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RESEARCH PAPER

Analysis of hydraulic fracturing additives by LC/Q-TOF-MS

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Abstract The chemical additives used in fracturing fluids can be used as tracers of water contamination caused by hydraulic fracturing operations. For this purpose, a complete chemical characterization is necessary using advanced analytical techniques. Liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (LC/Q-TOF-MS) was used to identify chemical additives present in flowback and produced waters. Accurate mass measurements of main ions and fragments were used to characterize the major components of fracking fluids. Sodium adducts turned out to be the main molecular adduct ions detected for some additives due to oxygen-rich structures. Among the classes of chemical components analyzed by mass spectrometry include gels (guar gum), biocides (glutaraldehyde and alkyl dimethyl benzyl ammonium chloride), and surfactants (cocamidopropyl dimethylamines, cocamidopropyl hydroxysultaines, and cocamidopropyl derivatives). The capabilities of accurate mass and MS-MS fragmentation are explored for the unequivocal identification of these compounds. A special emphasis is given to the mass spectrometry elucidation approaches used to identify a major class of hydraulic fracturing compounds, surfactants.

Keywords Hydraulic fracturing · Fracking · Environmental · High resolution · Time-of-flight mass spectrometry · Flowback waters · Produced waters

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Introduction

Hydraulic fracturing has become widespread in the last few years due to improvements in horizontal drilling technology and efficient gas production. The process of hydraulic fracturing consists of the injection of fracturing fluids (commonly known as *fracking fluids*) into deep wells at high pressures. Once the geologic formation is fractured, gas and oil can be recovered at the surface of the well. A large amount of water is used for fracturing the well, usually 2 to 5 million gal. More than half of the water remains down in the geologic formation, but the rest is recovered at the surface. Two commonly used terms, flowback water and produced water, have been used when addressing hydraulic fracturing samples. The flowback water is the immediate return of injected fracking fluids, and the produced water is the term used to describe the water that is mixed with formation water (native to the well) and returns at a later time, during the production of oil and gas recovery.

The environmental impacts of hydraulic fracturing have been previously reviewed [1, 2]. There have been some reports that indicate the migration of fracturing fluids and natural chemical components (mostly methane and radioactive elements) to nearby groundwater sources [3–10]. The specific impacts upon water resources and the slow contamination of shallow groundwater have also been reported in several studies [2, 3, 11, 12]. One of the concerns is the potential contamination of surface and groundwater supplies by fracking fluids or wastewater associated with this process. Furthermore, oil and gas companies have been reluctant to give details of what is exactly in their proprietary fluid mixes. But, changes are coming and companies are nowadays supposed to disclose what is in their mixtures according to recent regulations [13]. However, the compounds or families of compounds disclosed pertain to broad categories and the exact chemical compositions of the individual fluids are not listed. For

example, the FracFocus Chemical Disclosure Registry [14] contains information on a broad number of chemicals used at different wells across the USA. In a previous review by our group [15], a distinction between natural components from geologic formations and chemical additives used in fracturing fluids was made and categorized. In this work, we will focus on the accurate mass and high-resolution mass spectrometric analysis of several chemical additives used in fracturing fluids.

It is obvious that there is a current need to develop and identify specific methods that can detect the occurrence of chemical additives present in hydraulic fracturing fluids, so they can be used as tracers of water contamination associated with these processes. To date, some studies in the literature have attempted to determine hydraulic fluid components by mass spectrometric techniques. Some of these examples are the works by Orem et al. [16, 17], Strong et al. [18], Lester et al. [19], Maguire-Boyle et al. [20], Thacker et al. [21], and Thurman et al. [22]. Analyzed compounds in these previous works include polycyclic aromatic hydrocarbons, phthalates, alkyl phenols, aromatic amines, and polyethylene glycols among others. In order to understand the environmental fate and transport of many of these compounds, it is necessary to be able to detect them in their source water (fracking fluid and flowback/produced waters). For these reasons, advanced analytical techniques are needed in order to fully characterize specific individual components of fracking fluids.

Most of the works published to date used GC-MS techniques and, in a lesser extent, LC-MS techniques; the state-of-the-art methods for analyses of hydraulic fracturing waters were reviewed in a recent paper [15]. In this work, we focus on the use of liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (LC/Q-TOF-MS) for the detection and identification of several classes of organic chemical additives associated with hydraulic fracturing operations. The capabilities of accurate mass and MS-MS fragmentation are highlighted for the unequivocal identification of these compounds. We have focused here specifically on the accurate mass identification of several classes of biocides and surfactants used for fracking, and we have explored in detail the mass spectral fragmentation and ion structure elucidation used for the identification of these major classes of compounds.

Material and methods

Chemicals and reagents

Guar gum (99.9 %), glutaraldehyde (50 %), and alkyl dimethyl benzyl ammonium chloride (>95 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Cocamidopropyl dimethylamine (95 %) and cocamidopropyl hydroxysultaine (35 %) were provided by Lubrizol (Cleveland, OH, USA). HPLC grade acetonitrile and methanol were obtained from Burdick and Jackson (Muskegon, MI, USA). Formic acid was obtained from Sigma-Aldrich (St. Louis, MO, USA). An ultrapure water system (Arium 611-VF; Sartorius Stedim Biotech, Bohemia, NY, USA) was used. Individual stock solutions of standards (1000 μg/mL) were prepared in methanol or water and stored at −18 and 4 °C, respectively. From these solutions, working standard solutions were prepared by dilution with acetonitrile and water. The CAS numbers, elemental compositions, and chemical structures of the compounds studied can be found in Table 1.

Sample collection

Water samples were collected in baked glass (at 550 °C), 100-mL amber bottles with Teflon-lined caps to ensure sample integrity. All the samples were refrigerated, and sample processing and analysis were completed within 7 days for all the samples. No additives were placed in the samples to prevent contamination and sorptive removal. The samples of flowback and produced water were collected from different locations in Weld County, CO, USA. Samples were filtered through 0.45 μm PTFE filters.

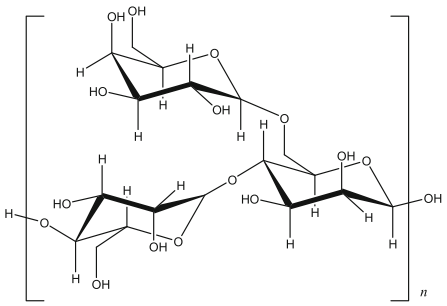
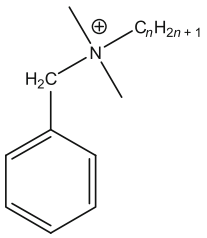
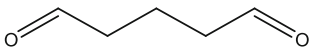
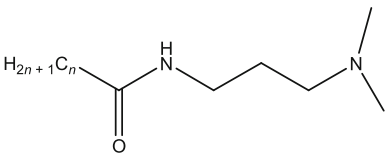
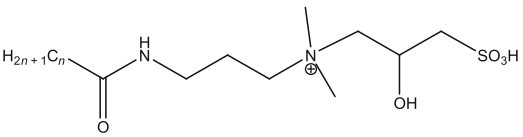
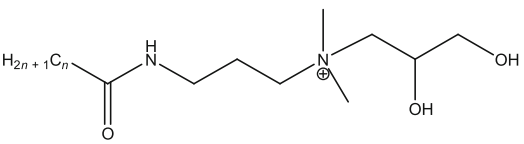
Chromatographic separation

The separation of chemical additives was carried out using an HPLC system (consisting of vacuum degasser, autosampler, and a binary pump) (Agilent Series 1290; Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed-phase C_8 analytical column of 150×4.6 mm and 3.5-μm particle size (Agilent Zorbax Eclipse Plus). Column temperature was maintained at 25 °C. The mobile phases A and B were water with 0.1 % formic acid and acetonitrile, respectively. The samples were injected (injection volume 10 μL) onto the column. Initial mobile-phase composition was 10 % B, held constant for 5 min, followed by a linear gradient to 100 % B at a flow rate of 0.6 mL/min, for a total run time of 30 min [23].

LC/Q-TOF-MS experiments

The HPLC system was connected to an ultra-high-definition quadrupole time-of-flight mass spectrometer (model 6540; Agilent Technologies, Santa Clara, CA, USA) equipped with electrospray Jet Stream technology, operating in positive ion mode, using the following operation parameters: capillary voltage of 3500 V, nebulizer pressure of 45 psig, drying gas of 10 L/min, gas temperature of 250 °C, sheath gas flow of 11 L/min, sheath gas temperature of 350 °C, nozzle voltage of 0 V, fragmentor voltage of 190 V, skimmer voltage of 65 V, and octopole RF of 750 V. LC-MS accurate mass spectra were recorded across the measured range *m/z* 50–1000 at 2 GHz.

Table 1 CAS numbers, elemental compositions, retention times, and chemical structures of additives found in fracturing fluids

Name	CAS number	Elemental composition	Ret. time (min)	Chemical structure
Guar gum	9000-30-0	$H(C_{18}H_{30}O_{15})_nOH$	2.4	
Alkyl dimethyl benzyl ammonium chloride (ADBAC)	63449-41-2	$C_{(n+9)}H_{(2n+14)}N^+$	18–24	
Glutaraldehyde	111-30-8	$C_5H_8O_2$	9–19 (polymeric forms)	
Cocamidopropyl dimethylamine (CAPDMA)	68140-01-2	$C_{(n+6)}H_{2n+14}N_2O$	13.8 ($C_{13}H_{28}N_20$)	
Cocamidopropyl hydroxysultaine (CAPHS)	68139-30-0	$C_{(n+9)}H_{2n+21}N_2O_5S^+$	14.2 ($C_{16}H_{35}N_20_5S$)	
Cocamidopropyl unknown (CAP unknown)	Unknown	$C_{(n+9)}H_{2n+21}N_2O_3^+$	13.3 ($C_{16}H_{35}N_20_3$)	

The data recorded were processed with MassHunter software. A reference solution was delivered using an external quaternary pump. This solution contains the following internal mass calibrants: purine ($C_5H_4N_4$) at *m/z* 121.0509 and HP-921 [hexakis-(1*H*,1*H*,3*H*-tetrafluoro-pentoxy)phosphazene] ($C_{18}H_{18}O_6N_3P_3F_{24}$) at *m/z* 922.0098. The instrument provides a mass resolving power of 30,000±500 (*m/z* 1522). The stability of mass accuracy was checked daily, and if values went above 2 ppm error, then the instrument was re-calibrated. When the instrument was operated in MS-MS mode, the isolation width was set at medium (*m/z* ~4) and collision energies of 10, 20, and 30 eV were used [23].

Results and discussion

Gel components

Gels are used in fracturing fluids in order to increase the viscosity of the liquid, thus enhancing the proppant (usually sand) to be

suspended in the mix and ultimately penetrate in the geologic formations to hold open the cracks created by the hydraulic fracturing. The fluids that contain gelling agents are commonly known as "gel-frac." The most common gelling agents are guar gum and cellulose, which are cross-linked polysaccharides [24]. Average molecular weights range from 50,000 to 8,000,000 [25]. No reports on guar gum analysis by LC-MS were found in the literature, and for this reason, we have included its mass spectrometry characterization here.

Guar gum

Chemically, guar gum is a polysaccharide composed of two sugars: galactose and mannose. The backbone is a linear chain of β-1,4-linked mannose monomers to which alpha-1,6-galactose units are linked at every second mannose, forming short side branches (Table 1). This unit repeats itself to form the cross-linked polymer. As expected from a gelling additive, guar gum forms an emulsion when dissolved in methanol or water. A clear diluted solution of 10 μg/mL of guar gum was analyzed by LC/Q-TOF-MS in positive ion mode, and the results are discussed below.

Only a single unit of guar gum ($C_{18}H_{32}O_{16}$) was detected at an early retention time (2.4 min), and no other major peaks corresponding to the cross-linked polymer were observed in the chromatogram. One of the reasons no other peaks were detected is because the mass range of the LC-MS only goes up to *m/z* 1000. However, this observation could also be due to the decomposition of the polymer itself under the high temperature of the electrospray source when it elutes from the column. Figure 1 shows the spectra obtained after the (a) full-scan and (b) MS-MS analysis of guar gum. As seen in Fig. 1a, a major ion at 527.1587 corresponding to the adduct of the guar monomer with sodium $[M+Na]^+$ was obtained. No protonated molecule was observed. This adduct formation with sodium is typical of most natural and artificial sugars [23] due to the presence of acetals in the molecule. A second major ion at 365.1057 was also observed corresponding to the fragmentation and loss of the galactose saccharide. A charge migration involving the sodium ion to the fragment generated occurs in this type of sodium adduct. Thus, the sodium ion remains as the charge in the fragment ions. The obtained MS-MS spectrum shown in Fig. 1b confirmed the occurrence of the 365 adduct ions. Furthermore, two more sodium adduct fragments at 203.0527 and 185.0423 were obtained,

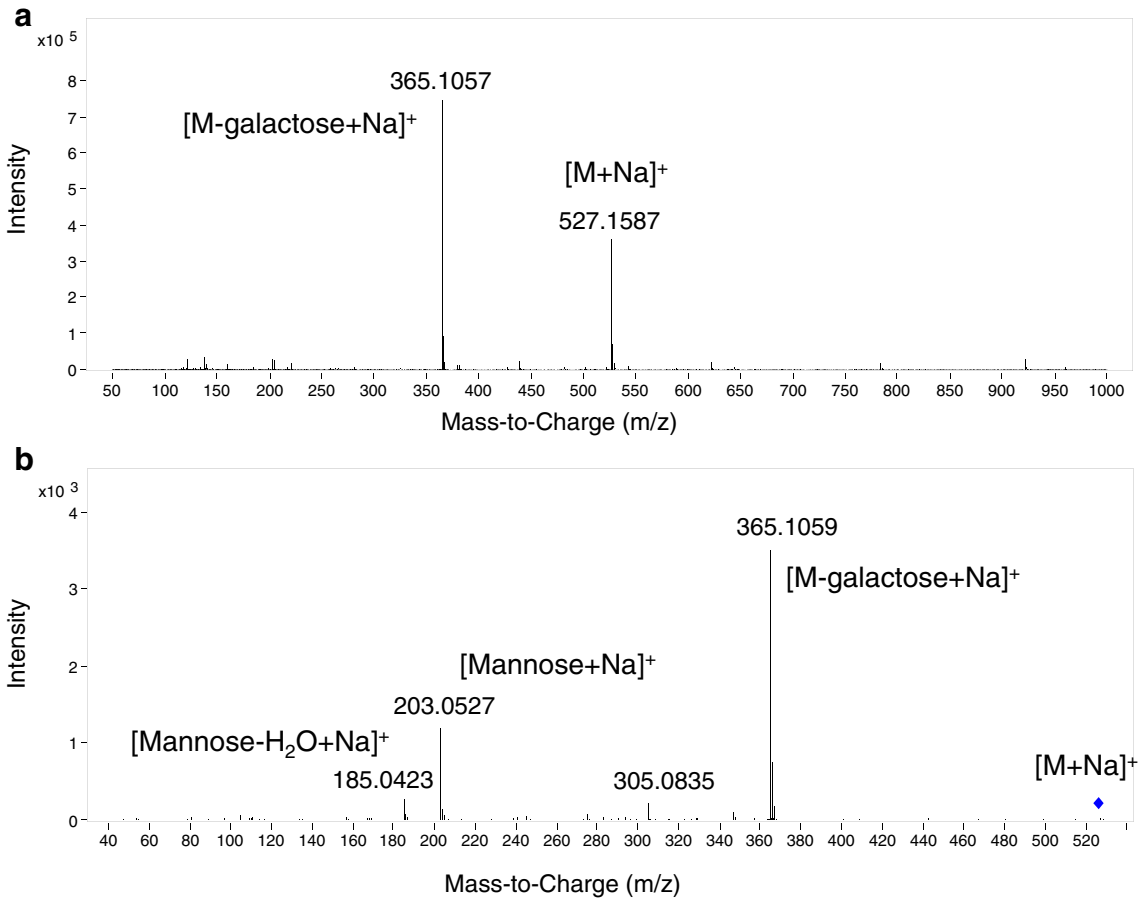


Fig. 1 (**a**) LC/Q-TOF-MS full spectrum and (**b**) MS-MS accurate mass spectrum of guar gum

which correspond to the fragmentation of the linked mannose saccharides (see Fig. 2 for detailed fragmentation pathway of guar). The exact masses for the specific fragment ions can be found in Table 2.

Biocides

Biocides are added to fracturing fluids in order to prevent the growth of bacteria in the water which is injected down the well. Biocides are perhaps the most important group of chemical additives used in hydraulic fracturing because the majority of compounds used for this purpose are toxic or exhibit toxic properties for aquatic organisms [24, 26]. Contrary to other compounds used in fracking fluids, biocides are regulated by the Federal Insecticide, Fungicide and Rodenticide Act, and they must be registered by the EPA [27]. In this paper, we focused on two important biocides that are commonly used in fracturing fluids: alkyl dimethyl benzyl ammonium chloride (ADBAC) and glutaraldehyde.

ADBAC

Commonly known also as benzalkonium chloride, alkyl dimethyl benzyl ammonium chloride is a quaternary amine with detergent and antimicrobial properties. ADBAC is popularly used in hundreds of cosmetic and cleaning products as well as in ophthalmologic solutions and sanitizers. In fact, its presence has been reported in the past in surface water and sediments associated with wastewater sources, as it is not removed by conventional treatment methodologies [28, 29]. Since ADBAC is a cationic surfactant, the analysis by LC-MS with positive ion electrospray is favored for this compound. This

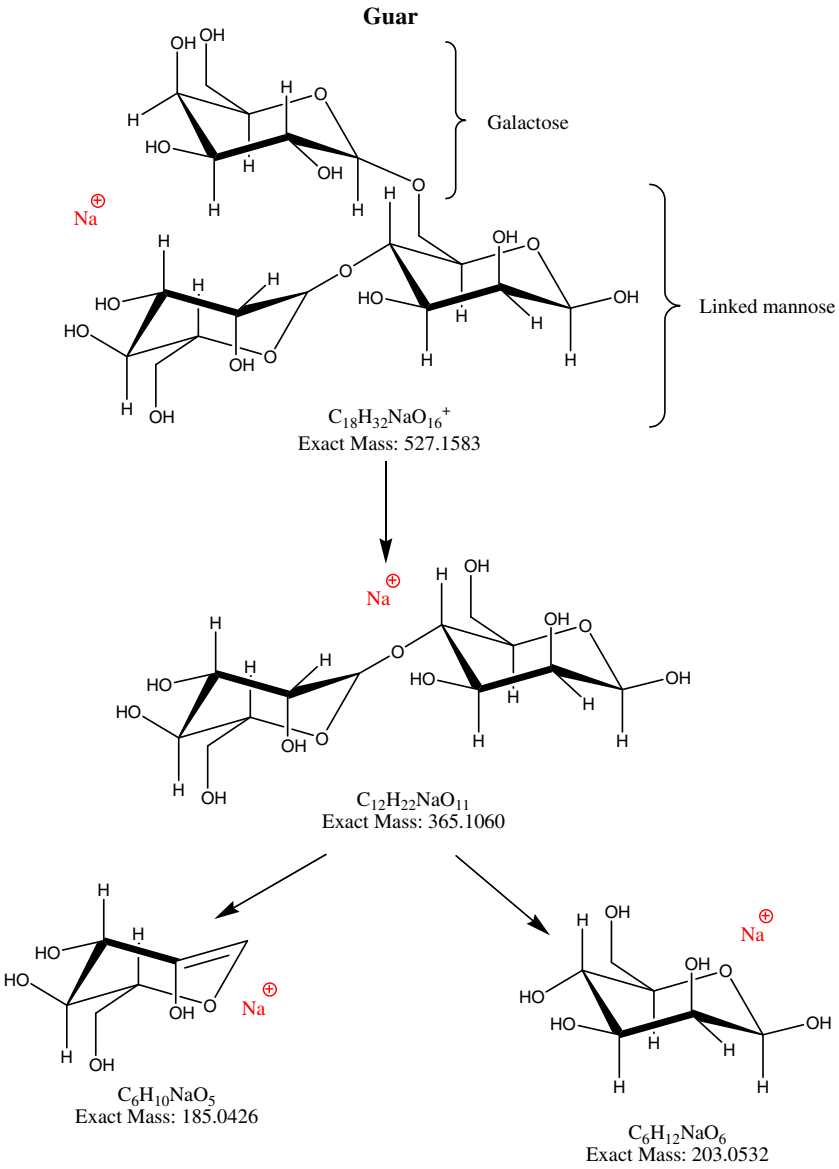


Fig. 2 Fragmentation pathway for guar gum by accurate mass

Table 2 Accurate masses, ions monitored, LODs, and detection frequencies (n=22) for hydraulic fracturing additives

Name	Ions detected	Accurate mass m/z	Fragment ions m/z	LOD (μg/L)	Detection frequencies in analyzed samples (%)
Guar gum	$[M+Na]^+$	527.1583	365.1060 203.0532 185.0426	200	0
Alkyl dimethyl benzyl ammonium chloride (ADBAC)	$[M]^+$ $[M]^+$ $[M]^+$ $[M]^+$	248.2373 (ADBAC-C_8) 276.2686 (ADBAC-C_{10}) 304.2999 (ADBAC-C_{12}) 332.3312 (ADBAC-C_{14})	156.1747 184.2060 212.2373 240.2686 91.0542[a]	10	54
Glutaraldehyde	$[2M+H_2O+Na]^+$ $[3M+H_2O+Na]^+$	241.1046 (dimer) 341.1571 (trimer)	223.0941 323.1465 123.0417[b]	500	0
Cocamidopropyl dimethylamine	$[M+H]^+$	201.1961 (CAPDMA-C_5H_{11}) 229.2274 (CAPDMA-C_7H_{15}) 257.2593 (CAPDMA-C_9H_{19}) 285.2900 (CAPDMA-$C_{11}H_{23}$)	156.1383 184.1696 212.2009 240.2322	5	15
Cocamidopropyl hydroxysultaine	$[M]^+$	339.1954 (CAPHS-C_5H_{11}) 367.2261 (CAPHS-C_7H_{15}) 395.2580 (CAPHS-C_9H_{19}) 423.2893 (CAPHS-$C_{11}H_{23}$)	156.1383 184.1696 212.2009 240.2322	50	15
Cocamidopropyl unknown derivative	$[M]^+$	275.2335 (CAP unknown-C_5H_{11}) 303.2642 (CAP unknown-C_7H_{15}) 331.2961 (CAP unknown-C_9H_{19}) 359.3274 (CAP unknown-$C_{11}H_{23}$)	156.1383 184.1696 212.2009 240.2322	5[c]	15

[a] Common fragment for all homologues

[b] Common fragment for all polymers

[c] LOD estimated from cocamidopropyl dimethylamine since no standard is available at this time

additive does not exist as a single molecular species; it rather contains a series of homologues ranging from C_8 to C_{16} [28]. In this work, we evaluated several flowback and produced water samples and confirmed its presence in 54 % of the samples. Figure 3a shows the total ion chromatogram of a produced water sample showing positive detections for a series of ADBAC homologues. The extracted ion chromatograms for three homologues from the sample are shown in Fig. 3b. In this particular case, the C_8, C_{10}, and C_{12} homologues were observed, a different distribution to the one found in common household products where the main homologues are usually C_{12} and C_{14} [28]. Note that the chromatography for these three compounds shows a broad tail, which is a result of secondary interactions of the fixed positive charge with the silica of the C-8 column used in this analysis. We prefer formic acid in order to get enhanced sensitivity for other compounds also present in these samples; however, for specific analysis of ADBAC, an ammonium formate buffer may be favored [28].

The fragmentation of these homologues is straightforward where the benzylic amine bond breaks (see Fig. 4). This fragmentation leads to the diagnostic ion at m/z 91.0542, commonly known as the *tropylium ion*, and the specific fragments corresponding to the unique alkyl chain substructure for each one of the homologues. Table 2 compiles all the exact masses for each homologue and their corresponding fragment ions. This represents the first reported finding for ADBAC homologues in hydraulic fracturing water samples. The fact that ADBAC is also used in commercial detergents and cleaning products makes this additive a non-specific tracer of water contamination due to hydraulic fracturing operations. Nevertheless, the characteristic distribution fingerprinting of the C_8 and C_{10} homologues could potentially be used as a unique tracing pattern for this type of additive.

Glutaraldehyde

Glutaraldehyde is mainly used not only as a biocide but also as a preservative and for industrial water treatment. Another use is to sterilize medical and dental tools. Its chemical structure is simple with two aldehyde groups (see Table 1). However, in aqueous solutions, the aldehyde groups become hydrated. In fact, glutaraldehyde has been shown to be in equilibrium with its hydrated forms (hemihydrate and dihydrate) and cyclic hemiacetal in water by Whipple and Ruta [30]. Furthermore, glutaraldehyde polymerizes via aldol condensation reactions and several different species can coexist in solution [31], as will be discussed here.

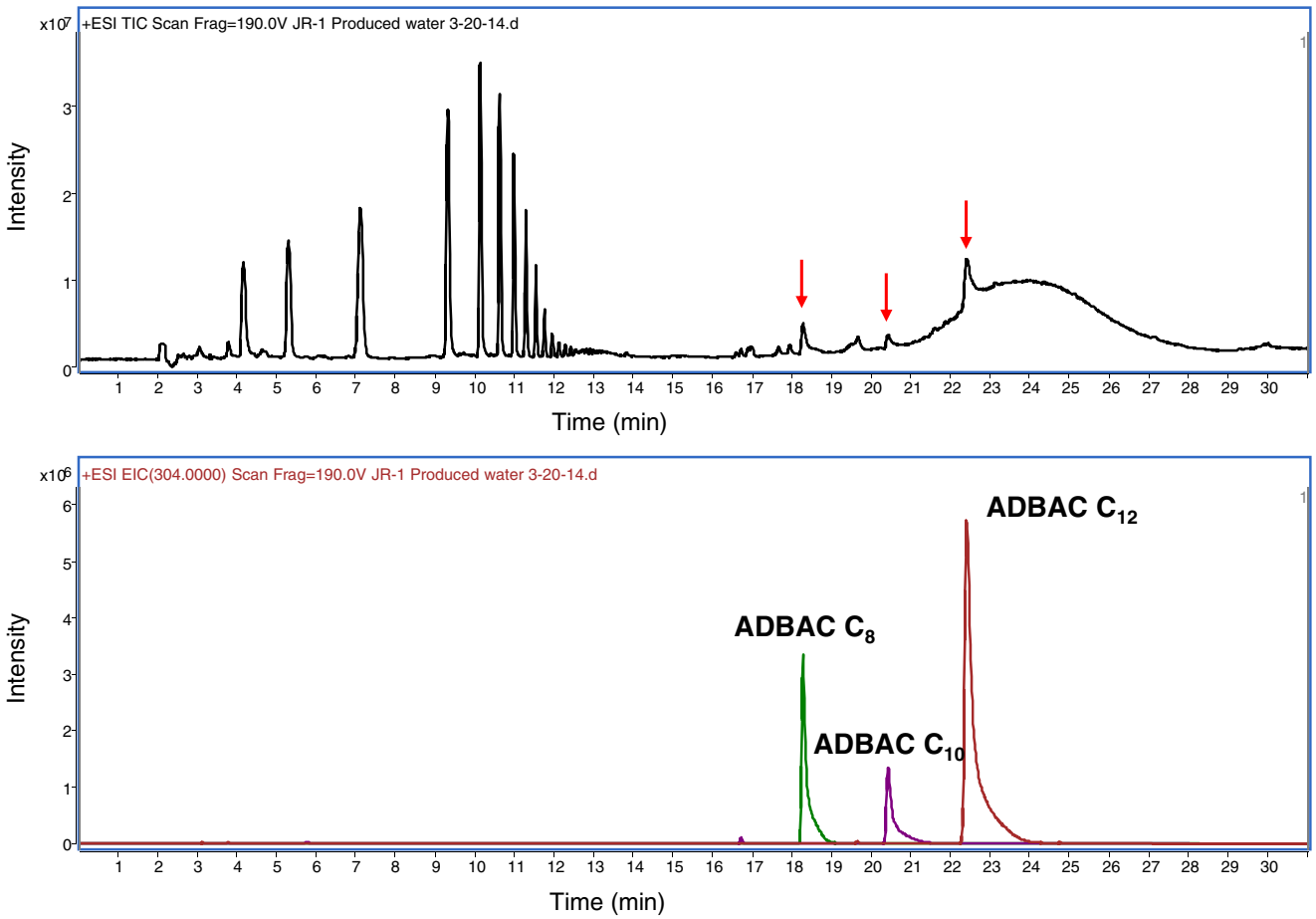


Fig. 3 (**a**) LC/Q-TOF-MS total ion chromatogram of a produced hydraulic fracturing water and (**b**) extracted ion chromatogram for three homologues of alkyl dimethyl benzyl ammonium chloride (*ADBAC*) for the same sample

The LC/TOF-MS analysis of this compound showed the presence of several chromatographic peaks with distinctive *m/z* values. One of the peaks had two major ions at *m/z* 241.1050 and 223.0944 (Fig. 5a). The ion at 241.1050 was identified as a dimerized molecule of glutaraldehyde formed via aldol condensation, which formed an adduct with a sodium ion under electrospray conditions. The molecule would have to be present in solution as a hemihydrate [30], and then, an aldol condensation would immediately occur to form the dimer. These data also supports the results found by Tashima et al. [32]. Furthermore, the dimer was fragmented under electrospray conditions and the mass spectrum also showed a water loss corresponding to the dehydration of the dimer to form the 223.0944 ion. It is important to note that the dehydration happens at the source since both spectrum peaks are detected at the same retention time. A dehydrated molecule in equilibrium would have a slightly different retention time, and it would be detected as a different chromatographic peak. Both of these chemical structures are shown in Fig. 5a.

Another detected peak in the chromatogram presented major ions at *m/z* 341.1575 and 323.1465 (Fig. 5b). The *m/z* 341.1575 ion represents the sodium adduct of the trimer of a hydrated glutaraldehyde, which also dehydrates to give the *m/z* 323.1465 ion under electrospray conditions, as similar to the dimerized molecule. Structures corresponding to these ions are also drawn in Fig. 5b. These dimers and trimers form in solution since they are chromatographically separated into broad peaks, and are not an electrospray source product. However, the dehydration (loss of water) is occurring in the heated mass spectrometer source, as observed in both spectra. By looking at the relative intensities of each of the ions in Fig. 5, one can see that as the molecule polymerizes, the loss of water in the source is favored, thus increasing the intensity for the lower mass ion compared to the higher mass ion. Finally, the MS-MS accurate mass spectrum of the ion at *m/z* 341.1575 is shown in Fig. 5c. As expected, the ion at *m/z* 123.0414 (a single molecule of glutaraldehyde) and its hydrated form at *m/z* 141.0520 were obtained and confirmed. Both species can be drawn as a hemiacetal structure as shown in Fig. 5c, and they match the findings from previous studies [30].

Other peaks corresponding to higher polymerizations (from masses at *m/z* 423, 523, 623, and 723) were seen in the chromatogram at higher retention times (results not

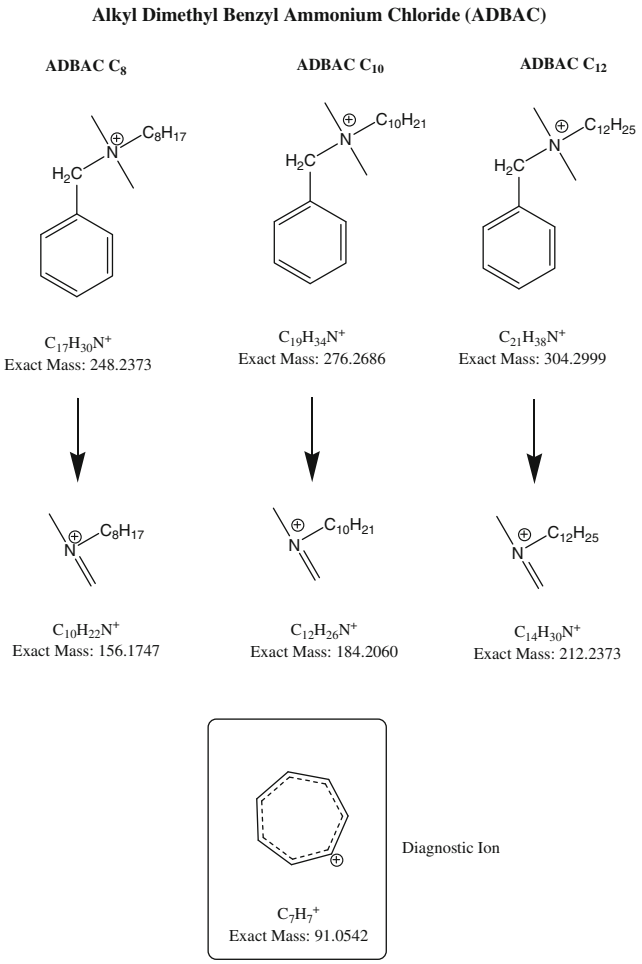


Fig. 4 Fragmentation pathway for three homologues of alkyl dimethyl benzyl ammonium chloride

shown), thus verifying the polymerization tendency of this molecule. These results showed that polymer chains up to 7 units were forming. A ring formation at the termination of the polymer structure may also form. All these polymeric species would exist in equilibrium in the fracking solution. No detections of glutaraldehyde were observed in flowback or produced waters. The limit of detection (LOD) for this compound is quite high (Table 2). This biocide is used at very low concentrations in fracking fluids (about 0.06 %), so it would require a sample preparation step to pre-concentrate this chemical and subsequently analyze it by LC-MS.

Surfactants

Surfactants are the group used as fracking fluid additives with the most diverse variety of compounds. The four main surfactant categories are neutral, cationic, anionic, and amphoteric. Neutral surfactants such as polyethylene glycols and linear alkyl ethoxylates have been previously identified in flowback and produced hydraulic fracturing waters [22], and they will not be discussed here. In this previous work, the use of accurate mass and the Kendrick mass defect using TOF was essential to assign individual chemical structures to each one of the surfactants identified in those samples. In this paper, we report the identification of three new classes of surfactants identified in fracking samples using high-resolution and accurate mass techniques. Cocamidopropyl surfactants are derived from coconut oil and dimethylaminopropylamine as well as from chemical reactions with sulfonates. Some classes are neutral (cocamidopropyl dimethylamines), and others are amphoteric (cocamidopropyl hydroxysultaines). In this section, we will discuss the two main families of cocamidopropyl surfactants. Because one of the side chains is identical to the different families, these compounds will present the same diagnostic ions after fragmentation as we will see next.

Cocamidopropyl dimethylamine

Fatty acid amidopropyl dimethylamines, also known as *amido-amines*, are commonly used in cosmetic products as antistatic and conditioning agents. In fracking fluids, these compounds are used as corrosion inhibitors as well as surfactants. They are synthesized from coconut fatty acids (of different chain lengths) derived from coconut oil after reaction with 3,3-dimethylaminopropylamine.

Diagnostic ions were used to identify this class of surfactants in the flowback/produced water samples. Figure 6 shows the total ion chromatogram (upper) and the extracted ion chromatogram (lower) of the ion at *m/z* 184.1696 for a flowback sample collected in the Denver-Julesburg Basin in Colorado. As seen in the extracted ion chromatogram in the lower chromatogram, the presence of three major peaks was noticed. The three peaks had accurate masses of 229.2274, 367.2261, and 303.2642. The peak at *m/z* 229.2274 was identified as cocamidopropyl dimethylamine (CAPDMA-C_7H_{15}) with the empirical formula of $C_{13}H_{28}N_2O$ (see Table 1). The confirmation of the identity of this compound was verified by injection of a standard. The MS-MS of this compound was discussed in an earlier work [19]. The C–N bond of dimethylamine is broken, giving rise to the diagnostic ion at 184.1696. It is important to note the usefulness of accurate mass since this same diagnostic ion (same nominal mass) occurs on the fragmentation of ADBAC discussed earlier. High-resolution accurate mass is crucial to distinguish these two diagnostic ions at 184.2060 and 184.1696 for ADBAC-C_{10} and cocamidopropyl dimethylamine C_7H_{15}, respectively.

Three homologue series of cocamidopropyl dimethylamine surfactants, corresponding to side alkyl chains of C_5H_{11}, C_7H_{15}, and C_9H_{19}, were also observed in other flowback water samples. However, the homologue corresponding to CAPDMA-C_7H_{15} was the major component observed in this sample and this is why it was discussed in detail above. Table 2 shows the exact masses for all the homologues

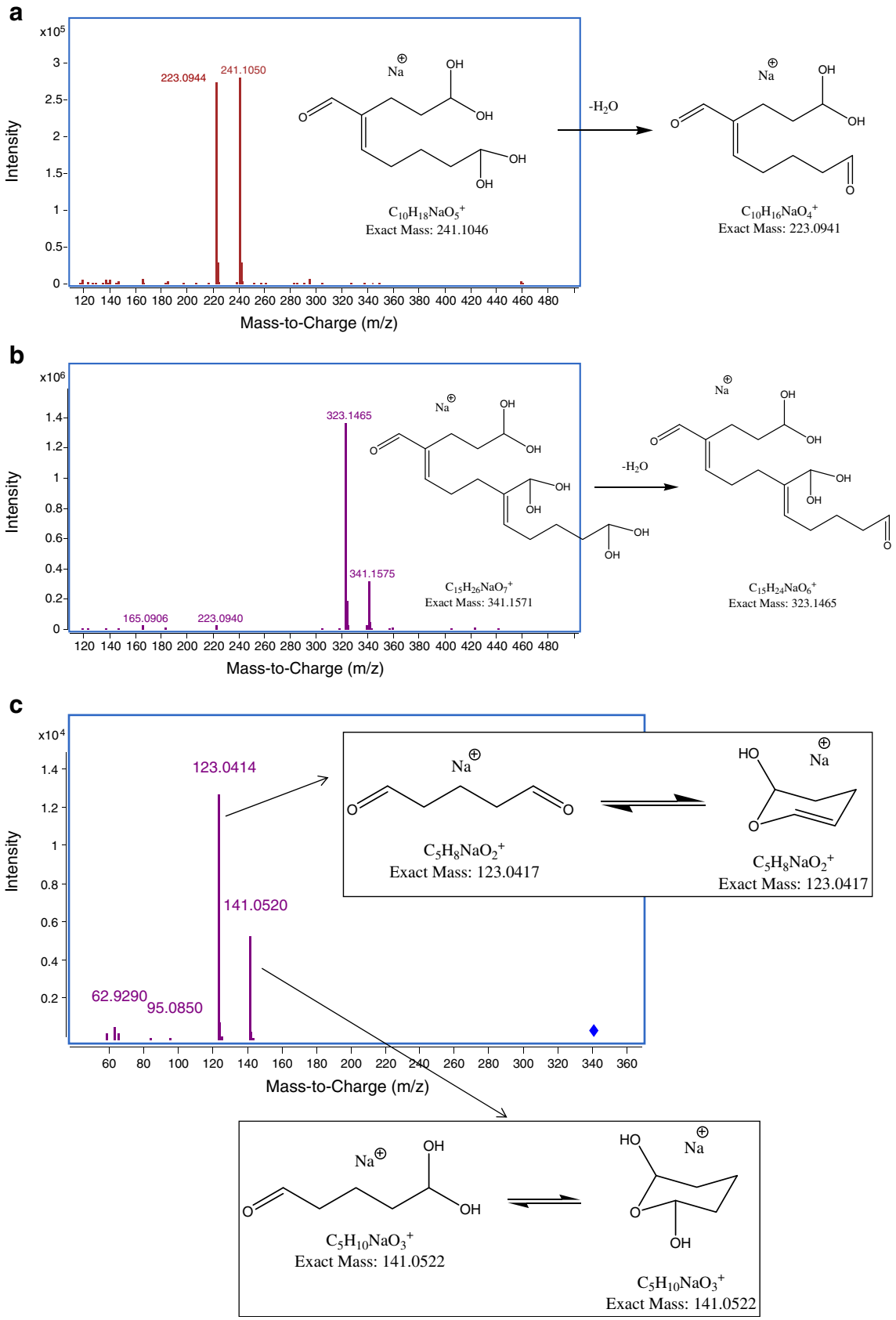


Fig. 5 LC/Q-TOF-MS accurate mass spectra of (**a**) dimer of glutaraldehyde and (**b**) trimer of glutaraldehyde and (**c**) MS-MS accurate mass spectrum of a trimer of glutaraldehyde

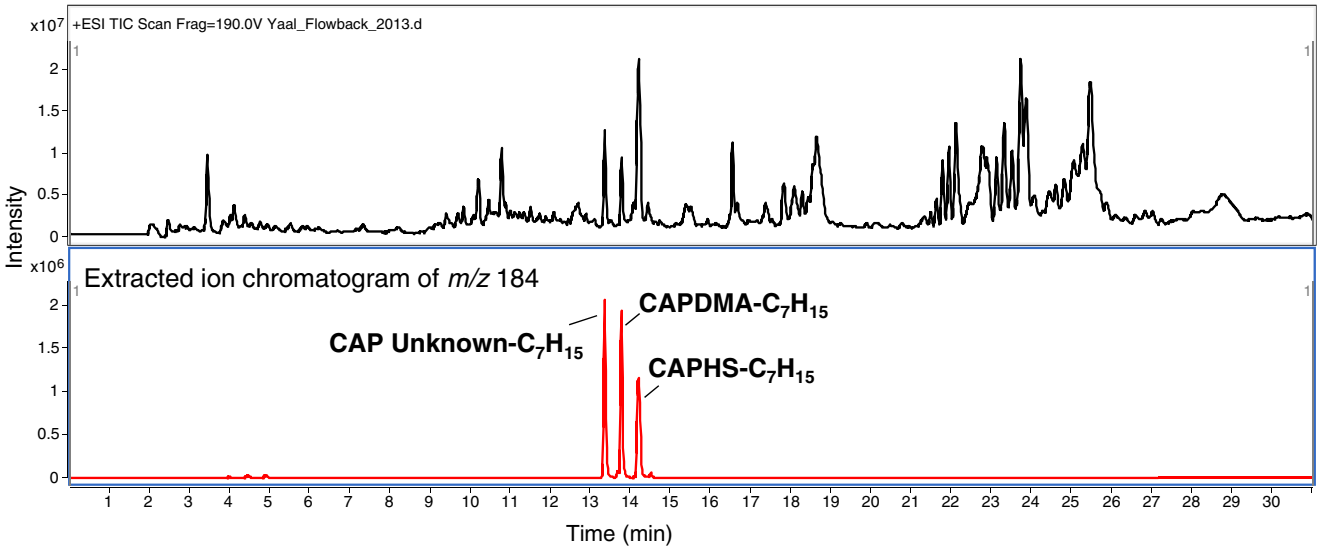


Fig. 6 (**a**) LC/Q-TOF-MS total ion chromatogram of a flowback hydraulic fracturing water and (**b**) extracted ion chromatogram for the diagnostic ion at *m/z* 184.1696 corresponding to cocamidopropyl surfactants. Peaks: *1* cocamidopropyl unknown derivative (CAP unknown C_7H_{15}), *2* cocamidopropyl dimethylamine (CAPDMA-C_7H_{15}), *3* cocamidopropyl hydroxysultaine (CAPHS-C_7H_{15})

belonging to this family of surfactants and their corresponding fragment ions.

Cocamidopropyl hydroxysultaine

From the diagnostic ion information at *m/z* 184 shown in Fig. 6, it was obvious that the other two peaks detected had to include the same backbone structure of the cocamidopropyl family. Therefore, an investigation of the spectral information of the peak at 367.2261 was carried out next. We quickly realized from the spectrum that a sulfur atom (relative intensity of the A+two ion is about 5 %) was present in the chemical structure of the ion. The molecular formula obtained was $C_{16}H_{35}N_2O_5S$. A quick search on the Web revealed that this compound was cocamidopropyl hydroxysultaine (CAPHS-C_7H_{15}), a common surfactant used in fracking fluids [33]. This compound eluted at a later retention time than the dimethylamine, which makes chromatographic sense, considering the more hydrophobic character of this compound. Hydroxysultaines are synthesized from the reaction of a cocamidopropyl dimethylamine and 1-chloro-2-hydroxypropane sulfonate. Similar to the previous compound discussed above, three series of homologues were observed for cocamidopropyl hydroxysultaine as well. Homologues with alkyl chains of C_5H_{11}, C_9H_{19}, and $C_{11}H_{23}$ were observed at earlier and later retention times, thus verifying the presence of these surfactants in flowback waters. In this case, the homologue with the alkyl chain of C_7H_{15} (chemical structure can be seen in Table 1) was the major component detected in one of the samples shown in Fig. 6. Table 2 shows the exact masses for all the homologues belonging to this family of surfactants and their corresponding fragment ions.

Cocamidopropyl derivative unknown

The third peak of the cocamidopropyl family had a mass at *m/z* 303.2642 and a shorter retention time compared to the other two discussed above. This was the most difficult compound to unravel from the mass spectral information. It was obvious that no sulfur isotope was present in the mass spectrum of this ion. From MS-MS analysis, only the two diagnostic ions at 184 and 127 were obtained verifying the common backbone structure, but no specific information on the other side of the chemical structure was available. The empirical formula obtained from the measured accurate mass was $C_{16}H_{35}N_2O_3$. A putative structure is proposed here (see Table 1). No other information could be obtained at this time from the literature, and standards are not available at this time. This molecule derives probably from a similar chemical reaction as those discussed above, or it could possibly be another surfactant not previously identified by mass spectrometry.

Conclusions

High-resolution mass spectrometry coupled with liquid chromatography has been used for the separation and identification of a group of additives that are present in hydraulic fracturing fluids and, thus, in flowback and produced waters. Accurate mass measurements and MS-MS data were essential to elucidate the chemical structures of the compounds analyzed. Using LC/Q-TOF-MS, accurate mass spectral information for guar gum, alkyl dimethyl benzyl ammonium chloride, glutaraldehyde, and cocamidopropyl surfactants is presented here. Analyses of flowback and produced waters confirmed

the presence of some of these chemical additives in hydraulic fracturing fluids. Cocamidopropyl amido-amines, a new family of surfactants, have been identified here and represent the first report of this class of compounds in hydraulic fracturing waters. The methodology presented in this paper will be highly useful for the analysis and tracing of these compounds in flowback, produced waters, surface waters, and groundwaters. It will also help in the development of water treatment strategies in order to minimize the environmental impact of hydraulic fracturing operations on water supplies.

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