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FTIR Approaches for Diuron Determination in Commercial Pesticide Formulations

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Two strategies have been developed for Diuron determination by FTIR spectrometry, an off-line extraction and stopped-flow determination and a fully mechanized procedure, based on the on-line extraction of Diuron and FIA−FTIR measurement of the extracts. The aforementioned procedures have been compared with a reference chromatographic method. The off-line FTIR spectra were obtained at a nominal resolution of 4 cm^{-1} from 4000 to 900 cm^{-1} by accumulating 25 scans. Diuron was determined using peak height measurements at 1582 cm^{-1} corrected using a baseline defined between 1562 and 1614 cm^{-1}. The waste generation of the off-line procedure was 3.4 mL chloroform for each sample, and the method provided a LOD of 40 $\mu g\ g^{-1}$, corresponding to 0.8% (w/w) Diuron in the original sample. The fully mechanized FIA method provided a LOD of 35 $\mu g\ g^{-1}$, which corresponds to 0.7% (w/w) in the solid sample and a maximum sampling frequency of the whole procedure of 30 h^{-1}, with a waste generation of 9.3 mL per sample, taking into account the volume of $CHCl_3$ required for sample dissolution and that need as a carrier. All those methods consume less organic solvent than a HPLC method, which involves the use of 39 mL of acetonitrile per sample and a sampling frequency of 12 h^{-1}.

KEYWORDS: Diuron; FTIR determination; flow injection analysis; stopped-flow; pesticide formulations

1. INTRODUCTION

Diuron (3(3,4-dichlorophenyl)-1,1-dimethylurea) is a substituted urea herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds, as well as mosses. It is used on noncrop areas and many agricultural crops such as fruit, cotton, sugar cane, alfalfa, and wheat. Diuron works by inhibiting photosynthesis. Diuron is slightly toxic for mammalians, the oral LD_{50} in rats being 3400 mg/kg (*1*).

Diuron may be found in formulations as wettable powders (80% w/w) (*2*) and suspension concentrates (50% w/v) (*3*).

Diuron determination can be carried out in different types of samples by high performance liquid chromatography (HPLC) (*4*−*7*), capillary electrophoresis (*8*, *9*), gas chromatography with electron capture (*10*, *11*), or mass spectrometry detection (*12*, *13*).

FTIR spectrometry has been employed for the quantification of different active principles in commercially available pesticide formulations, such as carbaryl (*14*), buprofezin (*15*), fluometuron (*16*), folpet and metalaxyl (*17*), and chlorpyriphos-ethyl (*18*), showing the high suitability of FTIR to carry out this kind of analysis. However, to our knowledge, there is no precedent on the determination of Diuron by using FTIR spectrometry.

One of the main drawbacks of the FTIR spectrometry is the general use of chlorinated solvents because of their high toxicity and environmental damage. Despite this, there is a widespread use of this type of solvent because of their high transparency in the mid-IR range and the high solubility of a great number of pesticides in them. However, to develop low contaminant procedures, the chlorinated waste generation and the reagent consumption must be minimized.

The aim of this work was the development of fast and low waste generation procedures that may be able to carry out in a simple way the precise and accurate determination of Diuron (*19*) in commercial formulations without any previous clean up or chromatographic steps, suitable to be employed in both the manufacturing process and in the quality control of finished products. In this sense, we propose a direct extraction of Diuron from agrochemicals using a reduced volume of chloroform and, after off-line filtration, its transport and introduction in a microflow cell and FTIR measurement in the stopped-flow mode. Alternatively, to reduce the sample manipulation and the operator exposition with the pesticide and chlorinated solvent, a mechanized approach, based on sample extraction in a vial followed by on-line filtration and continuous flow measurement, is also proposed to improve green analytical chemistry.

2. EXPERIMENTAL PROCEDURES

2.1. Apparatus and Reagents. A Nicolet (Madison, WI) Magna 750 FTIR spectrometer, equipped with a temperature-stabilized deuterated tryglycine sulfate (DTGS) detector, was employed for spectral

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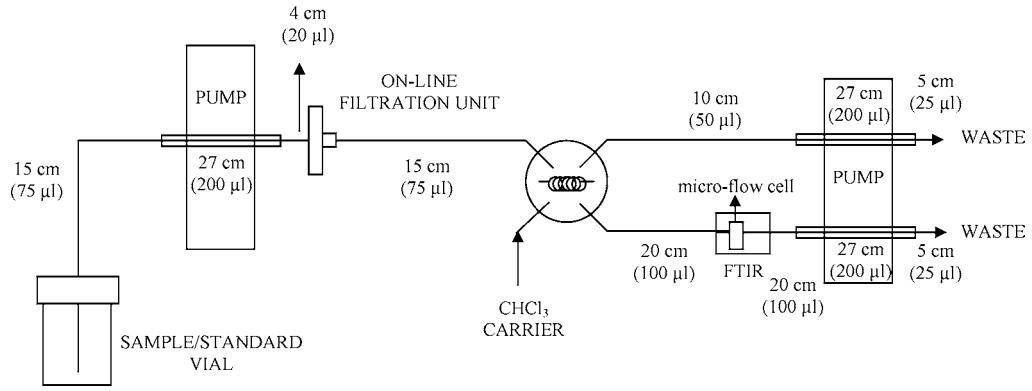

Figure 1. Manifold employed for the FIA–FTIR determination of Diuron in commercial pesticide formulations. Lengths of connections and an estimation of the internal volumes (values between parentheses) are indicated.

measurements, using a Specac (Orpington, UK) 10450 series micro-flow cell, with a ZnSe and CaF_2 window and a path length of 0.11 mm, that provides an internal volume of 5.5 μL. Spectra treatment and data manipulation have been carried out using Omnic 2.1 and QuantIR 1.2 software from Nicolet (Madison, WI).

To carry out the on-line extraction and FIA−FTIR determination of Diuron, the manifold depicted in **Figure 1** was made by employing a six-way Rheodyne 5041 injection valve (Cotati, CA) and two Gilson Minipuls peristaltic pumps (Villiers-le-Bel, France) furnished with Viton (iso-versinic) tubes (1 mm i.d. and 3 mm o.d.) placed before the filtration unit and after the measurement cell, to perform the Diuron extraction with $CHCl_3$ and sample transport and the carrier aspiration through the system while avoiding bubble formation. The connecting tubes employed in the setup were made of PTFE with a 0.8 mm i.d., and their lengths were adjusted to reduce the internal volume of the manifold. The filtration unit was made with a polypropylene 13 mm diameter syringe filter with a porous size of 0.45 μm. The six-way valve was used to select sample and standard injections and to insert a selected volume in the carrier stream.

A Hewlett-Packard HPLC Series 1050 high performance liquid chromatograph, equipped with a Kromasil C-18 column of 250 mm length and 4.6 mm i.d. with a 5 μm particle diameter was used. A variable wavelength UV−vis detector was employed for the analysis of Diuron formulations, this methodology being used as a reference procedure for the validation of FTIR measurements.

A Hewlett-Packard 8452 diode array spectrophotometer was employed for the measurements of UV spectra of Diuron standards.

The Diuron standard (99.4% w/w) was supplied by Fluka (Buchs, Switzerland). Analytical grade chloroform, stabilized with 150 mg L^{-1} amylene, was supplied by Scharlau (Barcelona, Spain) and employed for the preparation of samples and standards.

Wetting powder samples 1−3 were obtained directly from the Spanish market, containing approximately 80% w/w Diuron. Sample 4 was prepared from sample 1 by the addition of $CaCO_3$ with a final concentration of 40% Diuron. Sample 5, with a final content of 20% Diuron, was made from sample 2 by adding $CaCO_3$ and propylene glycol monooleate.

2.2. Reference HPLC Procedure. A total of 10 mg of sample was accurately weighed inside a 25 mL volumetric flask and diluted to the volume with CH_3CN. One milliliter of the slurry was diluted to 10 mL with CH_3CN and filtered through a 0.22 μm nylon filter. Twenty microliters of this solution was directly injected in a 85:15 acetonitrile/water mobile phase of 1 mL min^{-1}, and Diuron was determined in the isocratic mode by absorbance measurements at 254 nm. Area values of the chromatographic peaks obtained at 3.3 min for samples were interpolated in an external calibration established from five standard solutions of Diuron containing between 10.9 and 43.7 mg L^{-1}.

2.3. FTIR Off-Line Procedure. An accurate mass of sample (from 15 to 60 mg as a function of the Diuron content) was dispersed in 5 g of $CHCl_3$ by manual shaking. After homogenization, this slurry was off-line filtered, and afterward, the solution was introduced into the measurement cell by using a peristaltic pump. Then, the flow was stopped, and the FTIR spectra were recorded from 4000 to 900 cm^{-1}, using a nominal resolution of 4 cm^{-1}, accumulating 25 scans and employing a background spectrum of the cell filled with $CHCl_3$ measured in the same instrumental conditions.

A set of five Diuron chloroformic external standards, with concentrations from 1.3 to 4.5 mg g^{-1}, were prepared, and their FTIR spectra were obtained in the same conditions as those of the samples. Peak height absorbance values at 1582 cm^{-1} corrected using a linear baseline defined between 1562 and 1614 cm^{-1} were used for quantification purposes.

2.4. Flow Injection FTIR Procedure. A total of 15−60 mg of sample was weighed in a 10 mL vial, and 4 g of chloroform was added. The sample vial was installed in the manifold depicted in **Figure 1** on which the slurry was shaken and aspirated through an on-line connected 0.45 μm polypropylene filter. After that, 500 μL of the extract was sampled by using the sample loop of the injection valve and then injected in a chloroform carrier stream of 2.96 mL min^{-1}. The FTIR spectra, between 4000 and 900 cm^{-1}, were continuously recorded as a function of time, using a nominal resolution of 4 cm^{-1} and accumulating two scans per spectrum. Analytical measurements for Diuron were carried out from a representation of the peak height measurements at 1582 cm^{-1}, corrected with a linear baseline defined between 1562 and 1614 cm^{-1}, as a function of time (chemigram). The peak height values obtained for sample chemigrams were interpolated in an external calibration line established from the injection of five standard solutions containing between 0.7 and 4.7 mg g^{-1} Diuron, prepared in chloroform and measured in the same conditions as the samples.

3. RESULTS AND DISCUSSION

3.1. HPLC−UV Diuron Determination. Figure 2 shows the chromatograms of two Diuron standards containing 10.9 and 32.8 mg L^{-1} and that of a sample extract with a Diuron concentration of 20.5 mg L^{-1}. In this **Figure 2**, the UV spectrum of Diuron in CH_3CN in the wavelength region from 190 to 350 nm is also shown, in which case the presence of an intense band at 254 nm can be observed, which is extremely useful for Diuron monitoring. As can be seen in **Figure 2**, a sample diluted in CH_3CN and filtered provides the same chromatogram than the standards of pure Diuron.

The calibration line established in terms of area values of the chromatographic peaks obtained at a retention time of 3.3 min was $A = (8 \pm 6) + (70.4 \pm 0.2)C$ (mg L^{-1}), with a coefficient of determination $r^2 = 0.9999$. The limit of detection achieved, established from 3 times the standard deviation of the area values obtained for five independent injections of a standard containing 10.9 mg L^{-1} Diuron divided by the calibration slope, was 27 ng mL^{-1} that corresponds to 0.0013% w/w Diuron in the original sample. The sample injection frequency achieved using this procedure was 12 h^{-1}. For the validation of this method, we carried out recovery studies of

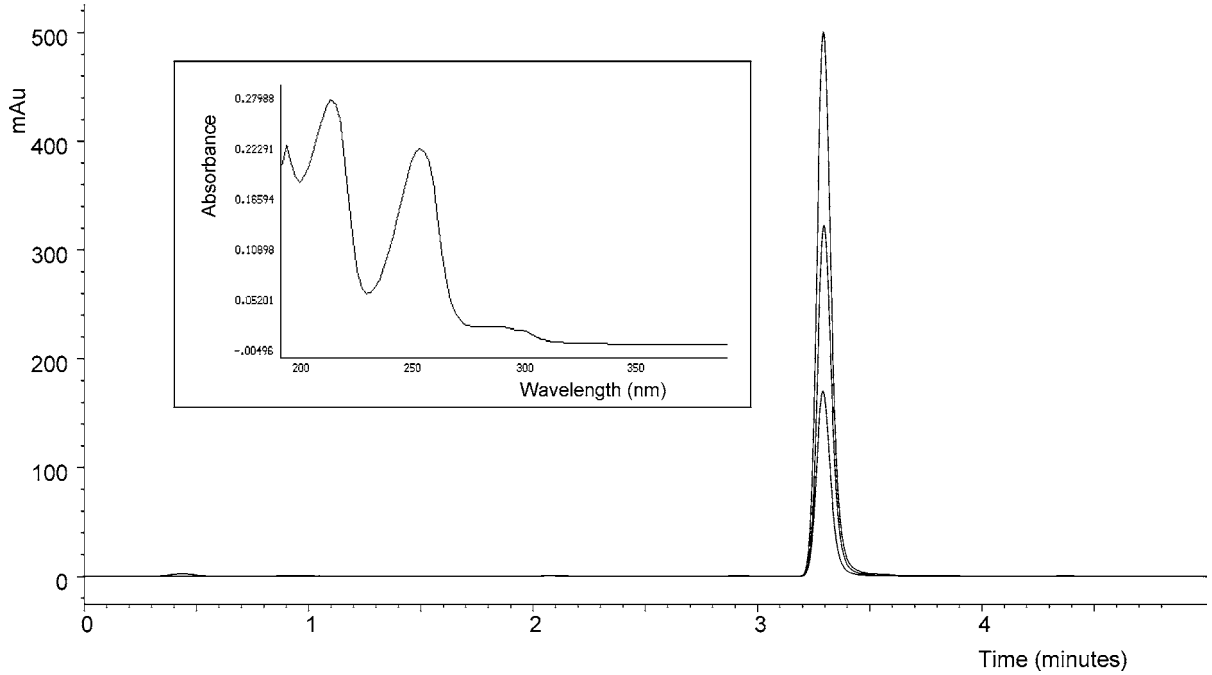

Figure 2. HPLC–UV chromatograms of two Diuron standards and a commercial sample extract with concentrations of 10.9, 32.8, and 20.5 mg L^{-1}, respectively. Inset: UV spectrum of a Diuron standard solution of 5.3 mg L^{-1} in CH_3CN obtained between 190 and 400 nm.

spiked pesticide samples and the analysis of synthetic samples (results not shown).

3.2. FTIR Absorbance Spectrum of Diuron. Figure 3 shows the spectra, in the wavenumber range of 1850−975 cm^{-1}, of a Diuron standard chloroformic solution of 2.7 mg g^{-1} and five insecticide sample extracts. As can be seen in **Figure 3**, the spectrum of every sample and that of the standard is very similar, and the same bands are present, thus indicating that practically only Diuron was extracted from the samples when $CHCl_3$ was used. The most intense bands were the carbonyl peak at 1672 cm^{-1} and the benzene ring stretching at 1514, 1477, and 1392 cm^{-1}. Other less important absorption bands are located at 1582 cm^{-1}, due to the C═C stretching in chloroalkenes, and 1297 and 1175 cm^{-1}, corresponding to amide and benzene ring breathing, respectively (*20*).

3.3. Selection of FTIR Bands for Diuron Determination. The object of this study was to find the measurement conditions that provide the best sensitivity and repeatability for Diuron determination. **Table 1** shows the figures of merit of different external calibration lines obtained from the main Diuron bands in the spectral region of 2000−1250 cm^{-1} and using different baseline and measurement criteria.

The limits of detection achieved, established from the standard deviation of six measurements of a blank solution divided by the calibration slope, varied from 10 to 86 $\mu g\ g^{-1}$, corresponding to 0.2 and 1.7% w/w Diuron in the original sample, respectively, for a sample mass of 15 mg, being adequate for the determination of this active principle in commercially available formulations.

Peak area values were in general 1 order of magnitude more sensitive than peak height ones. However, the band at 1582 cm^{-1} was selected because it does not overlap with any excipient band such as propylene glycol monooleate (see **Figure 4**) and because of the higher selectivity of this band in front of the carbonyl band at 1672 cm^{-1}. As can be seen in **Table 1**, the selected band peak height values provided have a lower LOD than the area ones. So, this measurement mode was selected and corrected with a baseline established from 1614 to 1562 cm^{-1} to avoid the effect of the presence of water in the formulations, which can interfere with the Diuron determination.

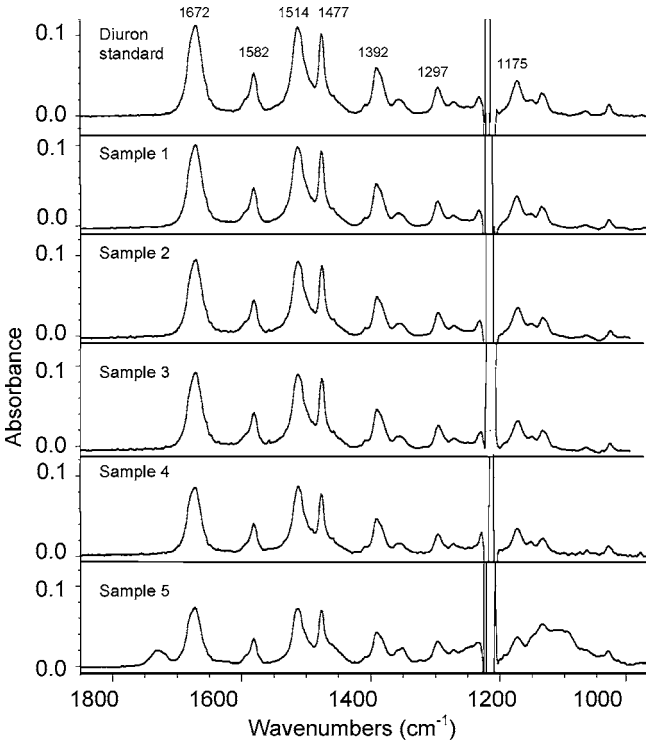

Figure 3. FTIR spectra of $CHCl_3$ solutions of a Diuron standard of 2.7 mg g^{-1} and three commercial pesticide formulations and two laboratory samples. Spectra are the average of 25 accumulated scans using a nominal resolution of 4 cm^{-1}. Commercial samples 1–3 containing 80% w/w Diuron and laboratory samples 4 and 5 with a Diuron content of 40 and 20% w/w, respectively. Note: mass of the different samples varies to provide a final concentration of Diuron of the same order than that of the standard.

Table 1. Analytical Characteristics for FTIR Determination of Diuron Using Different Measurement Modes, Bands, and Baseline Criteria

				calibration curve ($y = a + bC$ (mg g^{-1}))[a]					
band	measurement mode	wavelength	baseline correction	$a \pm s_a$[a]	$b \pm s_b$[a]	r^2[b]	LOD[c]	% LOD[d]	% RSD
1672	height	1672	1737–1633	0.0016 ± 0.0003	0.0349 ± 0.0001	0.9997	43	0.9	0.13
			1800	0.0012 ± 0.0003	0.0368 ± 0.0001	0.9998	25	0.5	0.15
	area	[1677–1 667]	1737–1633	0.013 ± 0.004	0.383 ± 0.002	0.9996	25	0.5	0.22
			1800	0.008 ± 0.004	0.405 ± 0.002	0.9997	10	0.2	0.11
1582	height	1582	1614–1562	0.0007 ± 0.0001	0.01500 ± 0.00006	0.9998	40	0.8	0.17
			1800	0.0003 ± 0.0001	0.01752 ± 0.00006	0.9998	32	0.6	0.39
	area	[1587–1577]	1614–1562	0.003 ± 0.001	0.1234 ± 0.0005	0.9997	48	1.0	0.35
			1800	0.003 ± 0.001	0.1216 ± 0.0005	0.9997	46	0.9	0.30
1514	height	1514	1556–1489	0.0004 ± 0.0002	0.0274 ± 0.0001	0.9997	72	1.5	0.31
			1556	0.0013 ± 0.0003	0.0329 ± 0.0001	0.9997	64	1.3	0.40
	area	[1519–1509]	1556–1489	0.007 ± 0.003	0.293 ± 0.001	0.9996	20	0.4	0.51
			1556	0.013 ± 0.004	0.358 ± 0.002	0.9996	32	0.6	0.12
1477	height	1477	1434–1490	0.0012 ± 0.0002	0.02299 ± 0.00006	0.9999	76	1.5	0.94
			1490	0.0010 ± 0.0001	0.02034 ± 0.00006	0.9999	83	1.6	1.41
	area	[1482–1472]	1434–1490	0.002 ± 0.002	0.1743 ± 0.0006	0.9998	28	0.6	0.87
			1490	0.000 ± 0.001	0.1468 ± 0.0006	0.9997	44	0.9	1.56
1392	height	1392	1425–1369	0.0003 ± 0.0001	0.01652 ± 0.00005	0.9998	50	1.0	1.77
			1407–1369	0.0004 ± 0.0001	0.01512 ± 0.00005	0.9999	44	0.9	1.46
	area	[1397–1 387]	1425–1369	0.001 ± 0.001	0.1439 ± 0.0006	0.9997	31	0.6	1.31
			1407–1369	0.001 ± 0.001	0.1309 ± 0.0005	0.9998	17	0.3	1.33
1297	height	1297	1282–1316	0.00017 ± 0.0008	0.00859 ± 0.00003	0.9999	86	1.7	0.44
	area	[1302–1292]	1282–1316	0.0002 ± 0.0006	0.0724 ± 0.0002	0.9998	57	1.1	2.10

[a] a and b are the intercept and the slope of the calibration lines. [b] Regression coefficient. [c] Limit of detection for the chloroform solution (in μg g^{-1}) obtained from the standard deviation of six measurements of a blank solution, established for a probability level of 99.6% ($K = 3$). [d] LOD in the original sample (% w/w).

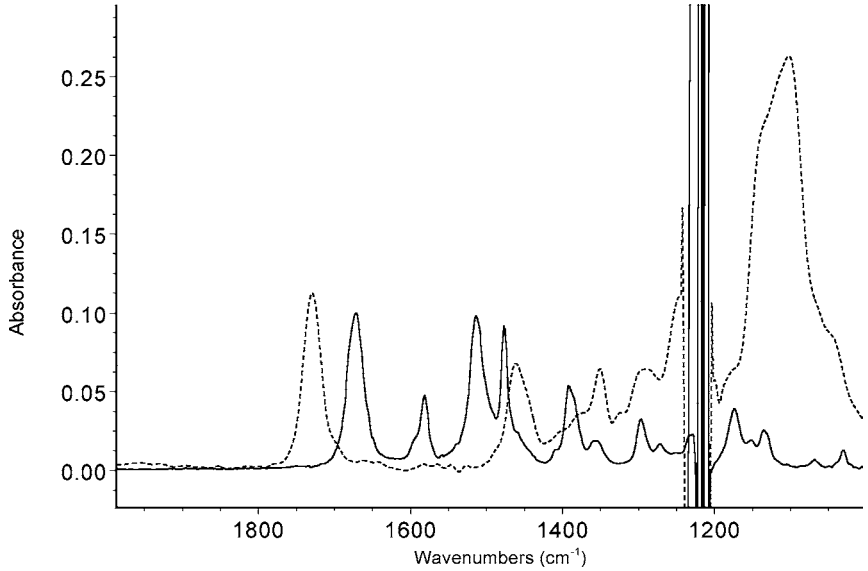

Figure 4. FTIR spectra of a Diuron standard chloroformic solution of 2.7 mg g^{-1} (solid line) and propylen glycol monooleate of 2.1 mg g^{-1} (dashed line).

4. OFF-LINE PROCEDURE

4.1. Off-Line Extraction of Diuron. A study of the time needed to carry out a quantitative extraction of Diuron by ultrasonic shaking was carried out, and it was confirmed that the extraction of Diuron from pesticide formulations was completed even without sonication. So it can be concluded that the high solubility of this compound in $CHCl_3$ permits a direct extraction from the samples by hand shaking.

4.2. Evaluation of the Matrix Effect on the Off-Line FTIR Diuron Determination. To ensure that the FTIR procedure was free from matrix effects, the slope of an external calibration line and that of a standard addition regression line were compared, obtaining $H = (0.0007 \pm 0.0001) + (0.01500 \pm 0.00006)C$ (mg g^{-1}) with $r^2 = 0.9998$ and $H = (0.054 \pm 0.001) + (0.0150 \pm 0.0002)C$ (mg added g^{-1}) with $r^2 = 0.999$, respectively, being that both slope values were statistically comparable for a confidence level of 95% (the t calculated value being 0.14, clearly lower than 1.71, the theoretical one).

5. ON-LINE PROCEDURE

5.1. Effect of Measurement Variables on the Determination of Diuron. The use of different sample injection volumes, from 100 to 500 μL, was tested to obtain as high a sensitivity as possible in the on-line measurement of Diuron. A volume of 500 μL was selected for further measurements because it provided peak height values statistically comparable with those found in the stopped-flow mode (see **Figure 5**), thus indicating the reduced dispersion of the solution from the injection loop to the measurement cell.

The effect of the carrier flow on the peak height values of the chemigrams of Diuron was studied in the range of 1−5 mL min^{-1} for an injection volume of 500 μL, and comparable data

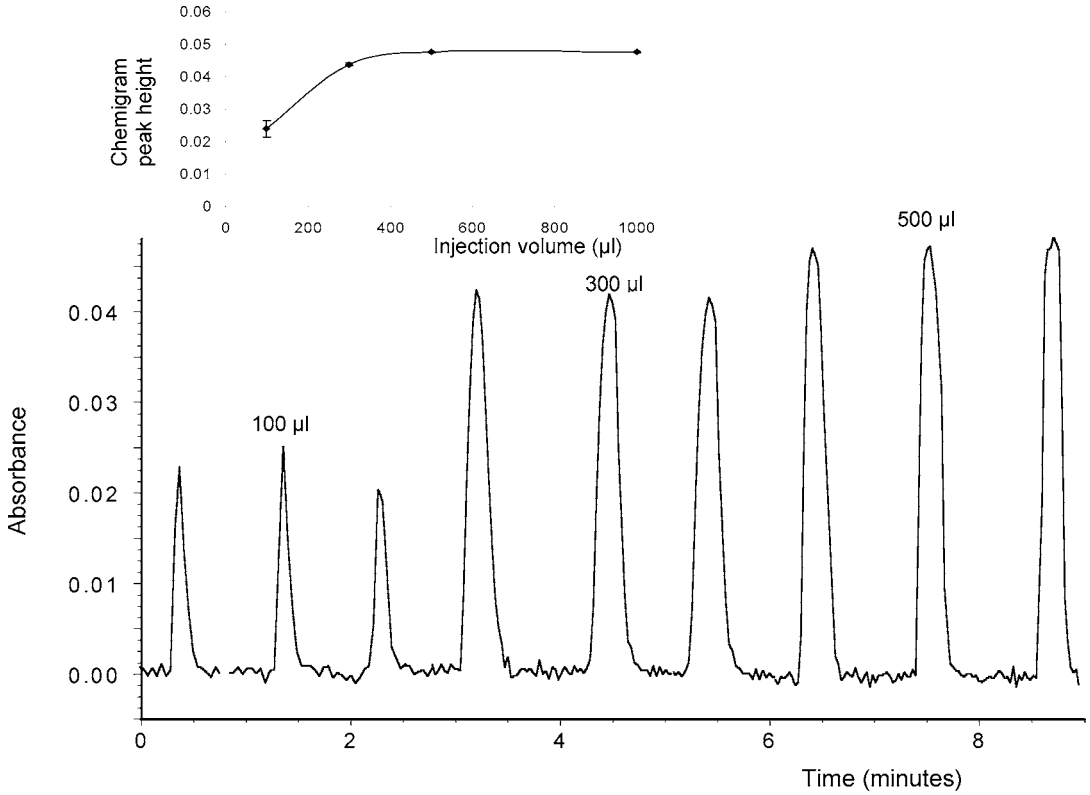

Figure 5. Effect of sample volume injected on the peak height of the Diuron chemigram established from measurements at 1582 cm^{-1} corrected using a baseline from 1614 to 1562 cm^{-1} on a Diuron standard solution of 3.13 mg g^{-1}. Experimental conditions: carrier flow 2.96 mL min^{-1}, nominal resolution 4 cm^{-1}, and two scans per spectrum. Values indicated correspond to the average of three independent injections ± the standard deviation. The peak height at 1000 μL corresponds to the Diuron standard solution measured in the stopped-flow mode, accumulating 25 scans. FIA recordings in this figure correspond to each one of the three injections made for the different volumes assayed.

Table 2. Determination of Diuron in Pesticide Formulations by Off-Line FTIR, FIA–FTIR, and HPLC–UV Procedures[a]

	FTIR			FIA–FTIR			HPLC–UV		
	$S = (0.0007 \pm 0.0001) + (0.01500 \pm 0.00006)Cr^2 = 0.9998$			$S = (-0.0001 \pm 0.0001) + (0.01296 \pm 0.00005)Cr^2 = 0.9999$			$S = (8\pm6) + (70.4 \pm 0.2)Cr^2 = 0.9999$		
sample	FTIR	CV (%)[b]	% relative accuracy error[c]	FIA–FTIR	CV (%)	% relative accuracy error	HPLC–UV	CV (%)	% active substance labeled
1	83.1 ± 0.3	0.4	0.5	80.8 ± 0.8	1.0	2.3	82.7 ± 0.3	0.4	80
2	82.6 ± 0.5	0.6	0.0	84 ± 2	2.4	1.7	82.6 ± 0.4	0.5	80
3	83.0 ± 0.7	0.8	0.0	84 ± 2	2.4	1.2	83.0 ± 0.4	0.5	80
4	40.1 ± 0.6	1.5	–0.5	42 ± 2	4.8	4.2	40.3 ± 0.5	1.2	40
5	20.8 ± 0.5	2.4	1.5	20.9 ± 0.4	1.9	2.0	20.5 ± 0.6	2.9	20

[a] Concentration values (% w/w) are the average of three independent analyses ± standard deviation. [b] Coefficient of variation for three replicates. [c] % error calculated as 100([FTIR] – [HPLC])/[HPLC], where [FTIR] and [HPLC] are the concentrations found using the FTIR or FIA–FTIR procedure and the HPLC–UV procedure, respectively.

were obtained with that found in the stopped-flow mode. However, using a carrier flow rate of 2.96 mL min^{-1}, the best precision of analytical data was found; thus, this value was selected, as a sample throughput of 30 h^{-1} was obtained.

5.2. Analytical Characteristics of FIA−FTIR Determination of Diuron. The sensitivity of the fully mechanized FIA−FTIR analysis of Diuron corresponds to 0.1296 absorbance units mg^{-1} mL. Using the recommended procedure, the limit of detection was 35 μg mL^{-1}, which correspond to 0.7% (w/w), for 20 mg of sample and provided a repeatability of 0.5% (expressed as relative standard deviation). For Diuron external calibration in the selected conditions, the expression $A = [-0.0001 \pm 0.0001] + [0.01296 \pm 0.00005]C$ (mg mL^{-1}) with $r^2 = 0.9999$ was found.

For actual sample analysis, a relative standard deviation between 1.0 and 2.8% for five replicate determinations and a maximum sampling frequency of the whole procedure of 30 h^{-1} was found.

6. COMPARISON BETWEEN THE DIFFERENT STRATEGIES ASSAYED

Commercially available Diuron formulations were analyzed by the HPLC−UV reference procedure and by the proposed FTIR method, using both off-line and FIA−FTIR measurements. As can be seen in **Table 2**, data found by the three methods are of the same order with average relative standard deviation values of 0.4−2.4% for stopped-flow measurements and 1.0−4.8% for FIA−FTIR measurements being the average accurate relative errors from −0.5 to 1.5% and from 1.2 to 4.2%, respectively, which is evidence that all the methods are comparable within their precision levels.

Additional statistical treatment of data in **Table 2** provides regression lines of $C_{FTIR} = (0.1 \pm 0.3) + (0.998 \pm 0.004)$-$C_{HPLC}$ with $r^2 = 0.9993$ and $C_{FIA-FTIR} = (0.6 \pm 0.7) + (0.99 \pm 0.01)C_{HPLC}$ with $r^2 = 0.997$ for the comparison between data found by FTIR in the stopped flow and FIA mode and those obtained by HPLC. The slope and intercept values of these equations are statistically comparable (t_{exp}= 0.50 and 0.33 for the stopped flow and t_{exp}= 1.00 and 0.86 for the FIA mode) with values of 0 and 1 for the intercept and slope of the regression line (t_{theor}=1.70) for a probability level of 95% and 30 degrees of freedom, thus indicating that methodologies developed do not require blank correction nor present systematic relative errors as compared with the reference procedure.

It must be indicated that the sensitivity provided by HPLC measurements is higher than that found by FTIR. However, for this kind of concentrate sample, the advantage offered by a strong reduction of the volume of organic solvent required (39.1 mL for HPLC, 3.4 mL for stopped flow FTIR, or 9.3 mL for FIA−FTIR measurements) and the increase of the sampling frequency from 12 h^{-1} in the case of HPLC to 30 h^{-1} for FIA−FTIR and 60 h^{-1} for the stopped flow FTIR clearly recommend the use of FTIR measurements for the control of Diuron concentration in pesticide formulations.

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