Development of a Headspace-Solid Phase Micro Extraction Method for the Analysis of Volatile and Semi-Volatile Organic Compounds from Polyurethane Resins for Leather Finishing

by

Antonia Flores, Sílvia Sorolla, Concepció Casas, Rosa Cuadros and Anna Bacardit

A³ Leather Innovation Center. Escola Politècnica Superior. Departament d'Informàtica i Enginyeria Industrial. Universitat de Lleida. Avda. Pla de la Massa, 8. 08700-Igualada

Abstract

Volatile organic compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs) arise from the chemicals used in the various stages of the leather manufacturing process. An important aim of the tanning industry is to minimize or eliminate VOCs and SVOCs, without lowering the quality of leather.

This paper shows the development of a new headspace-solid phase micro extraction coupled with gas chromatography–mass spectrometry (HS-SPME/GC-MS) method for the identification of VOCs and SVOCs emitted by newly designed polymers for the leather finishing operation. These new polymers are polyurethane resins designed to reduce the VOC and SVOC concentration. This method enables a simple and fast determination of the qualitative and semi-quantitative content of VOCs and SVOCs in polyurethane-type finishing resins. The chemicals that are of concern in this paper are the following: Dipropylene glycol Monomethyl Ether (DPGME), DBE-3 (a mixture of dibasic esters) and Triethylamine (TEA). The test conditions that have been determined to carry out the HS-SPME assay are the following: incubation time (2 hours), extraction temperature and time (40°C; 5 minutes) and the desorption conditions (280°C, 50 seconds).

Ten samples of laboratory scale resins were tested by HS-SPME followed by gas chromatography (GC-MS). DPGME and DBE-3 (a mixture of dimethyl adipate, dimethyl glutarate and dimethyl succinate) have been identified effectively. The compounds are identified by a quantitative method using external calibration curves for the target compounds. The technique is not effective to determine the TEA compound, since the chromatograms shown poor resolution peaks for the standard.

Introduction

Volatile Organic Compounds (VOCs) are hydrocarbons present in gaseous state at room temperature, or which are highly volatile at this temperature. VOCs refers to any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. VOCs play an important role in the environment and human health.[1] The health consequences can vary greatly, since it depends on the nature of the chemical compound, the degree of danger and the period of exposure to it; these consequences can range from the absence of known effects to a degree of severe toxicity.[2] The main concern with this type of compound is that some of them may become carcinogenic, mutagenic and reprotoxic (CMR) substances. In addition, some VOCs may cause annoying odors that, depending on the olfactory capacity of each human being, can cause rejection or mistrust among consumers. The environmental effects caused by VOC emissions are a matter of concern at the atmospheric level, since they destroy the ozone layer and, together with nitrogen oxides and sunlight, are precursors of tropospheric ozone formation and also produce the well-known photochemical smog.[1,3]

With the aim of reducing the adverse effects caused by VOC emissions, the European and Spanish legislation through the Directive 2010/75/EU and the Royal Decree 117/2003 regulates, limits and details a series of provisions for facilities and activities where organic solvents are used in their production processes.[1]

VOCs and SCOVs emissions are controlled by the legislation through the Annex VII of Directive 2010/75/EU, Activity No 13; being the limit from 75 to 150 g of solvent emitted per m^2 of leather product produced. The VOC emission levels to be in conformity with the Best Available Techniques (BAT) for the leather production in Europe are between 10-25 g/m^2 expressed as annual average values.

Organic solvents are used in certain stages of leather manufacturing, such as in post-tanning and especially during the finishing operations. Due to the current legislation, environmental problems, possible health effects and irritating odors that VOC emissions can generate, this sector is implementing improvements in the production system, minimizing or substituting solvent-based chemicals for less harmful products, to obtain a sustainable leather product, and preserving the highest quality. Even with these measures, leather finishing products are applied in concentrated quantities, which implies that VOC emissions can occur. For this reason, it is important to

Corresponding author email: anna.bacardit@udl.cat
Manuscript received February 1, 2021, accepted for publication March 28, 2021.

develop an analytical method to identify the presence of VOCs and Semi-Volatile Organic Compounds (SVOCs) compounds in finishing chemicals to go forward with the identification of critical compounds and to ensure that new polyurethane resins will comply with the expectations.[4]

One of the most widely used techniques for the determination of VOCs and SVOCs is Gas Chromatography coupled to Mass Spectrometry (GC-MS). The combination of high resolution, sensitivity and relatively short analysis time make the technology a routine used in most chemical laboratories.[5,6] Before the chromatographic analysis, the chemical compounds must be isolated and/or extracted from the matrices to be tested, being different techniques for this purpose; such as Liquid-Liquid extraction, Purge and Trap (P&T) or Solid Phase Extraction (SPE). Although some of these methods are useful for VOCs and SVOCs analysis, they have certain drawbacks, such as the sample handling and sample preparation time. Solvents are used in some of these extraction procedures and therefore, it must be managed correctly after the analysis. For this reason, VOC analytical testing techniques have improved and evolved to develop methods in which sample handling is minimal and practically zero solvent consumption.[7,8]

Pawliszyn and his colleagues developed the methodology in the early 1990s as a new method of sampling and sample preparation for further analysis by chromatography, which was later expanded by Zhang and Pawliszyn with the Headspace extraction modality (HS).[9-12] The HS sampling modality is applicable to both solid and liquid samples when the objective is the determination of volatile organic compounds in the sample or when the matrix is complex, since in this modality of extraction the fibber exposure to the sample is made without contact with the sample, thus extending its useful life.[13-15] Since its inception, this technique has been applied in various areas such as the environment, food, aromas and perfumes and also in pharmaceuticals. Among these, approximately 40% focus on applications about the environment and the amount of literature on this topic increases every year.[9]

Experimental

Chemicals and reagents

To assist the leather industry to improve production processes, a water-based synthesis of eleven polyurethane resins for the finishing of leather was developed in a pilot scale reactor. The substitution of organic solvents of great environmental concern by less harmful chemicals is one of the focus of this research. As the newly designed resins have to be analysed to determine their VOCs and SVOCs content, the start-up and performance of a test method to determine those compounds is of a great importance. The resins are identified from NV001 to NV011. NV001 resin is used as a reference for the HS-SPME method optimization.

This study is focused on three chemical compounds used in the synthesis of resins, which are the following: Dipropylene Glycol Monomethyl Ether (DPGME), DBE-3 (mixture of the dibasic esters dimethyl adipate, dimethyl glutarate and dimethyl succinate) and Triethylamine (TEA). It is emphasized that these chemical compounds are not routinely tested in laboratories. For this reason, this research is focussed to develop, optimize and validate a specific method of analysis by using the HS-SPME/GC-MS techniques.

Dipropylene Glycol Monomethyl Ether (DPGME) with a boiling temperature of 190°C and CAS No. 34590-94-8 is a mixture of isomers. The composition of the substance is as follows: 40-50% 1-(2-methoxypropoxy) -2-propanol (CAS No. 13429-07-7), 40-45% 1- (2-methoxy-1-methylethoxy) -2-propanol (CAS No. 20324-32-7), 2-5% 2- (2-methoxypropoxy) - 1-propanol (CAS No. 13588-28-8) and 3-5% 2- (2-methoxy-1-methylethoxy) -1-propanol (CAS No. 55956-21-3). These isomers are not purchased separately, which implies that the standard used in the study is Dipropylene glycol methyl ether, mixture of isomers (97%) (Sigma-Aldrich).

DPGME has low oral toxicity, both dermal and inhalation, and has no carcinogenic, reprotoxic, or mutagenic effects in humans. At the environmental level it is considered an easily biodegradable product in aerobic conditions, but only slightly degradable in anaerobic conditions. This chemical compound is often used in the manufacture of paints, varnishes, inks, and cleaners.[16]

The commercial product DBE-3 with CAS No. 95481-62-2 is a mixture of dibasic esters with a boiling range of 215-225°C, the composition of which is as follows: 89% dimethyl adipate (CAS No. 627-93-0), 10% dimethyl glutarate (CAS No. 1119-40-0) and 1% dimethyl succinate (CAS No. 106-65-0). Commercial standards for each component are purchased separately with a purity of> 99% (Sigma-Aldrich). This solvent is easily biodegradable, environmentally friendly and of low toxicity. DBE-3 can be a good alternative to conventional VOC-emitting solvents, including isophorone, glycol ethers, and glycol ether acetate, ketones with high boiling point, dichloromethane, butyl diglycol, acetone and cyclohexanone. This solvent is usually used in the synthesis of paints, coatings, lubricants and strippers, among other uses.[14,15]

TEA is an aliphatic amine with a boiling point of 90°C, CAS No. 121-44-8. It was purchased as a standard with a purity of ≥ 99% (Sigma-Aldrich). Like other amines, it presents an ammoniacal odour. The vapors given off by this chemical are dangerous to health, and they can irritate the nose, throat and lungs; and therefore, its handling must be carried out carefully. This compound can cause allergies and skin rashes if prolonged exposure occurs, and causes irritation in case of eye contact, being advisable to wear suitable clothing during its handling.[17]

For the extraction of the analytes, a syringe with a fiber packing is used and the selectivity and sensitivity of the extraction method depend on the composition of this fiber. In this work Carboxene / Polydimethylsiloxane SPME Sampling Fiber (CAR-PDMS) 75 µm from Supelco was used. Additionally, 20 mL vials and silicone / PTFE septums of SPME for testing of samples (Thermo-Scientific) and a Magnetic stirrer, stirring and heating bloc (Selecta) were used.

Chromatography

Detection of VOCs and SCOVs was performed by using a Gas Chromatograph (GC) from Agilent Technologies (Agilent 7820A) equipped with a single quadrupole Mass Spectrometry (MS) detector (Agilent 5975MSD). The chromatographic column used is a DB-5MS column (122-5532 Agilent Technologies, 30m length×0.25µm film×0.250 mm diam.)

A manual injection of the SPME fiber was made into the injection port of the chromatograph (Agilent Technologies, 7820A GC system). The carrier gas was helium at a constant flow of 1.2 ml/min. The injector temperature was 280°C; the oven temperature program started at 55°C for 1 minute followed by two ramps. The first ramp was an increase of 6°C/min until reaching 180°C, followed by another increase of 15°C/min until reaching 230°C for 3 minutes. It works with a Split 1:200 and the data acquisition was done in SCAN mode with a m/z range of 30-300. The identification of the compounds was carried out by means of the NIST 14 mass spectral library (version 2.2) followed by the corresponding standards injection.

HS-SPME Method

A diluted sample with ultrapure water of the resin was placed and sealed into a 20ml vial with a Teflon septum. The diluted sample was stirred during a determinate period (incubation time) to achieve the equilibrium conditions. VOCs and SCOVs were transferred to the air phase into the sealed vial, known as Head Space (HS). When the incubation time was finished, the compounds were extracted from the vial using the CAR-PDMS fiber (75 µm) for a certain period (exposition time) and a determinate temperature (extraction temperature). Once this step was completed, the SPME fiber was placed into the GC injection port to desorb the VOCs and SVOC compounds adsorbed by the fiber. The desorption temperature and the desorption time were also established during the method development. After the desorption process, the fiber was conditioned until the next analysis (300°C, 5min.).[15]

Optimizing the HS-SPME/GC-MS test conditions

SPME fiber

After the extraction process, the SPME fiber contained VOC and SVOC compounds. The selectivity and sensitivity of the extraction method depends on its composition. Conventional fibers for SPME consist of a silica fiber wrapped with a sorbent material, such as PDMS (polydimethylosiloxane), PA (polyacrylate), DVB (divinylbenzene), CW (cabowax) and CAR (carboxen) among others. In the last 20 years, these fibers have been improved and commercialized.[11,19]

The solid phase micro extraction (SPME) is a sample preparation technique used for the extraction of VOCs and SVOCs for many applications, coupled with gas chromatography to elute and determine these types of compounds in solid and liquid samples. The main advantages of this technique are speed, high sensitivity; it does not require sample handling or solvent extraction procedures being environmentally friendly extraction technique, speeds up the separation, and increases throughput. In addition, this technique is extremely cost-efficient in comparison to alternate extraction methods.

Previous research from A^3 Leather Innovation Center regarding the applications of the SPME technique for the determination of VOC and SCOV compounds, suggest that the most suitable fiber type is the CAR/PDMS 75 µm.[4] Other previous research work also recommend this type of fiber for VOC extraction.[9,20] The terms of use of the SPME fiber given by the supplier (Sigma-Aldrich) also bring recommendations to choose the fiber depending on the compounds to be identified and quantified. Before the first use of the SPME sampling fiber, it must be conditioned at 300°C during 30 minutes into the GC injector.

Sample stirring

Sample stirring favors the mass transport between the sample and the fiber coating; providing shorter extraction times and greater sensitivity in pre-equilibrium extractions. There are different stirring methods, such as magnetic stirring or vortex stirring; each having advantages and disadvantages. Ultrasound technology is not recommended, as it can heat the sample uncontrollably and damage the sampling fiber. To obtain reproducible results, it is important to maintain the same agitation, method and intensity.[13]

The stirring is finally established at 500 rpm in a stirring and heating unit, which does not imply a large investment.

Sample preparation

The SPME test methodology does not require sample manipulation. During the test condition optimization, the sample provides a too large area in the eluted sample, thus forcing to aqueous dilute the resin samples in ultrapure water of Milli-Q quality to obtain the optimum chromatographic signal. When selecting the appropriate sample volume to introduce into the sealed SPME vial, it must be selected to leave sufficient free space on the top of the sealed vial (Head Space). Therefore, the sample volume must be sufficient to be representative, but not to exceed the headspace of the vial.[13] Sample volumes between 1 and 5 ml were studied. The optimum sample was established at 3 ml, leaving enough space at the top of the vial (Head Space), and providing the optimum chromatographic signal.

Table I

Relation between the incubation time and eluted area for DPGME isomers

Incubation time (min.)	Area DPGME Isomer 1/Tr. 6.5 min	Area DPGME Isomer 2/Tr. 6.9 min
30	65,553,724	60,229,962
60	238,710,132	221,139,978
120	**374,986,795**	**361,222,771**
180	67,968,336	63,434,754

Time exposure

After the equilibrium phase of VOCs and SCOVs between the liquid phase and HS, the SPME fiber was introduced into the space of the sealed vial without contact with the liquid sample. NV001 resin was used to start up the test conditions. As it is shown in table I, the incubation time was determined in 2 hours at room temperature, since the optimum response was observed for the compounds object of concern. The HS-SPME remained at room temperature because the presence of volatile substances towards the Headspace of the vial was observed by means of vapor generation at 23-25°C. Two major peaks are eluted in the chromatogram, which corresponds to the isomers of DPGME. Although these isomers are known from the literature,[22] it is not possible to differentiate one from the other by the GC-MS technique.

As can be seen in the results shown in Table I, the fiber is saturated and produces a logarithmic signal giving a maximum point which in this case is at 120 minutes. From this point on, the signal decreases. Therefore, to optimize the assay, the optimum point must be sought, and in this case the incubation conditions of the sample are set at 120 minutes.

Extraction conditions

The extraction time is one of the most critical parameters in the SPME technique. The determination of the optimal extraction time depends mainly on the objective of the analysis.

If the main objective is to obtain a high productive level of analysis, it is necessary to work in pre-equilibrium conditions, which implies a shorter extraction time. In this case, it is essential to keep the same extraction and stirring times for each sample. If the exposure time varies during sampling, it will imply poor reproducibility. Consequently, it is advisable to use an automated SPME system when working under pre-equilibrium conditions in order to achieve good reproducibility. On the other hand, if the objective of the test is to obtain good sensitivity and reproducibility, it must work under equilibrium conditions Once equilibrium is reached, the amount of the compounds absorbed by the fiber remains constant. This fact implies that extraction can be performed both automatically and manually.[13]

The objective of this experimentation is to develop and validate a method for the determination of VOC and SCOV by HS-SPME, which implies good reproducibility and sensitivity. For this reason, it is preferable to establish the incubation time and afterwards, start to study the extraction time. Three different extraction times were tested, 3, 5 and 10 minutes.

Previous research made by the A^3 Leather Innovation Center of VOC content in leather revealed that the extraction temperature also influences the test. In the analysis of the resins object of concern, temperatures of 40°, 65° and 80°C are investigated.[4]

The optimum extraction time was established in 5 minutes, being the optimum extraction temperature 40°C; as it is shown in Tables II and III. A chromatogram with two major peaks is obtained, which after the analysis of the DPGME standard it is confirmed to correspond to the Dipropylene Glycol Monomethyl Ether isomers.

In Table I the incubation conditions of the samples were set. From the results obtained in Table II, the extraction time conditions are

Table II

Extraction time and eluted area for DPGME isomers

Extraction time (min.)	Area DPGME Isomer 1/Tr. 6.5 min	Area DPGME Isomer 2/Tr. 6.9 min
3	15,916,774	15,636,472
5	**22,455,845**	**21,768,777**
10	20,253,580	20,042,077

Table III

Extraction temperature and eluted area for DPGME isomers

Extraction temperature (°C)	Area DPGME Isomer 1/Tr. 6.5 min	Area DPGME Isomer 2/Tr. 6.9 min
40	**83,582,114**	**73,845,294**
65	12,273,871	12,674,859
80	17,785,430	17,947,846

set. As can be seen in the results of Table II, the maximum signal obtained in area is at 5 minutes. As in incubation conditions, a logarithmic signal is produced with a maximum point, after which the signal loses intensity.

Table III shows the results to set the temperature conditions. As can be seen, the maximum signal obtained is at 40°C, also producing a logarithmic signal.

Therefore, the final conditions that were set to optimize the analysis were 120 minutes of incubation of the sample, 5 minutes of extraction of the sample at 40°C.

Desorption and fiber reconditioning

Once the compounds are absorbed into the SPME fiber, the next step is to desorb those compounds in the gas chromatograph for their elution and determination by GC-MS. Desorption step is made into the injection port of the GC, using a specific liner for SPME methodology. The variables influencing the desorption process are time and temperature. The desorption temperature varies according to the type of sampling fiber used, since it depends on the fiber coating material. According to the manufacturer, the recommended desorption temperature range for CAR / PDMS 75 µm fiber is from 250° to 310°C. In this experimentation, the tested desorption temperatures were the following: 250°, 265° and 280°C. According to the results of Table IV, 280°C was established as the optimal desorption temperature. Once the desorption process is finished, the fiber is kept in the injection port for 10 minutes for conditioning and/or automatic cleaning between samples, without the need to manually enter said temperature, thus saving time by unifying two processes in one.

The tested desorption times were 40, 50 and 60 seconds. Although the initial desorption time was 40 seconds, the resolution observed of both DPGME isomers improves with a desorption time of 50 seconds, as shown in Table V. According to the manufacturer's recommendations, desorption time improves with longer times, a fact also observed in previous studies from the A[3] Leather Innovation Center.[4]

Table IV

Desorption temperature and eluted area for DPGME isomers

Desorption temperature (min.)	Area DPGME Isomer 1/Tr. 6.5 min	Area DPGME Isomer 2/Tr. 6.9 min
250	**220,075,820**	**168,452,741**
265	213,603,258	165,858,258
280	192,478,282	152,641,200

Table V

Desorption time and eluted area for DPGME isomers

Desorption time (seg.)	Area DPGME Isomer 1/Tr. 6.5 min	Area DPGME Isomer 2/Tr. 6.9 min
40	**194,825,462**	144,200,024
50	192,478,282	**152,641,200**
60	189,284,028	142,425,646

Table VI

Optimised conditions for the HS-SPME assay of polyurethane resins

SPME fiber	Units	CAR/PDMS 75µm
Sample volume	ml	3
Incubation time	hour	2
Stirring speed	rpm	500
Extraction temperature	°C	40
Extraction time	min.	5
Desorption temperature	°C	280
Desorption time	seconds	50
Fiber conditioning at 280°C	min.	10

Results

HS-SPME/GC-MS optimized method for VOV and SVOC determination

Once all the variables that influence the determination of VOC and SCOV have been optimized using the HS-SPME extraction methodology, it is concluded that the established test parameters are those indicated in Table VI.

Analytical calibration and quantification

Once the HS-SPME method was established for the extraction of volatile compounds and subsequent identification by GC-MS, all the aqueous-based resins from NV002 to NV011 were tested in duplicate. The identification of the compounds object of concern was primarily made by comparing their mass spectrum with the NIST database of compounds. Next, a verification of the target compounds was made reproducing the test conditions with the standards. Figure 1 shows the chromatogram of the resin NV004.

In Table VII, the two DPGME isomers, dimethyl glutarate and dimethyl adipate were identified.

It was observed that dimethyl succinate did not appear in the chromatograms of the resin samples.

Its exhaustion during the resin synthesis and/or the lower concentration in the commercial products are probably the causes of this phenomenon. On the other hand, just two of the four isomers of the commercial DPGME standard were detected and quantified.

Although triethanolamine is present in all the synthesized resins, a very poor resolution of this compound was observed in the chromatographic results, affecting its quantification. Determination of low-molecular weight amines by gas chromatography implies additional risks due to their high aqueous solubility, volatility, polarity and basic character. As the molecular mass of amine

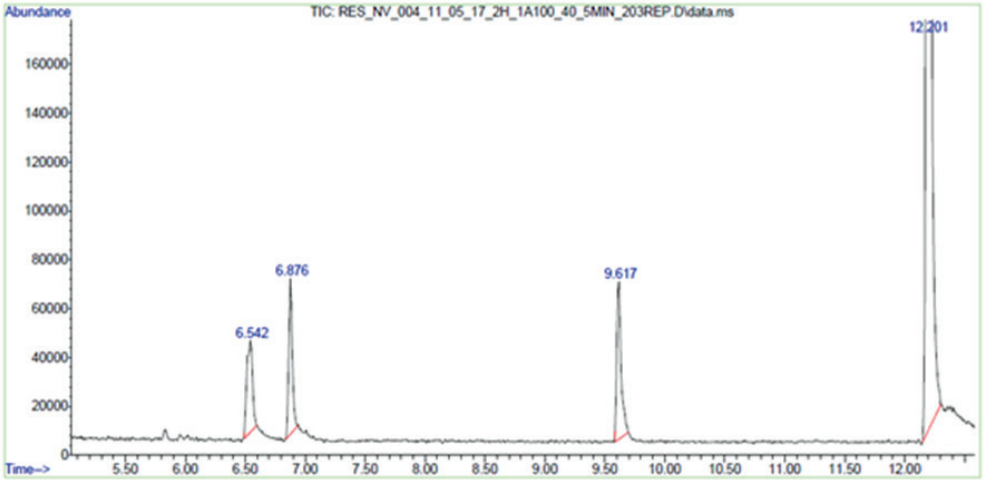

Figure 1. Resin NV004 chromatogram by HS-SPME/GC-MS

Table VII

Identification of VOC compounds from NV004 by HS-SPME/GC-MS

Peak	Ret. time (min.)	Area	% Area from total eluted	NIST identification	CAS Number
1	6.542	1,186,411	4.4	DPGME	Isomer 1
2	6.876	1,266,801	4.7	DPGME	Isomer 2
3	9.617	1,488,702	5.5	Dimethyl glutarate	1119-40-0
4	12.201	23,272,558	85.5	Dimethyl adipate	627-93-0

Table VIII

Calibration curves by external standard from the four target compounds

Compound	Concentration (mg/L)	R^2	Linear regression (Y= aX + b)
Dimethyl adipate	26.2 – 62.1 – 124.1 – 310.4 – 697.0 – 1241.4	0.9987	Y= 35265X – 793893
Dimethyl glutarate	9.2 – 26.6 – 66.6 – 103.2	0.9993	Y= 33068X + 64768
DPGME- Isomer 1	101.7 – 203.4 – 418.8 – 524.8 – 839.6 – 1049.5	0.9984	$Y= 256321X – 2.10^7$
DPGME- Isomer 2	101.7 – 203.4 – 418.8 – 524.8 – 839.6 – 1049.5	0.9992	$Y= 193423X – 1.10^7$

decreases, the relative effect of the amine group increases, which results in stronger sorption to polar stationary phases. In addition, amines tend to decompose in the GC column, and to sorb to exposed parts of the equipment and instrumentation. In general, chromatographic separation of aliphatic amines is much more difficult than separation of aromatic amines.[21]

The quantification of VOC and SCOV was carried out using an external standard method. Different concentrations of the standards were analysed applying the optimized test conditions. Table VIII specifies the linear regression resulting from each standard and its concentrations. The quantification values of the target compounds are indicated in Table IX.

LQ corresponds to the Limit of Quantitation according to the calibration standards curve of the target compounds.

LD corresponds to the detection limit, as no response had been detected from the target compounds.

Table IX

Concentration of the target compounds in the resin samples by HS-SPME/GC-MS.

Resin samples	g/l DPGME (Isomer 1)	RSD (%)	g/l DPGME (Isomer 2)	RSD (%)	g/l Dimethyl adipate	RSD (%)	g/l Dimethyl glutarate	RSD (%)
NV002	15.7	9.8	15.0	9.2	LD < 0.02	-	LD < 0.01	-
NV003	LQ = 10	-	LQ = 10	-	35.7	9.1	1.0	8.9
NV004	LQ = 10	-	LQ = 10	-	68.2	8.6	4.3	7.2
NV005	LD < 0.1	-	LD < 0.1	-	86.2	8.8	6.9	7.9
NV006	LD < 0.1	-	LD < 0.1	-	LD < 0.02	-	LD < 0.01	-
NV007	LQ = 10	-	LQ = 10	--	LD < 0.02	-	LD < 0.01	-
NV008	LD < 0.1	-	LD < 0.1	-	LQ = 3	-	LD < 0.01	-
NV009	LD < 0.1	-	LD < 0.1	-	0.1	9.0	LD < 0.01	-
NV010	44.1	9.7	42.2	8.4	ND	-	LD < 0.01	-
NV011	45.2	9.3	44.7	8.1	ND	-	LD < 0.01	-

Conclusions

The method for the extraction of VOC and SCOV prior to detection by GC-MS in new polyurethane water-based resins for leather finishing using the HS-SPME methodology has been optimized and validated for the determination of the target compounds: Dipropylenglycol monomethyl eter (DPGME) and DBE-3 in the basis of Dimethyl glutarate and Dimethyl adipate. The test method is not viable for TEA, since the peak resolution is poor and with low sensitivity. Next research tasks are focused to determine TEA by TD-GC-MSD.

Acknowledgements

This study has been carried out thanks to the Ministry of Economy and Competitiveness - Collaboration Challenges (MINECO) (Spain) through the NoVocs project "Innovative sustainable leather article free of Volatile Organic Compounds (VOC) and crosslinking agents" RTC-2016-4575-5 and the research entity A3 Leather Innovation Center (University of Lleida) (Catalonia).

References

1. MITECO; Ministerio para la transición ecológica., De compuestos orgánicos volátiles, 2019. [Online]. Available: https://www.miteco.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/emisiones/act-emis/compuestos_organicos_volatiles.aspx#. [Accessed: 18-Mar-2019].
2. RISTOX, "ISTAS: Compuestos orgánicos volátiles (COV)," 2010. [Online]. Available: http://risctox.istas.net/index.asp?idpagina=621. [Accessed: 18-Mar-2019].
3. E. Chorier, N. Blanc, J. C. Cannot, and A. Berthod, Headspace GC-MS for the determination of halogenated hydrocarbons, ethers and aromatic volatiles in fabric and leather, *JALCA* vol. **109**(10), pp. 322–329, 2014.
4. R. M. Cuadros Domènech, Contribució a la caracterització i disminució de l'ús de compostos orgànics volàtils en el sector adober, Universitat Politècnica de Catalunya, 2013.
5. J. W. Allwood and R. Goodacre, An introduction to liquid chromatography-mass spectrometry instrumentation applied in plant metabolomic analyses, *Phytochem. Anal.*, **21**(1), pp. 33–47, Jan. 2010.
6. M. C. Gutiérrez and M. Droguet, La Cromatografía de Gases y la Espectrometría de Masas: Identificación de compuestos causantes del mal olor, *Univ. Politécnica Catalunya*, vol. 122, pp. 35–41, 2002.
7. R. Cuadros, M. Alves, L. Olle, A. Bacardit, and J. Font, Characterization of the volatile organic compounds by HS-SPME-CG-MS in the leather sector., *JALCA* **108**(11), pp. 420–427, 2013.
8. H. Piri-Moghadam, F. Ahmadi, and J. Pawliszyn, A critical review of solid phase microextraction for analysis of water samples, *TrAC - Trends Anal. Chem.*, **85**, pp. 133–143, 2016.
9. G. Ouyang and J. Pawliszyn, SPME in environmental analysis, *Anal. Bioanal. Chem.*, **386**(4), pp. 1059–1073, Oct. 2006.
10. M. H. Tunick, S. K. Iandola, and D. L. Van Hekken, Comparison of SPME Methods for Determining Volatile Compounds in Milk, Cheese, and Whey Powder., *Foods (Basel, Switzerland)*, **2**(4), pp. 534–543, Nov. 2013.
11. H. Lan *et al.*, Modified zeolitic imidazolate framework-8 as solid-phase microextraction Arrow coating for sampling of amines in wastewater and food samples followed by gas chromatography-mass spectrometry, *J. Chromatogr. A*, **1486,** pp. 76–85, Feb. 2017.
12. A. Marsol-Vall, J. Eras, M. Balcells, B. Sgorbini, C. Cagliero, and C. Bicchi, Volatile composition and enantioselective analysis of chiral terpenoids of nine fruit and vegetable fibres resulting from juice industry by-products, *Hindawi J. Chem.*, **2017**, pp. 1–11, 2017.
13. MERCK, SPME for GC analysis, *Supelco*. pp. 1–28, 2018.
14. M. R. Reyes Ferrera, Determinació de fungicides en pells i en banys de procés del sector adober, Universitat Politècnica de Catalunya, 2015.
15. V. López-Grimau and M. C. Gutiérrez, Detección por GC-MS de Trimetilamina como causa del mal olor, *Univ. Politécnica Catalunya*, **128**, pp. 39–44, 2005.
16. OECD, Introduction Dipropylene Glycol Methyl Ether CAS N ° : 34590-94-8 (Isomers : 13429-07-7 , 20324-32-7 ; 13588-28-8 and 55956-21-3). UNEP PUBLICAIONS, pp. 1–99, 2001.
17. Kumbra Trading CO. LTD, What is Kumra making with it?, 2004. [Online]. Available: http://kumra.co.kr/3_produ02_4.html. [Accessed: 17-Feb-2020].
18. The Dow Chemical Company, Product Safety Assessment: ESTASOL™ Oxygenated Solvent Manufacture of Product, 2009. [Online]. Available: http://www.multisolgroup.com/Estasol-. [Accessed: 17-Feb-2020].
19. J. Torrens, M. Riu-Aumatell, E. López-Tamames, and S. Buxaderas, Volatile compounds of red and white wines by headspace-solid-phase microextraction using different fibers., *J. Chromatogr. Sci.*, **42**(6), pp. 310–6, Jul. 2004.
20. V. Gyorgy, Vas; Karoly, Solid-phase microextraction: a powerful sample preparation tool prior to mass spectrometric analysis, *J. MASS Spectrom. J. Mass Spectrom*, **39**, pp. 233–254, 2004.
21. J. Namieśnik, A. Jastrzębska, and B. Zygmunt, Determination of volatile aliphatic amines in air by solid-phase microextraction coupled with gas chromatography with flame ionization detection, *J. Chromatogr. A*, **1016**(1), pp. 1–9, Oct. 2003.
22. E. Lemazurier, A. Lecomte, F. Robidel, F. Bois, Propylene glycol monomethyl ether. A three-generation study of isomer B effects on reproductive and developmental parameters in rats. Toxicology and industrial health. **21**, 33-40. 10.1191/0748233705th213oa. 2005