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Multicommutation-NIR determination of Hexythiazox in pesticide formulations

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Abstract

A multicommutated flow-system was designed in order to increase analytical throughput and for controlling thermal effects on the NIR spectra for determination of Hexythiazox in pesticide formulations. An on-line standard addition was carried out showing the versatility and repeatability of multicommutation for the on-line mixing and dilution of solutions. Results obtained for commercial samples were statistically comparable with those obtained by an HPLC-reference method. Multicommutation-NIR allows the analysis of 52 samples per hour, in front of the 30 samples per hour analyzed by the NIR-batch procedure and the 7 samples per hour analyzed by HPLC-reference method.

Keywords: Multicommutation; NIR; Pesticides; Hexythiazox

1. Introduction

Hexythiazox (*trans*-5-(4-chlorophenyl)-*N*-cyclohexyl-4-methyl-2-oxothiazolidine-3-carboxamide) is a selective ovicide/miticide acaricide which is widely used in the treatment of some pests. It is applied at any stages of plant growth from budding to fruiting, inhibiting chitin synthesis in tetrachinid acari and *Phyllocnistis citrella* [1]. Spanish legislation specifies 1.00 mg kg^{-1} as a maximum tolerated limit in citrus [2]. However, there are not concluding studies about chronic and cancer dietary risk assessment in humans [3].

Methods for the determination of Hexythiazox at trace level include liquid chromatography with UV [4] or diode array detector [5], but basically with tandem mass spectrometry (MS), using electrospray ionization [6–9] or atmospheric pressure chemical ionization (APCI) [10–13]. Other techniques employed to Hexythiazox determination were voltammetry with hanging mercury electrode [14] and direct insertion probe MS [15].

These aforementioned techniques are adequate for pesticide analysis at trace levels but for routine control analysis of commercial formulations, in which the active ingredient is at the percentage level it is unnecessary the tremendous dilution involved in chromatographic procedures, also requiring an important consumption of solvents.

In the last years, vibrational techniques have been applied to the quality control of pesticides in commercial products [16] and different approaches have been proposed for FT-IR and FT-Raman spectrometric analysis. But it is noticeable that none method based on measurements in the near infrared region has been found in the literature.

Consumption of pesticides in the European Union reached 19,384 tonnes in 1999 [17] and the quality control of such volume of products requires methods as fast and automatable as possible. In this sense, a series of procedures based on the use of flow analysis (FA) FTIR have been proposed for the determination of single compounds and mixture of pesticides in commercial formulations [18–20].

Multicommutation is a flow analysis strategy widely developed in the 1990s, which combines the easiness of the adaptation of batch procedures to the flow ones with the versatility with regard to manifold real-time reconfiguration and has been coupled with different analytical techniques [21]. Multicommutation has been adapted to FTIR measurement in the mid IR for the determination of surfactants in detergent formulations [22]

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and benzene in gasolines [23], but there are no precedents on its use with NIR spectrometry.

In short, the main objective of this work is the development of a fast, simple and easily automatable method for the determination of Hexythiazox in agrochemical formulations by NIR spectrometry, showing the potential of multicommutation in the way of the enhancement of the analytical throughput and the insurance of a control over the negative effects caused by those factors affecting reproducibility of NIR measurements, as it can be temperature or the presence of suspended particles and bubbles [24].

2. Experimental

2.1. Apparatus

A Bruker MPA (Bremen, Germany) FT-NIR spectrometer, equipped with a quartz beamsplitter, an air cooled NIR source, an InGaAs detector and a 5 mm path length quartz micro flow cell was used for transmittance multicommutation-NIR measurements. Glass vials of 1 mL volume and 6.5 mm i.d. were used for batch measurements. The OPUS 4.2 software was used for controlling spectrometer and for the acquisition of data. The measurements in the continuous mode were carried out with the OPUS Chromatography utility.

Two NResearch 161K031 three-way solenoid valves (Stow, MA, USA) and a PC 486 microcomputer connected by the parallel port to a Toshiba ULN2803 chip were employed in the NIR-multicommutation procedure (see Fig. 1 for manifold details and sampling pattern).

The program which controls the multicommutation set-up by switching on/off the solenoid valves was made using Quickbasic 4.5 software.

Processing of individual spectra and transient recordings (chemigram) was carried out with Omnic 6.1 software from Nicolet (Madison, WI, USA).

A Gilson Minipuls 2 peristaltic pump (Villiers-le Bel, France) with a 1.20 $cm^3\ m^{-1}$ polyvinyl chloride Tygon tube was employed in the multicommutation set-up to aspirate the carrier, standard and sample solutions. Flow lines were made of PTFE tubing of 0.8 mm internal diameter.

A Vibromatic shaker and an Ultrasons water bath from J.P. Selecta (Barcelona, Spain) were used for mechanical and ultrasound assisted extraction assays.

A Dionex P680 High Performance Liquid Chromatograph (Sunny Vale, CA, USA), equipped with a C-18 reverse phase

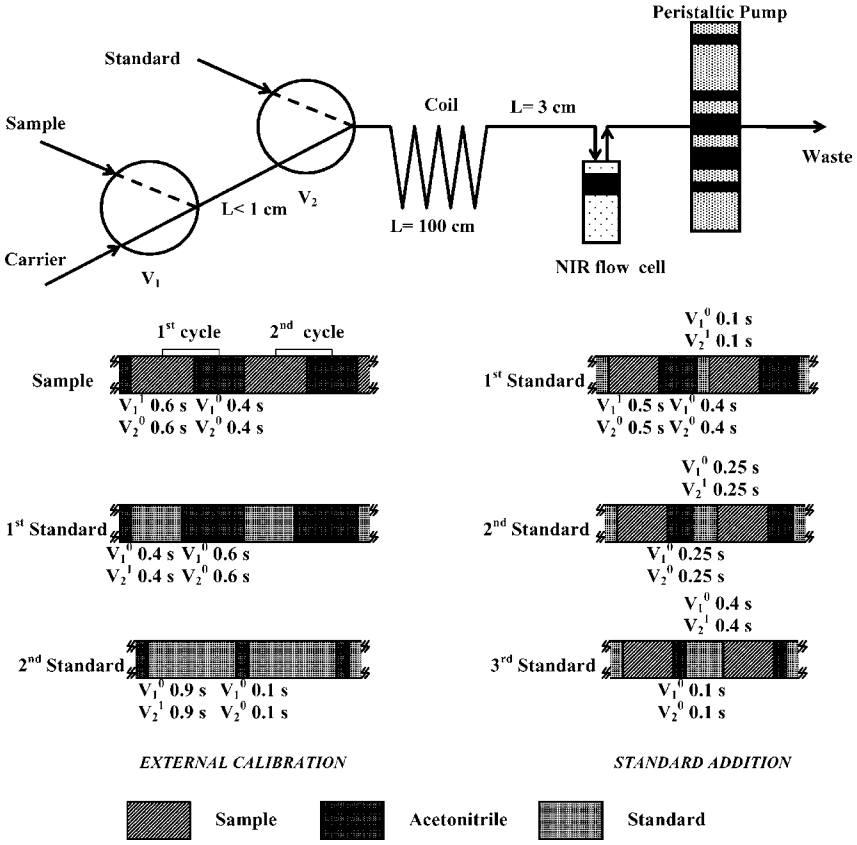

Fig. 1. Manifold employed for the determination of Hexythiazox by multicommutation-NIR spectrometry and the sampling pattern used for external and standard addition calibrations. *Note*: V_1 and V_2 are three-way solenoid valves. Peristaltic pump aspirates sample or standard solutions and acetonitrile carrier with a 1 mL min^{-1} flow-rate. The reaction coil was made with PTFE tubing of 0.8 mm internal diameter. Standard corresponds to a 7.93 mg mL^{-1} solution of Hexythiazox in acetonitrile. Sample is the extract obtained from a 1:10 (w/w) mixture of wettable powder sample and acetonitrile. Different solutions pass through valves by switching on (bit 1)/off (bit 0) them. Sampling pattern is exemplified for external calibration and standard addition, showing the first two cycles of aspiration for each replicate. V_i^j indicate the i valve in the j position ($j = 1$ switched on, $j = 0$ switched off).

(Kromasil) column (250 mm × 4.6 mm i.d. and 5 mm particle diameter) and an UVD 170U variable wavelength UV–vis detector, was employed in the HPLC method used as reference for determining Hexythiazox in agrochemical formulations.

2.2. Reagents and samples

Hexythiazox Pestanal® grade 99.9%, supplied from Riedel-de Häen was used to prepare standard solutions in the 3.5–18.7 mg mL^{-1} range.

Acetonitrile HPLC, gradient grade, from Scharlau (Barcelona, Spain) was employed as a solvent to prepare standard and sample solutions.

Wettable powder commercial formulations of pesticides containing Hexythiazox were obtained from Spanish market. Representative portions from laboratory samples were taken and stored in glass containers after their homogenization by mechanical shaking.

2.3. Reference procedure

A HPLC-UV procedure has been developed in our laboratory and used as a reference method for Hexythiazox determination in pesticide formulations.

0.1 g (±0.0001) of the wettable powder sample were accurately weighed inside a 10 mL glass vial and diluted with 1 g of acetonitrile. After a short mechanical shaking for ensuring the total extraction of the analyte from the solid matrix, the liquid was filtered. Thirty milligrams of the filtered sample solution were weighed in a glass vial and diluted with 8 g of acetonitrile. Twenty microlitres of this solution were injected in a 90:10 (v/v) acetonitrile/water mobile phase, after filtration through a 0.22 μm nylon filter, working in the isocratic mode and with 1 mL min^{-1} carrier flow rate. Hexythiazox was determined from peak area measurements at a retention time of 6.75 min from the chromatogram obtained at 210 nm. Data from samples were interpolated in an external calibration curve obtained from five acetonitrile standard solutions of Hexythiazox (ranging from 13.16 to 55.89 μg mL^{-1}) measured in the same conditions than samples.

2.4. NIR-batch procedure

0.1 g (±0.0001) of wettable powder samples were accurately weighed inside a 10 mL glass vial and diluted with 1 g of acetonitrile. After a short mechanical shaking, the liquid was filtered and placed inside a hermetically-capped glass vial of 1 mL internal volume and 6.5 mm i.d. The vial was introduced in a thermostatized sample holder at 30 °C and the NIR spectra between 12,000 and 4000 cm^{-1} were acquired after 2 min for reaching thermal equilibrium with the measured sample compartment, with a nominal resolution of 8 cm^{-1} and 15 accumulated scans per spectrum. The background single beam from the acetonitrile was obtained in the same conditions. For Hexythiazox measurement, it was selected the peak area values between 4948.6 and 4767.3 cm^{-1} corrected with a one-point horizontal baseline established at 4765 cm^{-1}. Hexythiazox concentration was obtained by interpolating peak area values of samples in a calibration line established from standard solutions ranged between 4.65 and 22.43 mg mL^{-1} measured in the same experimental conditions.

2.5. Multicommutation-NIR and recommended procedure

Fig. 1 shows the manifold employed in the multicommutation-NIR procedure and the sampling pattern for sample and standard solutions. Valve V_1 allows the aspiration of acetonitrile (carrier) when it is switched off (bit 0) or the aspiration of the sample solution when it is switched on (bit 1). Valve V_2 introduces the standard solution (bit 1, switched on) or those, which come from valve V1 (carrier or sample when V_2 is switched off). Switching on/off both valves with different sampling times provides the on-line mixing of all three solutions in variable ratios, allowing to get external calibration or standard addition with an unique standard solution and in the dilution range needed for each sample. The carrier solution flow rate was fixed at 1.00 mL min^{-1} taking into consideration that the 161K031 solenoid valve support ca. 30 psi. The programmed time for sampling pattern is indicated in Fig. 1 by V_i^j notation, being i the identification of valve and j that of its position, being valves identified as $j = 0$ and 1 for valve switched off and on, respectively.

Two strategies were suitable for multicommutation determination of Hexythiazox: external calibration and standard addition. For external calibration, each sample was aspirated by V_1 during 0.6 s and followed by 0.4 s of acetonitrile, repeating the sequence to 30 cycles, and each standard peak was obtained aspirating n s of the standard stock solution of 7.93 mg mL^{-1} through V_2 and $(1 - n)$ s of acetonitrile through V_1. n was varied from 0.4 to 0.9 to provide a calibration line in the 3.17–7.13 mg mL^{-1} concentration range.

3. Results and discussion

3.1. NIR spectra of Hexythiazox

Fig. 2 shows the typical NIR spectrum of a standard of Hexythiazox in acetonitrile and the spectrum of the acetonitrile extract of a commercial sample containing 10% (w/w) of Hexythiazox, using acetonitrile as a blank, obtained in the conditions specified in the NIR-batch developed procedure. As can be seen, Hexythiazox has a well-defined peak at 4859 cm^{-1}. It corresponds to the amide I and amide II bands [25]. The low solvent background between 5000 and 4500 cm^{-1} allows using this band for the determination of Hexythiazox in samples. On the other hand, the band at 4664 cm^{-1} is unsuitable for quantitative purposes because of the strong solvent absorbance between 4500 and 4250 cm^{-1}. No other useful bands appear in the NIR spectra between 12,000 and 4000 cm^{-1} using a standard solution of Hexythiazox in acetonitrile.

It was evaluated the use of different measurement conditions including peak area or peak height with different baseline corrections in order to obtain an adequate sensitivity, precision and

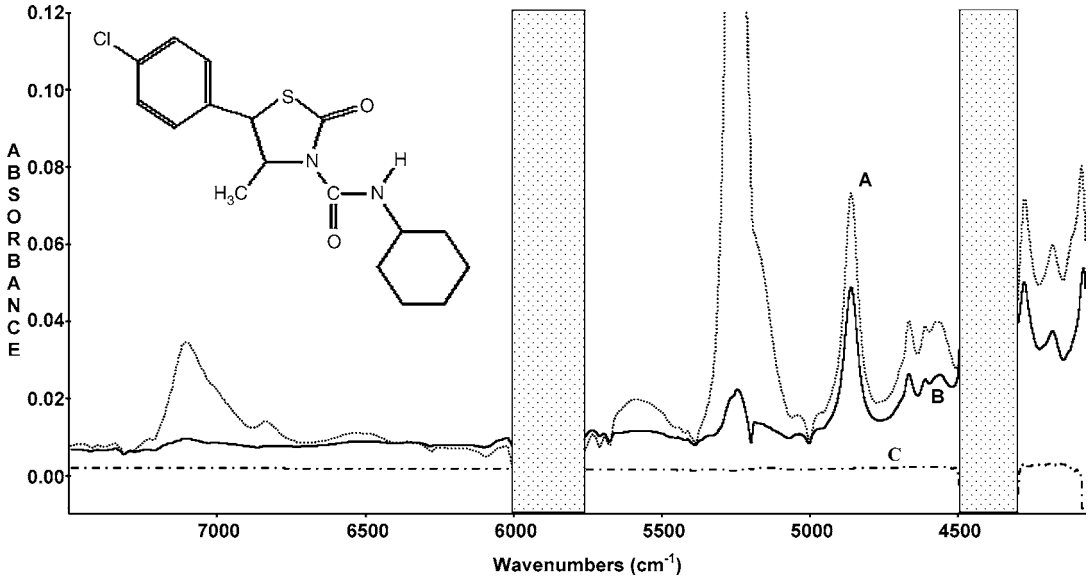

Fig. 2. NIR spectra of the acetonitrile extract (A) of a wettable powder sample, a standard (B) containing 6.8 mg mL^{-1} of Hexythiazox in acetonitrile and (C) acetonitrile blank. Hidden spectral regions are due to the high solvent background. *Inset*: Structural formula of Hexythiazox. Instrumental conditions: 8 cm^{-1} nominal resolution and 15 accumulated scans per spectrum.

accuracy. The peak area between 4948.6 and 4767.3 cm^{-1} corrected with a one-point baseline established at 4765 cm^{-1} was selected as measurement criterion for subsequent studies.

3.2. NIR-batch measurement conditions

A series of studies was carried out in order to select the experimental and instrumental conditions for NIR-batch measurements. Samples, standards and acetonitrile blank were put inside cylindrical glass vials of 6.5 mm i.d. and hermetically capped. As temperature has a great influence on the NIR spectra of Hexythiazox, it was necessary to wait for thermal equilibrium within filled glass vial and the thermostatically spectrometer vial holder before spectra acquisition. The temperature fixed for batch measurements was 30 °C, due to the difficulties to control external temperature, which was over 22 °C and sometimes over 25 °C. Two minutes were enough for reaching equilibrium. Vials were rotated before each measurement to consider the heterogeneity in the width of the glass vial walls, in order to minimize intravial and intervial variability of data, due to the variable optical path through those.

A nominal resolution of 8 cm^{-1} and 15 accumulated scans per spectrum were selected for spectra acquisition in the batch mode, also using a scanner velocity of 10 Hz, a zero filling factor of 2 and a Blackman–Harris 3-term apodization function for the spectra. These conditions of resolution and scan number (results not shown) were a good compromise between signal-to-noise ratio, sensitivity and acquisition time.

3.3. Hexythiazox extraction conditions

Preliminary studies on the effect of sample and solvent mass demonstrated that quantitative extraction of Hexythiazox from a sample containing 10.5%, w/w, was reached for 1.0 g of acetonitrile and 0.1 g of the wettable powder (WP) sample. Additional studies were carried out in order to evaluate the effect of additional ultrasonic or mechanical shaking time in Hexythiazox extraction from a mixture of acetonitrile and WP sample in the aforementioned quantities. From these experiences, it can conclude that it is obtained a total extraction of Hexythiazox from pesticide samples without requiring additional shaking. So, in subsequent studies, extraction was carried out by a slightly manual shaking, for ensuring a correct mixing between solid and liquid phases.

3.4. Analytical features for NIR-batch procedure

Table 1 summarizes the main features of the NIR-batch determination of Hexythiazox, by using external calibration and standard addition, and by the reference HPLC method. The content of Hexythiazox obtained by the three methods was statistically comparable for a probability level of 95% and with a precision level suitable for quality control exigencies. A calculated $t = 1.50$ was obtained for the comparison of NIR-batch external calibration data and HPLC mean results,

Table 1
Comparison of results obtained for Hexythiazox determination by both NIR-batch procedures and by HPLC-reference method

Method	% Hexythiazox (w/w) ± s[a]	Calibration line slope ± s[b]
HPLC-reference	10.6 ± 0.1	
NIR-batch external calibration	10.47 ± 0.03	0.294 ± 0.003
NIR-batch standard addition	10.6 ± 0.3	0.301 ± 0.006

[a] Standard deviation for three independent analysis.
[b] Standard deviation of calibration slope.

which is lower than the theoretical $t_{(95\%,\,7)} = 2.365$. On the other hand, the Cochran test indicates that NIR-batch standard addition and HPLC results were comparable ($t_{calculated} = 0.31$, $t_{(95\%,\,16)} = 2.120$. The absence of matrix effects was proved by comparing the slope of standard addition and external calibration curves.

Results from recovery studies were in the $102.3 \pm 0.9\%$ range for the determination of Hexythiazox at three spiked levels (4.2, 8.3 and 12.4 mg) to a sample extract containing 11.15 mg mL^{-1} of the analyte, showing once again the accuracy of the developed method and the lack of systematic errors.

3.5. Selection of the multicommutation-NIR parameters

In order to increase the sampling throughput and to provide a way for the automatization of the measurement step using FT-NIR spectroscopy it was evaluated the use of multicommutation with NIR. The set-up described in the Section 2 was employed and the on-line spectra recording was made using the OPUS-Chrom application.

It was studied the effect of accumulated scans and the flow rate on the width and height of the transient peaks obtained by measuring, as a function of the time, area between 4948.6 and 4767.3 cm^{-1}, corrected with a baseline established at 4765 cm^{-1}, for the 30 s injection of sample solution in the continuous mode, using acetonitrile as a carrier. It is reasonable to use a reduced number of accumulated scans as the flow rate increases, for the maintenance of a good signal-to-time resolution. So, each flow rate value required a fixed number of accumulated scans. Fig. 3 shows the effect of the pair flow-rate/accumulated scans on the aforementioned chemigram peaks features. As can be seen, four accumulated scans provides the highest peak height and repeatability with a medium peak width. It must be noticed that for 2 accumulated scans it was used a flow of 1.56 mL min^{-1}, for 3 scans 1.26 mL min^{-1}, for 4 scans 1.00 mL min^{-1} and for 5 scans 0.73 mL min^{-1}.

So, four accumulated scans and a flow rate of 1.00 mL min^{-1} was selected as a fixed condition for subsequent studies.

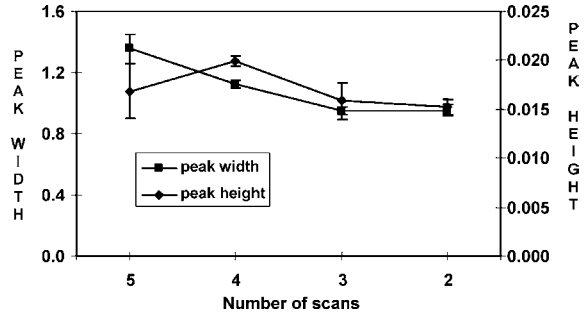

Fig. 3. Effect of the number of accumulated scans on the transient peak height and width of Hexythiazox NIR signals, for 30 cycles of aspiration per each replicate (0.5 s for the sample solution containing 7.5 mg mL^{-1} of Hexythiazox, and 0.5 s for carrier), with a coil length of 100 cm and a nominal resolution of 8 cm^{-1}. All the values correspond to the average ± standard deviation of three replicates, and the chemigram was obtained from the area between 4948.6 and 4767.3 cm^{-1} corrected with a baseline established at 4765 cm^{-1}.

The perfect mixing of sample and standard solutions with carrier for carrying out external calibration, on-line sample dilution or standard addition, depends on the coil length and the number of insertion cycles. In this sense, a study of the effect of coil lengths from 50 to 200 cm was studied. Results obtained evidenced that a 100 cm length coil provides excellent repeatability and reduced peak width. In order to reach the steady state for the mixing phenomena, different number of cycles of 0.5 s from a sample containing 7.5 mg mL^{-1} Hexythiazox and 0.5 s of carrier (dilution 1:1) were passed through a 100 cm coil. Working in these conditions 30 s were enough for reaching the steady state (see Fig. 4A). Finally, it was studied the effect of time between successive samplings on the chemigram features. Sensitivity was constant for a time over 45 s between successive replicates of 30 cycles each one (0.5 s of sample and 0.5 s of carrier), which is the minimum time required to return the chemigram baseline to zero (results not shown). So, a coil of 100 cm length, 30 cycles of sampling and 45 s between replicates were selected as fixed conditions for the multicommutation-NIR determination of Hexythiazox.

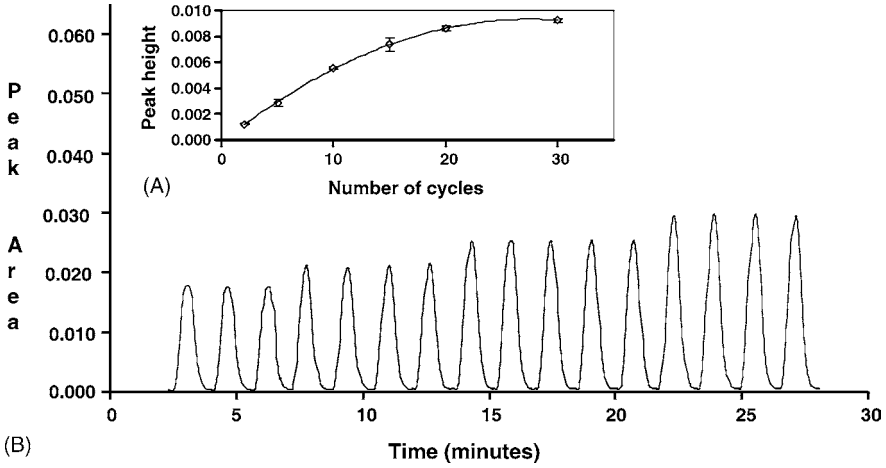

Fig. 4. (A) Effect of the number of aspiration cycles per replicate on the NIR signals found for Hexythiazox and (B) standard addition recordings found by multicommutation-NIR for Hexythiazox determination (see Fig. 1 for sampling pattern used). Experimental conditions: 4 accumulated scans, 8 cm^{-1} nominal resolution, 100 cm coil length, 1 mL min^{-1} flow-rate, aspiration cycle of 0.5 s sample and 0.5 s acetonitrile (for (B), 30 aspiration cycles and 45 s between replicates).

3.6. Multicommutation-NIR analysis of samples and on-line standard addition

The main trouble found in the NIR-batch method, developed for Hexythiazox determination, was the critical influence of temperature on the measurements. Changes in room temperature were inevitable during the development of this work, as a consequence of the spatial distribution of instruments used. So, repeatability data between days was really poor. For this reason, the multicommutation-NIR determination could improve the control over the background baseline and provide a high analytical throughput based on the use of a reduced number of standards. Data found using three replicates of two different standards, one with a concentration over the expected value for samples and the other one under the sample theoretical concentrations, sample content by interpolating sample peak height value between those obtained for the two different concentration level (3.17 and 7.13 mg mL^{-1}) peaks of standard. This strategy is suitable for quality control, where it is required a high sample measurement throughput.

Two samples were analyzed and results were calculated in the aforementioned conditions, obtaining a content of Hexythiazox of 10.7 ± 0.4 and 11.6 ± 0.1% (w/w), respectively. These values are in good agreement with those obtained by the HPLC-reference method, which were 10.5 ± 0.2 and 11.2 ± 0.3% (w/w) respectively and were statistically comparable at the 95% probability level ($t_{(95\%,\,4)} = 2.776$, $t_{calculated} = 1.11$ and 1.78 for samples 1 and 2, respectively). The variation coefficients for each sample analyzed by multicommutation-NIR were 4.2 and 1.0%, respectively, which are adequate for quality control purposes.

On the other hand, multicommutation has the advantage of preparing on-line dilutions with high precision. So, it is possible to carry out standard addition in the same way than external calibration, by aspirating sample, standard and carrier in different ratios, for constant sample aspiration and total aspiration times. The use of the standard addition method could minimize the temperature effects on the NIR measurements, in spite of the absence of a matrix as indicated in Section 3.4. Fig. 4B shows the typical transient peaks obtained for Hexythiazox analysis by on-line standard addition, that corresponds to a calibration line of Signal = 0.01782 + 0.00358*C*, *C* being the Hexythiazox concentration added in mg mL^{-1}, with an $r^2 = 0.998$. Results obtained using standard addition were statistically comparable with those obtained by the HPLC-reference method, as can be seen in Table 2. Standard addition and HPLC Hexythiazox values obtained for sample 3 were statistically comparable based on the use of the Cochran test ($t_{calculated} = 0.89$, $t_{(95\%,\,20)} = 2.086$).

Table 2
Comparison of results obtained for Hexythiazox determination by both multicommutation approaches and by HPLC-reference method

Method	% Hexythiazox (w/w) ± s[a]	Calibration line slope ± s[b]
HPLC-reference	10.5 ± 0.2	
NIR-multicommutation external calibration	10.7 ± 0.4	0.00362 ± 0.00003
NIR-multicommutation standard addition	10.6 ± 0.5	0.00358 ± 0.00004

[a] Standard deviation for three independent analysis.
[b] Standard deviation of calibration slope.

Table 3
Summary of the main analytical features of the NIR developed methods and HPLC-reference method used

Parameter	NIR-batch external calibration	NIR-multicommutation external calibration	HPLC-reference
LOD[a]	0.2 mg mL^{-1}	0.1 mg mL^{-1}	0.14 μg mL^{-1}
% R.S.D.[b]	0.2	0.8	0.05
Throughput (h^{-1})	30	52	7
Waste[c] (mL)	100	100	800

[a] LOD: limit of detection for $k = 3$, in mg mL^{-1} for both NIR methods and for in μg mL^{-1} HPLC-reference method.
[b] % R.S.D.: relative standard deviation of a standard solution for $n = 3$.
[c] Waste is calculated for 100 analysis and only for the measurement process.

Main features of NIR developed method compared with the HPLC reference method are summarized in Table 3. As can be seen, waste generation is reduced using both NIR methods, and the analytical throughput is increased in NIR methods in front of the HPLC-reference procedure.

4. Conclusion

NIR spectrometry offers a good alternative for pesticide analysis in commercial formulations in front of the use of HPLC methods, which are highly sensitive for residue analysis but involve high dilutions and low time-efficiency, which are unjustified for the concentration levels of samples. In the scope of quality control, multicommutation offers a fast and robust methodology for Hexythiazox determination in pesticide formulations providing the real-time control of the measurement process.

For the quantification of Hexythiazox by multicommutation-NIR, it was selected a calibration concentration range between 3.17 and 7.13 mg mL^{-1}, which correspond to the analysis of samples containing from 6 to 15%, w/w, being obtained a limit of detection of 0.1 mg mL^{-1} for a sample mass of 0.1 g.

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