Journal of Chromatography A, 1356 (2014) 283–288

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Short communication

Evaluation of hydrolysis and alcoholysis reactions in gas chromatography/mass spectrometry inlets

Guomin Ai*, Tong Sun, Xiuzhu Dong

State Key Laboratory of Microbial Resources, Institute of Microbiology, Chinese Academy of Sciences, No.1 West Beichen Road, Chaoyang District, Beijing 100101, China

ARTICLE INFO

Article history:
Received 5 March 2014
Received in revised form 9 May 2014
Accepted 11 June 2014
Available online 19 June 2014

Keywords:
Hydrolysis
Alcoholysis
Septum particles
GC inlet liner
Methanol
Ethanol

ABSTRACT

During gas chromatography/mass spectrometry (GC–MS) analyses using water and methanol as injection solvents, hydrolysis reactions after injecting water control and alcoholysis reactions after injecting methanol control or ethanol into a GC–MS system were observed and studied. Two dominant hydrolysis/alcoholysis product series were detected, and were identified as being HO—$(CH_3)_2$Si—OR and HO—$(CH_3)_2$Si—O—$(CH_3)_2$Si—OR, where R = H, methyl, or ethyl, when pure water, methanol and ethanol were injected. The chemical structures of the reaction products were cross-checked by injecting H_2O/D_2O and H_2O/MeOH/EtOH, and comparable EI mass fragmentation patterns were found. The water and alcohols injected reacted with silicones in septum particles which accumulated in the injection port liner after numerous injections, and both hydrolysis and alcoholysis reaction products gradually increased in concentration as the number of injections increased. Potential interferences from hydrolysis or alcoholysis reactions should be paid attention to, evaluated or eliminated when water or methanol was used as the GC or GC–MS solvent, and especially when underivatized methanol or ethanol was subject to GC and GC–MS analysis.

1. Introduction

Silicones have been used extensively as gas chromatographic (GC) stationary phases [1,2]. In addition, most septa used in GC instruments are made of silicone rubber materials, such as Agilent BTO® septa [3]. This type of silicone rubber-based septum may be prone to coring or shedding particles into the injection port liner after repeated injections, and this behavior is related to the inlet temperature and physical interactions with the syringe needle [3].

There has been much research into the thermal degradation of GC stationary phases, especially the degradation of silicones [1,4,5]. The formation of cyclic siloxanes from the thermal degradation of GC septum is also occasionally mentioned in such studies [4]. In addition to the thermal degradation of such GC stationary phases and GC septa, the re-activation of deactivated GC columns when water or alcohols such as methanol are introduced has been also observed based on the impairment of chromatographic performances that can be restored by resilylating the newly formed silanol groups on the column wall [6]. However, to the best of our knowledge, almost no hydrolysis or alcoholysis products of GC stationary phases resulting from water or alcohols injection have been identified and reported in the literature, and no information is available on the occurrence of hydrolysis or alcoholysis reactions between the silicones that is used in the GC inlet and the polar solvents (e.g., water, methanol and ethanol) that are injected into GC or GC–MS systems.

This short communication describes a study of the hydrolysis and alcoholysis reactions that occur in a GC inlet system when water and alcohols (methanol and ethanol) are injected, respectively. We started to acquire fundamental knowledge on the hydrolysis and alcohol hydrolysis products that may affect analytical performance and pose potential problem in identification of compounds in sample. The use of water and methanol as GC and GC–MS solvents, and the popular application of GC and GC–MS techniques for analyzing underivatized methanol and ethanol (such as distilled spirits), provided motivation for this study.

2. Experimental

2.1. Materials, reagents and chemicals

Methanol (LC/MS grade) was purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ, USA). Water (LC/MS grade) and absolute

* Corresponding author. Tel.: +86 10 64807429; fax: +86 10 64807429.
E-mail addresses: agm2006@163.com, aigm@im.ac.cn (G. Ai).

http://dx.doi.org/10.1016/j.chroma.2014.06.036
0021-9673/

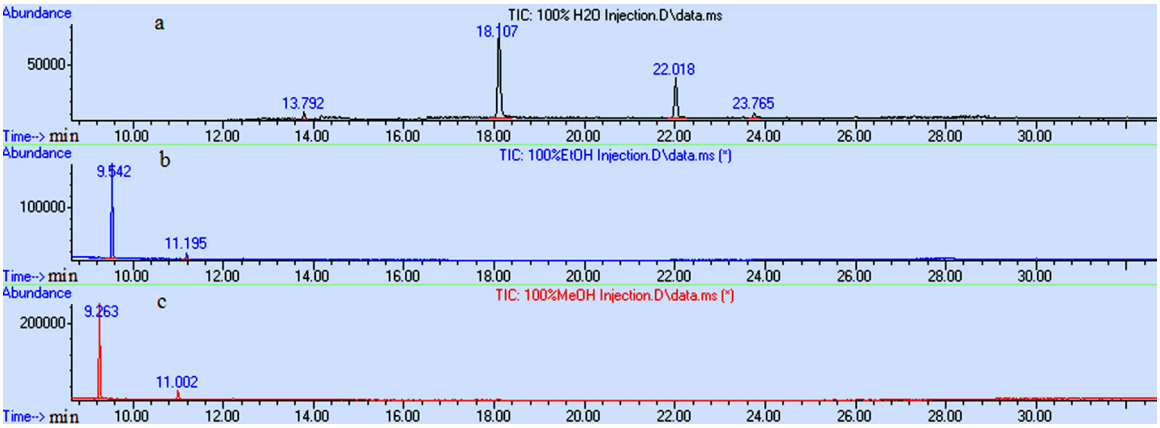

Fig. 1. GC–MS chromatograms of the separate injection of pure water (a), ethanol (b) and methanol (c), 0.2 μL each, in split (1/5) mode. Reaction products eluted at 9.263 and 11.002 min from 100% methanol injection, 9.542 and 11.195 min from 100% ethanol injection, and 13.792, 18.107, 22.018, and 23.765 min from 100% H_2O injection were detected.

ethanol (HPLC grade) were purchased from Duksan Pure Chemicals Co. Ltd. (Ansan, South Korea). D_2O (99.990% D) was purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. GC–MS analysis

GC–MS analyses were performed on an Agilent GC–MS system (7890A gas chromatograph and 5975C mass-selective detector; Agilent Technologies, Santa Clara, CA, USA) equipped with a DB-WAX column (30 m long, 250 μm i.d., 0.25 μm film thickness; Agilent Technologies). The inlet liner was an Agilent MS-certified split/splitless liner (part no. 5188–6576; 4.0 mm i.d., 870 μL volume, single taper, glass wool positioned in the middle of the liner). The septum was an Agilent BTO® septum (part no. 5183–4757; 11 mm diameter with "CenterGuide"). The GC conditions were as follows: split injection (injector temperature 230 °C, split 1/5 was used to place as much sample onto the column as possible); oven temperature, programmed from 35 °C (held for 3 min) to 47 °C at 5 °C/min, then to 100 °C at 25 °C/min, then to 145 °C at 2.5 °C/min, and then to 200 °C (held for 5 min) at 25 °C/min; the post-injection dwell time, 0.04 min; carrier gas and flow, He 1.0 mL/min; interface temperature, 160 °C. The injection volume was 0.2 μL. Under these conditions, the relative compounds to this work were (with elution times, in minutes, in brackets) methanol (3.8), ethanol (4.6), water (6.8), products 1 (9.3) and 2 (11.0) (from pure methanol injections), products 1 (9.5) and 2 (11.2) (from pure ethanol injections), products 1 (13.8), 2 (18.1), 3 (22.0), and 4 (23.8) (from pure water injections). The MS was used in electron impact (EI) ionization mode, with electron energy of 70 eV, an ion source temperature of 230 °C, and a quadrupole temperature of 150 °C. Data were acquired in full-scan (m/z 10–500) mode. Solvent delay of 12.0, 8.3, 9.0 and 8.55 min were used when pure water (and D_2O), methanol, ethanol, and a mixture of methanol and ethanol (1:1, v/v) were injected, respectively. Data were acquired and analyzed using Enhanced ChemStation (Version E.02.00.493, Agilent Technologies).

In order to measure changes in the responses of the reaction products as the number of injections increased, water and the mixture of methanol and ethanol (1:1, v/v) were alternately injected. For reducing the sample run time, a shorter GC oven program was run from the 32nd to the 59th, the 64th to the 129th, and the 134th to the 179th injections. The shorter GC oven program was: 100 °C, increased at 25 °C/min to 200 °C, which was held for 3 min. A solvent delay of 6.8 min (the total short run time was 7 min) was used, so that no analytes were detected during these sample runs.

3. Results and discussion

3.1. Reaction product peaks caused by water/alcohol injection

When pure water, methanol or ethanol was injected into the GC–MS system, four product peaks (eluted at 13.792, 18.107, 22.018, and 23.765 min) were found from water, two peaks (eluted at 9.263 and 11.002 min) were found from methanol, and two peaks (eluted at 9.542 and 11.195 min) were found from ethanol, as shown in Fig. 1. The retention times of all the product peaks were constant during all of the experiments. However, none of the product peaks were detected when either air injections or empty injections (manually started GC–MS runs without an injection) were performed. Therefore, we concluded that the peaks were for products of reactions between water or alcohol and the organic matter in the GC–MS (specifically in the GC) system. These reaction products were identified (or speculatively identified), and the positions in the GC system where the reactions took place were identified, as described below.

3.2. Identification of the hydrolysis/alcoholysis products

We acquired EI mass spectra of the water injection reaction products eluted at 18.11 and 22.02 min (a2 and a3 in Fig. 2), the methanol injection products eluted at 9.26 and 11.00 min (a1 and a2 in Fig. 3), and the ethanol injection products eluted at 9.54 and 11.20 min (b1 and b2 in Fig. 3). We found two reaction product series with m/z differences of 14 between the fragment ions, which were m/z 77 (a2 in Fig. 2), m/z 91 (a1 in Fig. 3) and m/z 105 (b1 in Fig. 3), and m/z 151 (a3 in Fig. 2), m/z 165 (a2 in Fig. 3) and m/z 179 (b2 in Fig. 3), from water, methanol and ethanol injection, respectively. The difference in the m/z ratios (14) is simply the difference in the molecular mass between water, methanol and ethanol, indicating the possibility that there were two kinds of hydrolysis and alcoholysis reactions. The fragment ion schemes for the six reaction products mentioned above were proposed and their chemical structures were identified and are shown in Fig. 4a. These results were confirmed using D_2O injections (b2 and b3 in Fig. 2). The chemical structures of the six hydrolysis/alcoholysis products were cross-checked using H_2O/D_2O injections and H_2O/MeOH/EtOH injections, which gave comparable mass fragmentation patterns.

In the case of water injection, the two minor reaction products eluted at 13.8 and 23.8 min were speculatively identified, and we did not take any more measures to confirm their chemical structures. Their proposed chemical structures and EI fragmentation patterns are shown in Fig. 4b.