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Inexpensive FIA method to determine trace levels of imazapyr by UV-detection enhanced with electrochemical polarization

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Abstract A new flow injection analysis method with spectro-electrochemical detection (FIA/SEC) to determine trace levels of imazapyr on water samples is presented. The non-chromatographic method involves the use of a bench photometer, a single-potential potentiostat, a low pressure pumping system and a home-made spectro-electrochemical flow detector (SEC-FD), specifically adapted for the described method and using a stainless steel/electrolytic lead/lead chloride (SS/e-$Pb/PbCl_2$) working electrode. The limit of quantification (LOQ) reached for the optimized work parameters was 0.02 µg/mL, the relative standard deviation (RSD) in the whole range of linear response was less than 2% and a wide linear response range from 0.005 to 6.0 µg/mL was obtained. A standard addition method was used to determine the imazapyr amount in natural waters containing commercial formulation of such herbicide, the Recovery % has values close to 105%. The method performance makes it suitable to analyze the legal imazapyr tolerances established by the U.S. EPA avoiding the use of expensive chromatographic equipments and/or complicated sample preparations.

1. Introduction

Imazapyr is a broad-spectrum non-selective herbicide in the imidazolinone family. Its main uses are vegetation control in forest, estuaries, residential and industrial sites, golf fields and railroad rights-of-way but it is also used in agriculture, e.g. in sugarcane, corn, sunflower, oil palm and rubber crop fields and also on pastures and rangeland.

Although imazapyr may suffer photolysis rapidly when is dissolved in water, with half-lives around 3 or 4 days; its

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persistence in soil may be higher than several months depending on the pH and the soil composition (Tu et al., 2001). It is also mobile in soil; therefore, the doses used and security periods must be carefully controlled to prevent environmental risks that could affect to non-target plants and cultures.

The U.S. Environmental Protection Agency (EPA) establishes legal imazapyr tolerances ('Reregistration Eligibility Decision for Imazapyr', 2006) ranged from 0.01 to 100.0 μg/mL (ppm) depending on the analytical matrix of samples (corn, grass, milk, meat, poultry, eggs, fish and some of its by-products). Also, the U.S. Food and Drug Administration (FDA) was published several methods to analyze imazapyr residues in different agricultural and food products ('Pesticides: Analytical Methods & Procedures, 2002) to comply with legal requirements. These methods are based on Gas Chromatography/Mass Spectrometry (GC/MS) or Capillary Electrophoresis/UV detection (CE/UV). They have Limits of Quantization (LOQ) of 0.01 and 0.05 μg/mL respectively and also include directions for a confirmatory analysis using Liquid Chromatography/Mass Spectrometry (LC/MS).

Other analytical methods have been published later having LOQ as lower as 1.0 ng/mL (ppb) in soil and solution samples. All of them are based on chromatographic methods requiring previous extraction stages (Anisuzzaman et al., 2000; D'Ascenzo et al., 1998c; D'Ascenzo et al., 1998b, 1998a; Furlong et al., 2000; Laganà et al., 1998; Liu et al., 1992; Marchese et al., 2001; Rodriguez and Orescan, 1998; Stout et al., 1996) or they are Enzyme-Linked ImmunoSorbent Assay (ELISA) immunoassay (Fischer and Michael, 1997). As it can be seen, all available analytical methods have in common the use of high performance equipment, which requires a high investment, both for purchase and for maintenance. They also require highly qualified and well-trained technical staff to run analytical protocols and, due to the stringent facilities needed, do not allow the in situ analysis of samples.

The electrochemical behaviour of imazapyr has been studied previously by using mercury electrodes. It exhibits an initial reduction peak associated to the 2,3-C=N double bond reduction in the imidazoline moiety (Mozo et al., 2010) (see Scheme 1) and some others at more negative potentials corresponding to the pyridinic ring reduction (Pintado et al., 2011). The peak positions are pH dependent and the reduction processes occur at more negative potentials for the more alkaline pH values. Both the imazapyr and its reduction products have absorbance bands at UV wavelengths. These last also absorb at the visible spectrum showing a yellow colour whose hue varies along with the pH of the electrolysed solution, being pale in acidic and orange in alkaline media. Such information leads to use the spectro-electrochemistry as detection strategy in a new

analytical method, looking for adequate levels of detection but using affordable instrumentation.

The combined use of an electrochemical signal to determine or derivate the analyte and the measurement of a spectroscopic property of such analyte in a spectro-electrochemical (SEC) approach can enhance the analytical performance of methods with such a detection system. The association of these two signals enhances the selectivity of the analysis and proves decisive when other electroactive and/or coloured compounds are presents in the sample. Although SEC has been applied in research on electrode processes involving coloured intermediates or products, the use of SEC detectors for routine analytical purposes is quite scarce and only a few research groups have some publications on the matter (Dewald and Wang, 1985; Heineman et al., 2009; Kaim and Fiedler, 2009; León et al., 2014; Morris et al., 2009).

In this work, a new flow injection analysis method with spectro-electrochemical detection (FIA/SEC) is presented to determine imazapyr content in water samples. The equipment required consists on a bench UV photometer, a low pressure pumping system and a single-potential potentiostat, all of them very affordable and friendly use. Also, a home-made flow-detector designed in our laboratory (León et al., 2013) and specially adapted for this method must be used, allowing both the optical determination and the polarization of appropriate electrodes to enhance the range of linear response and the limit of detection. The limit of quantification value reached is close to the legal tolerances of imazapyr. Moreover, the type of equipment used in this new method allows the automation of measures and also the miniaturization intended to in situ analysis of samples with compact and portable equipments.

2. Materials and methods

2.1. Reagents and solutions

Imazapyr (Pestanal) was purchased from Riedel as analytical standard (purity > 99.9%) and was used without further purification. Commercial presentation of imazapyr, Arsenal, was gently gifted by a local supplier of plant health products. All the other reagents used were of analytical grade.

Stock solution of 0.3 M NaCl was prepared to keep a saline concentration high enough; pH was adjusted to 0.5 with concentrated HCl, so the final ionic strength of solution was 0.6 M. This solution was used both to prepare imazapyr solutions of appropriate concentrations and as carrier solution. A fortified carrier solution with double concentration was used to conditioning real samples by mixing them 50:50.

The imazapyr solutions were stored in closed recipients and protected from sunlight to avoid the herbicide photolytic decomposition. The solutions were rejected after 3 days.

The electrolytic bath used for lead deposition is composed by a water solution of 3% (w/v) lead hexafluorosilicate, 14% (v/v) hexafluorosilicic acid and 1% (w/v) alimentary gelatine.

For the electrochemical reduction experiments, oxygen was removed by bubbling nitrogen through the solutions before their use.

All the solutions were prepared using low conductivity water (18 MΩ cm) purified from distilled water by a Millipore Milli-Q water system. All the experiments were carried out at room temperature.
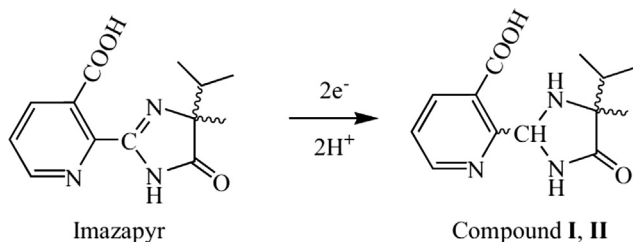
Scheme 1 Reduction mechanism of imazapyr in protic media.

The natural water used was taken from a well located in a residential area near of Seville city; it was used without any previous manipulation and was kept stored in a sample glass flask at $-4\,°C$ to its use.

2.2. Apparatus

UV absorption experiments were performed with a Varian Cary 1E (Aligent Inc., Santa Clara, CA) double beam UV–vis spectrophotometer, using standard quartz cuvettes or the new spectro-electrochemical cell as flow detector (SEC-FD).
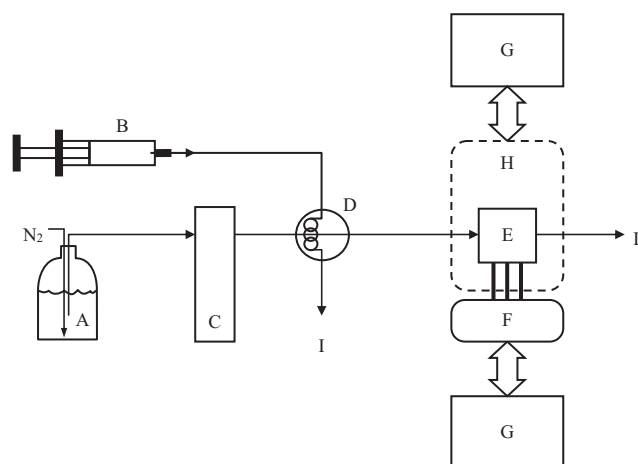
Potentiostatic electrochemical experiments were carried in a BAS 100B (BASi, West Lafayette, IN) three-electrode potentiostat interfaced to a PC. Galvanostatic lead coating were made with an Autolab PGSTAT20 (EcoChemie, Netherlands) electrochemical analyzer also interfaced to a PC. A C-3 Cell Stand for solid electrodes (BASi) was used for batch experiments. Platinum wire was used as auxiliary electrode in batch experiments and stainless steel (SS) pipe in flow experiments. An Ag/AgCl/NaCl$_{sat}$ electrode was always used as reference.

Circular dichroism (CD) experiments were carried with a spectropolarimeter Bio-Logic Mos-450 (Bio-Logic, Claix, France) and using fluorescence quartz cuvettes (10.0 mm width) or the new spectro-electrochemical cell as flow detector (SEC-FD).

A Gilson Minipuls3 (Gilson Inc., Middleton, WI) peristaltic pump coupled to an Omnifit (Diba Industries Inc., Danbury, CT) six-way manual injection valve (Code #: 001106) were used as part of the flow channel for FIA experiments. All tubing was made in PTFE 0.8 mm ID acquired from Supelco (Sigma-Aldrich).

2.3. FIA setup and procedure

The manifold arrangement of the FIA system used is a single flow-channel type and it's shown in Fig. 1. The saline solution described above was used as a carrier solution, with a flow rate of 1.0 mL/min. A loop of 200 µL was used to inject samples and standard solutions into the carrier stream. Appropriate amounts of solid analyte were dissolved in the carrier solution to make the standard solutions with the desired concentration; convenient dilutions were made from a stock concentrated solution for the lowest concentrations.

The UV detector wavelength was setting to 242 nm according to the bibliographic information and our own data for both direct and enhanced detection of imazapyr. The working electrode was polarized to -410 mV respecting to the Ag/AgCl/NaCl$_{sat}$ reference electrode.
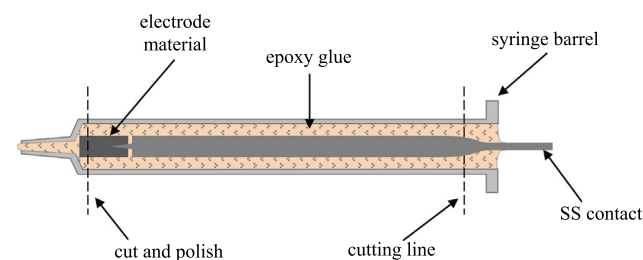
For real water samples determination, 10.5 mL/L of Arsenal was added to natural groundwater, according the use recommendations of supplier. Such sample solution was diluted in deionised water to get 6.0 µg/mL, within the linear range of detector. A standard addition procedure was carried out by adding three amounts of standard solution by increasing the imazapyr concentration in 6.0 µg/mL steps. Each solution, including sample and standard, was mixed 50:50 with fortified carrier solution to conditioning ionic strength and pH. Such solutions were injected five folds in the FIA system.

3. Results and discussion

3.1. Selecting the appropriate electrode material

To the best of the author's knowledge, all electrochemical studies published about imazapyr and imidazolinones were made on mercury electrodes; they have a high window of cathodic potentials for aqueous solutions and measures are highly reproducible. Obviously, this material has environmental issues if it is intended to use for analysis of residues in natural samples, so it is necessary to find a solid electrode material where imazapyr behaves similarly.

If a typical solid material is used, as glassy carbon or platinum, no reduction peak is observed because the solvent reduction occurs before the imazapyr one does, regardless of pH. The more adequate cathodic materials are sp metals such as Pb, Hg, Sn, Zn, Cd, Al, In ..., having the highest hydrogen overpotential (Torii, 2006). It's unusual to find commercial working electrodes for voltammetry made with such materials. Therefore, a set of electrodes were manufactured in a similar format than the carbon electrode (model MF-2012) available from BASi. Specifications, materials and dimensions of these electrodes are shown in Fig. 2.

Fig. 1 Schematic diagram of the FIA manifold. (A) Carrier solution; (B) Standards or samples; (C) Peristaltic pump; (D) Six-way sample injector; (E) Spectro-electrochemical cell; (F) Potentiostat; (G) PC; (H) Spectrophotometer; (I) Waste.

Fig. 2 Longitudinal section scheme of a home-made metallic electrode. A 1 mL syringe barrel filled with epoxy glue forms the electrode body. The electrode material is exposed after cut and polishes the left end (figure view). An internal stainless steel (SS) rod serves as electrical contact. Length of plastic body is 7.5 cm, total diameter is 6.4 mm and electrode material diameter is 3.0 mm.

The chosen materials were pure Zn, Pb, Sn and its azeotropic alloys Sn/Pb (62/38), Sn/Zn (15/85). These materials were melted in a crucible and were poured out into elongated ingots. After cooling, they were lathed as rods of 3.0 mm in diameter.

A small section, 6.0 mm long, of each was embedded in a plastic body formed by a jacket filled with epoxy glue. The outer jacket was the barrel of a disposable 1.0 mL syringe.

A stainless steel (SS) rod was inserted to make the electrical connection with the electrode when the glue was still fresh. The end connecting to the electrode is needle-shaped to ensure a good electrical contact. The protruding end is sized to external contact of the equipment used.

The surface of the electrode material is exposed when cut and polish the lower end of the syringe body, once the glue has completely cured. The polishing is done first with sandpaper and then with alumina powder getting smaller grain, a mirror-like surface of 3.0 mm in diameter must be obtained.

To check which material is the most suitable to reduce the imazapyr in acidic media, a set of differential pulse voltammograms (DPV) were performed on saline acidic solutions by using the home-made flat-shaped metallic electrodes (see Fig. S1 in Supplementary Material). The results shown that lead and tin electrodes have the highest hydrogen overpotential, therefore any of them can be the material of choice.

The spectro-electrochemical flow detector to be used requires tubular-shaped working electrodes, inside which circulate the solution and have to be installed by pressure (León et al., 2013). Both lead and tin are soft metals that can be easily deformed. Therefore, making a tube with these materials, with the suitable dimensions and rigid enough to be installed by pressing is very hard, almost impossible. So, a steel catheter should be used as supporting material, coating by electroplating with the electrode material in its inner face. Several electroplating experiments lead us to ensure (see microphotographs showed in Fig. S2 in Supplementary Material) that steel is better-coated with lead, so this is our final choice.

To check that imazapyr can be reduced on massive lead electrode, differential voltammetry measures were made at diffusion conditions and a signal is obtained at −1100 mV (see Fig. 3a). In addition, the signal should be reproducible without manipulating the electrode surface. It must be taken into account that for flow measurements, the working electrode will be the inside face of a leaded pipe which obviously cannot be polished before each measurement. Fig. 3b shows successive differential voltammograms of imazapyr on massive lead electrode. As can be observed, the first scan (on freshly polished electrode) is different, but the second and subsequent are quite similar.

The aspect of electrode surface after its use is whitish, perhaps due to the formation of a $PbCl_2$ layer by reaction with the chloride ions in the solution, which passivates and stabilizes the electrode behaviour. The working electrode nature can be said as m-Pb/PbCl$_2$ in these experiments.

The next challenge is to produce a compact layer of lead on a steel surface that behaves, from an electrochemical point of view, as the massive metallic lead. The most effective procedure is based on the industrial Betts process for lead purification (Betts, 1908). The electrolyte solution is based on hexafluorosilicate salts but now there are no lead anodes, so the lead contents of electrolyte must be controlled to avoid its depletion and a saturated bath is used. Lead is deposited on a flat SS circular electrode by applying a constant $10.0 \, mA/cm^2$ current density by 3 h. The cell potential observed while lead is electrolyzed should be around −500 mV. The theoretical thickness of lead reached was 100.0 μm and subjacent SS was completely coated as demonstrate the absence of early hydrogen evolution (see Fig. 3c) and the presence of the reduction peak of imazapyr.

A flat SS circular electrode was first used to establish and validate the electrolytic method but the final goal is to coat the inner surface of a catheter needle. This was done in the proper flow detector by recirculating the electrolytic solution at 1.0 mL/min and applying the current for the time required to obtain the desired thickness of lead. The geometry and arrangement of the electrodes in the flow detector make a non-homogeneous distribution of current in the working electrode. Therefore, the achieved lead thickness will not be uniform. To check whether it has reached a sufficient coating it must be tested by hydrogen evolution. A 24-h electrolysis gets the desired tubular shaped SS/e-Pb/PbCl$_2$ electrode.

3.2. Optimizing the working potential

Fig. 3 suggests that the working potential used must be −1100 mV. Nevertheless the imazapyr reduction potential at
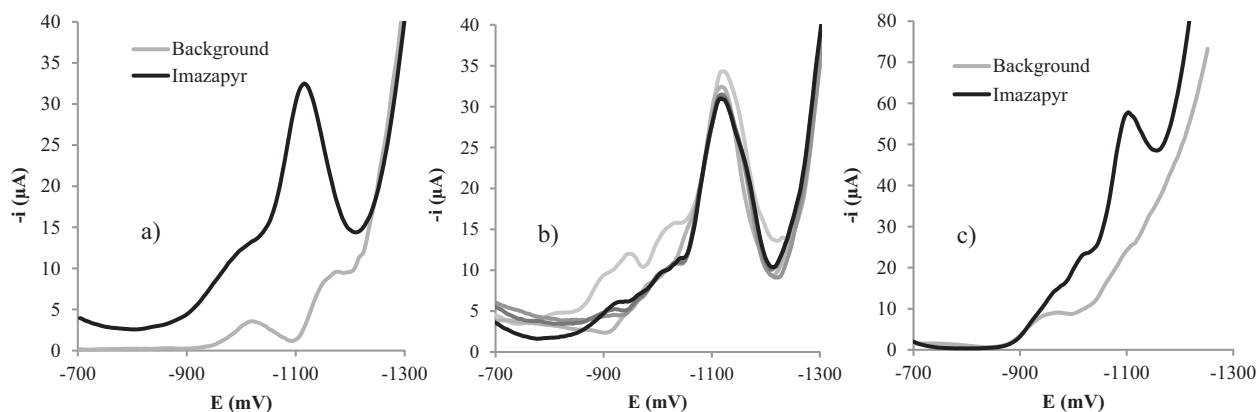
Fig. 3 Differential voltammograms of imazapyr on flat lead electrodes. (a) 1×10^{-3} M imazapyr on saline solution (pH = 0.5) over m-Pb/PbCl$_2$ electrode; (b) successive scans without manipulate the m-Pb/PbCl$_2$ electrode surface. (c) 1×10^{-3} M imazapyr on saline solution (pH = 0.5) over SS/e-Pb/PbCl$_2$ electrode.

flow-cell can drastically differ from the observed with flat electrodes in batch experiments because of the different geometry of electrodes, the different reference electrode used and/or the characteristic convective regimen of flow measurements among other reasons. So, experimental optimization of potential should be done by performing several amperometric measurements with different values of applied potential and keeping constant all the other experimental parameters such as the flow, concentration and injected volume of imazapyr samples. By plotting the maximum of UV absorbance over the applied potential it is possible to decide the optimal setting to $-410\,mV$ (see Fig. 4). More negative potentials than $-415\,mV$ cause hydrogen evolution and unstable baseline. Less negative potentials than $-380\,mV$ will not affect to the absorbance of imazapyr. Positive potentials can cause the lead oxidation and destroy the electrode. The UV absorbance response is used instead the amperometric because the first one is much more intense, thus less concentrated samples can be used.

3.3. Optimizing the working wavelength

The imazapyr present two absorption bands at the UV region, the bands at 200 nm and 240 nm can be associated to the imidazolinic and pyridinic rings respectively, being their maximum wavelengths pH dependent. When imazapyr is reduced, the 200 nm band will disappear and the 240 nm band is increased. As the reduction process affect to the 2,3-C=N double bond in the imidazoline ring (Mozo et al., 2010), it makes sense that the associated absorption band disappears. On the other hand, the 240 nm absorption band will rise because the interaction between both aromatic rings is changed during the reduction process. To check how electrolysis affects to the UV response, an electrolysis experiment was carried out in a flowing solution of imazapyr that recirculates and the solution was monitored by UV absorption every five minutes
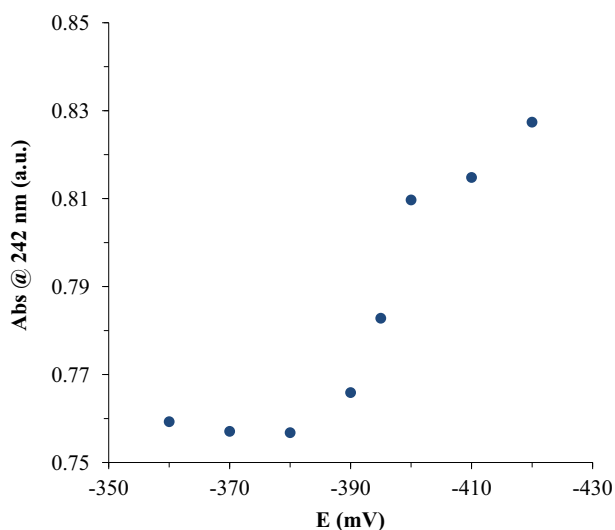
(Fig. 5). The zero of spectra was registered before applying the reduction potential. The observed behaviour is a net rising of absorption with a maximum at 242 nm and the absorbance is incremented by 0.25 absorbance units every 5 min of electrolysis. If the detector is tuned to 242 nm the best sensitivity can be obtained.
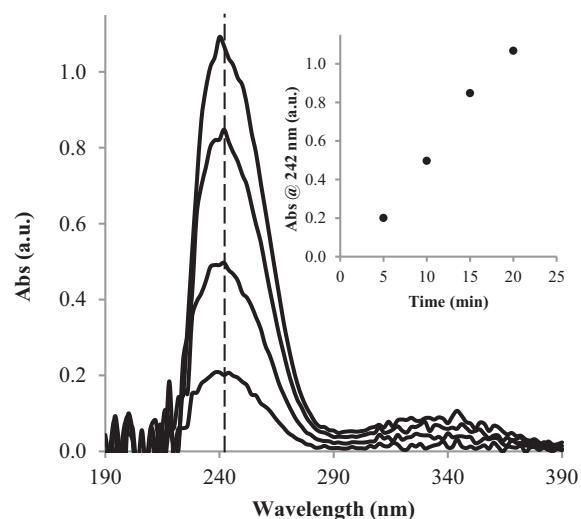
In general terms, the spectrophotometric methods are more sensitive than electrochemical ones about 10–100 fold, so an initial concentration of $2.0 \times 10^{-5}\,M$ of imazapyr must be used to avoid saturating the detector when electrolyze. Moreover, the reagent does not exhausted after the time shown in the Fig. 5 and three hours of electrolysis was required for its total consumption.

The applied potential modifies the spectroscopic properties of imazapyr because it modifies the molecule itself. This can be verified by analyzing the circular dichroism results obtained during an electrolysis procedure similar to that described above. The C4 position of imazapyr is a chiral carbon and the CD spectrum presents a small positive band at 260 nm and a six-fold greater negative band at 715 nm. When imazapyr is electroreduced the 2,3-C=N double bond will be saturated and a new chiral carbon is generated, as a consequence the CD bands will rise with the time of electrolysis similarly to what happens with the absorbance.

These results clearly indicates that the application of a bias potential to the lead electrode increases the imazapyr UV and CD absorption signals, this procedure would improve the analytical performance of a method as proposed in this paper when compared with the simple spectroscopic detection. Even more, the enhancement of spectroscopic properties of imazapyr can be regulated by controlling the time of electrolysis.

3.4. Optimizing the flow settings

Unfortunately the working conditions of continuous-flow analytical methods like FIA (Růžička and Hansen, 1988) do not allow analyte residence times at detector as long as desired.

Fig. 4   Dependence of absorbance intensity with applied bias potential. Each point represents the average value of five injections of imazapyr solutions (200 μL at 1×10^{-3} M) on saline carrier solution (pH = 0.5) flowing at 1 mL/min. Electrode: tubular shaped SS/e-Pb/PbCl$_2$ electrode.

Fig. 5   Consecutive UV spectra of imazapyr electrolysis experiment at $-410\,mV$. Initial conditions: 10 mL of 2×10^{-5} M imazapyr on saline solution (pH = 0.5); flow = 2 mL/min; time interval between spectra = 5 min.

It is necessary to adjust both flow rate and injection volume to tune the residence time and hence the conversion reached by electrolysis.

In an attempt to increase the residence time, the flow rate should be set to its lowest value. This setting affects to the analytical throughput and so a compromise must be reached. Moreover, the performance of the pumping system should also be considered, because a too slow flow in a peristaltic pump would result as the emergence of pulses in the baseline. Such type of considerations leads to selecting a 1.0 mL/min flow.

The conversion reached in an electrochemical process, besides depending on the contact time of the reactant and the electrode surface, also depends on the volume/interfacial surface relationship, the concentration, the applied potential and other factors. A way of increasing conversion is to reduce the injected volume of reactant while keeping constant the number of mols injected, so the highest proportion of that volume will be in contact with the electrode surface and also will have a greater amount of molecules undergoing reaction, decreases the volume also affects the signal produced by the detector and the limit of detection. Again a compromise solution is required which optimizes both parameters and an injection loop of 200 μL is used.

3.5. Checking the analytical performance

Once configured the FIA system and the detector, the method ability to detect imazapyr was checked and the analytical figure of merits were calculated. Therefore, a stock solution of imazapyr was prepared and dilutions with saline carrier solution at different concentrations were further injected fivefold for its determination. Fig. 6 shows the calibration curve obtained by plotting the average area under the FIA signal for five injections versus concentration of samples, the linear least square fitting has the equation Area = 4597 × [Imazapyr] (μg/mL) + 147 and a regression coefficient of 0.997. A FIAgram is also included as an insert.
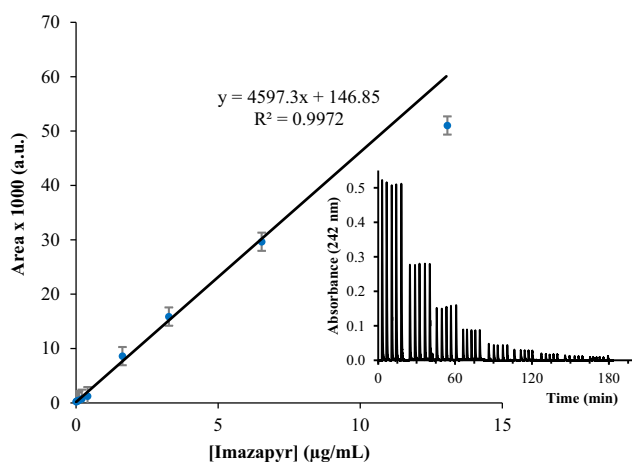
Fig. 6 Calibration curve for imazapyr FIA/SEC determination. Cell potential: −410 mV; wavelength: 242 nm; flow rate: 1 mL/min; injected volume: 200 μL; carrier solution: HCl/NaCl; ionic strength: 0.6 M; pH: 0.5. Insert: FIAgram of UV absorbance response.

A range of linear response greater than three decades is observed from 0.005 to 6.0 μg/mL, the average of relative standard deviation (RSD) in the whole range of linear response was less than 2%, and the limits of quantification (LOQ) and detection (LOD) calculated as 10σ/slope and 3σ/slope respectively were 0.02 and 0.007 μg/mL, where σ represents the standard deviation of the lowest measured concentration (Loock and Wentzell, 2012). The LOQ obtained makes the proposed analytical procedure appropriated for detecting imazapyr even below the EPA legal tolerances.

These data can be compared with those obtained from a typical spectroscopic determination by plotting the absorbance value at 242 nm versus the imazapyr concentration. The LOQ and LOD values, calculated as before, were 0.2 and 0.07 μg/mL respectively. That is, 10-fold the values obtained from the SEC detection. Also the linear range is only two decades width and covers concentrations 10-fold higher than before.

As the flow conditions were chosen somewhat arbitrarily, the calibration procedure was repeated by changing the flow rate to 0.5 mL/min (half the value previously used) and keeping all the other parameters the same values. The LOQ value now obtained increase by about 20%. Such result seems to contradict the direct relationship between the residence time and the magnitude of the obtained signal, but we must consider the definition of LOQ, which includes the statistical deviation of measures and the sensitivity of method, and therefore it is only indirectly related to the analytical signal magnitude.

If the flow is set to 1.0 mL/min, a single injection can be done in just 30 s, so the analytical throughput is 120 injections by hour. The only treatment that should be done at the sample is to acidify with concentrated HCl to pH equal to 0.5 and set its ionic strength at 0.6 M with NaCl. Furthermore, the extraction of imazapyr from soil samples with saline solutions is used by some authors (D'Ascenzo et al., 1998c; Marchese et al., 2001), so the extract can be directly analyzed by using the FIA method after the suitable conditioning. This avoids the solid-phase extraction stage before a chromatographic method to isolate the herbicide from the saline solution used and then simplify the method.

3.6. Method validation with real samples

To validate the proposed analytical method, samples of natural groundwater were analyzed in the FIA system by using the standard addition methodology. To assert that natural water is free of interfering compounds, a sample was conditioned 50:50 with fortified carrier solution and injected rendering a negligible variation of the baseline signal.

A sample was spiked with Arsenal, a commercial formulation of imazapyr, to a concentration in sample of 6.0 μg/mL. The sample was conditioned with fortified carrier solution, so the final concentration of Arsenal in cell was 3.0 μg/mL. The result obtained from standard addition method was 3.2 μg/mL. The RDS% for five injections was lower than 2.5% in the whole experiment.

To evaluate the sensitivity of determinations, a new sample was spiked to 3.5 μg/mL in cell by adding 6.0 μg/mL from Arsenal, and 1.0 μg/mL from standard solution. The analysis result was 3.6 μg/mL.

All these results were summarised in the Table 1. As can be observed, the Recovery% in both cases was close to 105%.

Table 1 Results from standard addition analysis of natural water samples.

Spiked Arsenal (µg/mL)	Spiked standard (µg/mL)	Cell concentration (µg/mL)	Detected (µg/mL)	Recovery (%)	RDS (%)
6.0	0.0	3.0	3.2 ± 0.2	107.0	2.4
6.0	1.0	3.5	3.6 ± 0.5	104.1	1.3

4. Conclusions

The results confirm that the spectro-electrochemical detection is a good strategy to analyze the imazapyr content in water samples. If the time of electrolysis is controlled, the UV absorbance measured can be enhanced to reach the desired limit of detection.

It was necessary to find the suitable electrode material and manufacture the electrode in the precise form needed by the detector. An electroplating flow method was developed to coating the inner surface of a stainless steel catheter with lead, so the tubular-shaped $SS/e\text{-}Pb/PbCl_2$ electrode was created. Then, the appropriate cell potential, the working wavelength and the flow parameters were optimized and a calibration curve was constructed. The analytical method is validated with real samples of natural water and commercial formulation of imazapyr, showing its applicability.

The method performance allows its potential use in routine analysis of imazapyr in a broad concentrations range of aqueous samples. The chemicals used are very accessible and inexpensive, and a single injection consumes only 200 µL of sample, taking 30 s each.

This work demonstrates that non-chromatographic methods such as the FIA/SEC now presented, can have analytical performance of the order of legally established requirements for reagents used in the agriculture and food industry and avoid the use of pre-processing stages to purify and concentrate. Generally, the FIA methods use more affordable equipment than the chromatographic and equally allow the automation. Also it is possible to miniaturize, making portable and compact instruments. They have less working parameters; they are more user friendly.

Acknowledgements

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2018.09.009.

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