Analytical pyrolysis of poly(dimethylsiloxane) and poly(oxyethylene) siloxane copolymers. Application to the analysis of sewage sludges

Analytical pyrolysis of poly(dimethylsiloxane) and poly(oxyethylene) siloxane copolymers. Application to the analysis of sewage sludges

Irene Coralli[1], Alessandro G. Rombolà[1], Cristian Torri[2], Daniele Fabbri[1]*

1. *Department of Chemistry "Giacomo Ciamician" c/o C.I.R.I. MAM Tecnopolo di Rimini, University of Bologna, via Dario Campana 71, 47192 Rimini (Italy).*
2. *Department of Chemistry "Giacomo Ciamician" and C.I.R.I. FRAME, University of Bologna, via Sant'Alberto 163, 48123 Ravenna (Italy).*

(*) Corresponding author: dani.fabbri@unibo.it

Abstract

Dimethicone (poly(dimethylsiloxane), PDMS) and its copolymers bearing a poly(ethylene glycol) (PEG) side chain (PEG-12 dimethicone and PEG-8 dimethicone) are utilised as ingredients in personal care products. These materials along with bis-PEG-18 methyl ether dimethyl silane were analysed by Py-GC-MS. The pyrolysates of dimethicone was dominated by cyclic dimethyl siloxanes from D_3 to over D_{10}. Besides D_n, the pyrolysates of PEG-dimethicone were featured by the presence of linear dimethyl siloxanes L_n. Hydroxylated siloxanes were also tentatively identified. Pyrograms were also characterised by PEG oligomers with different terminal groups (hydroxyl, ethyl, ethenyl). The molecular structure of pyrolysis products from the combined structural units of PDMS and PEG could not be assigned. Internal standard calibration protocols using pyrolysis products of PEG-12 dimethicone (L_6, L_8, L_9, and triethyleneglycol monoethyl ether) exhibited satisfactory linearity ($R^2 >$ 0.992) in the 0.75-58 µg range and repeatability (RSD < 15 %). Three samples of dried sewage sludge from a municipal water treatment plant were extracted with tetrahydrofuran and the extracts analysed by Py-GC-MS. The pyrograms were characterised by intense signals due to the lipid matrix (hydrocarbons, fatty acids, steranes, sterenes, sterols). D_n and L_n were identified indicative for the presence of siloxanes at levels around 60-290 µg g_{dw}^{-1}, while pyrolytic markers of PEG were not revealed. The recovery of PEG-12 dimethicone (17 µg) in spiked sample was 76 %. Galaxolide, galaxolide lactone and triclosan were identified in the pyrograms. The results of this study evidenced the potential of Py-GC-MS as a screening tool for the determination of cosmetic ingredients in sewage sludge.

1. Introduction

Polysiloxanes are inorganic polymers consisting of a backbone of alternating silicon and oxygen atoms, although the term silicones is often used to designate polysiloxanes with predominant

dimethylsiloxane units. Silicones are uniquely man-made materials that depending on their molecular weight and substituents can appear in different forms and properties. Therefore, ~~which make them useful~~ they have found applications in~~to~~ a variety of ~~applications in key~~ sectors such as agriculture, transportation, construction materials, electronics, energy, healthcare, industrial processes, personal care products and so forth [1–3]. The worldwide production of silicones is several million tons per year; the personal care production presented the third-largest application (industrial processes 35 %, construction materials 26 % and personal care products 17 %) [3]. Geographically, the largest silicon market is Europe and the categories products are toiletries, skin care, hair care, fragrances and make-up [3]. The predominant silicone involved in personal care products is poly(dimethylsiloxane) (PDMS), commercially known as dimethicone according to the International Nomenclature of Cosmetic Ingredients (INCI). Besides the homopolymer PDMS, copolymers bearing poly(oxyalkylated) substituents, especially poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) derivatives are widely used in personal care products [4]. They were originally called dimethicone copolyols and the name has been commercially replaced by PEG (or PPG) dimethicone and bis-PEG (or PPG) dimethicone [5]. Depending on the location of the poly(oxyalkylated) substituents, they are classified in three primary configurations: end-capped polysiloxanes, alkoxy-polysiloxane/polysiloxane copolymers and combinations of the latter [6].

In this study, attention was payed to PEG-dimethicones because these copolymers are widely used in pharmaceutical and personal care products [2], principally as emulsifiers [4] thanks to the presence of the water-soluble group (PEG) that makes dimethicones surface active and water-soluble, and because of their low toxicity [7]. Given their large use, it is expected that these products could enter wastewater treatment plants (WWTP). Thus, the knowledge on the occurrence of these polymers in treated wastewaters and sewage sludge is important in order to identify the existence of potential source of contamination in the environment.

As other water soluble or liquid polymers, PEG-dimethicones have not attracted the same attention of water insoluble solid polymers, such as microplastics, as potential environmental contaminants. However, water soluble polymers are produced in large quantity and could reach the environment when they are not efficiently removed by degradation or sorption in WWTP [8]. Moreover, some water-soluble polymers are persistent and should not be ignored just because they do not fall within the category of microplastics [9]. The analytical determination of trace concentrations of polymers in a complex heterogeneous matrix is challenging and requires selective and sensitive techniques as those based on mass spectrometry. In a proof of principle concept, Huppertsberg et al. [8] have identified PEG in wastewater effluents by mass spectrometry with in-source fragmentation technique that convert PEG into distinctive fragment ions ($C_4H_9O_2^+$, $C_6H_{13}O_3^+$, $C_8H_{17}O_4^+$ and $C_{10}H_{21}O_5^+$).

Analytical pyrolysis (Py) combined with gas chromatography-mass spectrometry (GC-MS) has demonstrated its validity for the determination of microplastics in various matrices [10–12]. Instead, the potential of Py-GC-MS to the analysis of liquid or water-soluble polymers in environmental samples has not been deeply investigated [13].

A fundamental step in developing new analytical methods by Py-GC-MS is the knowledge of the thermal behaviour of the polymers under investigation. Several articles reported on the analysis of PDMS [14–17] and PEG [18,19] by Py-GC-MS, but to the best of our knowledge no articles have been published dealing with Py-GC-MS of their copolymers (virtually between dimethylsiloxane and methylsiloxane bearing a poly(ethylene glycol) side-chain).

The main purposes of this study were (1) to gather information on the molecular composition of pyrolysates of dimethicone and PEG-dimethicones, (2) evaluate the potential of Py-GC-MS for their quali-quantitative analysis in complex organic matrices such as sewage sludge.

2. Experimental

2.1 Materials

Polydimethylsiloxanes from Dow Corning were kindly provided by Prof. Luca Valgimigli, University of Bologna. Namely, (INCI name (commercial name)): dimethicone (ACESIL 350), PEG-12 dimethicone (XIAMETER® OFX-0193 Fluid), PEG-8 dimethicone (FANCORSIL® LIM-1), and and bis-PEG-18 methyl ether dimethyl silane (DOWSIL™ 2501 Cosmetic Wax). Dimethicone and copolyols were dissolved in tetrahydrofuran (THF, Sigma Aldrich) to prepare calibration solutions with final concentrations in the 0.01-60 mg mL^{-1} range.

Tetrakis(trimethylsiloxy)silane (M_4Q, trisiloxane, 1,1,1,5,5,5-hexamethyl-3,3-bis[(trimethylsilyl)oxy]-, Sigma Aldrich) was employed as internal standard (i.s.); a solution of 100 mg L^{-1} (corresponding to 0.112 µg mg^{-1}) of M_4Q was prepared in THF. The notation used for methylsiloxanes is illustrated in figure 1, is M: $(CH_3)_3SiO_{1/2}$, D: $(CH_3)_2SiO_{2/2}$, T: $CH_3SiO_{3/2}$, Q: $SiO_{4/2}$; cyclic methylsiloxanes are termed D_n (n is the number of silicon atoms), siloxanol of D_5 is termed D_4D^{OH}; linear methylsiloxanes are indicated $MD_{n-2}M$ or more shortly L_n; a superscript to the right of a symbol denotes a group that replaced a methyl, thus siloxanol of D_5 is termed D_4D^{OH} [2]. Standard solutions of L_{2-5} and D_{3-6} (Sigma Aldrich) werewas prepared in THF at concentrations of 1 mg mL^{-1} .

Sewage sludge samples from the municipal WWTP of a local city were sampled in different steps of the depuration process: oxidized sludge (pre-treatment step), thick (primary settling), dewatered (biological thick sludge dewatered at the WWTP by centrifuges).

3

2.2 Sample preparation

Sludge samples were dried in an oven at 105 °C. After drying the quantity of solid matter originally present was calculated to be 1.0, 3.5 and 22.8 % for oxidized, thick and dewatered sludge, respectively. About 1 g, exactly weighed, of dried sewage sludge sample was extracted with 25 mL THF for 2 hours under reflux. THF is a good solvent for the extraction of PDMS [20]; preliminary tests showed that PEG-dimethicones were readily dissolved in THF. After solvent extraction, the mixture was centrifuged at 5000 rpm for 5 min, the supernatant was withdrawn and concentrated by rotary evaporation, the resulting solution was transferred into a 1.5 mL glass vial and concentrated to 0.5 mL by a gentle nitrogen stream. The vials were capped with PTFE cap composed of a central silicon septum protected internally by an aluminium foil and stored at -20 °C prior to Py-GC-MS analyses.

2.3. Py-GC-MS

Pyrolysis experiments were performed using a multi-shot pyrolyzer (EGA/PY-3030D Frontier Lab) interfaced to a GC-MS system (7890B and 5977B Agilent Technologies). For each experiment 5 µL of THF extracts and 5 µL, exactly weighed (± 0.01 mg), of calibration solution were injected inside a cup which free-fell into the pyrolyser furnace. The pyrolysis chamber interface temperature was set at 300 °C. Pyrolysis experiments were conducted ~~for 60 s~~ at 500 °C (60 s), a temperature which is higher than the maximum evolution rate of volatiles from PDMS [21] and PEG [22]. The pyrolysates were instantly introduced into the GC column fused silica capillary column (HP-5MS, stationary phase 5%-phenyl, 95%-methylpolysiloxane 30 m x 0.25 mm i.d. x 0.25 µm film thickness). The gas chromatograph was operated in a constant helium flow 1.0 mL min^{-1}~~, and a 1:20 split ratio~~. As peak ratio is inversely related to the amount of products entering the column, relatively low split ratios or even splitless conditions have been used in trace analysis of plastics [23]. In this study, a split ratio 20 was selected to favour polymer detection avoiding mass spectrum saturation. The oven programmed temperature was set at 40 °C for 5 min and a ramped rate of 10 °C min^{-1} to 300 °C where it was held for 10 min. Mass spectra were recorded under 70 eV electron ionisation in the *m/z* 35-600 interval at 2.6 scan sec^{-1}. Compound identification was based on injection of pure volatile methyl siloxanes, pyrolysis of PEG-200, NIST 14 library match, and comparison with literature.

2.4. Quantitation

Peak areas *A* were determined by integration of the peak in the extracted ion chromatogram of a single specific ion. Calibration protocol was constructed in the form of equation (1):

$$\frac{Ax \cdot Qis}{Ais} = aQx + b \qquad (1)$$

4

Ax is the peak area of the pyrolytic marker integrated at a specific *m/z*, *Ais* the peak area of i.s. (integrated at *m/z* 281), *Qx* the mass (µg) of the pyrolysed polymer, *Qis* the mass of the i.s. (µg, around 0.1 µg exactly calculated from the mass of the injected solution); *a* the slope (sensitivity) and *b* the intercept. Recovery was determined by spiking THF-extracted sewage sludge samples with a known quantity of PEG-12 dimethicone solution (corresponding to 17-19 µg of the copolymer in pyrolyser) and applying the overall analytical procedure. The limit of detection (LOD) was estimated as the quantity calculated to give a signal to noise ratio S/N = 3 at the retention time of the pyrolytic marker. Procedural and instrumental blank analyses were run periodically to check for potential contamination by environmental or instrumental (septum/column) contamination. Quantitative data were expressed as mean and percentage relative standard deviation (RSD) from three replicate analyses. RSD values were determined for repeatability estimates with calibration solutions of dimethicone (10 µg) and PEG-12 dimethicone (16 µg).

3. Results and discussion

3.1. Qualitative analysis

3.1.1. Pyrolysis products from the siloxane chain

The mass spectra of methylsiloxanes belonging to different groups (cyclic, linear and with hydroxyl groups) identified in the pyrolysates of the investigated polymers are presented in figure 2.

~~The example reported in figure 1a shows that~~ The pyrograms of dimethicone (an example is shown in figure 3a) were dominated by cyclic methyl siloxanes (D_n) in agreement with literature data on the pyrolysis of PDMS [21] [24]. It has been reported that the proportion of the various D_n formed upon thermal degradation decreases from D_3 to higher molecular species in a way which is not dependent on temperature and the type of chain ends (trimethyl or hydroxyl) [21]. The identification of D_3-D_6 was confirmed by the injection of pure standards (Table 1). The D_7 could be identified by the $[M-103]^+$ ion at *m/z* 415 following the elimination of methyl radical (15 u) from the molecular ion and the subsequent neutral loss of $Si(Me)_4$ (88 u) after skeletal rearrangement. $D_{>7}$ could be identified by published mass spectra [25]. In general, mass spectra of D_n are characterised by the absence of the molecular ion $M^{•+}$, the presence of $[M-15]^+$ ion for smaller rings, cyclic siloxanes without a methyl group ($[D_n-15]^+$ at *m/z* 207, 281, 355, 429) and linear $[Me_3Si(OSiMe_2)_{n=0-4}]^+$ ions (*m/z* 147, 221, 295, 369) produced from skeleton rearrangement [1,25]. It is worth noting that the mass spectra of cyclic siloxanes and linear α-ω diols are identical due to the loss of CH_3 and H_2O (33 u) [20]. The diol with n Si atoms typically elutes between D_{n+1} and D_{n+2} [26]. On this basis, the heptamethylhydroxycyclotetrasiloxane (D_3D^{OH}) was identified.

According to the fact that chain scission is not considered a dominant process in PDMS pyrolysis, linear dimethylsiloxanes (L_n or $MD_{n-2}M$) were barely or not even detected in the pyrolysates of dimethicone in accordance to literature [21,26,27]. The formation of linear siloxanes was ascribed to secondary reactions involving ring-opening of cyclic siloxanes catalysed by impurities on the walls of the pyrolysis reactor [27].

On the opposite, the pyrolysates of PEG-12 dimethicone (Figure 3~~1~~b) was featured by the evident occurrence of linear siloxanes. The presence of L_{3-5} was confirmed by the analysis of pure compounds (Table 1). Higher molecular weight (HMW) L_n species were tentatively identified by mass spectrum interpretation, order of elution and comparison with literature data [28]. Analogously to cyclic siloxanes, the identification of linear siloxanes by mass spectral interpretation is cumbersome due to the absence of $M^{\bullet+}$ and rearrangement reactions that lead to the formation of common ions. In addition, many of the isomeric siloxane products have the same mass spectra with a high risk of misinterpretation [20]. As an example, the mass spectrum of the internal standard (Q_4M) was identical to that of MD_2M.

The ion at *m/z* 221 resulted the second most abundant ion after the $(CH_3)_3Si^+$ ion (*m/z* 73) in the mass spectra of linear dimethylsiloxanes (figure 2) and can be used to highlight the presence of linear siloxanes with more than five Si atoms.

Similarly to PEG-12 dimethicone, the pyrograms of PEG-8 dimethicone were featured by the presence of linear dimethylsiloxanes (Figure 4~~2~~a) even though dominated by HMW~~higher molecular weight~~ species (L_8, L_9). ~~Both cyclic and linear species were minor products in comparison to the pyrograms of PEG-12 dimethicone.~~ L_n were not detected in the pyrolysates of bis-PEG-18 methyl ether dimethyl silane (figure 4~~2~~b).

The much higher proportion of evolved L_n from the co-polymers in comparison to dimethicone indicates that the pyrolytic behaviour of the siloxane chains was influenced by the presence of the PEG side chains. The formation of cyclic compounds involving "back-biting" reactions was probably less favoured than chain scission leading to linear species, probably due to steric hindrance. A similar explanation was advocated to explain higher proportion of linear over cyclic siloxanes from the pyrolysis of polysilalkylenesiloxanes [29].

By comparing figures 3b and 4a, a lower intensity of D_n and L_n peaks with respect to PEG was observed in the pyrogram of PEG-8 in comparison to that of PEG-12 dimethicone. It will be shown in section 3.2 that the lower intensity of siloxane peaks determined a lower sensitivity in the quantitative analysis of PEG-8 dimethicone. The different peak patterns is difficult to explain

without a precise knowledge of the chemical composition of the two copolymers. The values of x and y in the structural formulas of figures 3b and 4a are unknown and could assume different values in several commercial products [5].

PEG dimethicones are synthesised by hydrosilylation of the Si-H moieties of a silicone copolymer with allyl alcohol ethoxylate. The excess allyl alcohol ethoxylate remaining in the final product [5] could explain the higher proportion of PEG units in the pyrograms of PEG-8 dimethicone.

Table 1. Siloxanes formed upon flash pyrolysis of dimethicone and/or PEG-dimethicone. RT, retention time; ions, bold base peak; ID, identification based on "St.d" analyses of pure compound, "interpr." interpretation of mass spectrum or literature.

Compound	Abbr	RT, min	MW	ions m/z	ID
Hexamethyldisiloxane	L_2	2.89	162	147	St.d
Hexamethylcyclotrisiloxane	D_3	6.58	222	96, 191, **207**	St.d
Octamethyltrisiloxane	L_3	8.20	236	73, 103, 133, **221**	St.d
Unknown-1	-	9.23		193, **207**, 221	
Unknown-2	-	10.48		191, **207**, 223	
Unknown-3	-	10.71		133, 191, 193, **207**	
Unknown-4	-	10.79		96, 193, **207**	
Octamethylcyclotetrasiloxane	D_4	10.81	296	133, 249, 265, **281**	St.d
Decamethyltetrasiloxane	L_4	12.06	310	73, 191, **207**, 295	St.d
Heptamethylhydroxycyclotetrasiloxane	$D_3 D^{OH}$	12.97	298	126, 193, 251, **267**, 283	[26]

Unknown-5	-	13.52		193, **281**, 309	
Decamethylcyclopentasiloxane	D_5	13.54	370	**73**, 267, 355	St.d
Internal standard, Tetrakis(trimethylsiloxy)silane	M_4Q, IS	14.03		73, 147, **281**, 369	i.s.
Dodecamethyl pentasiloxane	L_5	14.90	384	73, 147, **281**, 369	St.d
α,ω-dioloctamethyltetrasiloxane	$M^{OH}D_2M^{OH}$	15.89	314	133, 249, 265, **281**	[20]
Unknown-6		16.01		**73**, 267, 281, 355	
Dodecametylcyclohexasiloxane	D_6	16.09	444	**73**, 325, 341, 429	St.d
Unknown-7	-	16.14		**73**, 267, 281, 341	
Tetradecamethylhexasiloxane	L_6	17.23	458	**73**, 147, 221, 443	[28]
Tetradecamethylcycloheptasiloxane	D_7	18.34	518	**73**, 147, 281, 415, 503	[25]
Hexadecamethyl heptasiloxane	L_7	19.27	532	**73**, 147, 221, 517	Interpr.
Hexadecamethyl cyclooctasiloxane	D_8	20.36	592	73, 221, **355**, 577	[25]
Octadecamethyl octasiloxane	L_8	21.09	606	**73**, 147,	Interpr.

				221, 591	
Octadecamethyl cyclononasiloxane	D_9	22.07	666	**73,** 147, 429,	[25]
Eicosamethyl nonasiloxane	L_9	22.73	680	73, 147, 221	Interpr.
Eicosamethyl cyclodecasiloxane	D_{10}	23.60	740	73, 147, 221	[25]

3.1.2. Pyrolysis products from the PEG side chain

As expected, the pyrograms of PEG-8 and PEG-12 dimethicones were featured by pyrolysis products formed by the thermal degradation of PEG side chains (Figures 3~~1~~b and 4~~2~~a).

Table 2. GC-MS data of pyrolysis products of PEG-12 and PEG-8 dimethicone. A, B end groups in the formula: A-(CH₂-CH₂-O)ₓ-B, CE cyclic ether (crown ether). Tentative structural assignment based on the analysis PEG200 (for diols HO-(CH₂-CH₂-O)ₓ-H), library match (> 80 % without background correction), elution order on the same GC stationary phase ([18,19]).

A	B	X	formula	RT min	m/z
CH_3-CH_2-O	CH_3-CH_2	1	$C_6H_{14}O_2$	5.93	59, 74, 45
CH_3-O	H	2	$C_5H_{12}O_3$	9.50	45, 59, 90
HO	**H**	**2**	**$C_4H_{10}O_3$**	**10.1**	**45, 75, 76**
CH_3-CH_2-O	H	2	$C_6H_{14}O_3$	10.9	45, 59, 72
CH_2=CH-O	H	2	$C_6H_{12}O_3$	11.1	45, 89, 101
CH_3-CH_2-O	CH_3-CH_2	2	$C_8H_{18}O_3$	11.2	45, 72(73), 59
CH_2=CH-O	CH_2=CH	2	$C_8H_{14}O_3$	12.5	45, 117, 73
HO	**H**	**3**	**$C_6H_{14}O_4$**	**15.0**	**45, 89, 58**
CH_3-CH_2-O	H	3	$C_8H_{18}O_4$	15.5	45, 72(73), 59
-	-	4 (CE)	$C_8H_{16}O_4$	15.7	45, 89, 43
CH_3-CH_2-O	CH_3-CH_2	3	$C_{10}H_{22}O_4$	16.5	45, 73(72), 59
-	-	4 (CE ester)	$C_8H_{14}O_5$	17.6	102, 45, 103
HO	**H**	**4**	**$C_8H_{18}O_5$**	**18.4**	**45, 89, 58**
CH_3-CH_2-O	H		$C_{10}H_{22}O_5$	19.1	45, 72(73), 59
-	-	5 (CE)	$C_{10}H_{20}O_5$	19.2	45, 89, 43
CH_3-O	H	5	$C_{11}H_{24}O_6$	21.6	45, 59, 89
HO	**H**	**5**	**$C_{10}H_{22}O_6$**	**21.8**	**45, 89, 58**
CH_3-CH_2-O	H	5	$C_{12}H_{26}O_6$	22.2	45, 73, 59
-	-	6 (CE)	$C_{12}H_{24}O_6$	22.3	45, 89, 73
CH_3-CH_2-O	CH_3-CH_2	4	$C_{12}H_{26}O_5$	22.8	45, 73(72), 59

-	-	6 (CE ester)	$C_{12}H_{22}O_6$	24.0	45, 103, 43
CH$_3$-O	H	6	$C_{13}H_{28}O_7$	24.4	45,59,89
HO	**H**	**6**	$C_{12}H_{26}O_7$	**24.5**	**45, 89, 59**

It is known that the thermal degradation of PEG occurs at relatively low temperatures with the homolytic cleavage of the C-O bonds and H transfer reactions leading to oligomeric pyrolysis products containing –(CH$_2$-CH$_2$-O)$_n$- units terminated with hydroxyl and/or ethoxyl end groups; the strongest C-C bonds are cleaved at higher temperatures with formation of methoxyl end groups, while the dehydration of hydroxyl ends brings about the formation of vinyl ether end groups [22,30]. Besides linear species, pyrolysis products with a cyclic ether end group [18] and crown ethers [19] were also formed. This molecular complexity became evident in the pyrograms of PEG copolymers and the polymer bis-PEG-18 methyl ether dimethyl silane (constituted by a silicon atom with two PEG substituents) that were characterised by clusters of several peaks separated by 2-4 minutes. The structural assignment of the various oligomer families was difficult because PEG pyrolysis products display very similar mass spectra lacking molecular ion [30]. The PEG structural unit -CH$_2$-CH$_2$-O- is preserved in the structure of the pyrolysis products and after ionization is responsible for the loss of 44 u (ethylene oxide). As said above, the various pyrolysis products differ in their end groups X-(O-CH$_2$-CH$_2$-)$_n$, namely hydroxy (X=H), methoxy (X = CH$_3$), ethoxy (X=CH$_3$-CH$_2$), vinyl ether (X= CH$_2$=CH). The aldehyde group is also a possible end group even though generally not abundant [31]. Pyrolysis products with two different end groups (e.g. methyl and ethyl ethers) exhibit both the ion series of each terminal group complicating the identification. Common intense ions of linear and cyclic species were found at *m/z* 45 (CH$_3$-CH$_2$-O$^+$), *m/z* 59 (CH$_3$-CH$_2$-O-CH$_2^+$), *m/z* 73 (CH$_3$-CH$_2$-O-CH$_2$-CH$_2^+$) and *m/z* 89 (CH$_3$-CH$_2$-O-CH$_2$-CH$_2$-O$^+$) [32]. Some of PEG-derived pyrolysis products tentatively identified in the pyrolysates of copolymers are listed in Table 2. As an example, pyrolysis products eluting in the first portion of the pyrogram of PEG-12 dimethicone are evidenced in Figure 5~~3~~.

3.1.3. *Other pyrolysis products*

Distinctive pyrolysis products of the PEG dimethicones containing both siloxane and ethylene oxide moieties could not be identified with a reliable degree of certainty. As explained above, linear siloxanes were characteristic of the copolymers, but they did not provide molecular evidence for the presence of the PEG side chains. GC-MS data of unknown pyrolysis products of PEG-8 and PEG-12 dimethicone, not detected in the pyrolysates of PDMS and bis-PEG-18 methyl ether dimethyl silane, are reported in Table 1 (unknowns) and Table 3. Four pyrolysis products of Table 3 (# 1, 2, 3 and 5) were characterized by mass spectra exhibiting a base peak at *m/z* 133. An ion at *m/z* 133 occurred

only at relatively low abundance in the mass spectra of a few dimethylsiloxanes (Table 1). The m/z 133 ion is the base peak in the mass spectrum of dimethyldiethoxysilane ($[M-CH_3]^+$) and the second most abundant peak of the mass spectrum of methyltriethoxysilane ($[M-OCH_2CH_3]^+$) [1], thus it is assigned to $(CH_3)Si(OCH_2CH_3)_2^+$. On this ground, the empirical formula of m/z 133 could be $C_5H_{13}O_2Si^+$, while other possibilities are $C_4H_9O_3Si^+$ and $C_4H_{13}OSi_2^+$.These pyrolysis products are tentatively assigned to the fragmentation of methyl-propyloxy PEG siloxane units or secondary reactions between dimethylsiloxane and PEG fragments. An interesting compound of this family was the compound eluting at 9.05 min with a mass spectrum presenting an even ion at m/z 188.

Table 3. Unidentified peaks in the pyrograms of PEG-8 and PEG-12 dimethicones. Peak numbers correspond to the peak labels of Figure 5̲3̶.

#	min	m/z (% abundance)
1	9.05	119 (77), **133** (100), 145 (31), 173 (84), 188 (26)
2	9.24	**133** (100), 147 (29), 177 (74)
3	9.71	**133** (100), 147 (15), 175 (40)
4	9.76	**101**(100), 116 (58), 145 (28), 160 (17)
5	9.94	**133** (100), 149 (15), 177 (36)
6	10.0	**193** (100), 209 (52)

3.2. Quantitative analysis

The determination of the polymer quantity in a given sample by Py-GC-MS is typically carried out from the peak area of a pyrolysis product characteristic of the polymer. This approach is followed for instance in the analysis of microplastics where polymer-specific pyrolytic markers were utilised for quantitation (for example, styrene trimer for polystyrene, terminal n-alkadienes for polyethylene, and 2,4-dimethyl hept-1-ene for polypropylene [10,12]). The potential of the same approach in the case of PEG-12 dimethicone was investigated in this study exploiting the results shown in Section 3.1. Dimethicone and its PEG-copolymers produced cyclic dimethylsiloxane (D_n) upon pyrolysis. The calibration curves of the most intense species D_{3-6} exhibited different linearity (R^2 from 0.905 to 0.976) for dimethicone in the investigated concentration range (0.09-3.7 µg, n = 6). D_6 is proposed for quantitation in real samples because lower MW cyclic species were occasionally found in blank

analyses and gave the lower R^2 values. When D_6 was applied as quantitation marker for PEG-12 dimethicone the linearity, evaluated in the 0.75-58 µg range (n = 5), was satisfactory (R^2 = 0.995). The sensitivity was much higher for dimethicone (from equation (1), a = 9.0 10^{-3}) than PEG-12 dimethicone (a = 0.25 10^{-3}) in accordance to the fact that the copolymer contains less D units for the same mass of polymer. This relevant difference in sensitivity between polymer types indicates that D_6 cannot be adequately used for the quantitation of silicones as a family.

Besides, D_6, the following pyrolytic markers were investigated for PEG-12 dimethicone: the linear siloxanes L_6, L_8, and L_9, and the triethyleneglycol monoethyl ether (TGE, $C_8H_{18}O_4$). These markers were chosen because relatively intense, successfully identified and eluted in a time region less impacted by products evolved from the sewage sample matrix. The ions at m/z 221 for $L_{6,8,9}$ and m/z 45 for $C_8H_{18}O_4$ were selected for calculating the calibration protocols and evaluate the method performance. The GC peak of L_7 overlapped with that of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol that exhibits an intense satellite ion at m/z 221; due to this interference L_7 was not selected for quantitation.

The obtained figures of merit of the method using the pyrolytic markers $L_{6,8,9}$ and TGE are presented in Table 4. Calibration curves gave R^2 = 0.993 for L_6, R^2 = 0.999 for $L_{8,9}$ and R^2 = 0.992 for TGE. The repeatability by analysing a calibration solution (17 µg) was rather good, in general below 10 % in accordance with the typical precision of Py-GC-MS [15]. In comparison to D_6, the sensitivity of TGE and L_6 were similar, while those of L_8 and L_9 slightly lower. The sensitivity of these markers was lower for PEG-8 than PEG-12 dimethicone. The PEG-8/PEG-12 sensitivity ratios of TGE, L_8 and L_9 (L_6 was not detected in PEG-8 dimethicone pyrolysates) were 0.79 ± 0.04, 0.21 ± 0.01 and 0.029 ± 0.01, respectively. The pyrograms of PEG-12 and PEG-8 dimethicones presented differences in the relative distribution of D/L products-, probably due to the different length of the blocks in the original copolymers. However, this hypothesis cannot be confirmed as x and y in the structural formulas of figures 3 and 4 are unknown. The pyrolytic markers could not be detected in the pyrolysate of 0.07 µg of sample, whereas the pyrogram from 0.75 µg exhibited distinct peaks of $L_{6,8,9}$ and TGE successfully identified by mass spectral match after background correction. The LOD estimated from the analyses of the calibration solutions (S/N = 3 criterion) occurred in the 0.04-0.4 µg range (Table 3). When the quantity of analysed sample is 1 g, as in this study, the procedural LOD would be less than 0.4 µg$_{PDMS}$ g^{-1} corresponding to 0.15 µg$_{Si}$ g^{-1} in terms of silicon when considering the $(CH_3)_3SiO$ unit of 74 u. The LOD by Py-GC-MS is comparable to that of other analytical methds. For instance, the LOD by SEC-ICP-HR/MS and ICP-MS were reported to be 1.2 µg$_{Si}$ g^{-1} [26] and 0.1 µg$_{Si}$ g^{-1} [33], respectively. However, these methods did not provide molecular speciation. The recovery, determined by analysing spiked sewage samples previously extracted with THF, was 76 %

using L_6 as pyrolytic marker. This value can be considered acceptable for trace contaminants in complex matrices providing support to the validity of the Py-GC-MS procedure.

Table 4. Figures of merit of the Py-GC-MS procedure in the analysis of PEG-12 dimethicone. (TGE: CH_3CH_2-O-$(CH_2$-CH_2-$O)_{32}$-H); m/z quantitation ion in bold;

Marker min	m/z (%)	R^2	Sensitivity	LOD µg	RSD %	Recovery %	RSD %
D_6 16.1 min	73(100), 341(41), **429**(20), 342(15), 147(14)	0.995	0.0025	0.4	20	76	2
TGE 15.5 min	**45**(100), 72(30), 73(27), 59(20), 89 (21)	0.992	0.0028	0.1	10	69	5
L_6 (MD_4M) 17.2 min	73 (100), **221** (83), 147(73), 281(29), 443(4)	0.993	0.0022	0.04	15	74	4
L_8 (MD_6M) 21.1 min	73(100), **221**(75), 147(56), 207(28), 295 (23)	0.999	0.0015	0.1	4.0	66	6
L_9 (MD_7M) 22.7 min	73(100),**221**(81), 147(58), 207(27), 295(26)	0.999	0.0012	0.2	2.7	68	5

3.3. Py-GC-MS of sewage sludge extracts

3.3.1. Polysiloxanes

Pyrograms of oxidized, thick and dewatered sludges, previously dried and extracted in THF, were mainly dominated by fatty acids, alkanes, alkenes, sterols and sterenes from the matrix. An example is shown in Figure 64. The chemical nature of the pyrolysate indicates that lipids constituted the main chemical family extracted by THF. Cyclic dimethyl siloxanes from D_3 to D_7 could be revealed by retention time and mass spectrum matching. The [M-15]$^+$ ions were particularly distinctive for the rapid individuation of cyclic dimethylsiloxanes in the extracted ion chromatogram mode. Volatile cyclic siloxanes are known to be present in sewage sludges [2], however, their presence in the pyrolysates was excluded because the samples were dried before extraction and any volatile D_n would have been eliminated by volatilisation. Hence, D_3-D_7 were pyrolysis products indicative of the occurrence of polysiloxanes. Pyrolysis products of PEG could not be detected. Analogously, putative PEG-PDMS pyrolysis products (Table 3) could not be revealed, with the exception of the compound eluting at 9.23 min (Table 1).

By assuming that D_6, one of the possible pyrolytic marker selected for quantitation in Section 3.2, was released solely from the pyrolysis of dimethicone (PDMS), the concentrations calculated from the calibration protocol were 99, 105 and 61 µg g_{dw}^{-1} for the oxidized, thick and dewatered sludge samples, respectively. The corresponding RSD (n = 3) were 14, 16 and 17 %, respectively. The concentration values were within the ranges reported in other studies [33–36] using different analytical techniques (see Table 5).

Table 5. Examples of concentrations of siloxanes in sewage sludges reported in the literature with different methods (μg_{Si} were converted into μg_{PDMS} using the 74/28 conversion factor).

Input source of WWTP	Country	Analytical technique	Concentration µg$_{PDMS}$ g$_{dw}^{-1}$	References
Domestic	Australia	ICP-AES	360	[35]
Domestic	Japan	ICP-AES	144	[33]
Domestic and industrial	Maryland	FAAS	254 ± 14	[36]
Domestic and industrial	USA Canada	GPC-ICP-AES	1124 ± 1367	[34]
Domestic	Italy	Py-GC-MS	61-105[1] 225-289[2]	Present study

1- From calibration with dimethicone using D_6.

2- From calibration with PEG-12 dimethicone using L_6.

The absence of pyrolytic markers of PEG units in the analysed sludge samples may suggest that PEG-dimethicones were not present in the matrices at levels detectable by the method. Nonetheless, recovery experiments showed that the copolymer at the level of 17 µg g^{-1} in spiked samples could be successfully identified and quantified (section 3.2). This level is much lower than those typically reported for silicones in sewage samples (Table 5) evidencing the good performance of the method for the requested application. As PEG is highly biodegradable [7] and microorganisms in sewage sludges degrade PEG [37–40], it is probable that the PEG side chain of dimethicone copolyolys could have been degradeds. Degradation could result in copolymers with shorter PEG-chains. Another hypothesis is that the copolymer was totally distributed in the water phase (wastewater) due to its

water-solubility. However, water was not eliminated by centrifugation before drying, so any copolymer present in the water phase should have ended up in the dried sample. Notably, the occurrence of the L_6 pyrolytic marker of PEG-12 dimethicone could be revealed in all the samples at the correct retention time in the extracted ion chromatograms at m/z 221. All the characteristic ions of the mass spectrum obtained from the analysis of the standard PEG-12 dimethicone were detected, as exemplified in the inset of Figure 65.

Although the identification of PEG-dimethicone copolymers could not be confirmed by PEG markers, the linear siloxanes were considered indicative for the presence of dimethicone copolymers. In order to give a rough estimation of the level of their occurrence, the concentrations of copolymers were calculated from the calibration protocol for PEG-12 dimethicone using the L_6 pyrolytic marker. The obtained values were 245 µg g_{dw}^{-1} ($\pm$ 15 % RSD), 289 µg g_{dw}^{-1} ($\pm$ 14 %) and 225 µg g_{dw}^{-1} (8 %) for the oxidized, thick and dewatered sludge samples, respectively. Although these values could not be reliably assigned to original PEG-dimethicones, they suggest that dimethicone copolymers could be a significant fraction of total polysiloxanes in sewage sludge. This hypothesis was further supported by looking at the L_6/D_6 GC peak area ratios at m/z 221 to m/z 429. These ratios were in the range 0.1-0.3 for real samples, significantly higher than that of dimethicone (0.001), indicating that the level of linear siloxanes could not be solely assigned to the pyrolysis of the PDMS homopolymer (dimethicone). Nevertheless, the ratios were lower than those found in the analysis of standard PEG-12 dimethicone in spiked sewage samples (7 $\pm$ 3 % RSD). These findings suggest that the investigated sewage samples contained both PDMS homopolymers and copolymers. The nature of these copolymers could not be definitively associated to PEG due to the absence of PEG markers. Besides differences in the chemical nature of silicones, the quantitation was complicated by different factors that make it difficult quantitation of polysiloxanes as a whole family. As discussed above, the sensitivity of pyrolytic markers was different for the different polymers, the commercial copolymers have different composition and may contain unreacted material. In addition, the fact that ionization and fragmentation efficiencies [8] and peak areas are dependent on the molecular weight of the polymers [15].

3.3.2. Additional information from Py-GC-MS. Personal care products

Interestingly, a closer insight into the pyrograms of sewage sludges revealed the occurrence of ingredients of personal care products and cosmetics in all the analysed samples. The fragrance galaxolide was identified at retention time 22.6 min and mass spectrum matching with that of injected pure standard (Figure 75). Its degradation product lactone-galaxolide was further tentatively identified at 25.7 min (m/z 257, 272). Here, for the first time these cosmetic ingredients were revealed

by Py-GC-MS. Triclosan was also tentatively identified at 25.0 min (*m/z*: 146, 218, 288, 290). These compounds were typically reported in samples from WWTP by GC-MS [41–43].

4. Conclusions

Flash pyrolysis of PEG dimethicones produced cyclic dimethyl siloxanes and ethylene oxide derivatives evolved from the PDMS and PEG chains, respectively. In addition, linear dimethyl siloxanes were produced which were proposed as pyrolytic markers of siloxane copolymers as they were not present in the pyrolysates of the homopolymer. The chemical structure of pyrolysis products indicative of the polyoxyethylene methylsiloxane moiety remained elusive. Even though not specific of PEG dimethicones, linear dimethyl polysiloxanes were selected for the development of a novel Py-GC-MS procedure for the analysis of siloxane copolymers in sewage sludges. The satisfactory values of precision, recovery, sensitivity, limit of detection and its performance in the analysis of sewage sludge samples demonstrated the potential of the Py-GC-MS method for complex matrices. Lipids were extracted by the organic solvent concurrently with siloxanes causing an important matrix effect. Thus, further improvements of the Py-GC-MS method will require clean-up steps to separate lipids from siloxanes. Incidentally, the occurrence of galaxolide fragrance and biocide triclosan was revealed by Py-GC-MS showing that the technique can be extended to the determination of a wide range of personal care products with a single analysis.

References~~EFERENCES~~

[1]   A.L. (Editor) Smith, Winefordner, J. D. (Series Editor), Kolthoff, I. M., Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications - The Analytical Chemistry of Silicones, Jhon Wiley & Sons, Inc, 1991.

[2]   C. Rücker, K. Kümmerer, Environmental Chemistry of Organosiloxanes, Chem. Rev. 115 (2015) 466–524. https://doi.org/10.1021/cr500319v.

[3]   Global Silicones Council, Socio-economic evaluation of the global silicones industry, Amec Foster Wheeler Environment & Infrastructure UK Limited, 2016.

[4]   J. Nikitakis, B. Lange, International cosmetic ingredient dictionary and handbook, 16th edition, Personal Care Products Council, Washington, DC, 2016.

[5]   A.J. O'Lenick, Silicones for personal care, 2nd ed, Allured Pub, Carol Stream, III, 2008, ISBN: 978-1-932633-36-8.

[6]   Safety Assessment of Polyoxyalkylene Siloxane Copolymers, Alkyl-Polyoxyalkylene Siloxane Copolymers, and Related Ingredients as Used in Cosmetics | Cosmetic Ingredient Review, Washington, 2015.

[7] F. Kawai, Biodegradation of Polyethers (Polyethylene Glycol, Polypropylene Glycol, Polytetramethylene glycol, and Others), Biopolymers Online. (2005). https://doi.org/10.1002/3527600035.bpol9012.

[8] S. Huppertsberg, D. Zahn, F. Pauelsen, T. Reemtsma, T.P. Knepper, Making waves: Water-soluble polymers in the aquatic environment: An overlooked class of synthetic polymers?, Water Research. 181 (2020) 115931. https://doi.org/10.1016/j.watres.2020.115931.

[9] H.P.H. Arp, H. Knutsen, Could We Spare a Moment of the Spotlight for Persistent, Water-Soluble Polymers?, Environ. Sci. Technol. 54 (2020) 3–5. https://doi.org/10.1021/acs.est.9b07089.

[10] J. La Nasa, G. Biale, D. Fabbri, F. Modugno, A review on challenges and developments of analytical pyrolysis and other thermoanalytical techniques for the quali-quantitative determination of microplastics, Journal of Analytical and Applied Pyrolysis. 149 (2020) 104841. https://doi.org/10.1016/j.jaap.2020.104841.

[11] R. Peñalver, N. Arroyo-Manzanares, I. López-García, M. Hernández-Córdoba, An overview of microplastics characterization by thermal analysis, Chemosphere. 242 (2020) 125170. https://doi.org/10.1016/j.chemosphere.2019.125170.

[12] N. Yakovenko, A. Carvalho, A. ter Halle, Emerging use thermo-analytical method coupled with mass spectrometry for the quantification of micro(nano)plastics in environmental samples, TrAC Trends in Analytical Chemistry. 131 (2020) 115979. https://doi.org/10.1016/j.trac.2020.115979.

[13] M. Julinová, L. Vaňharová, M. Jurča, Water-soluble polymeric xenobiotics – Polyvinyl alcohol and polyvinylpyrrolidon – And potential solutions to environmental issues: A brief review, Journal of Environmental Management. 228 (2018) 213–222. https://doi.org/10.1016/j.jenvman.2018.09.010.

[14] J.C. Kleinert, C.J. Weschler, Pyrolysis gas chromatographic-mass spectrometric identification of poly(dimethylsiloxane)s, Anal. Chem. 52 (1980) 1245–1248. https://doi.org/10.1021/ac50058a020.

[15] C.J. Weschler, Polydimethylsiloxanes associated with indoor and outdoor airborne particles, Science of The Total Environment. 73 (1988) 53–63. https://doi.org/10.1016/0048-9697(88)90186-6.

[16] J.P. Lewicki, R.L.F. Albo, C.T. Alviso, R.S. Maxwell, Pyrolysis-gas chromatography/mass spectrometry for the forensic fingerprinting of silicone engineering elastomers, Journal of Analytical and Applied Pyrolysis. 99 (2013) 85–91. https://doi.org/10.1016/j.jaap.2012.10.021.

[17] J. Maurer, K. Buffaz, G. Massonnet, C. Roussel, C. Burnier, Optimization of a Py-GC/MS method for silicone-based lubricants analysis, Journal of Analytical and Applied Pyrolysis. 149 (2020) 104861. https://doi.org/10.1016/j.jaap.2020.104861.

[18] X. Han, Y.H. Hu, Z.K. Lin, S.F. Li, F.Q. Zhao, Z.R. Liu, J.H. Yi, L.Y. Zhang, X.N. Ren, Effects of fullerenes on thermal behaviors of polyethylene glycol, J Therm Anal Calorim. 93 (2008) 927–932. https://doi.org/10.1007/s10973-007-8715-2.

[19] Z. Lin, T. Wang, X. Han, D. Han, S. Li, Comparative studies on low-temperature pyrolysis products of pure PEG and PEG/nano-Co3O4 by Py-GC/MS, Journal of Analytical and Applied Pyrolysis. 81 (2008) 121–126. https://doi.org/10.1016/j.jaap.2007.09.010.

[20] S. Varaprath, D.H. Stutts, G.E. Kozerski, A Primer on the Analytical Aspects of Silicones at Trace Levels-Challenges and Artifacts – A Review, Silicon Chem. 3 (2006) 79–102. https://doi.org/10.1007/s11201-006-9005-8.

[21] N. Grassie, I.G. Macfarlane, The thermal degradation of polysiloxanes—I. Poly(dimethylsiloxane), European Polymer Journal. 14 (1978) 875–884. https://doi.org/10.1016/0014-3057(78)90084-8.

[22] R. P. Lattimer, Mass spectral analysis of low-temperature pyrolysis products from poly(ethylene glycol), Journal of Analytical and Applied Pyrolysis. 56 (2000) 61–78. https://doi.org/10.1016/S0165-2370(00)00074-7.

[23] L. Hermabessiere, C. Himber, B. Boricaud, M. Kazour, R. Amara, A.-L. Cassone, M. Laurentie, I. Paul-Pont, P. Soudant, A. Dehaut, G. Duflos, Optimization, performance, and application of a pyrolysis-GC/MS method for the identification of microplastics, Analytical and Bioanalytical Chemistry. 410 (2018) 6663–6676. https://doi.org/10.1007/s00216-018-1279-0.

[24] J.P. Lewicki, B.P. Mayer, C.T. Alviso, R.S. Maxwell, Thermal Degradation Behavior and Product Speciation in Model Poly(dimethylsiloxane) Networks, J Inorg Organomet Polym. 22 (2012) 636–645. https://doi.org/10.1007/s10904-011-9625-0.

[25] G.R. Pickering, C.J. Olliff, K.J. Rutt, The mass spectrometric behaviour of dimethylcyclosiloxanes, Organic Mass Spectrometry. 10 (1975) 1035–1045.

[26] F. Chainet, L.L. Meur, C.-P. Lienemann, J. Ponthus, M. Courtiade, O.F.X. Donard, Characterization of silicon species issued from PDMS degradation under thermal cracking of hydrocarbons: Part 2 – Liquid samples analysis by a multi-technical approach based on gas chromatography and mass spectrometry, Fuel. 116 (2014) 478–489. https://doi.org/10.1016/j.fuel.2013.08.010.

[27] G. Camino, S.M. Lomakin, M. Lageard, Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms, Polymer. 43 (2002) 2011–2015. https://doi.org/10.1016/S0032-3861(01)00785-6.

[28] V.Yu. Orlov, Dissociation of methylsiloxane under electron bombardment, Zhurnal Obshchei Khimii. 37 (1967) 2300–2307.

[29] D. Allan, S.C. Radzinski, M.A. Tapsak, J.J. Liggat, The Thermal Degradation Behaviour of a Series of Siloxane Copolymers - a Study by Thermal Volatilisation Analysis, Silicon. 8 (2016) 553–562. https://doi.org/10.1007/s12633-014-9247-6.

[30] K. Voorhees, S. Baugh, D. Stevenson, An Investigation of the Thermal-Degradation of Poly(ethylene Glycol), J. Anal. Appl. Pyrolysis. 30 (1994) 47–57. https://doi.org/10.1016/0165-2370(94)00803-5.

[31] H. Arisawa, T.B. Brill, Flash pyrolysis of polyethyleneglycol Part I: Chemometric resolution of FTIR spectra of the volatile products at 370–550°C, Combustion and Flame. 109 (1997) 87–104. https://doi.org/10.1016/S0010-2180(96)00124-1.

[32] M.M. Fares, J. Hacaloglu, S. Suzer, Characterization of degradation products of polyethylene oxide by pyrolysis mass spectrometry, European Polymer Journal. 30 (1994) 845–850. https://doi.org/10.1016/0014-3057(94)90013-2.

[33] N. Watanabe, T. Nakamura, E. Watanabe, E. Sato, Y. Ose, Distribution of organosiloxanes (silicones) in water, sediments and fish from the Nagara River watershed, Japan, Science of The Total Environment. 35 (1984) 91–97. https://doi.org/10.1016/0048-9697(84)90371-1.

[34] N.J. Fendinger, D.C. Mcavoy, W.S. Eckhoff, B.B. Price, Environmental occurrence of polydimethylsiloxane, Environ. Sci. Technol. 31 (1997) 1555–1563. https://doi.org/10.1021/es9608712.

[35] G.E. Batley, J.W. Hayes, Polyorganosiloxanes (Silicones) in the aquatic environment of the Sydney region, Mar. Freshwater Res. 42 (1991) 287–293. https://doi.org/10.1071/mf9910287.

[36] R. Pellenbarg, Environmental poly(organosiloxanes) (silicones), Environ. Sci. Technol. 13 (1979) 565–569. https://doi.org/10.1021/es60153a013.

[37] E.L. Fincher, W.J. Payne, Bacterial utilization of ether glycols, Applied Microbiology. 10 (1962) 542–547.

[38] C. Borstlap, C. Kortland, Effect of substituents in the aromatic nucleus on the biodegradation behavior of alkylaryl sulfonates, Journal of the American Oil Chemists Society. 44 (1967) 295–297. https://doi.org/10.1007/BF02635617.

[39] S.J. Patterson, C.C. Scott, K.B.E. Tucker, Nonionic detergent degradation: III. Initial mechanism of the degradation, Journal of the American Oil Chemists' Society. 47 (1970) 37–41. https://doi.org/10.1007/BF02541454.

[40] N. Obradors, J. Aguilar, Efficient biodegradation of high-molecular-weight polyethylene glycols by pure cultures of Pseudomonas stutzeri., Applied and Environmental Microbiology. 57 (1991) 2383–2388.

[41] M. Biel-Maeso, C. Corada-Fernández, P.A. Lara-Martín, Removal of personal care products (PCPs) in wastewater and sludge treatment and their occurrence in receiving soils, Water Research. 150 (2019) 129–139. https://doi.org/10.1016/j.watres.2018.11.045.

[42] A.M. Peck, Analytical methods for the determination of persistent ingredients of personal care products in environmental matrices, Anal Bioanal Chem. 386 (2006) 907–939. https://doi.org/10.1007/s00216-006-0728-3.

[43] S. Ramos, V. Homem, L. Santos, Development and optimization of a QuEChERS-GC–MS/MS methodology to analyse ultraviolet-filters and synthetic musks in sewage sludge, Science of The Total Environment. 651 (2019) 2606–2614. https://doi.org/10.1016/j.scitotenv.2018.10.143.
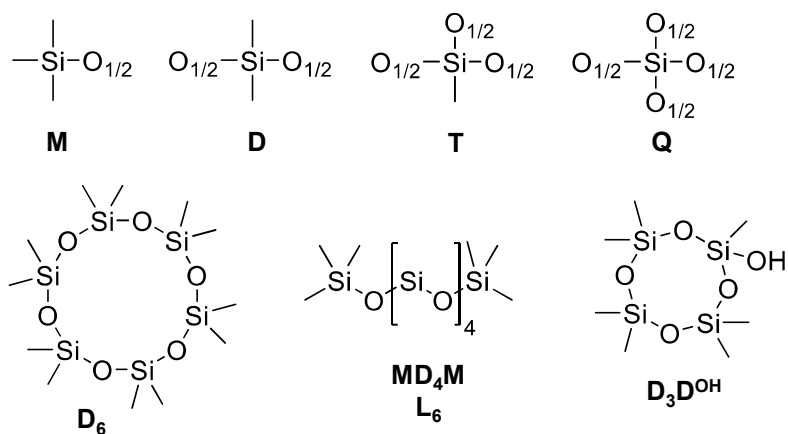
Figure 1

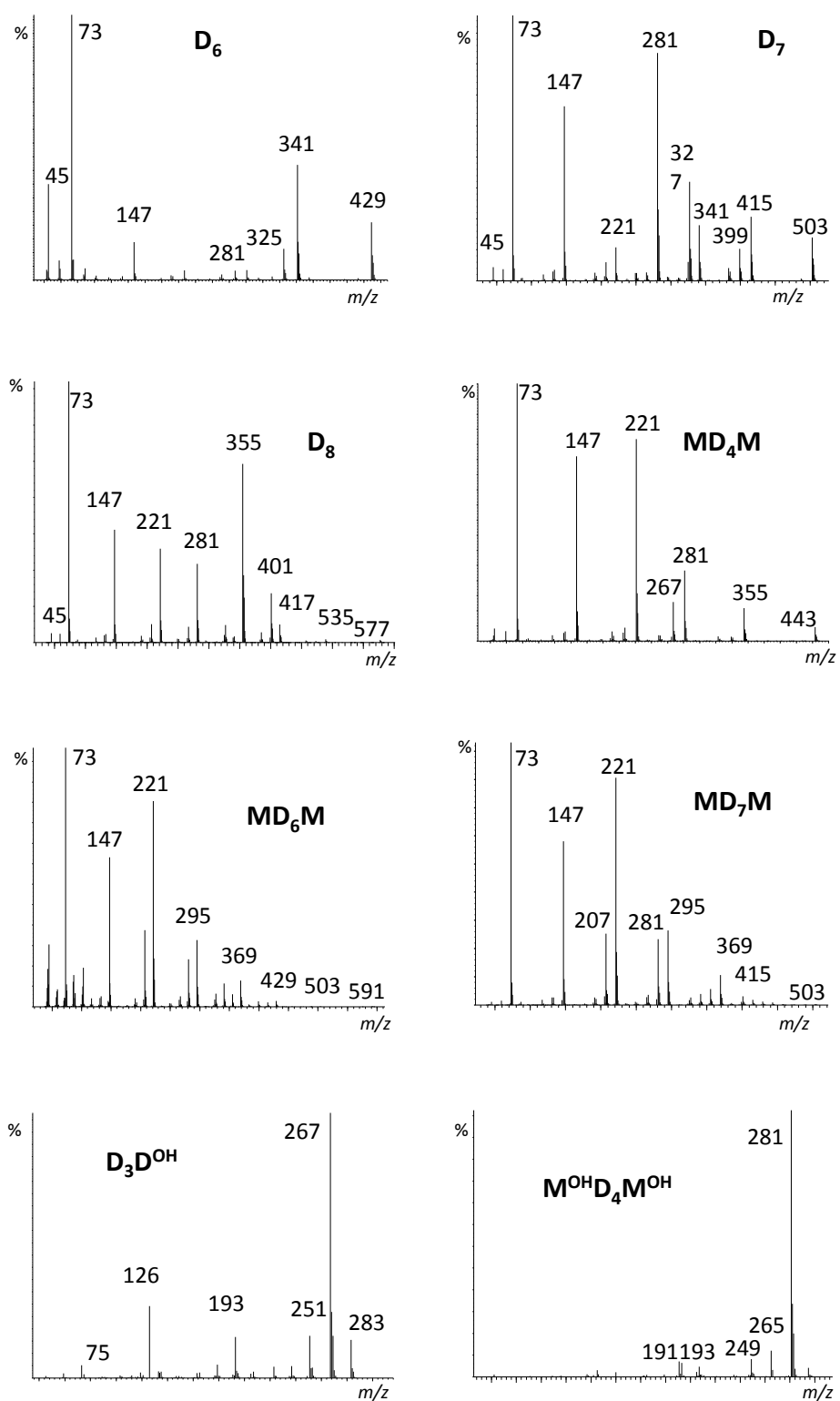*Shorthand notation for methylsiloxanes with examples of structural formulas.*

Figure 2

Mass spectra of some methylsiloxanes found in the pyrolysates of dimethicone (D_7 and D_8) and PEG-12 dimethicone (all expect D_7 and D_8).
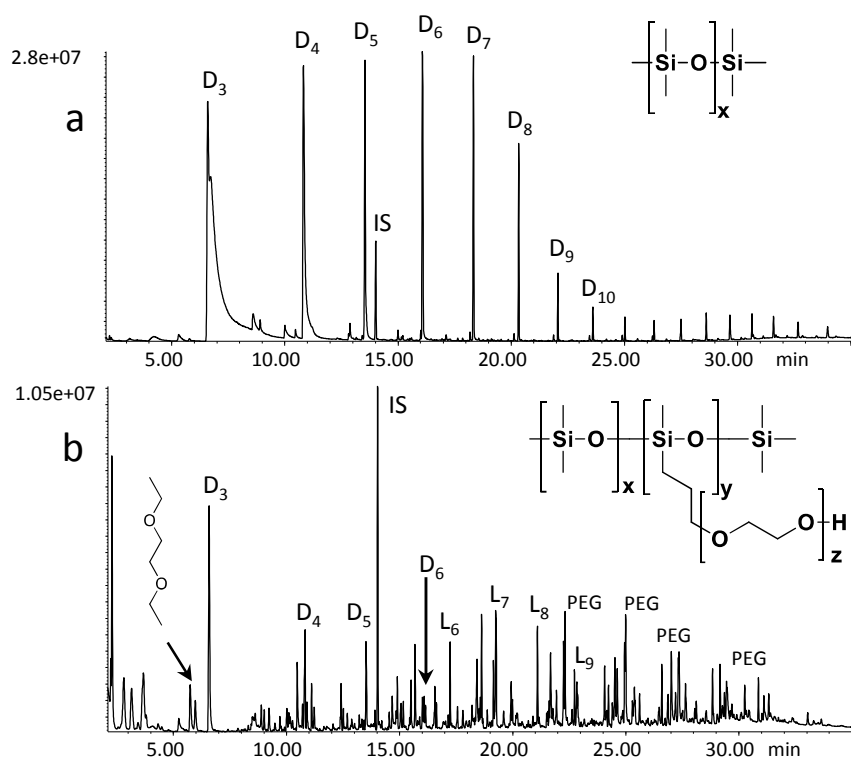
Figure 3
TIC-pyrograms of (a) dimethicone (45 µg) and (b)PEG-12 dimethicone (40 µg). PEG: peak clusters from PEG pyrolysis. IS: internal standard. The chemical structure of the polymers is shown on the top of each pyrogram (z ≈ 12 for PEG-12 dimethicone, x and y are unknown*).*
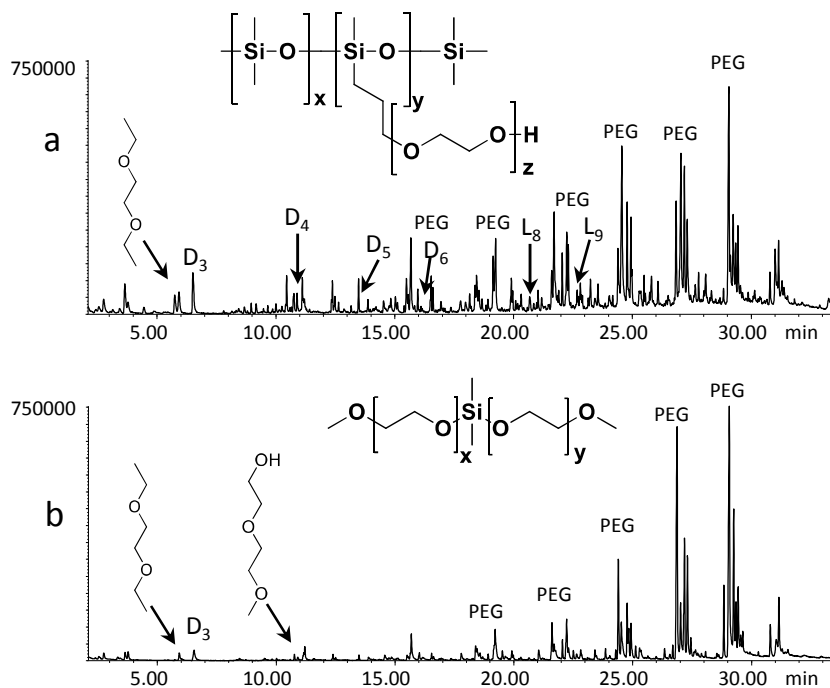
Figure 4

TIC-pyrograms of (a) PEG-8 dimethicone and (b) bis-PEG-18 methyl ether dimethyl silane. PEG: peak clusters from PEG pyrolysis. The chemical structure of the polymers is shown on the top of each pyrogram (z ≈ 8 for PEG-8, x and y are unknown).
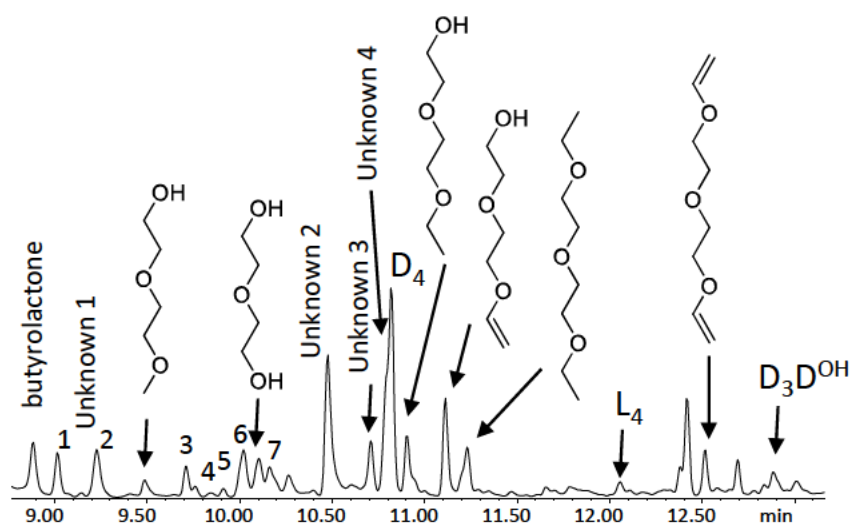
Figure 5

TIC-pyrogram of PEG-12 dimethicone in the 8.8-13.2 min elution region. GC-MS data of Unknown 1-4, PEG derived products and peak numbers refers to tables 1, 2 and 3, respectively
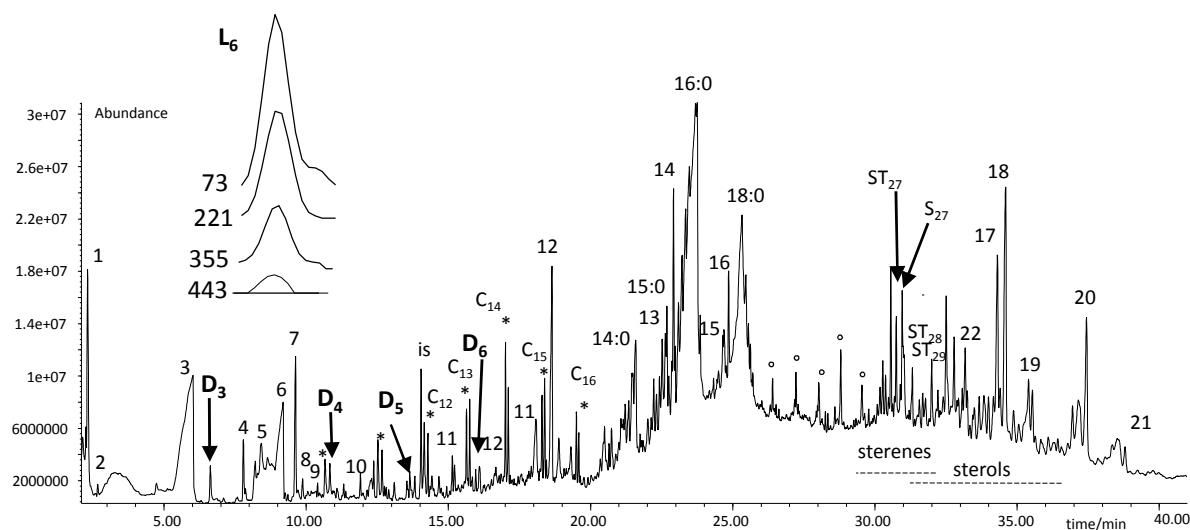
Figure 6

TIC-pyrogram of sewage sludge thick. Tentative identification: **1**: THF; **2**: benzene; **3**: tetrahydrofuranol; **4:** xylene; **5**:styrene; **6**: butyrolactone; **7**: *m/z* 41, <u>74</u>, 102 m/z (unknown); **8:** C3-benzene; **9**: 64, 78, 106 (1,2-dithiolane); **10**: C4-benzene; **11**:C6-benzene; **12**, heptylbenzene; **13**: galaxolide; **14**: 2-heptadecanone; **15**: galaxolide lactone; **16**: 3-octadecanone; **17**: *m/z* 249, 389, 404 (unknown); **18**:16-hentriacontanone; **19**:hexadecanoic acid hexadecyl ester; **20**:Octadecanoic acid, hexadecyl ester; **21**:9-octadecenoic acid, hexadecyl ester. 14:0, 15:0, 16:0, 18:0 fatty acids; ST27, ST28, ST29: C_{27}, C_{28} and C_{29}-sterenes; S27: cholestane; (*): *n*-1-alkene, *n*-alkanes; (°): *m/z* 57,71, 239. In the inset, the mass chromatograms at *m/z* 73, 221, 355 and 443 at the retention time of L_6 (17.2 min).
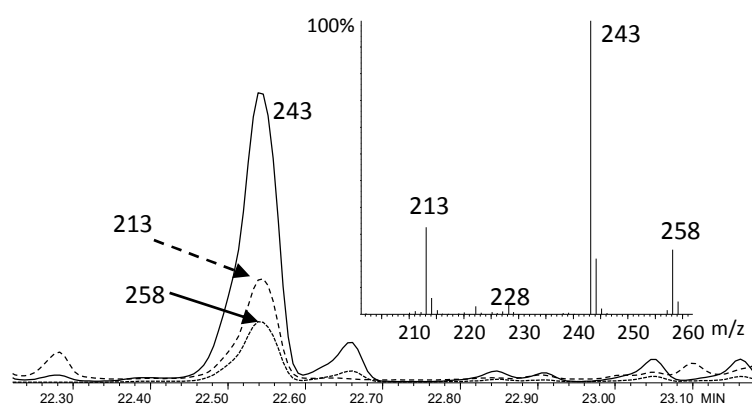
Figure 7
Py-GC/MS of oxided sludge. Extracted ion chromatograms at *m/z* 213, 243 and 258 and mass spectrum at 22.46 min attributed to galaxolide.