



3.5. Overview of other potential methods for the study of plastics degradation

As it was already pointed out any technique capable of identification of plastic may be also of used for the description of degradation progress over a large time interval. There are some of the possible candidates which were used for identification of plastics and are also referred to in the Chapter 1.

3.5.1. Determination of the molar mass

The molar mass (degree of polymerisation) is one of the fundamental characteristics of the plastic determining its properties. Its changes may be followed e.g. by viscometry which requires that the polymer is dissolved.

3.5.2. Non-invasive techniques

There is a big challenge to enlarge the applicability of some methods by non-invasive examination of the extent of degradation. One of the ambitions is to develop nondestructive analytical techniques suitable not only for identifying plastics but also for the estimation of the degradation extent. The most important appears SPME-GCMS detection of volatile organic compounds (VOCs) in the vicinity of the plastics exposed to normal conditions.





Polymer families	Styrenic	Polyolefins	Acrylics	Polyamide	Poly(phenylene oxide)	Polyurethanes	Cellulose esters
Types of commercial plastic	Polystyrene Acrylonitrile-butadiene-styrene	Polyethylene Polypropylene Polybutylene	Homo- and co-polymeric poly(methyl methacrylate)	Nylon type 6	Poly(2,6-dimethyl-1,4-phenylene oxide)	Polyester-based and polyether-based polyurethanes	Celluloids

Figure 45. The list of polymers for VOC examination

3.5.2.1. SPME-GCMS analyses of volatile organic compounds (VOCs)

In recent years, it has been shown that SPME-GCMS (solid phase micro extraction-gas chromatography coupled with mass spectrometry) is a sensitive, reliable and fast technique for collecting a large range of volatile organic compounds from a wide variety of matrices (Pawliszyn 1999). The technique has been successfully applied for measuring indoor air pollutants as well as for screening odoriferous compounds and for controlling emissions from some synthetic polymers (Albertsson *et al.* 2006; Espert *et al.* 2005; Gröning and Hakkarainen 2002; Hakkarainen 2008; Hakkarainen *et al.* 2003; Hanh *et al.* 2010; Thiébaud *et al.* 2007). Our aim was to assess the potential of SPME-GCMS as in-situ non invasive analytical tool for identifying plastics as well as their degradation based on their VOC emissions. Thirteen commercially produced plastics from ResinKit™ which are also widely present in museum collections were selected and tested. A brief survey of the main emission profiles obtained is presented and the use of SPME-GCMS for identifying volatile markers, additives, monomers and odoriferous compounds as well as compounds possibly dangerous to health is evaluated and discussed. They belong to seven main polymer families namely styrenics, polyolefins, acrylics, polyamides, poly(phenylene oxide), polyurethanes and cellulose ester-based polymers (Figure 45). Among them, the polyurethane samples chosen were flexible foams in which the isocyanate hard domain is made up of aromatic toluene diisocyanate and the polyol soft domains are based on poly(propylene oxide) glycol (Sample 1) or adipate ester (Sample 2). Celluloid samples are made up of cellulose nitrate plasticised with camphor or triphenyl phosphate. Polystyrene and acrylonitrile-butadiene-styrene are the most common polymers of the styrenic family.

3.5.2.2. VOCs from the reference set of plastics

From all the thirteen samples, well-resolved chromatographic fingerprints of VOCs emitted were obtained. It may be of interest





Compound	Retention time (min)	Molar mass	Main mass fragments Base peak noted in orange
ADDITIVES			
INHIBITORS AND ANTIOXIDANTS			
Glycerol diacetate	28.7	176	43,103,145
2,4-di-tert-butylphenol	32.9	206	191,206
2,5-di-tert-pentylbenzoquinone	36.5	248	177,191,233,248
Benzoate, 2-ethylhexyl-	37.7	234	70,105,112
Bisphenol A	46.9	228	119,213,228
PLASTICISERS			
2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB™)	34.9	286	43,71,243
Phthalate, diethyl-	34.9	222	149,177
Phthalate, diisobutyl-	40.8	278	149,197,223
Phthalate, dibutyl-	42.7	278	149,197,223
OTHER COMPOUNDS			
<i>n</i> -Acetic acid	2.4	60	43,45,60

Figure 46. “Non-specific” volatile organic compounds from the set of plastics

that more than 200 different were detected and identified. Two categories of VOCs can be distinguished: the “non-specific” (Figure 46) and the “specific” ones (Figure 47). “Non-specific” VOCs are either compounds detected from most plastics and as such are considered as ubiquitous, or compounds detected only once or other compounds the formation of which cannot be clearly explained. The “specific” VOCs are representative of the polymer nature and are mainly monomer residues from the synthesis.

“Non-specific” VOCs can be divided in two categories namely “additives” and “other compounds”. Additives are inhibitors, antioxidants and plasticisers. Three compounds considered as inhibitors and antioxidants that are well-known as toxic plastic additives were identified predominantly. They are: 2,4-di-tert-butylphenol, 2,5-di-tert-pentylbenzoquinone and bisphenol A. Glycerol diacetate and benzoate 2-ethylhexyl- were also identified. They are food additive and flavouring substance, respectively. Four predominant plasticisers were also detected. Among them, the 2,2,4-trimethyl-1,3-pentanediol diisobutyrate is largely used plasticiser in the manufacturing of flexible plastic and especially for soft surface products. Previous indoor air case studies have indicated that it could contribute to odour and hardly to sensory irritation. Phthalate esters are produced for various industrial uses and used primarily





Compound	Retention time (min)	Molar mass	Main mass fragments Base peak noted in orange	Relative percentage
STYRENICS				
POLYSTYRENE				
Toluene	4.7	92	91,92	1.1
Benzene, ethyl-	9.1	106	91,106	27.7
Xylene (para)	9.8	106	91,106	3.0
Styrene	11.5	104	78,103,104	100.0
Benzene, isopropyl-	13.4	120	105,120	1.5
Styrene, methyl-	14.6	118	91,117,118	0.4
Benzene, <i>n</i> -propyl-	15.0	120	91,120	1.4
Benzaldehyde	15.5	106	77,105,106	5.4
Phenol	16.7	94	66,94	1.2
Benzeneacetaldehyde	19.2	120	91,120	1.6
Acetophenone	20.0	120	77,105,120	1.5
Hexanoic acid, 2-ethyl-	22.3	144	73,88,101,116	0.7
Propane, 1,3-diphenyl-	36.4	196	92,105,196	0.2
Cyclobutane, 1,2-diphenyl- (isomers)	38.6	208	78,104,208	1.8
ACRYLONITRILE-BUTADIENE-STYRENE				
Benzene, ethyl-	9.1	106	91,106	9.2
Styrene	11.5	104	78,103,104	6.0
Phenol	16.7	94	66,94	100.0
Acetophenone	20.0	120	77,105,120	5.1
Hexanoic acid, 2-ethyl-	22.3	144	73,88,101,116	8.9
Butyldiglycol	24.1	162	45,57,87,132	4.1
POLYOLEFINS				
LOW DENSITY POLYETHYLENE				
<i>n</i> -Undecane	21.4	156	57,71,85	12.1
<i>n</i> -Dodecane	24.7	170	57,71,85	31.4
Dodecane, 2-methyl-	26.3	184	57,71,85,141	2.6
Dodecane, 3-methyl-	26.7	184	57,71,85,155	2.8
<i>n</i> -Tridecane	27.6	184	57,71,85	29.1
Cyclohexane, <i>n</i> -heptyl-	28.8	182	82,83,182	2.7
Tridecane, 4-methyl-	29.2	198	57,71,85,154	4.6
Tridecane, 2-methyl-	29.4	198	57,71,85,154	7.2
Tridecane, 3-methyl-	29.5	198	57,71,85,168	7.2
<i>n</i> -Tetradecane	30.3	198	57,71,85	100.0
Tetradecane, 5-methyl-	31.6	212	43,57,85,154	3.4
Tetradecane, 4-methyl-	31.8	212	57,71,85,168,169	5.7
Tetradecane, 2-methyl-	32.1	212	57,71,85,168,169	9.5
<i>n</i> -Pentadecane	32.8	212	57,71,85	88.4
Tetradecane, 3-methyl-	32.9	212	57,71,85,182,183	7.6
Pentadecane, 6-methyl-	33.9	226	57,71,85,154	1.9
Pentadecane, 5-methyl-	34.0	226	43,57,85,168	2.9
Cyclohexane, <i>n</i> -nonyl-	34.1	210	82,83,210	2.7
Pentadecane, 2-methyl-	34.3	226	57,71,85,182,183	4.6
Pentadecane, 3-methyl-	34.5	226	57,71,85,197	2.8
<i>n</i> -Hexadecane	35.2	226	57,71,85	29.8
<i>n</i> -Heptadecane	37.5	240	57,71,85	6.8





POLYPROPYLENE				
<i>n</i> -Undecane	21.4	156	57,71,85	60.9
<i>n</i> -Dodecane	24.7	170	57,71,85	46.2
Undecane, 2,6-dimethyl-	25.0	184	57,71,98,113	9.7
<i>n</i> -Tridecane	27.6	184	57,71,85	30.5
Tridecane, 2-methyl-	29.4	198	57,71,85,154	9.7
Tridecane, 3-methyl-	29.5	198	57,71,85,168	10.4
<i>n</i> -Tetradecane	30.3	198	57,71,85	100.0
Tetradecane, 4-methyl-	31.8	212	57,71,85,168,169	10.0
Tetradecane, 2-methyl-	32.1	212	57,71,85,168,169	13.4
<i>n</i> -Pentadecane	32.8	212	57,71,85	96.7
Tetradecane, 3-methyl-	32.9	212	57,71,85,182,183	13.9
Pentadecane, 2-methyl-	34.3	226	57,71,85,182,183	21.0
<i>n</i> -Hexadecane	35.2	226	57,71,85	28.6
<i>n</i> -Heptadecane	37.5	240	57,71,85	5.3
POLYBUTYLENE				
<i>n</i> -Tridecane	27.6	184	57,71,85	13.4
Cyclohexane, <i>n</i> -heptyl-	28.8	182	82,83,182	4.0
Tridecane, 4-methyl-	29.2	198	57,71,85,154	5.0
Tridecane, 2-methyl-	29.4	198	57,71,85,154	7.0
Tridecane, 3-methyl-	29.5	198	57,71,85,168	6.6
<i>n</i> -Tetradecane	30.3	198	57,71,85	63.4
Tetradecane, 5-methyl-	31.6	212	43,57,85,154	3.9
Tetradecane, 4-methyl-	31.8	212	57,71,85,168,169	6.0
Tetradecane, 2-methyl-	32.1	212	57,71,85,168,169	10.4
<i>n</i> -Pentadecane	32.8	212	57,71,85	48.1
Tetradecane, 3-methyl-	32.9	212	57,71,85,182,183	9.9
Cyclohexane, <i>n</i> -nonyl-	34.1	210	82,83,210	2.5
Pentadecane, 2-methyl-	34.3	226	57,71,85,182,183	4.0
Pentadecane, 3-methyl-	34.5	226	57,71,85,197	2.1
<i>n</i> -Hexadecane	35.2	226	57,71,85	8.1
<i>n</i> -Heptadecane	37.5	240	57,71,85	2.5
ACRYLICS				
HOMO-POLY(METHYL METHACRYLATE)				
Methacrylate, methyl-	3.4	100	41,69,100	100.0
CO-POLY(METHYL METHACRYLATE)				
Acrylate, ethyl-	3.1	100	55,99	27.3
Methacrylate, methyl-	3.4	100	41,69,100	100.0
POLYAMIDE				
NYLON TYPE 6				
Caprolactame	26.8	113	30,55,84,113	100.0
POLYPHENYLENE OXIDE				
POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)				
Styrene	11.4	104	78,103,104	13.6
Phenol	16.7	94	66,94	100.0
Benzoquinone, 2,5- or 2,6-dimethyl- (isomers)	21.7	136	39,68,79,108,136	42.8
Hydroquinone, 2,5- or 2,6-dimethyl- (isomers)	30.4	138	95,123,138	5.3
Cyclobutane, 1,2-diphenyl- (most probable isomer)	38.6	208	78,104,208	2.6
POLYURETHANES				
POLYESTER-BASED POLYURETHANE				
Diethylene glycol	18.0	106	45,75	variable





POLYETHER-BASED POLYURETHANE

Glycol derivatives (e.g. ethylene, propylene, dipropylene, tetrapropylene glycol)	-	62,76,134,250	59,87,101,103	variable
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Cellulose ester-based polymers

CELLULOIDS

Camphor isomer	21.5	152	41,95,108,137,152	50.1
Camphor isomer	23.4	152	81,95,108,152	100.0
Isoborneol isomer	23.5	152	41,67,95,110,139,152	0.3
Borneol isomer	23.8	152	41,67,95,110,139,152	0.3
Camphor isomer	24.5	152	41,95,108,137,152	54.0

Figure 47. “Specific” volatile organic compounds from the set of plastics

as plasticisers in plastics. The release of phthalates from artefacts into the atmosphere can be linked to their migrations through polymeric materials followed by their evaporations from the plastic surface. In recent years, considerable attention has been paid to human exposure to phthalates because they are suspected to cause various health injuries. With environmental purposes, several SPME methods were successfully developed for extraction of phthalates from various matrices and recently from water samples including bottled mineral waters (Cao 2008; Luks-Betlej *et al.* 2001). In the present research, others phthalates widely used were not detected but the extraction method applied was not optimized for trapping the largest range of phthalate esters. Among the “other compounds” category, five linear acids (*n*-C1 and *n*-C6 to *n*-C9) which are more or less ubiquitous acids were also detected. They have various chemical origins and cannot be thus considered as specific compounds. 2-ethyl-1-hexanol was also identified. It is one of the most important alcohols used for various chemical syntheses. It is also generally considered to be a degradation product of di(2-ethylhexyl) phthalate (DEHP), the largest phthalate ester used as a general purpose plasticiser.

2-ethyl-1-hexanol has often been detected in plastic emissions and mainly from poly(vinyl chloride) based materials. Indoor air complaints (unpleasant odour and/or irritation symptoms) have been correlated with its presence (Järnström *et al.* 2008).

Concerning styrenic plastics, in agreement with earlier publications on the volatiles obtained for polystyrene and acrylonitrile-butadiene-styrene, styrene monomer is present in the chromatograms of the two polymers (Vilaplana 2010). Traces of three oligomers of styrene namely 1,3-diphenylpropane and (trans/cis) isomers of 1,2-diphenylcyclobutane were also detected for polystyrene. These dimers are formed through side reaction during processing of polystyrene. The lack of such dimers in the emission of the acrylonitrile-butadiene-styrene sample can be easily explained by the lower initial abundance of polystyrene in this copolymer.





Ethylbenzene is the second and third most abundant specific compound emitted by polystyrene and acrylonitrile-butadiene-styrene, respectively. It is known to affect nerves' system after a long time exposition. Methylstyrene can also be considered as specific VOC of styrenic polymers. The presence of benzaldehyde, phenol and acetophenone is due to oxidized fragments of styrenic polymers (Vilaplana 2010). It should be underlined that the specific volatile markers like styrene and ethylbenzene allow distinguishing styrenic family from the other tested families, although it does not allowed going further in the polymer identification.

For polyolefins (low density polyethylene, polypropylene and polybutylene), the most abundant compounds released were linear and branched alkanes. Finding this range of alkanes as well as the predominance of tetradecane and pentadecane is most probably due to their high affinity with the coating of the fibre. Volatile signatures from polyolefins are typically series of linear and branched alkanes, which, however, do not allow discriminating between the three tested polymers but allow distinguishing polyolefins from the other plastics.

Some specific and volatile monomers were also detected on the SPME extracts of acrylic, polyamide and poly(phenylene oxide) samples. They are methylmethacrylate and ethylacrylate for acrylics, caprolactame for polyamide 6, and isomers of dimethylbenzoquinone and phenol for poly(phenylene oxide). These compounds are marker monomers and their occurrence permit to identify unambiguously the nature of their polymeric matrix.

As it was already pointed out the chromatogram of the SPME extract of polyether- and polyester-based polyurethane samples revealed the presence of glycol derivatives and diethylene glycol, respectively which can be considered as volatile markers for polyurethanes (Lattuati-Derieux *et al.* 2011). As expected camphor can be considered as a marker for celluloid used as a plasticiser, the camphor continuously diffuses through the sample matrix.

3.5.2.3. FTIR and NIR spectroscopy

Using a portable unit and a database of reflectance spectra that are signatures of various plastics, researchers could swoop into a museum and efficiently identify the composition of artefacts within a relatively short time and trace the changes, if there are any, in dependence on time and/or conditions of expositions. Again the well advanced degradation process is needed to trace some differences.

Agnès Lattuati-Derrieux

