Characterization of silane-based hydrophobic admixtures in concrete using TOF-MS

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ABSTRACT

Silane-based hydrophobic admixtures especially alkyltrialkoxysilanes are used as water repellent agents for the surface protection of concrete. To optimize the structure of alkyltrialkoxysilanes in terms of their performance and their long term durability it is important to understand the chemical reactions taking place between the silicon organic compounds and the materials on which they are applied. For this purpose the characterization of alkyltrialkoxysilanes and their reaction products in concrete is necessary. Therefore we adapted an analytical method based on time-of-flight mass spectrometry (TOF/MS) combined with electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI). Monomeric alkyltrialkoxysilanes could be analyzed by the former method, reaction products which could be identified as Silsesquioxanes (SSOs) by the latter one. The results indicate that ESI-TOF/MS and MALDI-TOF/MS serve as a reliable and convenient tool to characterize monomeric silane-based hydrophobic admixtures as well as their reaction products resulted from hydrolysis and condensation.

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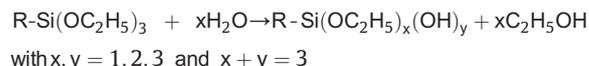
1. Introduction

1.1. Chemical behavior of silanes on mineral materials

Concrete in buildings and structures is exposed to various environmental factors that lead to damages and its deterioration. In particular, the capillary uptake of chloride containing aqueous solutions, e.g., de-icing salts or sea water, can lead to fast corrosion of the reinforcement. To prevent this and other damaging processes surface protection systems for cement-based materials are needed. One type of these protection systems is based on silicon organic compounds, e.g. alkyl groups containing trialkoxysilanes. These so-called silanes are sprayed onto the concrete surface and during the penetration into the concrete by capillary transport, the silane reacts under the prevailed alkaline conditions forming a very thin water repellent polymer resin of siloxane species that covers the pore walls [1,2]. The alkyl group of the silane molecule is responsible for the water repellence of the resin. Both performance and durability of the water repellent treatment depend on the penetration profile in the concrete characterized by the penetration depth and content of the formed siloxanes. Previous experiments have shown that the chemical reaction of alkylalkoxysilanes on mineral materials is a complex process consisting of several steps [3]. The reaction process is determined by several factors, such as the type and amount
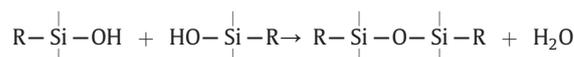
of silane, temperature, solvent, concrete composition (w/c, pore system) and pH-value of the treated concrete [4]. Fig. 1 shows the chemical reactions during hydrophobizing of cementitious materials.

The basic reaction of silane to siloxane species consists of two steps (Fig. 2):In a first step a) "hydrolysis" the alkoxygroups are replaced with hydroxygroups forming silanols releasing alcohol under alkaline conditions or by certain catalysts like Sn-organic compounds. In a second step b) "condensation" silanol species react to siloxane species forming $Si-O-Si$-bonds.

a)

$$R\text{-}Si(OC_2H_5)_3 \;+\; xH_2O \rightarrow R\text{-}Si(OC_2H_5)_x(OH)_y + xC_2H_5OH$$
with $x, y = 1, 2, 3$ and $x + y = 3$

b)

$$R-\overset{|}{\underset{|}{Si}}-OH \;+\; HO-\overset{|}{\underset{|}{Si}}-R \rightarrow R-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-R \;+\; H_2O$$

The reaction of crosslinking of siloxanes forming 3D-resins is related to that of condensation: Two hydroxyl groups of siloxane species react while releasing water.

Hydrolysis and condensation influence each other. The total reaction is complex and due to the trifunctionality of alkyltrialkoxysilanes many

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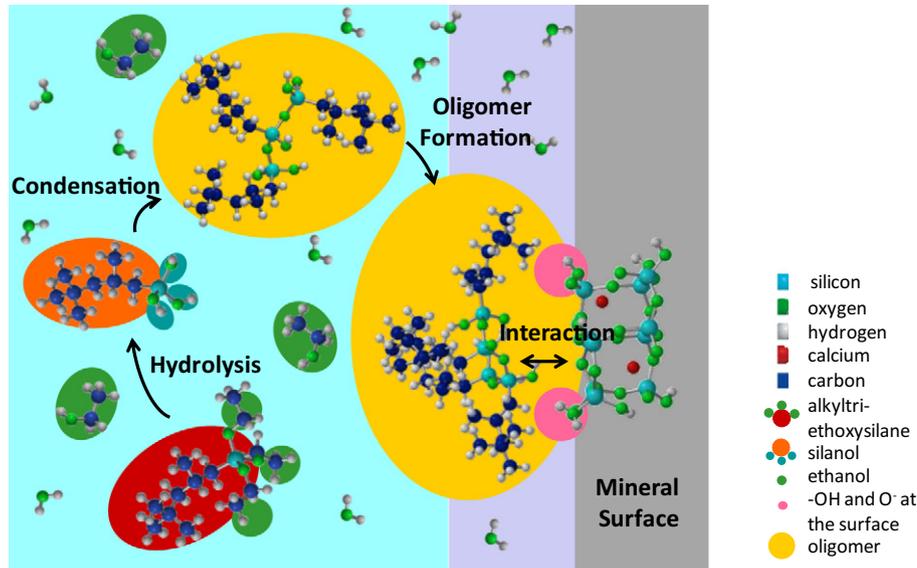*E-mail address:* hartmut.herb@hs-karlsruhe.de (H. Herb).

Fig. 1. Schematic diagram of chemical reactions during hydrophobizing of cementitious materials with Isooctyltriethoxysilane [5].

species are possible. The chemical reactivity of the silanes depends on their structure e.g. the chain length, isomeric constitution of the alkyl group, and the structure of the alkoxy groups [6]. Commonly used components in applications in the construction industry are Isobutyltriethoxysilane, Isooctyltrimethoxysilane, Isooctyltriethoxysilane (IUPAC: Triethoxy (2,4,4-trimethylpentyl)silane), and it's isomeric form n-Octyltriethoxysilane with molecular formula $C_8H_{17}(OC_2H_5)_3$. By means of computational chemistry energetic conditions of different reaction products of alkyltrialkoxysilanes were investigated to obtain the preferential reaction process [5]. It was shown that the formation of siloxane species starts with monomeric silanol compounds in aqueous environment followed by condensation steps. Different species consisting of up to 10 Si-atoms with cyclic structure were investigated.

1.2. Methods for characterization of reaction behavior of silanes

Fourier-Transformation Infrared Spectroscopy (FTIR) is often applied for qualitative and quantitative analysis of silane-based water-repellents. The investigation is based on signals caused by CH-vibration of the alkylgroups. This method is used to determine the penetration profiles of silanes which are applied to concrete. It represents a quality control for the treatment with silanes [7]. However, this method does not give the same selectivity for the characterization of individual components in complex polymer mixtures as other used methods like Pyrolysis–GC [8] provide. An analytical tool for the characterization of individual species is mass spectrometry as the output is their mass-to-charge ratio. Superplasticizer, polymer-based additives and other organic binders in the field of building materials are analyzed with this method [9, 10]. In particular, time-of-flight mass spectrometry (TOF/MS) allows

analyzing the chemical structure with high resolution and high sensitivity. Especially for TOF/MS two ionization techniques are common: electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI). Compared to conventional ionization techniques such as electron impact ionization (EI) or secondary ion technique (SIMS) where organic molecules are usually fragmented these methods are more gentle and therefore allow the analysis of intact organic molecules and polymers.
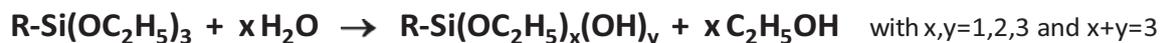
However, the complicated chemical processes determining the properties of polysiloxanes as well as their degradation have hardly been studied so far. The formation of various species due to the trifunctionality of alkyltrialkoxysilanes poses the main difficulty during analysis of such systems. Up to now there is no suitable method for the characterization of the chemical structure of polysiloxanes formed in the presence of cementitious materials. Our investigation aims to explore the applicability of the TOF/MS method to characterize the chemical composition of alkyltrialkoxysilanes on the surface of cementitious materials. Especially the reaction products during hydrolysis, condensation and crosslinking catalyzed by alkaline media were analyzed. A potential application for this method is the investigation of possible deterioration processes of polysiloxanes [11].

2. Experimental section

2.1. Chemicals

In this study Isooctyltriethoxysilane $C_8H_{17}Si(OC_2H_5)_3$ in high purity was used as alkyltrialkoxysilane compound made by Wacker Chemie

a)

$$R\text{-}Si(OC_2H_5)_3 + x\,H_2O \rightarrow R\text{-}Si(OC_2H_5)_x(OH)_y + x\,C_2H_5OH \quad \text{with } x,y=1,2,3 \text{ and } x+y=3$$

b)

$$R\text{-}\overset{|}{\underset{|}{Si}}\text{-}OH + HO\text{-}\overset{|}{\underset{|}{Si}}\text{-}R \rightarrow R\text{-}\overset{|}{\underset{|}{Si}}\text{-}O\text{-}\overset{|}{\underset{|}{Si}}\text{-}R + H_2O$$

Fig. 2. Polycondensation of silanes: a) hydrolysis under ethanol release and b) condensation.

Table 1
Parameter of cement paste specimens and curing conditions.

Cement	CEM I 42,5 R
w/c	0,5
Size	$10 \times 10 \times 2$ mm
Storage # 1	20 °C, 80% RH
Duration # 1	42 days
Storage # 2	20 °C, 80% RH
Duration # 2	46 days

(Burghausen, Germany). Ethanol (absolute), tetrahydrofuran (THF) of HPLC grade quality and sodium hydroxide (suprapur) were purchased from VWR (Darmstadt, Germany). All other chemicals mentioned were supplied by Sigma-Aldrich (Taufkirchen, Germany) unless otherwise specified. Ultrapure water was produced by a Milli-Q Gradient system (Millipore, Eschborn, Germany). The cement chosen for the experiments was an ordinary Portland cement (CEM I 42.5 R from Heidelberger Zement, Wetzlar plant, Germany).

2.2. Instruments

ESI-TOF/MS was performed using a Q-Star Pulsar i (AB Sciex, Darmstadt, Germany) to analyze low molecular weight compounds such as monomeric alkyl-triethoxysilanes. The analyte (c = 10 ppm) was dissolved in ethanol, saturated with $NaNO_3$, to provide the necessary ionization by Na-ions and infused at a flow-rate of 5 µl/min directly into the ESI ion source by a syringe pump (Harvard Apparatus, Holliston, MA, USA) (diameter: 4.61 mm). Usually 20 spectra were accumulated. The mass calibration was achieved by using a 100 ppm solution of "M600" (AB Sciex) in acetonitrile/water (1:1).

MALDI-TOF/MS was performed using a 4700 Proteomics Analyzer and a 4800 Plus MALDI TOF/TOF Analyzer (AB Sciex, Darmstadt, Germany). They were equipped with a pulsed Nd-YAG-laser (wavelength: 355 nm, pulse width: 3 ns, frequency: 200 Hz). The laser intensity was optimized for resolution and signal-to-noise ratio. Usually 1000 spectra in the positive ion mode and reflector mode were accumulated. Spectra were recorded in a m/z range between 700 and 2200. Focus mass was set on 1400. Welled sample plates were used. 2,5-dihydroxybenzoic acid (DHB, gentisic acid) was selected as matrix. Sodium iodide (NaI) was added to provide the necessary ionization by positive charged Na-ions. Both the matrix and cationizing agent were

dissolved in THF with a concentration of 20 mg/mL (DHB) and 20 mmol/mL (NaI). 25 µL matrix solution and 2.5 µL ionizing agent were mixed with 2.5 µL of the sample. Two coatings (0.5 µL each) were performed on the MALDI plate, removing the solvent by evaporation at room temperature. In every experiment mixtures of the matrix and cationizing agent in THF were also monitored. Spectra were calibrated by use of polypropylene glycols (AB Sciex, Darmstadt, Germany) for external calibration. All parameters concerning instrument settings were optimized in preliminary tests.

2.3. Experiments with alkyltrialkoxysilane in solution

An aqueous solution of sodium hydroxide (NaOH) and THF was used to simulate only the alkaline environment of cementitious materials without any interference of solid matrix like sorption or transport effects. According to a pH-value of pore solution in concrete around 12.5 caused by hydroxides mainly KOH at a concentration of 0.2 mol/L was chosen. For the reaction 100 µL of Isooctyltriethoxysilane was dissolved in 300 µL THF and 28 µL of aqueous NaOH solution was added in a closed 2 mL PE tube. The mixture was stirred using a magnetic stirrer at room temperature. After 7 days a sample was taken and diluted with THF (1 to 100) for measuring with MALDI-TOF/MS. Also a sample without Isooctyltriethoxysilane was measured (blank test).

2.4. Preparation and leaching of treated specimens

For simulating solid matrices of concrete specimens e.g. plates of hardened cement paste were made by mixing cement and pure water by hand and cured under defined conditions (Table 1, # 1). They were thoroughly treated with Isooctyltriethoxysilane by submerging for 24 h and afterwards stored under defined conditions (Table 1, # 2).

For analyzing the reaction products of Isooctyltriethoxysilane the treated specimens were subjected to leaching by THF. For that purpose, they were placed directly into the solvent (static tank test) at room temperature without any enhanced procedures. The solid/liquid-ratio was 2 to 5 (m/V in g/mL). After at least 24 h the specimens were removed and the extracts were analyzed using MALDI-TOF/MS without any further purification or enrichment. Also, specimens not treated with Isooctyltriethoxysilane were handled by this procedure (negative control).
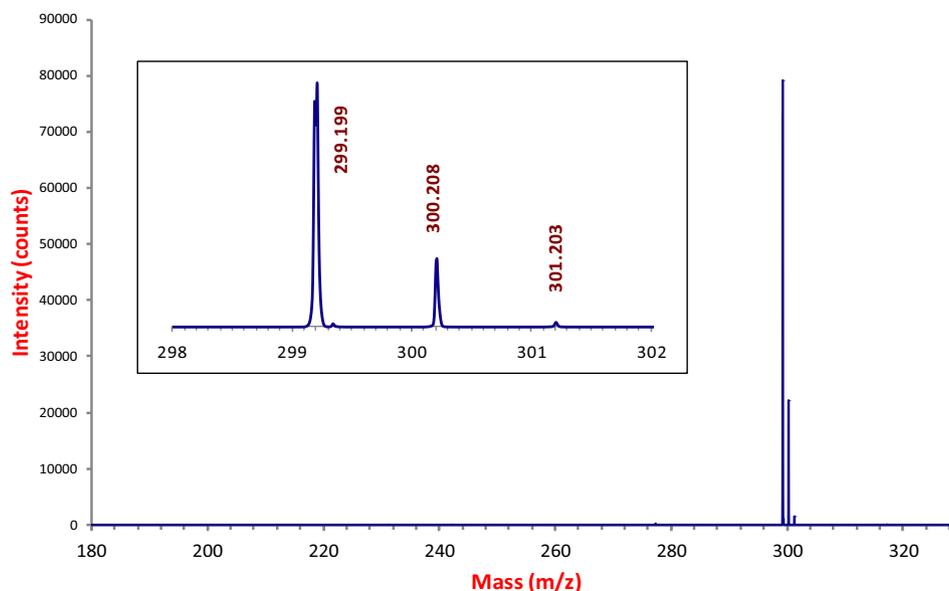

Fig. 3. ESI-TOF mass spectra of Isooctyltriethoxysilane (c = 100 ppm, $[M + Na^+]$-adduct, solvent: ethanol, ionizing agent: $NaNO_3$).
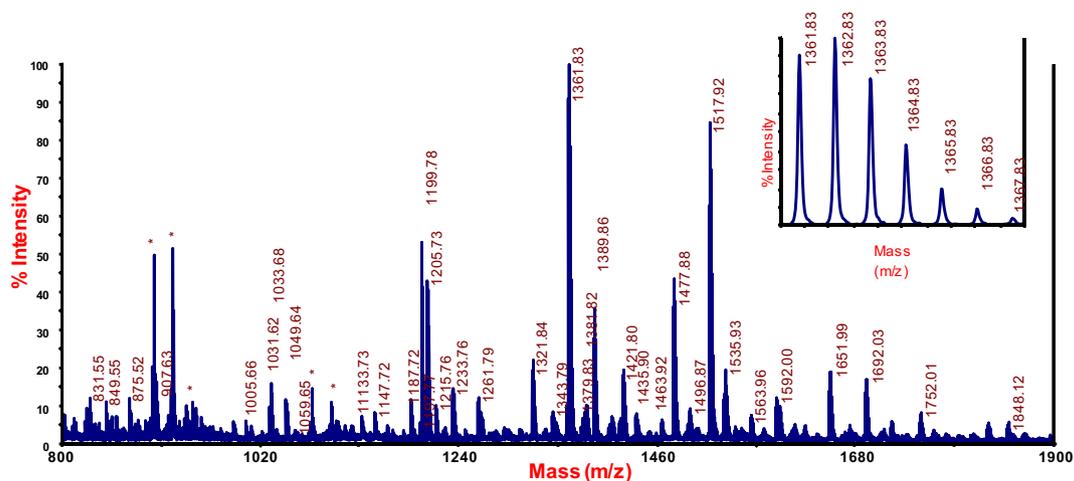
Fig. 4. MALDI-TOF mass spectra of alkaline treated Isooctyltriethoxysilane (*: peaks are also found in the negative control).

3. Results and discussion

3.1. Characterization of monomeric compounds

Monomeric compounds were analyzed by ESI-TOF mass spectrometry. Fig. 3 shows the obtained mass spectra of Isooctyltriethoxysilane. The presence of three peaks in the inset is due to the isotopic distribution mainly caused by the Si-atom (^{28}Si: 92.23%, ^{29}Si: 4.67%,^{30}Si: 3.1%). It shows an equidistance of m/z = 1 between the isotopic peaks. So, only single-charged sodium adducts, e.g. the molecular mass plus 22.990 [M + Na$^+$], are generated. The obtained masses from spectra are compared with theoretical masses. The experimental (299.199) and predicted values (299.202) are in perfect agreement. The compound is selectively identified by its [M + Na$^+$]-adduct.

3.2. Siloxane species in alkaline solution

First, siloxane species were characterized in solutions for exclusively studying the influence of an alkaline environment avoiding any interference through sorption or transport effects of solid materials. Fig. 4 shows the MALDI-TOF/MS mass spectra of Isooctyltriethoxysilane exposed to an alkaline environment for 7 days. There was no significant difference in the spectra even after several days. Only the m/z range between 800 and 1900 is shown because at low mass the MALDI spectra

are dominated by peaks caused by matrix compounds (DHB, NaI, THF). This part of the spectra is not shown. No peaks of siloxane species were detected above 1900 u.

The isotopic distribution in the inset (cluster with monoisotopic peak with m/z = 1361.83) of Fig. 4 shows an equidistance of m/z = 1 between the peaks. So, only single charged adducts appear which can mainly be assigned to [M + Na$^+$] species and less to [M + H$^+$] species, respectively.

The obtained masses from the spectra are compared with theoretical masses. These were calculated using the monoisotopic mass of potential siloxane species based on the trifunctionality of the alkyltrialkoxysilanes and their reaction by hydrolysis, condensation and crosslinking. Table 2 shows this calculation as an example for a siloxane species consisting of 4 Si-atoms and three, four and six bridging O-atoms based on Octyltriethoxysilane. It is not likely that all these species are present in the system, as it is only a mathematic calculation for adjusting measured masses.

As shown with ESI-ionization an excellent correlation was found between experimental and predicted values. Besides the peaks that can be attributed to siloxane some more peaks of unknown species which are also found in the negative control were detected.

The peaks could be assigned to Si – O – Si bonds containing species which are generally called silsesquioxanes (SSOs) [12]. They can be described by the formula [13,14]:

$$T_n(OH)_x(OC_2H_5)_y \text{ where } T = RSiO_{1.5-m/2n} \text{ and } x + y = m$$

Table 2
Calculation of siloxane species and their masses based on Octyltriethoxysilane is exemplarily shown for a species consisting of 4 Si-atoms. Measured species are marked in bold, R = Isooctyl.

Formula	M (mass of species) [u]	M + H$^+$ (mass of hydrogen adduct) [u]	M + Na$^+$ (mass of sodium adduct) [u]
$Si_4O_3(OR)_6$	882.63	883.64	905.62
$Si_4O_3(OR)_5(OH)$	854.60	855.61	877.59
$Si_4O_3(OR)_4(OH)_2$	826.57	827.57	**849.56**
$Si_4O_3(OR)_3(OH)_3$	798.54	799.54	821.53
$Si_4O_3(OR)_2(OH)_4$	770.50	771.51	793.49
$Si_4O_3(OR)_1(OH)_5$	742.47	743.48	765.46
$Si_4O_3(OH)_6$	714.44	715.45	737.43
$Si_4O_4(OR)_4$	808.56	809.56	**831.55**
$Si_4O_4(OR)_3(OH)_1$	780.52	781.53	803.51
$Si_4O_4(OR)_2(OH)_2$	752.49	753.50	775.48
$Si_4O_4(OR)_1(OH)_3$	724.46	725.47	747.45
$Si_4O_4(OH)_4$	696.43	697.44	719.42
$Si_4O_6(OR)_2$	734.48	735.49	757.47
$Si_4O_6(OR)_1(OH)_1$	706.45	707.46	729.44
$Si_4O_6(OH)_2$	678.42	679.43	701.41

Table 3
Assignment of MALDI-TOF/MS peaks (monoisotopic [M + Na$^+$]-adducts unless noted) of products of Isooctyltriethoxysilane treated with NaOH (R = Isooctyl-; n.a.: not assigned; n.c.: not calculable due to overlay with other peaks).

m/z	Assignment	Intensity [%]	m/z	Assignment	Intensity [%]
831.55	$T_4(OR)_4$	11	1361.82	$T_8(OH)_2$	100
849.55	$T_4(OR)_4(OH)_2$	10	1379.83	$T_8(OH)_4$	5
875.52	$T_3(OH)_3$	11	1381.90	$T_7(OR)_5(OH)_2$	n.c
1005.65	$T_5(OR)_4(OH)_1$	5	1389.85	$T_8(OR)_1(OH)_1$	36
1031.69	$T_6(OH)_2$	8	1421.80	n.a.	18
1033.69	$T_5(OR)_5$	n.c	1435.89	$T_8(OR)_2(OH)_2$	7
1049.63	$T_6(OH)_4$	11	1463.91	$T_8(OR)_3(OH)_1$	5
1133.72	$T_6(OR)_3(OH)_1$	7	1477.88	n.a.	43
1147.73	n.a.	7	1517.92	$T_9(OH)_1$	85
1187.71	$T_7(OH)_1$	11	1535.93	$T_9(OH)_3$	19
1199.79	n.a.	53	1563.96	$T_9(OR)_1(OH)_2$	7
1205.74	$T_7(OH)_3$	42	1591.99	$T_9(OR)_2(OH)_1$	8
1215.74	$T_7(OR)_1$	9	1652.03	$T_{10}(H^+\text{-}adduct)$	18
1233.76	$T_7(OR)_1(OH)_2$	13	1692.02	$T_{10}(OH)_2$	17
1261.79	$T_7(OR)_2(OH)_1$	11	1752.01	n.a.	8
1321.84	$T_8(H^+\text{-}adduct)$	22	1848.12	$T_{11}(OH)_1$	5
1343.79	T_8	5			

Fig. 5. Possible structure of the species $T_8(OH)_2$.

The structures of these silsesquioxanes may vary from the perfect polyhedra following the formula $(RSiO_{1.5})_n$ ($n =$ even number ≥ 6), also denoted as T_n or POSS (polyhedral oligomeric silsesquioxanes) to partially hydrolyzed and condensed frameworks. In case of partially condensed frameworks ($m > 0$) the number of intramolecular cycles c can be calculated by the equation:

$$c = (n-m)/2 + 1. \tag{1}$$

The minimum value of delta (n-m) is -2, representing a linear/branched chain without any intramolecular cycles. Monomeric alkyltriethoxysilanes could be described as $T_1(OC_2H_5)_3$.

Table 3 shows the peak assignment for the spectra of the silsesquioxanes formed by reaction of Isooctyltriethoxysilane shown in Fig. 4. The intensity of the peaks is normalized using the highest peak which was set at 100%. Only peaks with intensities more than 5% are listed.

It can be seen that the reaction of iso-octyltriethoxysilane in an alkaline environment – as commonly present in concrete – leads to the formation of various species. An inorganic network (Si–O–Si bonds) is built by means of adding water and NaOH as a catalyst. Species – present after hydrolysis, condensation and crosslinking – with masses of up to 1900 u containing 3 to 11 Si-atoms were detected. The delta (n-m) of partially condensed species ranges from 0 to 10, i.e. 1 to 6 intramolecular cycles according to Eq. (1). The species $T_8(OH)_2$ shows the highest

intensity. A possible molecular structure of $T_8(OH)_2$ is an open cage structure with 4 intramolecular cycles as shown in Fig. 5.

More generic e.g. not specific for silane based hydrophobic admixtures, structures of silsesquioxanes with completely or incompletely condensed frameworks like cage structure, partial cage structure, open structure and ladder structure are shown elsewhere [13]. Other recorded predominant species are $T_9(OH)_1$ and $T_7(OH)_3$. All predominant species show a high degree of hydrolysis. In general they are fully hydrolyzed as no species with ethoxy groups could be detected. They also show a high degree of condensation with delta (n-m) > 2.

3.3. Extractable siloxane species from specimens

Fig. 6 shows the MALDI-TOF/MS mass spectra of Isooctyltriethoxysilane detected in the extracts of specimens prepared by means of an extraction with THF. These spectra are illustrated in the 800–1900 m/z range, since no peaks of siloxane species were detected below or above. The extractable species could be identified as silsesquioxanes and the peaks can be assigned to corresponding compounds as shown in Table 4. The intensities of the peaks are normalized to the highest siloxane peak, set as 100%, and only peaks with an intensity higher than 5% are listed. Besides the assigned siloxane peaks, some peaks of an unknown species as well as signals of a species, that has also been found in the negative control – caused by matrix compounds (cement paste, DHB, NaI, THF) – can be seen in the spectra.
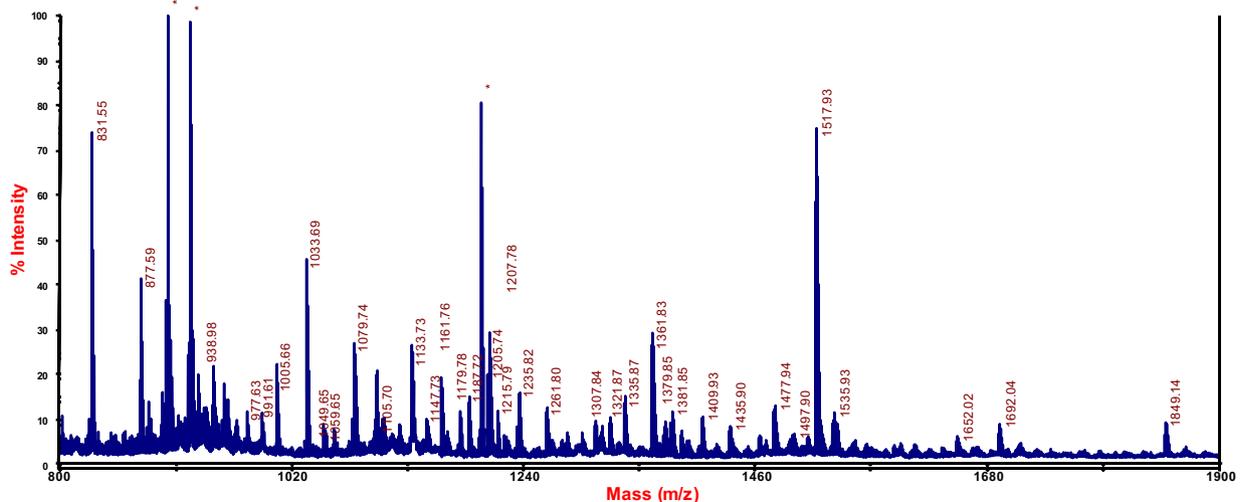

Fig. 6. MALDI-TOF mass spectra of leached Isooctyltriethoxysilane products (*: peaks are also found in the negative control).

Table 4

Assignment of MALDI-TOF/MS peaks (monoisotopic [M + Na$^+$]-adducts unless noted) of products of Isooctyltriethoxysilane leached from hardened cement paste; (R = Isooctyl; n.c.: not calculable due to overlay with other peaks; n.a.: not assigned).

m/z	Assignment	Intensity in %	m/z	Assignment	Intensity in %
831.55	$T_4(OR)_4$	74	1215.74	$T_7(OR)_1$	13
877.60	$T_4(OR)_5(OH)_1$	42	1235.82	$T_6(OR)_6$	16
931.58	$T_5(OR)_2(OH)_1$	20	1261.79	$T_7(OR)_2(OH)_1$	12
959.62	$T_5(OR)_3$	15	1307.83	$T_7(OR)_3(OH)_2$	10
977.62	$T_5(OR)_3(OH)_2$	12	1321.84	$T_8(H^+$-adduct)	10
991.61	$T_6(H^+$-adduct)	11	1335.86	$T_7(OR)_4(OH)_1$	16
1005.65	$T_5(OR)_4(OH)_1$	23	1361.82	$T_8(OH)_2$	30
1033.69	$T_5(OR)_5$	46	1379.83	$T_8(OH)_4$	10
1049.63	$T_6(OH)_4$	9	1381.90	$T_7(OR)_5(OH)_2$	n.c
1059.65	$T_6(OR)_1(OH)_1$	8	1409.93	$T_7(OR)_6(OH)_1$	11
1105.69	$T_6(OR)_2(OH)_2$	10	1435.89	$T_8(OR)_2(OH)_2$	8
1133.72	$T_6(OR)_3(OH)_1$	27	1477.94	n.a.	12
1147.73	n.a.	10	1517.92	$T_9(OH)_1$	75
1161.75	$T_6(OR)_4$	20	1535.93	$T_9(OH)_3$	10
1179.76	$T_6(OR)_4(OH)_2$	12	1652.03	$T_{10}(H^+$-adduct)	6
1187.71	$T_7(OH)_1$	16	1692.02	$T_{10}(OH)_2$	9
1205.74	$T_7(OH)_3$	20	1848.12	$T_{11}(OH)_1$	10
1207.79	$T_6(OR)_5(OH)_1$	n.c.			

Species with masses of up to 1900 u containing 4 to 11 Si-atoms could be detected. The delta (n-m) of partially condensed species ranges from 0 to 10, i.e. 1 to 6 intramolecular cycles according to Eq. (1). $T_9(OH)_1$, a fully hydrolyzed species with 5 intramolecular cycles shows the highest peak intensity.

The used method of MALDI-TOF/MS implies that the analytes are soluble in the solvent used for the extraction. If there are any reaction products of Isooctyltriethoxysilane on the surface of the specimens which are insoluble in the used solvent they cannot be detected by this method. Hence our leaching process of siloxane species with THF as a solvent is not quantitatively approached.

The comparison of the results of the leached species with those formed in aqueous solutions of NaOH shows a congruency regarding the mass range. The species with a lower degree of hydrolysis as well as those with a lower degree of crosslinking show some higher intensity in the leached sample. So the ratio of condensation versus hydrolysis is somewhat higher. It can be seen that the alkaline environment of the aqueous NaOH solution and THF as a solvent leads to results similar to those obtained by the environment of the specimens, i.e. species which are similar in chemical structure are formed. So the alkaline environment of the hardened cement paste is mainly responsible for the reaction path of the Isooctyltriethoxysilane in concrete. The comparison of these results with modeling results by means of computational chemistry shows, that there is a good correlation between the detected species by MALDI-TOF–MS and the theoretical ones [5].

4. Conclusions

The combined use of ESI-TOF/MS and MALDI-TOF/MS enabled us to characterize silane-based hydrophobic admixtures, e.g. alkyltrialkoxysilanes and their reaction products as intact species formed under alkaline conditions like they prevail in concrete and other cementitious materials. Operating in the positive ion mode mainly Na-adducts of species could be detected and selectively identified by their masses. Monomeric alkyltrialkoxysilanes could be characterized by ESI-TOF. The reaction steps hydrolysis, condensation and crosslinking of alkyltrialkoxysilanes with hydroxide as a catalyst form more complex siloxane species which are called Silsesquioxanes (SSOs). These SSOs were further characterized by MALDI-TOF/MS. The various species detected are mainly fully hydrolyzed and consist of intramolecular cycles caused by the alkaline environment of concrete. These data can be used to establish a relationship between the chemical structure and the chemical reactivity which is important for the development of new silane-based water repellents with an increased durability. Also, it enabled us to analyze if an unknown cementitious material has been hydrophobized by alkyltrialkoxysilanes and which compounds e.g. which kind of alkyl- and alkoxygroups were used. So, TOF-MS is a high-performance tool for analyzing silane-based hydrophobic admixtures.

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