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Accurate Mass Analysis of Hydraulic Fracturing Waters

Using the Kendrick mass defect with the Agilent LC/Q-TOF MS

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Abstract

To detect a set of polypropylene surfactants that may be used as clay stabilizers, scale inhibitors, or surfactants, water samples from hydraulic fracturing were analyzed using a combination of UHPLC and Q-TOF-MS. Because of their structure, with the accurate mass measurement of the Q-TOF, a Kendrick mass defect tool was developed and used to help separate the mixture of polypropylene surfactants and their adducts, present in many hydraulic fracturing samples. This Application Note discusses the chromatography associated with the polypropylene-glycol surfactants, in regards to the multiple isomers that form. The polypropylene-glycol surfactants (PPGs) make excellent tracers of hydraulic fracturing wastewaters, since they are not commonly detected in surface and groundwater samples. PPG surfactants have been detected in approximately 20 samples from Colorado, North Dakota, Oklahoma, and Texas.

Introduction

Hydraulic fracturing, sometimes called fracking, is the process of removing gas and oil from clay-rich deposits that were previously unproductive because of the low yield of hydrocarbons. The combination of horizontal drilling at great depth (7,000 to 10,000 feet below the surface), and the use of a mixture of water, proppants (sand), surfactants, biocides, and other chemicals, has enabled the economic recovery of both gas and oil. This process of hydraulic fracturing has revolutionized gas and oil recovery during the last 10 years. It has created a booming oil business in the western United States, especially in Colorado, Texas, and the Dakotas. One of the concerns with hydraulic fracturing is the large volumes of water that are needed per well, approximately 3–5 million gallons, depending on the depth of the well. Less than half of this water returns to the surface where either recycling or disposal is required. For proper handling, it is critical to know the constituents of this wastewater, organic and inorganic. Thus, there is a need for rapid and accurate measurement of the chemicals in these waters.

This Application Note used a combination of ultrahigh performance liquid chromatography (UHPLC) followed by quadrupole time-of-flight mass spectrometry (Q-TOF-MS) to separate and identify many of the chemicals present in the wastewaters. One of the key tools for this process is the Kendrick mass defect. This tool takes advantage of the fact that the polymeric chemicals used in the proppant mixture are based on a polyethylene or polypropylene glycol structure. Various functional groups are added to the end of the surfactants to give the proper hydrophilic/hydrophobic balance needed to move both oil and gas through a sand and water mixture. This Application Note shows how the authors applied LC/Q-TOF-MS with the Kendrick mass defect tool to ascertain the structure of the polypropylene surfactants and their adducts. This Application Note is useful to those who analyze hydraulic fracturing wastewaters, and to those involved with these types of surfactant mixtures in general.

Experimental

Instruments

The Agilent 1290 Infinity II LC was used to separate the surfactant mixtures, and was coupled to an Agilent 6545 Q-TOF LC/MS equipped with electrospray Jet Stream technology. Table 1 shows the instrument conditions.

Sample collection

Wastewater samples were collected from various locations in the western United States, including Colorado, North Dakota, Oklahoma, and Texas. To obtain a representative set of both produced and flowback samples, the samples required the cooperation and assistance of oil companies and their partners. This was accomplished with the help of the Environmental Defense Fund and their partners in industry. The samples were collected on-site from oil/water/gas separators. Samples were stored at 4 °C for up to one month before analysis.

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 mm
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
Postrun	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. Optimum mass accuracy was obtained with 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 m/z 922.0098.

Results and discussion

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

Figure 1 shows the positive ion electrospray total ion current (TIC) chromatogram for the analysis of a produced water sample from Colorado. This chromatogram shows several sharp narrow peaks in the PEG region as well as peaks that are rounded but symmetrical in the PPG region (Figure 1).

Figure 1 shows two distinct mass zones, the earlier region is a PEG region, on which we have published several journal articles[1,2]. The PEG region has mass differences of 44.0262 mass units on average (retention time of 9–12.5 minutes). The second region of the chromatogram has mass differences of 58.0419 ±0.0002 mass units (retention time of 12.5–19 minutes). This second region suggests a polypropylene unit (CH_2-$CH(CH_3)$-O) or PPG region, rather than a polyethylene unit (PEG region). Because of the repeatable unit of 58.0419, it is possible to apply the Kendrick mass scale to help identify the compound of interest, as well as its polymeric series and that of its adducts.
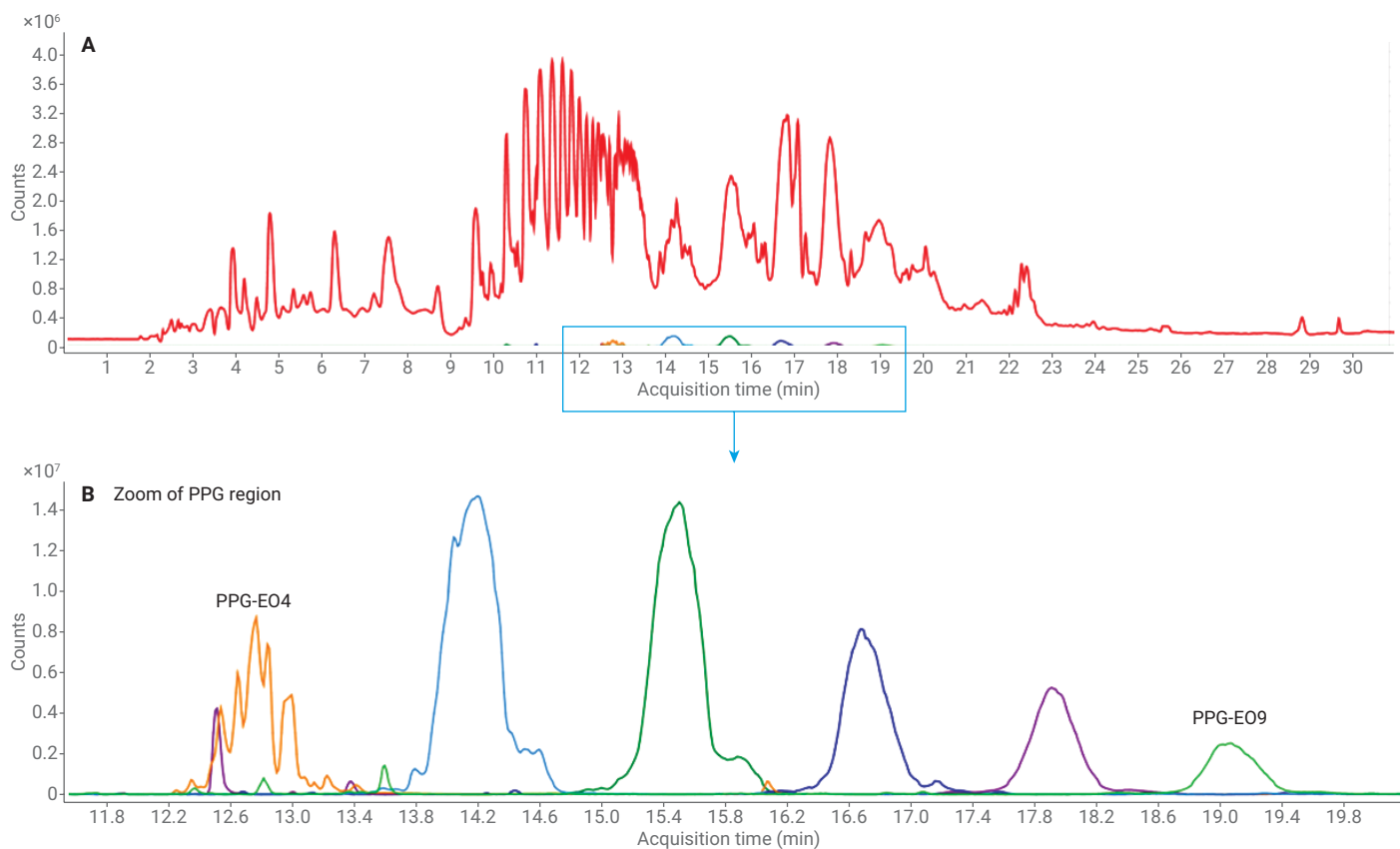

Figure 1. UHPLC/Q-TOF-MS with the TIC of a produced water sample, JR-5, from a recently fractured well that shows an area of the chromatogram with a mass separation of 58 mass units from 12 to 19 minutes. The zoomed area is shown in B.

Kendrick mass scale

Table 2 shows the result of applying the Kendrick mass scale to a series of masses in a produced water sample from hydraulic fracturing, sample JR-5 from Colorado. To understand a series of hydrocarbons that differed in mass by a methylene group, CH_2, Kendrick used a filtering technique, which is named after him[3]. The Kendrick mass scale has been applied to other series, but only recently to PEGs[1] and PPGs[2]. The application of the Kendrick mass scale first involves the determination of the Kendrick mass scaling factor. This factor is determined by dividing the nominal mass of the repeating polypropylene glycol unit (58 mass units) by the calculated exact mass of the same unit (58.04186481) for a scaling factor of 0.999278714. When this scaling factor is multiplied by the measured accurate mass, the resulting mass is called the Kendrick mass. The Kendrick mass defect is defined as the Kendrick nominal mass minus the Kendrick accurate mass, which for PPG-PO4 is 273 − 272.971 = 0.029. All PPGs in Table 2 have the same Kendrick mass defect within an error of 0.001.

The concept of the Kendrick mass is that if two compounds have the same repeating chemical structure, that is, $(CH_2(CH_3)CH-O)$, there will be an addition of the exact mass of that group, that is, 58.0419 mass units, to each new compound in the chromatogram. Thus, when the scaling factor is multiplied by the measured masses, all ions that differ by the $CH_2(CH_3)CH-O$ group will have the same Kendrick mass defect. Thus, it is only necessary to obtain the correct formula and structure for one of the unknown polypropylene glycols. All other unknown polypropylene glycols can be calculated as either one unit longer or shorter depending on the gain or loss of the 58.0419 unit.

MS/MS Identification of PPG surfactants

Once the Kendrick series is identified, an ion is selected for MS/MS analysis. Figure 2 shows a typical mass spectrum for the produced water sample, JR-5, with three prominent adducts for the suspected PPG-PO7. The adducts are proton, ammonium, and sodium.

Based on matching the retention times of the adducts, either the proton or the ammonium adduct is then chosen for MS/MS analysis. Figure 3 shows the fragmentation pattern for the PPG-PO7 standard, which matched the fragmentation of the putative PPG-PO7 sample.

Table 2. Kendrick mass for a suite of polypropylene glycol surfactants from PPG-EO4 to PPG-EO9, with an average mass difference of 58.0419 ±0.0002 mass units, from a produced water sample (JR-5) from hydraulic fracturing located in Colorado. The ion measured is the sodiated adduct.

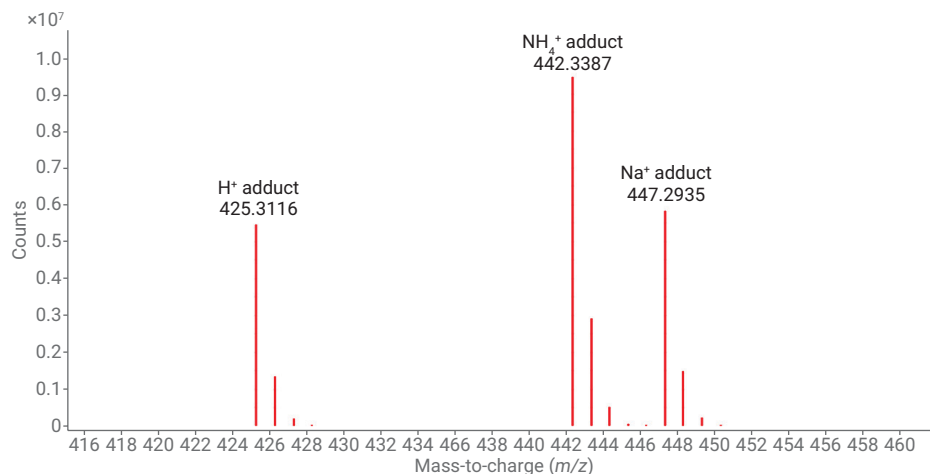| Retention time (min)	Ion measured m/z	Kendrick mass	Kendrick mass defect	Ion adduct
12.9	273.1676	272.971	0.029	Na+PPG-PO4
14.4	331.2094	330.971	0.029	Na+PPG-PO5
15.6	389.2515	388.971	0.029	Na+PPG-PO6
16.4	447.2935	446.971	0.029	Na+PPG-PO7
17.6	505.3349	504.970	0.030	Na+PPG-PO8
18.8	563.3764	562.970	0.030	Na+PPG-PO9

Figure 2. The MS spectrum of a putative PPG-PO7 with the proton, ammonium, and sodium adducts shown.

The fragmentation first involves the loss of water from the protonated PPG-PO7 (Figure 3). Then, the protonated molecule proceeds to undergo the neutral losses of 58.0419 ±0.002 in a zipper-like fashion until the last propylene group with a mass of m/z 59.0495. The loss of water indicates that the surfactant ends with an OH. This is also confirmed by multiplying the number of repeating units by its mass (58) and subtracting the result from the molecular mass, in this case 18. This is one of the simplest fragmentation patterns one will see in the identification of surfactants. If the surfactant ended with another moiety, this could be determined by the remaining fraction and the accurate mass measurement. Now that we have confirmation of the PPG-PO7, we can extend the Kendrick mass defect to all of the compounds in Table 2, from PPG-PO4 to PPG-PO9. This is the power of using the Kendrick mass defect with closely related surfactant mixtures.

Another interesting feature of the polypropylene glycol surfactants is their chromatography, which is shown in the zoomed part of Figure 1. Notice that the peaks are approximately one minute wide. This widening of the peaks is caused by the presence of many isomers for the PPG surfactant mixture[2]. PEGs have only one isomer, and give sharp peaks of approximately 12 seconds wide. In contrast, the PPGs have more than 10 tetramers for PPG-PO4, which increases exponentially with each new addition of 58 mass units. Notice the partial separation of the tetramers for the PPG-PO4 in the zoomed portion of Figure 1. This effect is caused by the fact that the PPG molecule is asymmetrical. Thus, the result is that there are 100s of possible isomers by PPG-PO9, with different retention times but the same accurate mass. These isomers
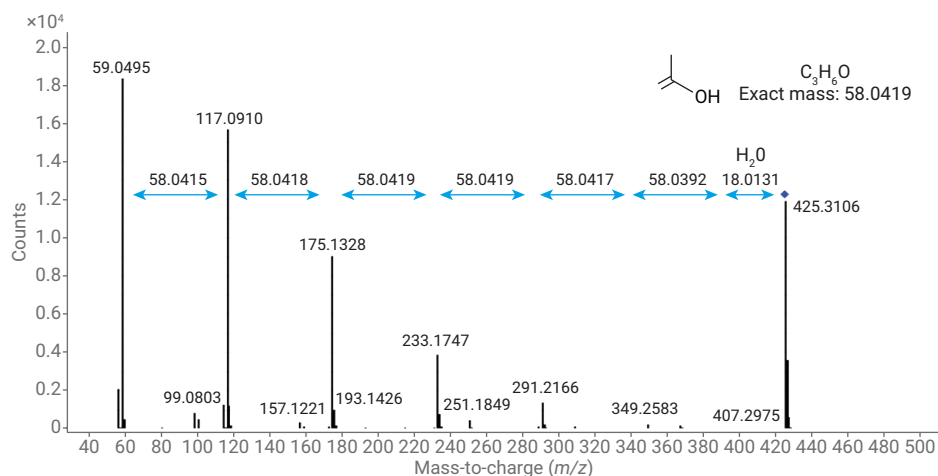

Figure 3. MS/MS analysis of PPG-PO7.

lead to the broadening of peaks from 10–12 seconds per compound to over one minute wide. This characteristic shape of the longer-chain PPGs was found in nearly all hydraulic fracturing water samples (that is, ~20 samples) that we have analyzed and published[2]. Thus, PPGs are good indicators of hydraulic fracturing wastewater, since they are not typically found in water samples.

An accurate mass database of PPG compounds

Once the PPGs are identified (Table 2), it is possible to carry out the process of PPG identification automatically on new samples using a Personal Compound Database (PCD), an accurate mass database inside the MassHunter Software. The database is constructed using a program called the Personal Compound Database Library (PCDL). The formula, name, and structure are entered into the library. Different settings are used to search the unknown samples, such as accurate mass and retention time windows. This process can be automated to rapidly identify PPGs in unknown wastewater samples from hydraulic fracturing using either a PCD or

a PCDL. We used a PCD only (no spectra) on approximately 20 samples from Texas, North Dakota, Oklahoma, and Colorado with detections of the PPGs in most of the samples. This work was carried out with cooperation from the Environmental Defense Fund.

Conclusions

The 1290 Infinity II LC and 6545 LC/Q-TOF-MS enabled the characterization of polypropylene glycol surfactants from hydraulic fracturing water samples. Applying the Kendrick mass defect to the accurate masses of these PPGs facilitates their rapid identification using MassHunter software. A PCDL can then be constructed and used to identify these compounds in wastewater samples from hydraulic fracturing. Finally, polypropylene surfactants make excellent tracers of hydraulic fracturing wastewaters, since they are not commonly detected in surface and groundwater samples, and are commonly found in hydraulic fracturing wastewaters.

References

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3. E. Kendrick. A mass scale based on $CH_2 = 14.0000$ for high resolution mass spectrometry of organic compounds. *Analytical Chemistry* **1963**, *35*, 2146–2154.

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