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Chromatographic approaches for determination of low-molecular mass aldehydes in bio-oil

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ABSTRACT

HPLC–UV and GC/MS determination of aldehydes in bio-oil were evaluated. HPLC–UV preceded by derivatization with 2,4-dinitrophenylhydrazine allows separation and detection of bio-oil aldehydes, but the derivatization affected the bio-oil stability reducing their quantitative applicability. GC/MS determination of aldehydes was reached by derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride. Two approaches for this reaction were evaluated. The first: "in solution derivatization and head space extraction" and the second: "on fiber derivatization SPME", the latter through an automatic procedure. Both sample treatments allows the quantification of most important aliphatic aldehydes in bio-oil, being the SPME approach more efficient. The aldehyde concentrations in bio-oil were ~2% formaldehyde, ~0.1% acetaldehyde and ~0.05% propionaldehyde.

1. Introduction

Renewable energy sources play an important role solving environmental problems and securing energy provision. Biomass is a renewable source that can be used as fuel, being wood agricultural and forest residues some of the most available. It is possible to convert biomass in a more useful energy source through thermal conversion. Pyrolysis is a thermal decomposition that occurs in absence of oxygen. In fast pyrolysis, the biomass, i.e. wood sawdust, decomposes generating mainly vapors, aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid called "bio-oil" (crude pyrolysis liquid) is formed [1,2].

Bio-oil contain between 10 and 30 wt% of water and hundreds of oxygenated organic compounds like pyrolytic lignin (15–20%), aldehydes (10–20%), organic acids (10–15%), anhydrosugars (5–10%) and other compounds [3,4]. Some of these are highly reactive, producing instability of bio-oil. This composition makes bio-oil a very complex matrix from the analytical point of view.

In the context of phenol/formaldehyde resin formulation, the aldehyde fraction of bio-oil is very important. Additionally, the toxicity of some volatile aldehydes, especially formaldehyde (Permissible exposure limit (PEL) in air at working places is 0.75 mg L^{-1} [5]) demands their quantification in bio-oil. The presence of hydroxyacetaldehyde (glycolaldehyde), formaldehyde and acetaldehyde in bio-oil, has been previously described [2–4,6]. Determination of hydroxyacetaldehyde has been carried out using direct injection to a gas chromatograph coupled to a mass selective detector for identification of compounds and flame ionization detector coupled to the system (GC/MS/FID) for quantification [6]. Other aldehydes, as propionaldehyde and different substituted furaldehydes, can also be detected and quantified using this system [6].

On the other hand, quantification of formaldehyde and acetaldehyde in bio-oil has not been deeply achieved yet. Determination of these aldehydes in bio-oil using high performance liquid chromatography (HPLC) preceded by derivatization with 2,4-dinitrophenylhydrazine (DNPH) has been mentioned in only one reference, without enough information about the analytical quality of the obtained results [7]. This approach has been widely described in the literature for determination of carbonyl groups in different matrixes, like water, air, alcoholic beverages, food, and other, but not in bio-oil [8–13]. On the other hand, determination of carbonyl groups in bio-oil has been usually based on the quantitative reaction between hydroxylamine hydrochloride and a variety of aldehydes and ketones in pyridine. Due to the specific oximation reaction, other bio-oil components do not interfere. This allowed the implementation of a routine analysis method. The typical carbonyl content in fresh bio-oil has been ranged between 4 and 6 mol carbonyl kg^{-1} liquid [14].

GC is a technique usually used for determination of aldehydes, preceded by derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA). This reaction provides

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thermal stability and volatility to the oximes, which are amenable for GC analysis. The US Environmental Protection Agency (EPA) method 556 propose the extraction of oximes derivatives from water by liquid–liquid extraction (LLE) using different solvents and reagents [15]. Headspace (HS) and solid phase micro-extraction (SPME) are other approaches for aldehydes determination. Low molecular-mass aldehydes in pharmaceutical formulations have been determined by direct derivatization and extraction in a HS system [16]. The same procedure was used for quantification of aldehyde traces in aqueous solutions [17]. The aldehyde extraction by SPME has also been described through *on-fiber* derivatization (OFD) using PFBHA adsorbed on the fiber, then the fiber is exposed to the sample using HS-SPME mode, followed by GC. This procedure has been applied to different matrixes, like water, human blood, food and beer [18–22]. These technologies have not yet been evaluated for aldehyde determination in bio-oil samples.

Due to the complexity of bio-oil matrix, the determination of aldehydes requires high selectivity of the analytical method. In this research, different methods for low-molecular-aldehydes determination in bio-oil samples are evaluated and discussed, including derivatization with DNPH and HPLC separation of derivatives, derivatization in solution with PFBHA followed by the headspace extraction and direct injection into the GC/MS system, which was abbreviated with the acronym D-HS-GC/MS. The last method evaluated involves an automatic chemical fiber modification with PFBHA for on-fiber derivatization and extraction of aldehydes-PFBHA and desorption in the GC/MS system. This method was abbreviated as OFD-HS-SPME–GC/MS.

2. Experimental

2.1. Chemicals and materials

Formaldehyde 37%, 2,4-dinitrophenylhidrazine, valeraldehyde 97%, methanol and acetonitrile (both HPLC grade) were purchased from Merck (Darmstadt, Germany). Acetaldehyde 99.5%, propionaldehyde 97%, 2-furaldehyde 98%, glicolaldehyde (dimer) and *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride, were obtained from Sigma (St. Louis, MO, USA). Deionized water (18 mΩ) was produced with a Millipore Milli-Q water purification system (Bedford, MA, USA).

2.2. Instrumentation and separation conditions

2.2.1. HPLC–UV

HPLC analyses were carried out with a Merck Hitachi HPLC system equipped with a Hitachi L-2200 auto-sampler, a Hitachi L-2130 pump and a Hitachi L-2400 UV detector (Merck KG, Darmstadt, Germany). Data processing was done using an Interactive Graphics Software, version 6.20 from Varian Inc. (Palo Alto, CA, USA). A Shim-Pack VP-ODS 25 cm × 4.6 mm column was employed at room temperature with a mobile phase constituted by acetonitrile (A) and water (B). The gradient started with 45% of A for 1 min, increasing to 65% of A in 5 min and keeping this proportion for 9 min, decreasing to 60% A in 16 min and maintaining this condition for 25 min, followed by a washing step with 100% A for 25 min. The flow rate was 1.5 ml min^{-1}, detection at 360 nm and sample injection volume 10 μL.

2.2.2. GC/MS

GC/MS analysis were performed with a HP 6890 Series gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) equipped with Combi PAL CTC-G6500 autosampler (CTC Analytics AG, Zwingen, Switzerland) a split/splitless injector and a HP 5973 mass-selective detector. The system operation was controlled by a HP ChemStation G1701AA, version A.03.00 and Cycle Composer Software 1.4.0. The chromatographic separation was performed using a VF-1701 (14% cyanopropyl/phenyl, 86% polydimethylsiloxane) column (Varian) of 60 m × 0.25 mm I.D., 0.25 μm film thickness and as mobile phase, electronic helium grade 6.0 (99.9999%) at 2 mL min^{-1} as flow. The GC/MS transfer line was kept at 280 °C and the detection was carried out in scan mode with electron energy of 70 eV. The ionization source was set at 230 °C and analyzer temperature at 150 °C.

Two temperature programs were optimized, one for D-HS-GC/MS (program 1) and other for HS-SPME–GC/MS (program 2). Program 1: The initial temperature was 80 °C, with an increase of 3 °C min^{-1} up to 150 °C (ramp 1), 40 °C min^{-1} up to 280 °C (ramp 2), and a final clean-up at 280 °C for 5 min. The injection port temperature was 260 °C and the injection volume was 1000 μL using the split mode. Program 2: The initial temperature was 45 °C, with an increase of 3 °C min^{-1} up to 150 °C (ramp 1), 40 °C min^{-1} up to 280 °C (ramp 2), and a final clean-up at 280 °C for 5 min. The injection port temperature was 260 °C and using system split mode with 10 min of desorption time from the fiber.

2.3. Solutions

2.3.1. Standards and bio-oil sample preparation for HPLC–UV

Aldehyde standards were prepared in acetonitrile and stored at 4 °C.

Five mg of 2,4-DNPH were dissolved in 5 mL of a solution containing 1.25 mL HCl (37%, v/v), 3.12 mL water and 625 μL of acetonitrile.

250 μL of bio-oil were dissolved in 4 mL of acetonitrile/water 50/50% (v/v) and diluted with mobile phase. 100 μL of 2,4-DNPH solution and 500 μL of diluted bio-oil were mixed for derivatization reaction.

2.3.2. Standards and bio-oil sample preparation for GC/MS

All aldehyde standard stock solutions and internal standard (valeraldehyde) were prepared in methanol. Subsequent dilutions were prepared in deionized water at the moment of analysis. The PFBHA solution was prepared in methanol/water 50/50% (v/v) in a concentration of 10 mg mL^{-1}. All solutions were stored at 4 °C. Bio-oil samples were diluted with water (0.5–10, v/v), producing the pyrolytic lignin precipitation, which was separated by centrifugation. The aqueous phase was diluted again with water (0.5–50, v/v). This last solution constituted the diluted bio-oil.

The solutions used for D-HS-GC/MS were prepared in headspace vials (10 mL) with magnetic screw caps, with 2 mL of diluted bio-oil, 100 μg L^{-1} of internal standard and 1 mg mL^{-1} of PFBHA solution.

Two solutions were used for OFD-HS-SPME–GC/MS, the first was 2 mL of PFBHA (3 mg mL^{-1}) and the second was 2 mL the diluted sample with internal standard (100 μg L^{-1} of valeraldehyde). They were placed in different 20 mL-headspace vials with magnetic screw caps.

2.4. Statistical analyses

Experimental design of OFD-HS-SPME–GC/MS and D-HS-GC/MS were carried out using the MODDE 7.0.0 software, Umetrics AB (Umeå/Malmö, Sweden).

3. Results and discussion

3.1. HPLC–UV method

The reaction between low molecular mass aldehydes and 2,4-DNPH for hydrazones formation is performed at room temperature (15–25 °C) for 30 min [15–18]. Considering the high variability of bio-oil aldehydes (aliphatic aldehydes, furaldehyde

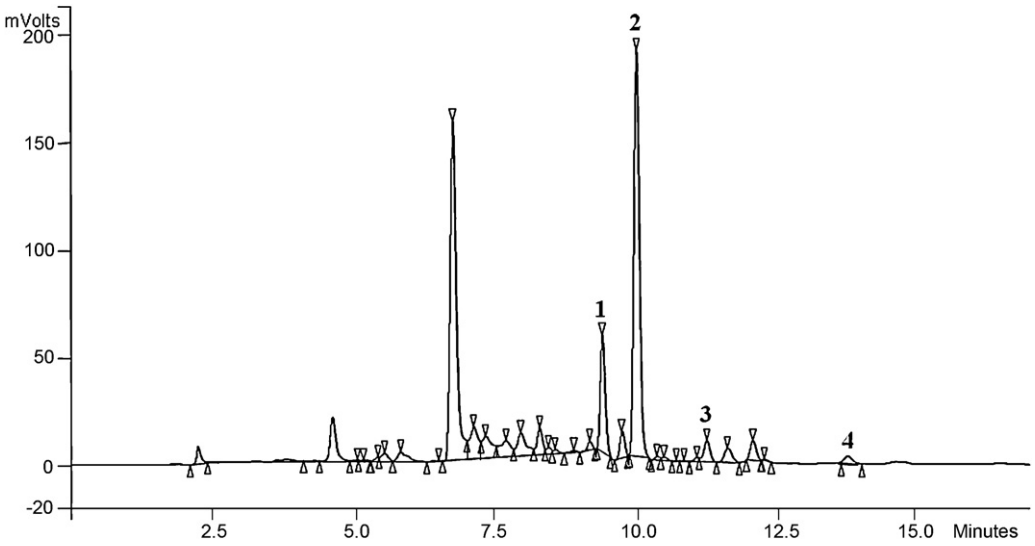

Fig. 1. HPLC chromatogram of 2,4-dinitrophenylhydrazones of aldehydes in bio-oil samples. Peaks: 1 = glycolaldehyde-DNPH, 2 = formaldehyde-DNPH, 3 = acetaldehyde-DNPH and 4 = 2-furaldehyde-DNPH.

and glycolaldehyde) it was necessary to optimize this reaction. The optimal conditions for derivatization were 0.15 μmol of DNPH at 40 °C for 30 min. In Fig. 1 is shown the aldehyde-2,4-dinitrophenylhydrazone HPLC chromatogram of a bio-oil sample.

The separation of principal bio-oil aldehydes is achieved under the optimized separation conditions (see Fig. 1), however the presence of interferences is observed. Besides, from the quantitative point of view a non linear response was obtained for glycolaldehyde. This is due to the hydrates production in aqueous solution, which affected the 2,4-hidrazones formation. Although derivatization with formaldehyde was quantitative, a narrow linear range was observed for quantitative purposes (1.5–7.0 mg L^{-1}).

It is possible to apply this approach for air samples or other less complex matrixes, but bio-oil contains a high diversity of functional groups and chromophores, which produce interferences in detection and quantification. This is due to the use of basic or acid reagents for derivatization reactions, which generate unwanted sample reaction and instability of bio-oil. A more selective method, without these reagents, is required.

To improve analytical selectivity, PFBHA derivatization combined with GC, is an alternative system that can be used for complex matrixes, considering that PFBHA solution preparation does not require aggressive reagents, that can produce instability of bio-oil matrix. Two alternatives based on this approach are presented and discussed below for low-molecular mass aldehyde determination in bio-oil samples.

3.2. Optimization of D-HS-GC/MS method

This method is based on aldehyde derivatization in solution using PFBHA and direct HS extraction of oximes, being necessary only one step for sample treatment. A method for determination of low-molecular mass aldehydes in pharmaceutical excipients has been previously described with the following conditions: derivatization at 80 °C for 20 min, syringe temperature was set at 105 °C and agitation speed at 500 rpm. [16]. In this case, considering the complexity of the bio-oil matrix, these parameters of sample treatment were evaluated using an experimental design. The temperature was evaluated between 35 and 85 °C, agitation between 250 and 700 rpm and derivatization time between 5 and 70 min. The optimized HS derivatization/extraction conditions were; derivatization at 85 °C for 60 min and agitation at 350 rpm. Higher temperatures produce evaporation of aqueous solution which decreases the efficacy of the HS process. The significant representative equation of derivatization/extraction variables for each aldehyde determination in bio-oil by HS approach is presented below:

Formaldehyde

$$y = 2.458^{+06}(\pm 295,601) + 558,143X_1(\pm 198,918) - 793,458\,X_2(\pm 209,268) - 53,309X_3(\pm 214,856) - 1.478^{+06}X_3^2(\pm 357,597)$$

Acetaldehyde

$$y = 55,527.1(\pm 6202.1) + 15,111.2\,X_1(\pm 4173) + 24,421.6X_2(\pm 4391) - 12,977.5X_3(\pm 4508) - 32,186.7X_3^2(\pm 7503)$$

where X_1 is reaction time, X_2 derivatization temperature and X_3 agitation. This method was validated by analysis of variance (ANOVA) using MODDE 7.0.0.0 software.

Fig. 2 shows the chromatogram of aldehyde-PFBHA oximes in a bio-oil sample, using the optimized extraction conditions. Valeraldehyde was used as internal standard.

Isomers of each aldehyde, except formaldehyde-PFBHA oxime, are produced in the derivatization reaction of bio-oil, causing two peaks for each analyte in the chromatogram. The resolutions in all cases were higher than 2.5, showing enough selectivity for aldehyde separation between them and with interfering signals. The selectivity was evaluated by comparison of mass spectra obtained for each chromatographic signal from bio-oil sample whit those of the standard solution.

3.3. Optimization of ODF-HS-SPME–GC/MS method

The optimization of this method was addressed in two steps. The first was the evaluation of fiber coating, especially from the point of view of bio-oil matrix interferences. After that, the evaluation of optimal HS-SPME condition for on-fiber modification, derivatization and extraction was carried out using an experimental design.

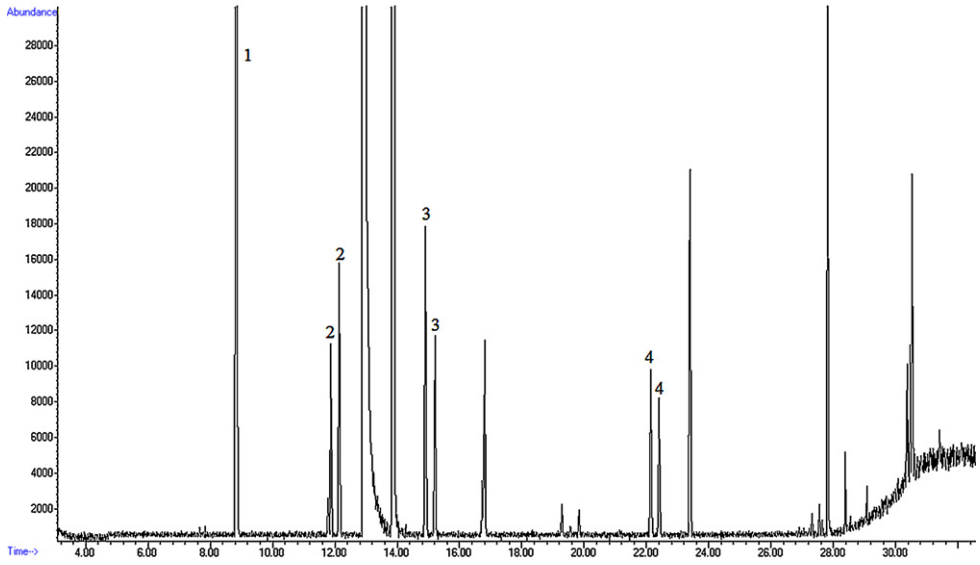

Fig. 2. Typical D-HS-SPME–GC/MS total ion count mass chromatogram of PFBHA aldehyde oxime in a bio-oil sample. Peaks: 1 = formaldehyde-PFBHA oxime; 2 = acetaldehyde-PFBHA oximes; 3 = propionaldehyde-PFBHA oximes and 4 = valeraldehyde-PFBHA oximes (internal standard).

3.3.1. Evaluation of fiber coating for bio-oil samples

Extraction of PFBHA-aldehydes in water samples has been described using DVB/PDMS fiber [19–23]. Due to complexity of bio-oil matrix, which contains a large amount of volatile compounds, which can interfere with aldehyde HS-SPME, determination of fiber selectivity in presence of these interferences is required. Regarding this, the evaluation of three different fibers with different polarities was carried out. The experiment was carried out at different temperatures, and the capacity to absorb/adsorb the most volatile interferents present in bio-oil and their effect on derivatization reaction was measured. The evaluation was performed by fiber exposure in the HS of an aqueous fraction of bio-oil by 30 min. The fibers evaluated were: polyacrylate (PA), carboxen/polydimethylsiloxane (CAR/PDMS), divinylbenzene/polydimethylsiloxane (DVB/PDMS) at 30 °C, 40 °C and 60 °C. Fig. 3 presents the results for the three assayed fiber.

Aromatic compounds in the aqueous fraction of bio-oil were the most abundantly extracted with the three fibers. Phenolic compounds have more affinity with PA fiber at higher temperature, while benzaldehyde derivatives are better extracted with CAR/PDMS at lower temperature. These results are consistent with the polarity and volatility of evaluated analytes and show that the better option is DVB/PDMS, because at all essayed temperatures, the efficiency was less for the interfering aromatic compounds.

3.3.2. Automatic sequence for OFD-HS-SPME–GC/MS

This procedure was carried out in two steps. The first was the chemical modification of the fiber with PFBHA. The second step was the "on-fiber derivatization" of aldehydes present in HS-sample. These steps were carried out by an automated procedure achieved with a CTC Combi Pal autosampler controlled by Cycle Composer software. The procedure started with the chemical fiber modification by PFBHA impregnation (3 mg mL^{-1}, 250 rpm, 40 °C and 10 min), whose parameters are resumed in Table 1 (step 1). In this step, the creation of a "virtual injector" in the autosampler in order to obtain the PFBHA impregnation was necessary. In the second step (Table 1), the impregnated fiber exposure to HS-sample (250 rpm, 40 °C and 30 min), followed by desorption in the GC injector was possible creating two methods in the autosampler. The first step was "Desorbed into virtual injector" and the second "Desorbed into real injector", enabling the sequential fiber impregnation and derivatization/extraction of aldehydes in the same autosampler. An important parameter was the agitation speed, because high velocity can produce fiber breaking.

The main advantage of automatic OFD-HS-SPME–GC/MS is to reduce the human intervention with the consequent improvement of reproducibility of sample treatment.

3.3.3. Optimization of aldehyde extraction/derivatization in bio-oil samples by OFD-HS-SPME–GC/MS

Using the automatic developed approach, chemical modification of fiber by PFBHA sorption and "on-fiber" aldehyde derivatization were optimized in a single experimental design. In literature, the main factors affecting this technique has been studied separately each one, but in this research it was performed using a central composite face-centre design, considering each variable and its interactions. The optimized variables and their high and low values are presented in Table 2. The responses were studied for formaldehyde, acetaldehyde, and propionaldehyde and the evaluation included 30 runs and 4 central points.

The significant representative equation of the procedure for each aldehyde is presented below:

Formaldehyde

$$y = 970.5(\pm 59.5) - 295.1X_1(\pm 44.3) - 4.4X_2(\pm 44.3) + 87.8X_3(\pm 44.3) - 429.5X_4(\pm 44.3) - 425.2X_5(\pm 44.3) + 410.1X_4^2(\pm 74.2) + 332.7X_1 * X_4(\pm 47.0) + 188.1X_1 * X_5(\pm 47.0) - 350.5X_2 * X_3(\pm 47.0) + 434.3X_4 * X_5(\pm 47.0)$$

Table 1
Parameters for automatic sequence in OFD-HS-SPME–GC/MS.

	Step 1	Step 2
Pre incubation time (m:ss)	3:30	0:30
Incubation temperature (°C)	40	40
Agitator speed (rpm)	250	250
Agitator on time (m:ss)	0:05	0:05
Agitator off time (m:ss)	0:02	0:02
Vial penetration (mm)	31	31
Extraction time (m:ss)	10:00	30:00
Desorb to	GC-Iny 2 (virtual injector)[a]	GC-Iny 1 (real injector)
Injection penetration (mm)	44	54
Desorption time (m:ss)	0:05	11:00

[a] Virtual injector in an autosampler, after PFBHA impregnation on-fiber.

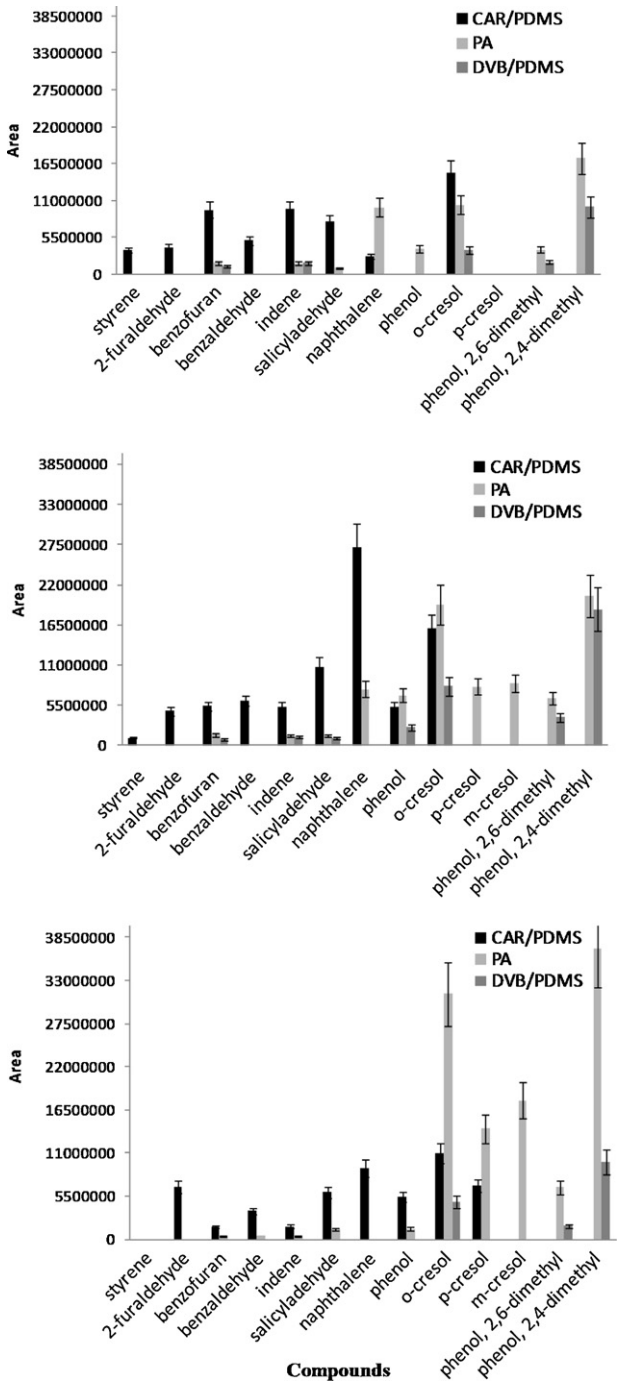

Fig. 3. Evaluation of different polymer coatings to various extraction temperatures. (A) 30 °C; (B) 40 °C and (C) 60 °C.

Table 2
Experimental variables studied.

Experimental variables	Identification	Low	High
PFBHA (mg L^{-1})	X_1	1.0	10.0
Temperature adsorption PFBHA in fiber (°C)	X_2	27.0	50.0
Agitation time in adsorption PFBHA in fiber (min)	X_3	5.0	30.0
Agitation time in de derivatization reaction (min)	X_4	5.0	60.0
Temperature derivatization la reaction (°C)	X_5	35.0	60.0

Acetaldehyde

$$y = 936.2\,(\pm 110.6) - 366.8\,X_1(\pm 82.4) + 179.1\,X_2(\pm 82.4) + 34.8\,X_3(\pm 82.4) - 532.6X_4(\pm 82.4) - 508.8\,X_5(\pm 82.4) + 596.5X_4^2(\pm 137.9) + 437.3X_1 * X_4(\pm 87.4) + 297.3X_1 * X_5(\pm 87.4) - 338.7X_2 * X_3(\pm 87.4) + 666.6X_4 * X_5(\pm 87.4)$$

Propionaldehyde

$$y = 678.5\,(\pm 79.8) - 335.9\,X_1(\pm 59.5) + 152.7X_2(\pm 59.5) + 66.1X_3(\pm 59.5) - 442.5X_4(\pm 59.5) - 478.9X_5(\pm 59.5) + 445.9X_4^2(\pm 99.5) + 321.4X_1 * X_4(\pm 63.1) + 182.8X_1 * X_5(\pm 63.1) - 222.1X_2 * X_3(\pm 63.1) + 385.6X_4 * X_5(\pm 63.1)$$

Analysis of variance (ANOVA), using MODDE 7.0.0 software was applied for evaluation and validation of these models and explained correctly the behavior of the compounds in the experimental domain. Therefore, the models were accepted, however due to the differences in the optimal condition for each aldehyde, a compromise was necessary, applying a multiple responses optimization with this purpose. Table 3 shows the optimum values for each aldehyde, and those obtained by compromise using the multiple responses optimization. Fig. 4 is shown a typical chromatogram of a bio-oil sample, obtained under the described conditions.

In literature the reaction between aldehydes in water samples and PFBHA (17 mg mL^{-1}) is described [23,24]. Considering the high cost of this reagent, the concentration reduction was tested at levels of 0.5, 1.0, 10.0 and 17.0 mg mL^{-1}. The oxime signal in bio-oil samples decreased at 0.5 mg mL^{-1}, while between 1.0 and 17.0 mg mL^{-1} constant signals were observed. Finally a concentration of 1 mg mL^{-1} was used. The PFBHA adsorption temperature was similar for acetaldehyde and propionaldehyde, but less for formaldehyde, being the optimal at 40 °C. The optimal agitation time for fiber PFBHA adsorption was less than 10 min for formaldehyde and acetaldehyde and 15 min for propionaldehyde. Regarding the formaldehyde importance for its use in resin formulation, the agitation time was fixed considering its optimal condition. The derivatization temperature was optimal at 35 °C, however, because in the first step 40 °C was used, this temperature was maintained with the purpose to decrease the analysis time without cooling the system.

3.4. Analytical parameters OFD-HS-SPME–GC/MS and D-HS-GC/MS method and applications

Calibration curves were constructed for both developed methods. Whereas there is no reference material available, the recoveries were determined adding two concentration levels (50 and 100 μg L^{-1}). The intermediate precision using three different bio-oil samples analyzed by triplicate ($n = 9$) was determined. The principal analytical parameters are summarized in Table 4.

Significant differences in calibration curve slopes, detection limits, recoveries and intermediate precision, for the two proposed methodologies were observed. OFD-HS-SPME–GC/MS was more favorable for bio-oil aldehyde determination because its sensitivity. No statistical difference was observed between concentrations of formaldehyde, acetaldehyde and propionaldehyde obtained in bio-oil samples ($n = 5$) by OFD-HS-SPME–GC/MS and by D-HS-GC/MS methods. This was demonstrated ($\alpha = 0.05$) using t test, showing a p-value higher than 0.05. Finally, in Table 5 the quantitative results for aldehydes in different bio-oil samples are shown.

Table 3
OFD-HS-SPME–GC/MS optimal conditions.

Experimental variables	Formaldehyde	Acetaldehyde	Propionaldehyde	Optimum[a]
PFBHA (mg L^{-1})	1	1	1	1
Temperature sorption PFBHA in fiber (°C)	27	50	50	40
Agitation time in sorption PFBHA in fiber (min)	10	10	15	10
Agitation time in derivatization reaction (min)	20	30	30	35
Temperature of derivatization reaction (°C)	35	35	35	40

[a] Obtained by multiple responses optimization method.

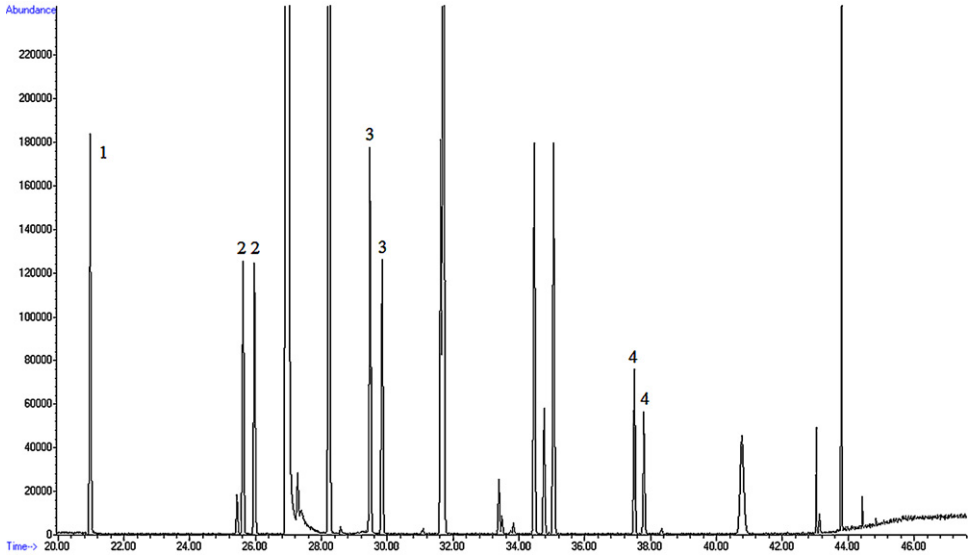

Fig. 4. Typical OFD-HS-SPME–GC/MS total ion count mass chromatogram of PFBHA aldehyde oxime in bio-oil sample. Peaks: 1 = formaldehyde-PFBHA oxime; 2 = acetaldehyde-PFBHA oximes; 3 = propionaldehyde-PFBHA oximes and 4 = valeraldehyde-PFBHA oximes (internal standard).

Table 4
Comparison of analytical parameters of OFD-HS-SPME–GC/MS and D-HS-GC/MS.

	OFD-HS-SPME–GC/MS			D-HS-GC/MS		
	Formaldehyde	Acetaldehyde	Propionaldehyde	Formaldehyde	Acetaldehyde	Propionaldehyde
Calibration curve	$y = 0.0107x + 0.1982$	$y = 0.0162x + 0.0093$	$y = 0.0182x + 0.2143$	$y = 0.0305x - 0.0303$	$y = 0.0213x - 0.4547$	$y = 0.0331x - 0.8298$
R	0.9970	0.9831	0.9871	0.9989	0.9835	0.9769
LD[a] (μg L^{-1})	0.2	4.4	6.4	1.2	7.1	15.2
Linear range	LQ[d]-200	LQ-200	LQ-200	LQ-350	LQ-350	LQ-350
Recovery[b] % (bio-oil samples)	89.9	84.7	81.8	89.5	73.5	66.1
Intermediate precision[c] (RSD)	8.1	6.8	11.5	8.4	5.2	23.3

[a] LD: detection limit.
[b] Aldehydes added (50–100 μg L^{-1}) in bio-oil samples.
[c] Three different bio-oil, analyses for triplicate ($n = 9$).
[d] LQ: quantification limit.

Table 5
Determination of aldehyde-PFBHA oxime in bio-oil samples, by two optimized method.

Bio-oil samples	Formaldehyde (wt%)		Acetaldehyde (wt%)		Propionaldehyde (wt%)	
	D-HS	OFD-HS-SPME	D-HS	OFD-HS-SPME	D-HS	OFD-HS-SPME
1	1.6 ± 0.3	1.9 ± 0.2	0.08 ± 0.03	0.03 ± 0.01	0.03 ± 0.02	0.012 ± 0.007
2	0.8 ± 0.2	1.3 ± 0.3	0.03 ± 0.01	0.01 ± 0.01	ND	LD > LQ
3	1.8 ± 0.3	2.2 ± 0.2	ND	0.03 ± 0.01	ND	LD > LQ
4	0.9 ± 0.1	1.7 ± 0.2	0.09 ± 0.04	0.12 ± 0.07	ND	0.04 ± 0.01
5	1.1 ± 0.3	1.7 ± 0.2	0.07 ± 0.01	0.04 ± 0.01	ND	0.010 ± 0.005
6	3.2 ± 0.5	3.6 ± 0.4	ND	0.05 ± 0.01	ND	0.023 ± 0.007
7	2.1 ± 0.4	2.4 ± 0.3	0.06 ± 0.01	0.02 ± 0.01	ND	0.014 ± 0.003
8	2.3 ± 0.4	2.0 ± 0.2	0.11 ± 0.04	0.03 ± 0.01	ND	0.010 ± 0.003

Quantitative determination of propionaldehyde by D-HS-GC/MS was not possible in most of the bio-oil samples, because the low concentration of this aldehyde, while OFD-HS-SPME–GC/MS allows it determination due to its pre-concentration on the fiber. However, the principal disadvantages of OFD-HS-SPME was the brief life time of the fiber (20 bio-oil samples) and because the carry over effect, which requires a continuous cleaning process of the fiber at 280 °C during 30 min, reducing it life span.

The results of this research show interesting levels of formaldehyde in the studied bio-oil samples (0.8–3.2 wt%), allowing it use in phenol/formaldehyde resin production. Detection limit for formaldehyde by OFD-HS-SPME–GC/MS is 0.2 $\mu g\,L^{-1}$, significantly below the PEL (750 $\mu g\,L^{-1}$).

4. Conclusions

The quantitative determination of main aliphatic aldehydes in bio-oil can be done by GC–MS preceded by PFBHA derivatization and HS extraction or HS-SPME extraction using a DVB/PDMS fiber. In contrast, HPLC–UV determination preceded by DNPH derivatization is affected by the own derivatization reagent, producing a non linear or a very narrow linear range, useless for bio-oil samples. Both developed methods show no statistical difference between the aldehyde concentrations obtained in bio-oil samples, however the sample treatment based on HS extraction has enough selectivity, but pre-concentration on a chemically modified fiber is more effective, from the sensitivity perspective. The concentration of formaldehyde found in bio-oil is interesting, considering its possible use in industrial production of phenol/formaldehyde resin.

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