Accurate Mass Analysis of Hydraulic Fracturing Waters: Identification of Polyethylene Glycol Surfactants by LC/Q-TOF-MS

Application Note

Authors

E. Michael Thurman and Imma Ferrer
Center for Environmental Mass Spectrometry
Department of Environmental Engineering
University of Colorado
Boulder, CO
USA

Abstract

A combination of UHPLC followed by LC/Q-TOF-MS was used to detect suites of polyethylene glycol compounds (PEGs) that occur in flowback water samples from hydraulic fracturing. The Kendrick Mass Defect was applied to differentiate the various adducts within a suite of PEGs. A database of the accurate masses along with their retention times by UHPLC has been designed to enable rapid and accurate analysis of either groundwater or flowback samples from hydraulic fracturing. Forty PEGs and their various adducts and multiply-charged ions can be identified in less than 2 minutes of computer time.

Agilent Technologies

Introduction

Hydraulic fracturing (fracking) extracts oil and gas by forcing fluids into oil and gas rich shale deposits. The fracking fluids contain a mixture of proppants (sand), surfactants, biocides, inorganic salts, and other compounds intended to facilitate the release of the trapped gas. More than 7,000 wells have been drilled in Colorado alone, and reports of groundwater contamination have occurred most notably in Wyoming, New York, and Pennsylvania [1]. The first water that returns from the fracking process (flowback) has the potential to contaminate nearby aquifers or surface water. Care is taken to recycle the flowback water, or to dispose of it properly, although the Safe Drinking Water Act does not apply to hydraulic fracturing solutions [2]. Thus, there is a demand for tracer compounds that are indicative of the presence of contamination by hydraulic fracturing and do not occur in the subsurface [2].

In this application note, a combination of ultra high performance liquid chromatography (UHPLC) followed by quadrupole time-of-flight tandem mass spectrometry (Q-TOF-MS/MS) was used to detect a bimodal distribution of polyethylene glycols that may be used as indicator compounds for groundwater or surface water impacted by flowback waters. The Kendrick Mass Defect [2,3] was applied in a novel application to differentiate the various adducts of a suite of glycols, in particular, the proton, ammonium, and sodium adducts of each of the chains of glycols. The database of the accurate masses along with their retention times by UHPLC is needed to provide a rapid and accurate analysis of either groundwater or surface water samples using Agilent MassHunter Software.

Experimental

Instruments

Separation of the analytes was carried out using an Agilent 1290 Infinity LC System coupled to an Agilent 6540 Ultra High Definition (UHD) Accurate-Mass Q-TOF LC/MS system equipped with electrospray Jet Stream Technology. The instrument conditions are shown in Table 1.

Sample collection

The flowback sample was collected on October 14, 2014 and obtained from Weld County, Colorado, with the help of James Rosenblum, University of Colorado, Department of Environmental Sustainability.

Table 1. LC and Q-TOF MS Conditions and Analysis Parameters

LC run conditions	
Column	Agilent ZORBAX Eclipse XDB-C8, 4.6 × 150 mm, 3.5 µm
Column temperature	25 °C
Injection volume	10 µL
Mobile phase	A) 0.1% formic acid in water v/v B) Acetonitrile
Linear gradient	10% B for 5 minutes; 10% B to 100% B over 25 minutes
Flow rate	0.6 mL/min
Post run	12 minutes
Q-TOF MS conditions	
Ion mode	ESI, positive
Drying gas	10 L/min
Gas temperature	325 °C
Nebulizer gas	45 psig
Sheath gas	11 L/min at 350 °C
Capillary voltage	4,000 V
Nozzle voltage	1,000 V
Fragmentor voltage	190 V
Skimmer voltage	45 V
Octopole RF	750 V
Mass range	*m/z* 50–1,000
Detector rate	2 GHz
Resolving power	30,000 at *m/z* 1,522

Data analysis

The data were processed with Agilent MassHunter Software. Accurate mass measurements of each peak from the total ion chromatograms were obtained by means of an automated calibrant delivery system using a low flow of a calibrating solution (calibrant solution A, Agilent Technologies, Inc.) that contained the internal reference masses purine *m/z* 121.0509 and HP-921 at *m/z* 922.0098. The instrument provided a typical mass resolving power of 30,000 at *m/z* 1522.

Results and Discussion

UHPLC/Q-TOF-MS analysis of hydraulic fracturing waters

The positive ion electrospray total ion current (TIC) chromatogram for the analysis of the flowback water exhibits two distinct zones, or a bimodal distribution (Figure 1). First is a polar series of peaks at a retention time of 4–12 minutes, and second is a less-polar zone that elutes from 12–14 minutes. The series of peaks in both zones are separated by a nominal mass of 44 mass units, which suggest a glycol structure consisting of CH_2-CH_2-O (Table 2). Furthermore, the accurate mass data in Table 2 show that the differences for the first seven peaks are 44.0266, on the average. A similar result was also observed for the second region between 12–14 minutes in Figure 1 (data not shown). There is an apparent repeatable relationship among the chromatographic peaks, which makes it is possible to apply the Kendrick mass scale [3].

Kendrick mass scale

Kendrick used a filtering technique (scaling factor) named after him to better separate and understand a series of hydrocarbons that differed in mass by a methylene group, CH_2. The Kendrick mass scale has been applied to other series, but only recently to the polyethylene glycol structures and linear alkylethoxylates in flowback and produced waters from hydraulic fracturing by Thurman *et al*. in 2014 [2].

The application of the Kendrick mass scale first involves the determination of the Kendrick mass scaling factor, which is determined as the ratio of the nominal mass of the repeating glycol unit, (CH_2CH_2-O), divided by the exact calculated mass of the same glycol unit. This is equal to 44/44.026214748, which gives a scaling factor of 0.999404559. When this scaling factor is multiplied by the measured accurate mass, the resulting mass is called the Kendrick mass [2]. For example, Table 2 shows the Kendrick masses for some of the chromatographic peaks in Figure 1.

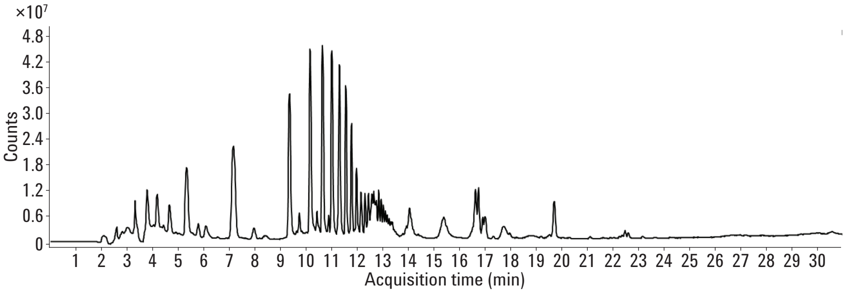

Figure 1. UHPLC/Q-TOF-MS chromatogram of a flowback sample from a recently hydraulic fractured well, which shows a bimodal distribution of polymers that differ by 44.026 mass units, a hydrophilic zone at 4–12 minutes and a second less-polar zone at 12–14 minutes.

*Table 2. Kendrick Mass for a Suite of Polyethylene Glycols Found in Flowback Water with an Average Mass Difference of 44.0266**

Retention time (min)	Ion (*m/z*) measured accurate mass	Kendrick mass	Ion adduct
3.5	173.0776	172.975	Na + PEG-EO-3
4.2	217.1048	216.975	Na + PEG-EO-4
5.4	261.1309	260.975	Na + PEG-EO-5
7.3	305.1586	304.975	Na + PEG-EO-6
9.5	349.1830	348.975	Na + PEG-EO-7
10.2	393.2095	392.975	Na + PEG-EO-8
10.7	437.2373	436.977	Na + PEG-EO-9
10.7	432.2830	432.026	NH_4 + PEG-EO-9
11.0	476.3067	476.023	NH_4 + PEG-EO-10
11.3	520.3333	520.023	NH_4 + PEG-EO-11

*JR-5 sample from Weld County, Colorado, based on a scaling factor of 0.999404559.

The concept of the Kendrick mass defect can then be applied, which is that if two compounds have the same repeating chemical structure, that is, $(CH_2CH_2\text{-}O)$, then there will be an addition of the exact mass of $CH_2\text{-}CH_2\text{-}O$ to each new compound in a chromatogram. Thus, when the scaling factor is multiplied by the measured masses, all the ions that differ by the $CH_2\text{-}CH_2\text{-}O$ group will have exactly the same mass defect (within the error of accurate mass measurement, which is typically ±0.001 mass units). These results are shown in Table 2.

For example, Table 2 shows that the measured accurate masses for ions at retention times of 3.5 to 10.7 minutes all had different mass defects ranging from 0.0776 to 0.3333. However, after multiplying by the appropriate Kendrick mass scaling factor for the glycol unit $(CH_2CH_2\text{-}O)$ of 0.999404559, only two mass defects, 0.975 and 0.023, were found for this suite of 9 ions (Table1). The fact that all of the Kendrick mass defects for each type of ion adduct are nearly identical means that each of the compounds increases by one ethylene glycol unit, or an accurate mass of 44.0262. Thus, it is only necessary to obtain the correct formula and structure for one of the glycols, and then all others can be calculated as either one unit longer or shorter depending on the gain or loss of the 44.0262 mass unit.

Using the measured mass of 305.1586 (a sodium adduct in Table 2), which also shows a proton adduct at *m/z* 283.1753 in Figure 2, a formula can be determined using MassHunter Software, as shown in Figure 2. The proton adduct at 283.1753 is first highlighted, followed by using the **Generate Formula** option to determine the best formula, shown in Figure 2 as $C_{12}H_{26}O_7$, which is the neutral molecular formula.

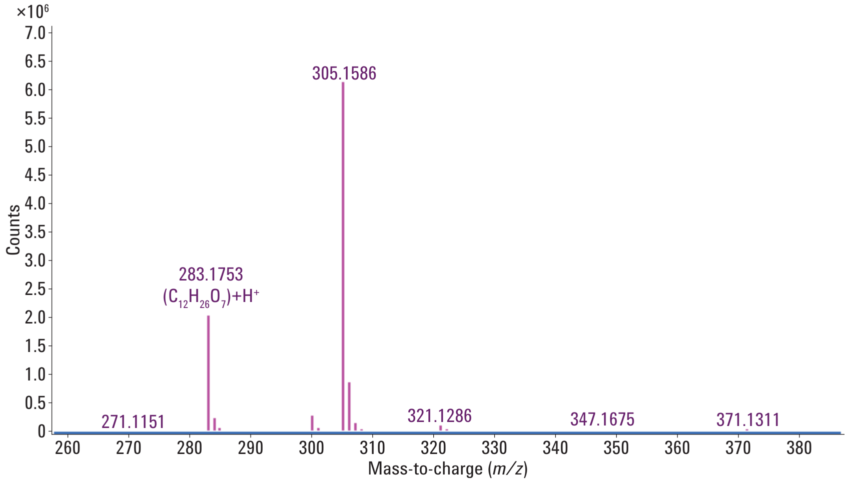

Figure 2. Q-TOF-MS scan from 7.060 to 7.409 minutes, showing the proton adduct at m/z 283.1753 along with the formula generated in Agilent MassHunter Software. The sodium adduct of the ion is also shown at m/z 305.1586.

Analysis by MS/MS of the *m/z* 283.1753 can determine if the spectrum will match a polyethylene glycol structure, as shown in Figure 3. The mass spectrum consists of a series of 44.026 mass unit losses that translate into a simple PEG structure [4]. The polyethylene glycol unit is equal to $HO\text{-}(CH_2CH_2O)_n\text{-}H$, which means that the chain length of the unit must be n = 6, since this length provides the correct formula of $C_{12}H_{26}O_7$. Table 2 can then be used to assign PEG-7 and PEG-8 to the higher mass ions, as well as PEGs -3, -4, and -5 to the lower mass ions, since all of the compounds with the same Kendrick mass differ by one glycol unit.

Figure 4 shows the mass spectrum for PEG-9 at a retention time of 10.6 minutes with three major ions at *m/z* 415.2539, 432.2830, and 437.2378. The mass differences among these three ions are 17 and 22, which indicate that the proton adduct is at 415.2539. What is important to note about the PEG-9 is that the major adduct ion for PEG-9 is no longer the sodium adduct, but rather the ammonium adduct (compare Figures 2 and 4). The mobile phase does not contain ammonium; thus, the ammonium adduct is formed from trace levels of ammonium present in the mobile phase and sample [2]. This shift to the ammonium adduct at PEG-9 has been attributed to a cage-like structure that surrounds the ammonium ion more readily (that is, energetically) and favors the ammonium ion over the sodium ion adduct [2]. The same is true for ammonium adducts of PEG-10 and PEG-11.

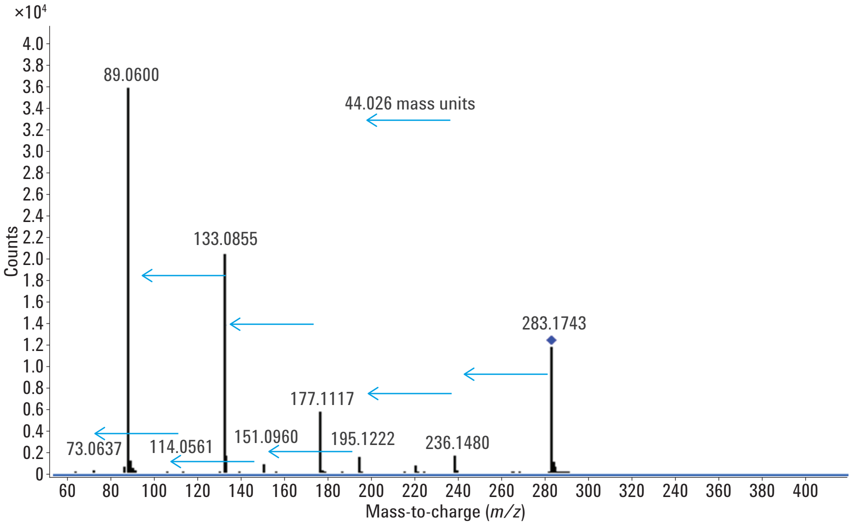

Figure 3. MS/MS spectrum of the m/z 283.1743 proton adduct from Figure 2.

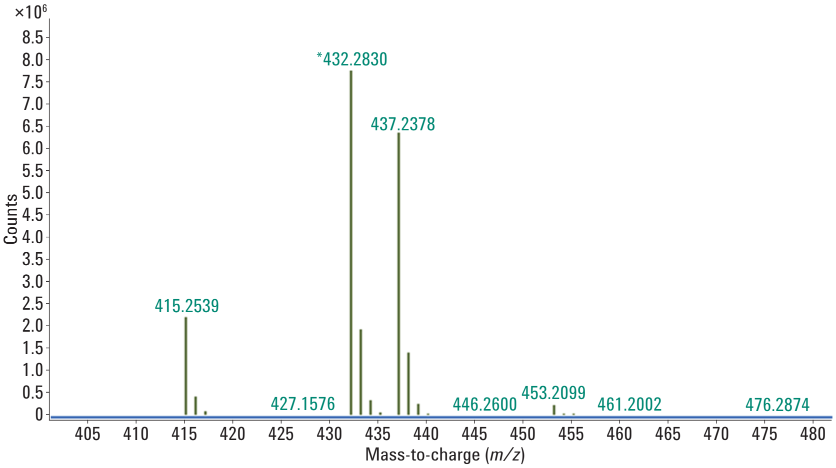

Figure 4. The mass spectrum at 10.6 minutes for PEG-9, with the major ion being the ammonium adduct at m/z 432.2830.

An accurate mass database of PEG compounds

After the application of this Kendrick mass scale, it was possible to identify proton, sodium, and ammonium adducts of the various PEGs shown in Figure 1. These enabled the construction of an accurate mass database of these PEG ions and adducts. It also allowed subsequent use of the MassHunter Software to find the > 40 different PEGs shown in Figure 1, as well as their various ion adducts, in less than 2 minutes of computer time. Identification of these PEGs may enable their use as indicators of contamination of aquifers or surface water by hydraulic fracturing.

Conclusions

The Agilent 1290 Infinity LC System and Agilent 6540 LC/Q-TOF-MS enabled the UHPLC/MS/MS characterization of two sets of representative polyethylene compounds from hydraulic fracturing flowback samples. Applying the Kendrick mass scale to the accurate masses of these PEGs and other ethoxylated surfactants [2] facilitates their identification using Agilent MassHunter Software, and the construction of a database of such compounds present in flowback samples. This database can, in turn, enable the use of these compounds as unique tracers of hydraulic fracturing.

References

1. D. M. Kargbo, R. G. Wilhelm, D. J.Campbell. "Natural gas plays in the Marcellus Shale: Challenges and potential opportunities" *Environ. Sci. Technol.* **44**, 5679-5684 (2010).
2. E. M. Thurman, I. Ferrer, J. Blotevogel, T. Borch. "Analysis of hydraulic fracturing flowback and produced waters using accurate mass: identification of ethoxylated surfactants" *Anal. Chem*. **86**, 9653-9661 (2014).
3. E. Kendrick. "A mass scale based on CH_2 = 14.0000 for high resolution mass spectrometry of organic compounds" *Anal. Chem.* **35**, 2146-2154 (1963).
4. I. Ferrer, E. T. Furlong, E. M. Thurman, in *Liquid Chromatography/Mass Spectrometry*, *MS/MS and Time-of-Flight MS: Analysis of Emerging Contaminants*, Ferrer, I. Thurman, E. M, Eds.; ACS Symposium Series 850; American Chemical Society: Washington, D.C. pp 376-393.

Acknowledgements

The authors thank James Rosenblum of the University of Colorado for sample collection and for sharing the flowback sample for this application note.

www.agilent.com/chem

Printed in the USA
February 18, 2015
5991-5473EN