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Investigations on the metabolism of alkyl polyglucosides and their determination in waste water by means of liquid chromatography–electrospray mass spectrometry

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Abstract

Alkyl polyglucosides (APGs) were analyzed by reversed-phase liquid chromatography coupled to mass spectrometry with electrospray ionization. Analytes were separated according to the chain length of the alkyl homologues, whereas the separation of isomeric forms of the glucose moiety was achieved partially. Depending on the structure of the glucose ring the alkyl monoglucosides show a distinct affinity in terms of the formation of sodium and ammonium adduct ions. Metabolism of isomer pure alkyl monoglucosides was studied on a testfilter device to gather information about the degradation behavior and to obtain eventually poorly degradable metabolites. In spite of unsuccessful detection of any metabolites such as ‘‘polyglucoside alcanoic acids’’, a degradation pathway was proposed including the cleavage of the glucosidic bond as initial step. In addition, a method for the determination of APGs in municipal waste water effluent was developed using solid-phase extraction on reversed-phase material. Recovery rates were in the range of 66 to 98% for three spiked alkyl monoglucosides and a quantitation limit of 0.2 $\mu g\ l^{-1}$ was achieved. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Surfactants; Alkyl polyglucosides

1. Introduction

Alkyl polyglucosides (APGs) are non-ionic surfactants produced on basis of renewable feedstocks such as glucose and fatty alcohols deriving from starch and palm oil [1]. They have been known since 1893 but it is only in the last few years that they have been manufactured on an industrial scale. These surfactants consist of a complex mixture of a variety of homologues and isomers, including stereoisomers, binding isomers and ring isomers within the glucose moiety (Fig. 1). The global production rate in 1997 amounted to $8 \cdot 10^{7}$ kg [2]. Even if they are unlikely to become a main surfactant like soap, alkylbenzene sulfonates, alcohol ether sulfates or alcohol ethoxylates they play an important role as co-surfactants.

Due to favorable properties in terms of foaming performance, synergism with other surfactants and skin compatibility they are increasingly used in cleaning agents and detergents [3]. After usage in household products the APGs are discharged into the domestic sewage which is treated in the waste water treatment plant (WWTP). Compared to the ‘‘commodity’’ surfactants mentioned above for which comprehensive data compilation on influent concentrations, removal efficiency during biological treatment and effluent concentrations exist [4–6], there is little information available on the corresponding values of APGs. To the author’s knowledge there exist no data on effluent concentrations in

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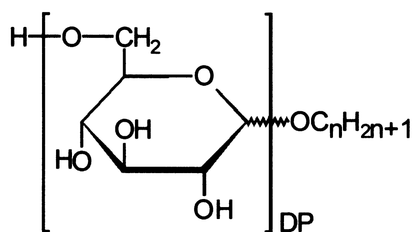

DP (degree of polymerization): 1,2 - 1,7
n: 8, 10, 12, 14, 16

Fig. 1. Simplified chemical structure of alkyl polyglucosides.

WWTPs. Calculated concentrations for German WWTPs for influent, effluent and receiving water are expected to be in the range of 10, 0.1 and 0.01 mg l^{-1} respectively [6].

In order to evaluate the biodegradation of APGs, a series of tests including the closed bottle-test, the modified Organisation for Economic Co-operation and Development screening test and the coupled units-test was carried out [7,8] allowing one to conclude the environmental acceptability of the non-ionic surfactants. However, these test methods are all based on the determination of sum parameters such as dissolved organic carbon (DOC), chemical oxygen demand (COD) or biological oxygen demand (BOD). Consequently no information is gathered regarding the metabolism pathway or the degradation kinetics.

To obtain such data a substance specific analytical method is essential enabling both the separation of the complex surfactants mixtures and the identification of individual constituents. Furthermore, a suitable testing device must be available for the isolation of metabolites.

As for the analytical determination of APGs several methods are described in the literature, e.g., colorimetric determination [9] or thin-layer chromatography [10]. Since these methods exhibit rather low sensitivity they were only used for bulk chemicals or formulations. For detecting APGs at low level concentrations as occurring in environmental samples more sophisticated methods like gas chromatography–mass spectrometry (GC–MS) are required [11]. To perform a GC determination the APGs have to be derivatized prior to analysis as they are not sufficiently volatile. This time-consuming step can be circumvented by using high-performance liquid chromatography (HPLC). Due to the lack of any chromophoric group in the surfactant molecule UV detection is fairly insensitive. However, mass spectrometry coupled to HPLC is the detection method of choice since it provides valuable information.

With regard to degradation studies a testing system based on the concept of Sontheimer was applied by the German chemical industry in order to determine the microbial poorly degradable fractions of DOC in sewage effluents. Later, this device was modified enabling one to study the degradation behavior of persistent organic compounds [12]. The filters are based on a biological fixed-bed reactors on which microorganisms are immobilized on glass beads.

A series of different classes of chemical compounds including aliphatic amines, aromatic sulfonates, organic acids and phosphates were investigated [12]. The formation of sulfophenyl carboxylic acids as primary degradation products of linear alkylbenzene sulfonates was also studied in depth [13].

This paper describes a new analytical protocol for the separation of APGs using HPLC coupled via an electrospray (ES) interface to a mass-selective detector. Degradation studies were carried out on a testfilter device spiked with three alkyl monoglucosides. Samples of this testfilter were investigated by means of LC–ES-MS with respect to the occurrence of metabolites. A simple analytical procedure for the determination of APGs in spiked municipal waste water was developed including solid-phase extraction (SPE), LC separation and MS detection.

2. Experimental

2.1. Reagents and standards

Technical blends of APGs were kindly supplied by Henkel (Düsseldorf, Germany). These mixtures contained alkyl homologues with mainly C_8/C_{10}- and

C_{12}/C_{14}-oligomers. Individual pure C_8, C_{10} and C_{12}-β-monoglucosides used for spiking were purchased from Sigma (Deisenhofen, Germany). The C_5 homologue used as internal standard was also provided by Sigma. The mobile phase was prepared from HPLC-grade acetonitrile (LiChrosolv, Merck, Darmstadt, Germany) and Milli-Q water (Milli-Q-Plus 185, Millipore). The reagent grade solvents hexane, acetone and methanol used were obtained from Merck.

2.2. High-performance liquid chromatography

For HPLC analysis a Perkin-Elmer binary pump PE 200 was used. The separations were carried out on a Superspher 60 RP-select B (5 μm) column (125×2.1 mm I.D.) which was thermostated at 35°C. A gradient was used in the separation. Mobile phase A consisted of acetonitrile–water (adjusted with ammonia to pH 7.9) (80:20, v/v), and mobile phase B consisted of water (adjusted with ammonia to pH 7.9)–acetonitrile (95:5). The gradient was initially held constant at 100% B for 2 min, then progressed within 2 min to 75% B. In the following 15 min B was increased linearly to 50% B. In order to elute unknown compounds from the column B was further reduced to 30% within 1 min and held constant for another 3 min. Finally the eluent composition was reset to the starting conditions and held until equilibration. Flow-rate was 0.2 ml min^{-1}, and the volume of the injection loop was 100 μl.

2.3. Mass spectrometry

A Perkin-Elmer Sciex API 150 MCA mass spectrometer equipped with a TurboIon interface was used. Data were acquired in full scan mode in a range of 200–600 u, cycle time was 0.7 min. For quantifying APGs in the testfilter samples as well as in the effluent samples, MS was operated in the negative-ion mode and acquisition mode was set to the selected ion monitoring (SIM) mode. The ion source conditions were as follows: positive mode (negative mode): source temperature: 400°C, ionspray voltage: +4.2 kV (−3.0 kV), orifice voltage: +35 V (−28 V). Nitrogen was used as heater gas with a flow-rate of 7 l min^{-1}.

2.4. Testfilter device

River Rhine water sample was continuously pumped from a 10-l storage tank upflow into a glass column (diameter: 5 cm, height: 23 cm, volume: 310 ml) in a closed loop. The pump (Concept b, ProMinent, Heidelberg, Germany) regulated the flow-rate to 15 ml min^{-1} and a membrane pump aerated the water in the storage tank via a glass frit. The glass column was packed with the carrier material up to a height of 18 cm. PTFE tubings (diameter: 6 mm) connected the individual components of the testfilter system. The whole set-up was kept away from light to prevent any photocatalytic degradation and the growth of algae. All experiments took place at 20°C.

2.4.1. Carrier material

Siran carrier (No. 023/02/300, Schott Engineering, Mainz, Germany): Siran carriers are native, porous sintered glass used for the immobilization of microorganisms (diameter: 2 to 3 mm, surface: 80 m^2 l^{-1} or 0.2 m^2 g^{-1}, porous diameter: 60 to 300 μm, mass: 450 g l^{-1}).

2.4.2. Preparatory phase

The water in the testfilter plant was replaced weekly with fresh river Rhine water to initiate biofilm formation on the carrier materials for a period of 50 days. Water quality, degradation rate and sorption capacity were monitored daily by measuring DOC, conductivity, dissolved oxygen, pH value, spectral adsorption $\alpha_{254\ nm}$ and temperature.

2.4.3. Sampling and sample preparation

In the storage tank of the testfilter device, 10 l of fresh river Rhine water were spiked with the different test compounds at a concentration of 1 mg l^{-1}. Samples of 50 ml were taken in short intervals, stabilized with 1 ml formaldehyde (37%) and stored for short period of time at 5°C. Untreated river Rhine water was also analyzed as control to check for background concentration. Prior to injection samples were filtered through a 0.45-μm glass fiber filter and the internal standard was added (final concentration: 250 μg l^{-1}). Measurements were carried out in the (–)-mode by LC–ES-MS.

2.5. Analysis of waste water treatment plant effluents

A SPE method was developed for the enrichment of APGs in spiked WWTP effluents. The solid-phase material (100 mg of LiChrolut EN, purchased from Merck) was manually filled into glass cartridges and was consecutively conditioned with 3×2 ml hexane, 3×2 ml acetone, 3×2 ml methanol and 6×2 ml water. A 100-ml volume of the spiked sample previously filtered through a glass fiber filter (0.45 μm) was sucked through the cartridge with a flow-rate of approximately 20 ml min^{-1}. The cartridges were then dried for 1 h with nitrogen and eluted three times with 1 ml methanol. The extracts were reduced under a gentle stream of nitrogen until dryness and then filled up to 1 ml with the LC eluent.

3. Results and discussion

3.1. Separation and detection by liquid chromatography–electrospray mass spectrometry

Applying LC–ES-MS the separation and identification of individual components in a technical blend of APGs was enabled. The detection is possible in both the positive and negative ionization modes.

Fig. 2A shows a typical LC–ES-MS chromatogram from a standard mixture of APGs registered in the negative ion mode with a scan range from 200–600 u. The obtained complex peak pattern is resolved by extracting the masses of the molecular ions $[M-H]^-$ of the constituents. In Fig. 2B and C the extracted ion chromatograms of the alkyl monoglucosides (C_8, C_{10} and C_{12}) and alkyl diglucosides (C_8, C_{10} and C_{12}) are depicted. The masses of the corresponding ions are summarized in Table 1.

The order of elution depends on the length of the alkyl chain as well as on the number of glucose units. Increasing chain length results in increased retention time. On the other hand the introduction of a second glucose moiety leads to weaker retardation on the C_8 column owing to higher hydrophilicity of the molecule. The C_8-, C_{10}- and C_{12}-monoglucosides are entirely separated according to the alkyl chain length (Fig. 2B). Moreover, a separation with regard to the ring isomery of the glucose moiety, i.e., pyranosidic or furanosidic form, is achieved. Peaks arising from stereoisomeric α- and β-alkyl monoglucosides are partially resolved. As for the alkyl diglucosides (Fig. 2C) the peak pattern of a specific alkyl homologue is much more complex compared to the corresponding monoglucoside. This is due to the higher number of possible isomers including ring isomers, stereoisomers and binding isomers. In the latter case the two glucose rings may be linked by a 1,4- or 1,6- glucosidic bond.

With the selected ion masses beside the assigned monoglucosides also a series of signals with low intensity are occurring which are indicated as 7*, 8* and 9* in Fig. 2B. These signals originate from fragment ions of diglucosides which are formed by the loss of one glucose unit resulting in fragments having the same mass as the corresponding alkyl monoglucosides.

The spectra of the octyl monoglucoside registered under positive and negative ionization mode are displayed in Fig. 3A and B. In the (+)-mode the molecule ion peak of both the sodium and the ammonia adduct is detected, whereas in the (−)-mode the base peak is assigned exclusively to $[M-H]^-$. In both cases characteristic fragmentation of the parent compound occurs tracing back to the cleavage of the glucosidic bond. In the (+)-mode three glucose fragments are detected, whereas in the (−)-mode a single glucose fragment is observed. The assignment of the daughter ions is listed in Table 2. The impact of the orifice voltage on the fragmentation pattern was investigated for C_{10}-β-glucopyranoside, showing that in the (−)-mode the intensity of the fragment ion m/z 161 relative to the one of the molecular ion rises with increasing voltage (set to −20, −50 and −80 V), whereas the intensity of $[M-H]^-$ (m/z 319) runs through a maximum (U_{max}: −28 V). When ES-MS is set to the positive mode the formation of the sodium and ammonium adduct ion is strongly dependent on the orifice voltage. Ramping this parameter from 0 to +100 V displays a rapid decrease of the intensity of $[M+NH_4]^+$, while the intensity of $[M+Na]^+$ is rising until a maximum at +35 V.

In the positive ionization mode a distinct selectivity of the monoglucosides with respect to the formation of adduct ions is observed. In dependence of the

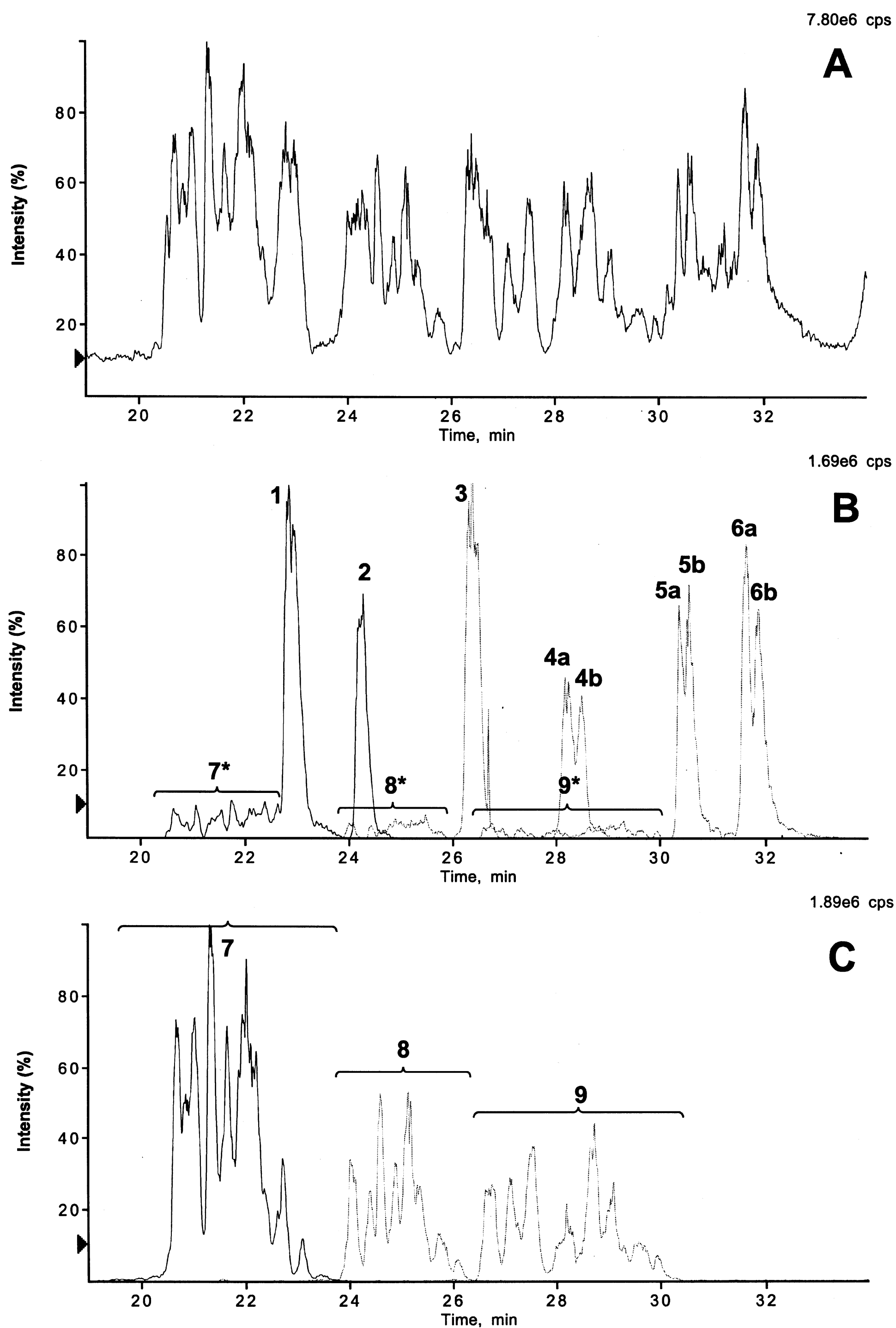

Fig. 2. (A) LC–ES-MS chromatogram (total ion current; TIC) of a standard solution, (B) extracted ion chromatogram (XIC) of C_8-, C_{10}- and C_{12}-monoglucosides and (C) XIC of C_8-, C_{10}- and C_{12}-diglucosides (1, 2: C_8-monoglucoside, 3, 4: C_{10}-monoglucoside, 5, 6: C_{12}-monoglucoside, 7: C_8-diglucoside, 8: C_{10}-diglucoside, 9: C_{12}-diglucoside).

Table 1
LC–ES-MS ion masses (m/z) of different molecular and quasi-molecular ions of alkyl mono- and diglucosides (as assigned in Figs. 2 and 5)

Compound	Number	Ion mass (m/z)		
		$[M-H]^-$	$[M+NH_4]^+$	$[M+Na]^+$
C_8-Monoglucoside	1, 2	291	310	315
C_{10}-Monoglucoside	3, 4	319	338	343
C_{12}-Monoglucoside	5, 6	347	366	371
C_8-Diglucoside	7	453	472	477
C_{10}-Diglucoside	8	481	500	505
C_{12}-Diglucoside	9	509	528	533

ring form (glucopyranoside or glucofuranoside) and the stereoisomery (α- or β-alkyl monoglucoside) a different affinity towards Na^+ and NH_4^+ appears. The molecular structures of the four possible isomers are shown for the octyl homologue in Fig. 4.

The SIM chromatogram of C_8-, C_{10}- and C_{12}-monoglucosides (ion masses as listed in Table 1) is displayed in Fig. 5A. The corresponding XIC showing the adduct ions $[M+Na]^+$ and $[M+NH_4]^+$ are given in Fig. 5B and C. While the alkyl glucofuranosides exhibit a higher tendency to form the sodium adduct, the alkyl glucopyranosides are preferably detected as ammonium adduct ion. Also the α- and β-isomers of the glucofuranosides manifest a much higher selectivity towards Na^+ and NH_4^+ compared to the two corresponding glucopyranosides. The following statements can be made exemplary for the dodecyl monoglucoside (5, 6): (a) α-glucofuranoside (6a) has a much higher affinity towards Na^+ compared to β-glucofuranoside (6b), (b) the peak of α-glucofuranoside (6a) is the most intensive signal among the four $[M+Na]^+$ signals, (c) α-glucopyranoside (5a) and β-glucopyranoside (5b) show no discrimination of Na^+ or NH_4^+ in terms of the formation of the corresponding adducts. These observations can be explained by specific interactions of the cation with the glucose moiety. Since the Na^+ and NH_4^+ have different ion radii (Na^+: 0.95 Å, NH_4^+: 1.43 Å) their coordination with the glucose moiety – presumably via hydroxy groups – depends on the spatial availability which is determined by the constitution and configuration of the glucose part. Further investigations regarding the impact of the ion size should be carried out using potassium as competitive adduct ion as the radius of this cation (1.33 Å) is comparable to that of ammonium.

It is noteworthy that sodium adduct ions are formed and detected even without addition of any sodium salt to the LC eluent. Seemingly the ions originate from impurities in the solvent and standards. Since the concentration of sodium is not adjusted to a certain level, the observations in terms of the formation of sodium and ammonia adducts may vary qualitatively. As recently described [14] a higher content in sodium resulted in the detection of $[M+NH_4]^+$ only for the glucopyranoside, whereas the sodium adduct is formed from both the glucopyranoside and the glucofuranoside.

Due to the limited reproducibility of adduct ion formation in the (+)-mode the following studies were carried out in the negative-ion mode.

3.2. Biodegradation

River Rhine water was spiked with 1 mg l^{-1} of each octyl-, decyl- and dodecyl-β-monoglucoside and continuously pumped through the filter bed. The temporal evolution of the test substance concentrations was followed up by LC–ES-MS. In Fig. 6 relative concentration of each homologue is plotted vs. time. The biodegradation curve shows a sigmoidal-shaped course that can be subdivided into a lag phase, where the acclimatization of the microorganisms to the test substances occurs (0 to 13 h), a degradation phase, in which the compounds are metabolized (13 to 21 h) and a plateau phase, in which degradation is nearly complete (after 1 day). During the first period a slight dependence of the adaptation rate on the alkyl chain length is observed

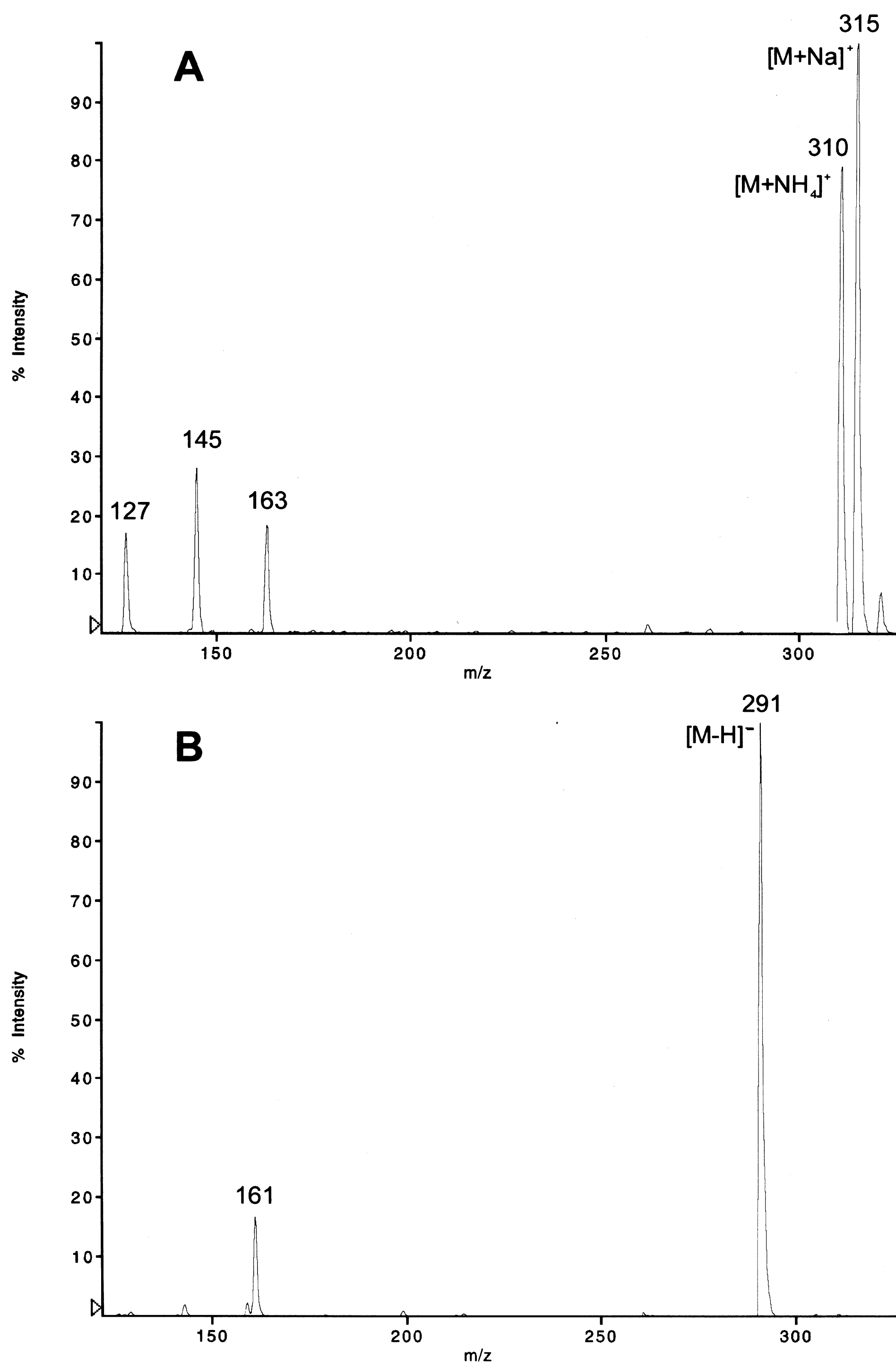

Fig. 3. LC–ES-MS spectra of octyl glucopyranoside under negative (A) and positive (B) ionization.

Table 2
Fragments of alkyl monoglucosides under (+)- and (−)-ionization in LC–ES-MS

Ionization mode	Ion mass (m/z)	Fragment
Positive	127	$[Glucose\text{-}3H_2O+H]^+$
Positive	145	$[Glucose\text{-}2H_2O+H]^+$
Positive	163	$[Glucose\text{-}H_2O+H]^+$
Negative	161	$[Glucose\text{-}H_2O\text{-}H]^-$

– increasing chain length goes along with faster degradation – whereas almost no difference is apparent in the final degradation phase.

The degradation behavior of the linear alkylbenzenesulfonates (LASs) submitted to the same test protocol was recently studied in our laboratory [13]. The primary degradation of these anionic surfactants was nearly complete after a period of 22 days at a test concentration of 5 mg l^{-1}. The half life period was 5 days compared to about 18 h in case of APGs. Thus the degradability potential of the latter is significantly higher for the applied assay.

The testfilter samples were also investigated with respect to the occurrence of possible metabolites. A breakdown pathway of the APGs is derived from the metabolism of LASs and alcohol ethoxylates, which are degraded by ω-oxidation of the alkyl chain resulting in carboxylic acids [15,16]. These are in turn further degraded by β-oxidation releasing acetyl-CoA. The corresponding mechanism for APGs is shown in Fig. 7, I. The search for the masses of the corresponding ''polyglucoside alcanoic acids'' (C_8-acid: m/z 322, C_{10}-acid: 350, C_{12}-acid: 378) using LC–ES-MS was unsuccessful. Neither in the (−)-mode where the masses of $[M-H]^-$ and $[M-CO_2\text{-}H]^-$ were investigated nor in the (+)-mode where the supposed acids should have been detected as the possible adduct ions $[M+Na]^+$ or $[M-H+2Na]^+$ was any indication of the presence of ''polyglucoside alcanoic acids'' given. An explanation for the non-detectability of those carboxylic

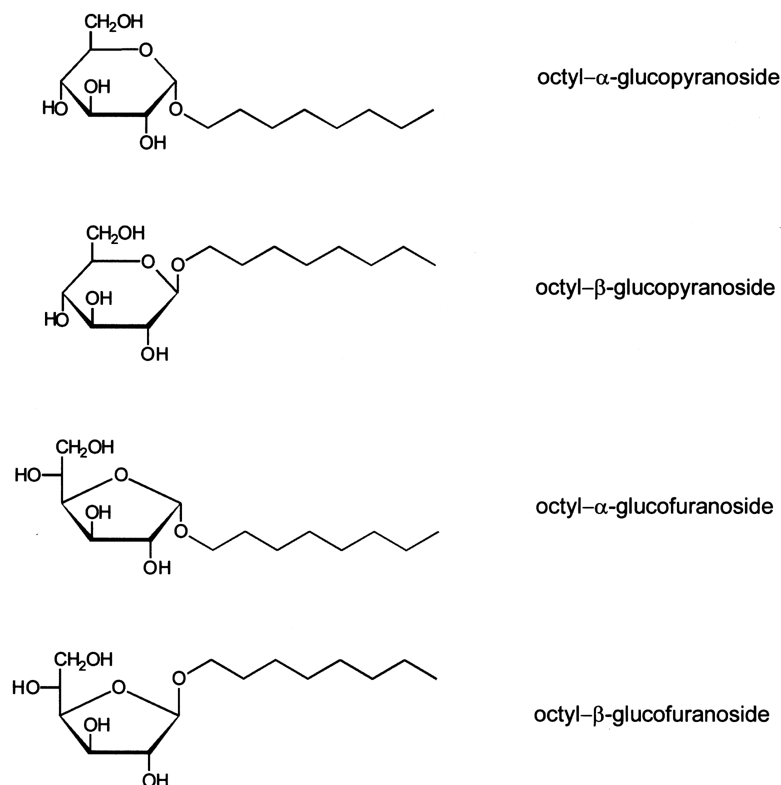

Fig. 4. Structures of ring and stereoisomers of octyl monoglucoside.

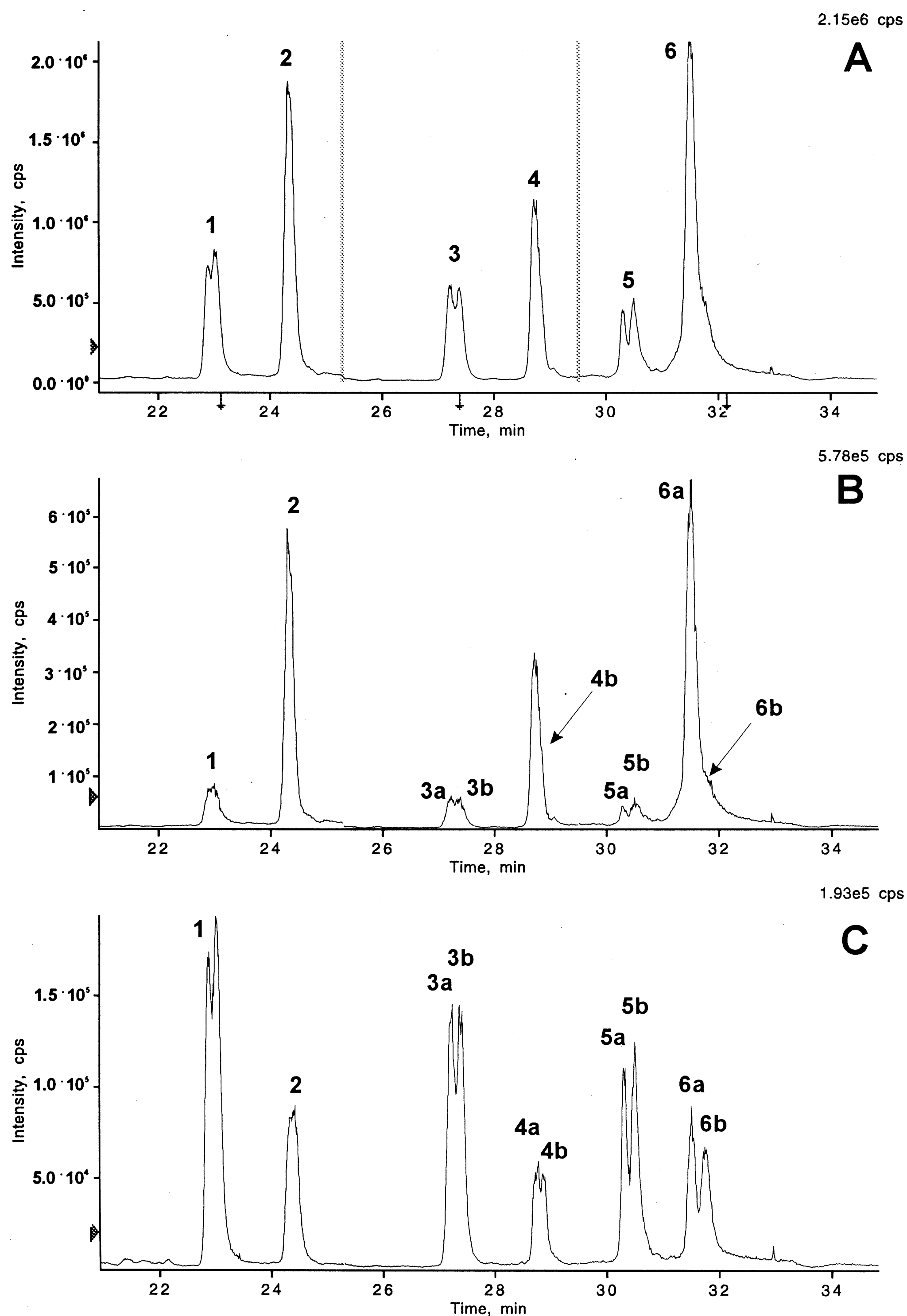

Fig. 5. (A) SIM chromatogram of C_8-, C_{10}- and C_{12}-monoglucosides in the (+)-mode, (B) XIC of $[M+Na]^+$, (C) XIC of $[M+NH_4]^+$ (1: C_8-glucopyranoside, 2: C_8-glucofuranoside, 3: C_{10}-glucopyranoside, 4: C_{10}-glucofuranoside, 5: C_{12}-glucopyranoside, 6: C_{12}-glucofuranoside, a: α-glucoside, b: β-glucoside).

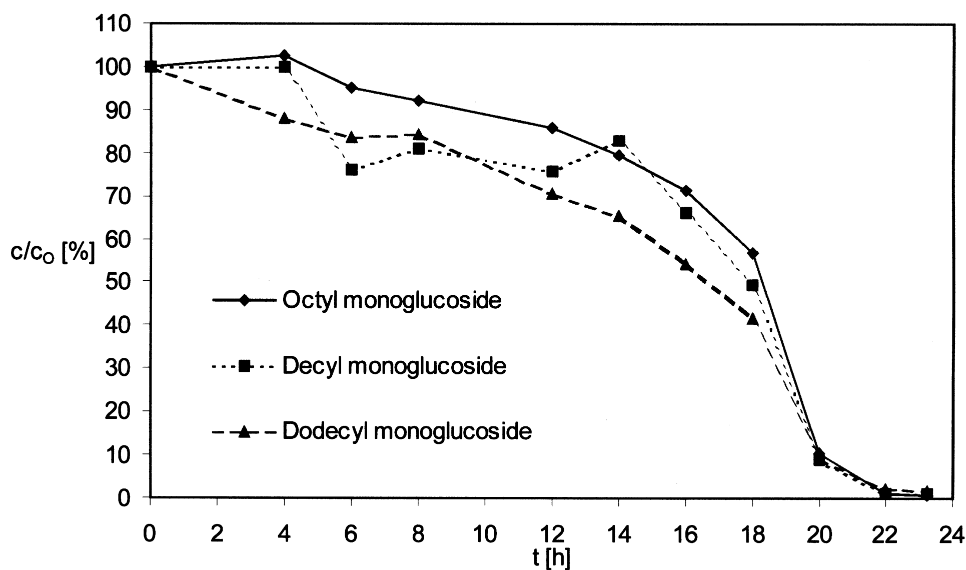

Fig. 6. Degradation curve of C_8, C_{10}- and C_{12}-β-glucopyranosides [$c_0(t_0)$=100%].

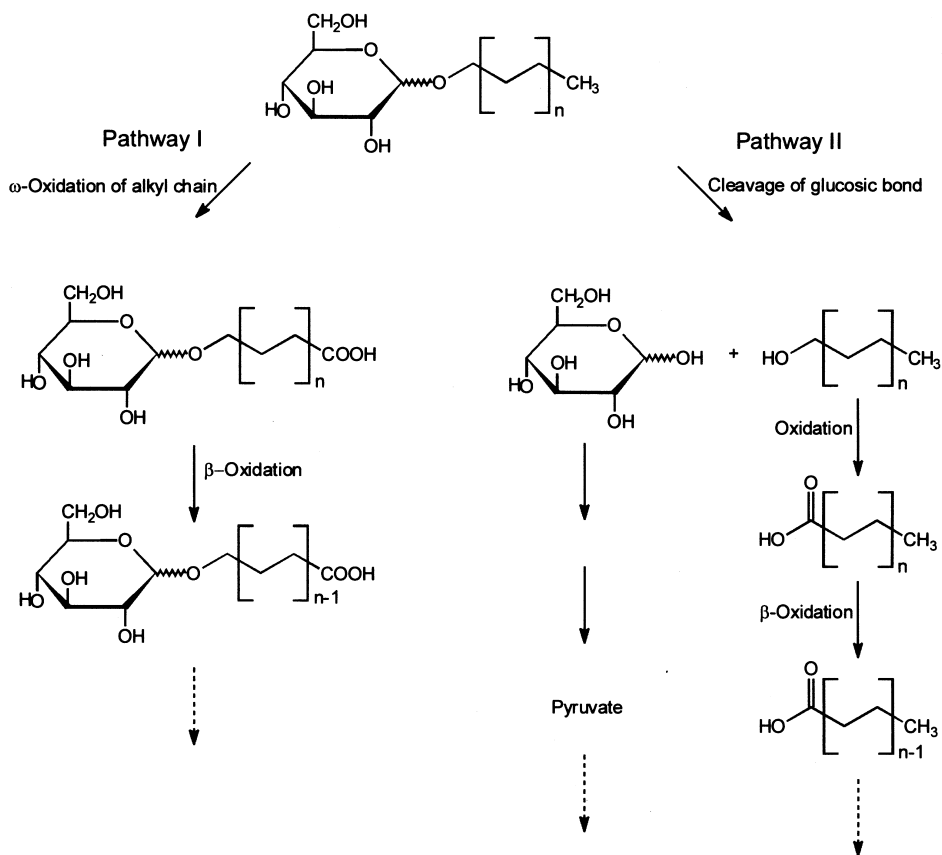

Fig. 7. Possible degradation pathways of alkyl glucopyranosides.

acids can be explained by a different degradation mechanism. This pathway (Fig. 7, II) encompasses the cleavage of the glucosidic bond leading to glucose and the fatty alcohol. In this case the glucose is rapidly further metabolized via pyruvate, whereas the fatty alcohol is oxidized to the corresponding acid which subsequently undergoes the classical fatty acid degradation mechanism. The lack of detection of the fatty acids which were also investigated with LC–ES-MS can be traced back to a fast intracellular metabolism.

3.3. Determination in waste water

An analytical protocol was developed enabling the detection of APGs – namely C_8-, C_{10}- and C_{12}-β-glucopyranosides – in spiked effluents from a municipal WWTP. After extraction of the aqueous samples on solid-phase cartridges the obtained extracts were separated via HPLC. The following detection was performed with ES-MS set to the SIM mode with negative ionization.

For quantitation purposes an external calibration was prepared in the concentration range from 5 to 200 μg l^{-1}. Calibration graphs (six points) exhibit good linearity for each of the three analytes with correlation coefficients better than 0.998 using C_5-glucopyranoside as internal standard and higher than 0.994 without internal standard.

In a first experiment the SPE was carried out on RP-C_{18}. This material which usually can be used for the enrichment of non-polar to medium-polar substrates proved to be inappropriate for the APGs as recovery rates for samples spiked at 1 μg l^{-1} were lower than 25%. Much better recoveries were achieved with the styrene–divinylbenzene based solid-phase LiChrolut EN material frequently applied for the enrichment of mid-polar to polar compounds. Results for effluent samples spiked at 0.2, 0.5 and 1 μg l^{-1} with a mixture of the three APG homologues were found to be in the range of 66 to 98% (mean 81% for $n=6$). A LC–ES-MS chromatogram of an extract is given in Fig. 8 showing that the three alkyl monoglucosides can clearly be identified.

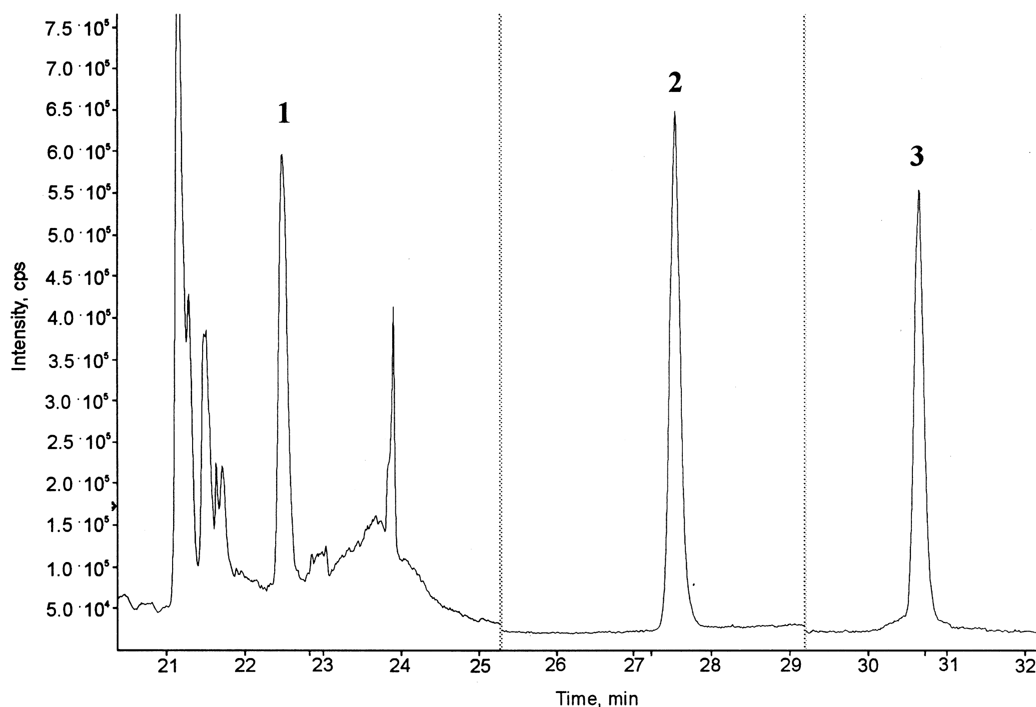

Fig. 8. LC–ES-MS chromatogram from effluent extract (spiked concentration 1 μg l^{-1}) (1: C_8-glucopyranoside, 2: C_{10}-glucopyranoside, 3: C_{12}-glucopyranoside).

When spiked effluent samples are measured directly, i.e., without sample enrichment on solid-phase material, concentrations of down to 10 μg l^{-1} are unambiguously detectable.

An influent sample from a WWTP receiving municipal sewage water was analyzed applying the developed methodology. The overall concentration for three detected monoglucosides (C_{10}, C_{12} and C_{14}) was 2 μg/l, whereas no APGs were detectable in the corresponding effluent from the same plant.

Acknowledgements

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