the second one containing other four non-noble metals (Ag, Cu, Co, and Ni). Every working electrode has a contact diameter of 1 mm. Not only how the metal sensors are fixed inside of the steel body is important, but also the connection between the sensors and the cables connected to the measurement system. In this sense, each array of sensors has been connected to the measurement system using cables soldered to a crimp-on terminal. Next, each steel cylinder has been filled up with epoxy resin in order to fix the metal sensors, separate them and guarantee the contact surface of 1 mm in diameter for all the sensors. In the end, in order to guarantee a full contact of all the sensors, the overflowing resin of the metal sensor was sanded (Fig. 1).

The selection of the metal sensors used to develop the arrays has been made according to our previous experience [18,42] and papers published before [43,44]. In addition, a calomel electrode has been used (Radiometer Analytical, XR 100) as reference electrode.

Fig. 1. Example of the designed electrode arrays.

2.4. Laboratory analyses

Attending to the experience acquired in previous works [18,42,43] and the preliminary tests with glyphosate in buffer dissolution, a pulse train (Fig. 2) has been designed and used in order to carry out the voltammetric measurements.

Electrochemical analyses have been done by using the FraPlus-Mini device to samples with five different concentrations of glyphosate, three different ones of ammonium nitrate, and three different ones of liquid humus dissolved in a buffer solution of 0.1 M sodium dihydrogen phosphate adjusted to a pH of 6.7 with a few drops of NaOH. As a result of these combinations a global amount of 31 samples (thirty plus the buffer sample) per series have been selected attending to an appropriate distribution of glyphosate, ammonium nitrate and humus concentrations (Table 1).

During the voltammetric analyses, dissolutions were measured for three times in order to assure repeatability of the samples. In this way, it was possible to perform three series of assays (with three repetitions and five iterations each one) to create sufficient data volume (279 assays) to construct and validate a mathematical model by using SOLO © software (Eigenvector Research Inc.)

3. Results and discussion

3.1. Voltammetric analyses

A data base has been obtained as a result of the three series of assays (A, B and C) measured by pulsed voltammetry with the designed pulse train, to the 31 samples of known glyphosate, ammonium nitrate, and liquid humus concentrations in buffer solution. This data base is composed by 999 values of intensity for each one of the 279 assays made. Before starting the statistical treatment, the five iterations of every measure were averaged, as well as the three measures of the same sample, obtaining 93 measures to be statistically treated. This is to simplify the data base and diminish variations among measurements to build the mathematical model. In this data base, three of the 93 measures are buffer measures, which have been subtracted from each one of the measurements of the corresponding series. Therefore, we had to statistically treat 90 measures of the intensity response produced by the dissolved substances.

The voltammetric response to the five glyphosate concentrations in presence of the maximum concentration of ammonium nitrate and humus was in the way shown in Fig. 3.