Accutest Laboratories

Field and Analytical Challenges

Practical Quantitation Limits, Method Detection Limits, Interferences and Dilution Challenges

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Introduction

- Fracturing fluids vary significantly in consistency and viscosity.
- Samples received were predominantly representative.
- Samples received in our laboratory were either prepared the same day of receipt or within a day after
- Matrices varied from DI water like consistency to a thick paint like consistency (all samples were free flowing).
- Samples were preserved per regulatory requirements other than VOA's.

Parameters and Methods

- Acrylamide – SW846 – 8316
- Metals – Method 200.8 / 245.1
- Cyanide/ Weak and dissociable, Total – SM 4500 CN E & I
- Fecal and Total Coliform – SM 9222D & B
- Total Phenolics – EPA Method 420.1
- Herbicides – SW846 – 8151
- Ion Chromatography – EPA Method 300
- Residual Chlorine – SM 4500 CL G
- VOA's – EPA Method 624
- SVOA's – EPA Method 625
- Pesticides/ PCB's – EPA Method 608
- 2,3,7,8 – TCDD – EPA Method 1613B
- Halo Acetic Acids – EPA Method 552.3
- 1, 2 – Dibromoethane – EPA Method 504.1

Fracturing Fluid Analyses Parameters
500 Series

Method	Analyte	PQL, ug/L
EPA 552.3	Dibromoacetic Acid	0.8
EPA 552.3	Dichloroacetic Acid	0.8
EPA 552.3	Monobromoacetic Acid	1.6
EPA 552.3	Monochloroacetic Acid	0.8
EPA 552.3	Trichloroacetic Acid	0.8
EPA 552.3	Haloacetic Acid	0.8
EPA 504.1	1,2-Dibromoethane	0.025

Fracturing Fluid Analyses Parameters 600 Series

Method	Analyte	PQL,ug/L
EPA 608	4,4´-DDD	0.05
EPA 608	4,4´-DDE	0.05
EPA 608	4,4´-DDT	0.05
EPA 608	Aldrin	0.05
EPA 608	alpha-BHC	0.05
EPA 608	Aroclor 1016	1
EPA 608	Aroclor 1221	1
EPA 608	Aroclor 1232	1
EPA 608	Aroclor 1242	1
EPA 608	Aroclor 1248	1
EPA 608	Aroclor 1254	1
EPA 608	Aroclor 1260	1
EPA 608	beta-BHC	0.05
EPA 608	Chlordane	0.5
EPA 608	delta-BHC	0.05
EPA 608	Dieldrin	0.05
EPA 608	Endosulfan I	0.05
EPA 608	Endosulfan II	0.05
EPA 608	Endosulfan sulfate	0.05
EPA 608	Endrin	0.05
EPA 608	Endrin aldehyde	0.05

Fracturing Fluid Analyses Parameters 600 Series (continued)

Method	Analyte	PQL,ug/L
EPA 608	gamma-BHC	0.05
EPA 608	Heptachlor	0.05
EPA 608	Heptachlor epoxide	0.05
EPA 608	Methoxychlor	0.05
EPA 608	Toxaphene	1
EPA 624	1,1,1-Trichloroethane	1
EPA 624	1,1,2,2-Tetrachloroethane	1
EPA 624	1,1,2-Trichloroethane	1
EPA 624	1,1-Dichloroethane	1
EPA 624	1,1-Dichloroethene	1
EPA 624	1,2,4-Trichlorobenzene	1
EPA 624	1,2-Dibromo-3-chloropropane	5
EPA 624	1,2-Dichlorobenzene	1
EPA 624	1,2-Dichloroethane	1
EPA 624	1,2-Dichloropropane	1
EPA 624	1,3-Dichlorobenzene	1
EPA 624	1,4-Dichlorobenzene	1
EPA 624	2-Chloroethyl vinyl ether	5
EPA 624	Acrolein	50
EPA 624	Acrylonitrile	5

Fracturing Fluid Analyses Parameters 600 Series (continued)

Method	Analyte	PQL,ug/L
EPA 624	Bromodichloromethane	1
EPA 624	Bromoform	1
EPA 624	Bromomethane	1
EPA 624	Carbon tetrachloride	1
EPA 624	Chlorobenzene	1
EPA 624	Chloroethane	1
EPA 624	Chloroform	1
EPA 624	Chloromethane	1
EPA 624	Dibromochloromethane	1
EPA 624	Dibromomethane	1
EPA 624	Epichlorohydrin	10
EPA 624	Ethylbenzene	1
EPA 624	Methylene chloride	1
EPA 624	Styrene	1
EPA 624	Tetrachloroethene	1
EPA 624	Toluene	1
EPA 624	Trichloroethene	1
EPA 624	Vinyl chloride	1
EPA 624	cis-1,2-Dichloroethene	1
EPA 624	cis-1,3-Dichloropropene	1
EPA 624	m,p-Xylene	2
EPA 624	o-Xylene	1

Fracturing Fluid Analyses Parameters 600 Series (continued)

Method	Analyte	PQL,ug/L
EPA 624	trans-1,2-Dichloroethene	1
EPA 624	trans-1,3-Dichloropropene	1
EPA 624	1,3-Dichloropropylene	1
EPA 624	Trihalomethane, Total	1
EPA 624	Xylenes,Total	1
EPA 625	1,2,4-Trichlorobenzene	5
EPA 625	1,2-Diphenylhydrazine	5
EPA 625	2,4,6-Trichlorophenol	5
EPA 625	2,4-Dichlorophenol	5
EPA 625	2,4-Dimethylphenol	5
EPA 625	2,4-Dinitrophenol	25
EPA 625	2,4-Dinitrotoluene	5
EPA 625	2,6-Dinitrotoluene	5
EPA 625	2-Chloronaphthalene	5
EPA 625	2-Chlorophenol	5
EPA 625	2-Nitrophenol	5
EPA 625	3,3´-Dichlorobenzidine	10
EPA 625	4,6-Dinitro-2-methylphenol	25
EPA 625	4-Bromophenyl phenyl ether	5
EPA 625	4-Chlorophenyl phenyl ether	5

Fracturing Fluid Analyses Parameters 600 Series (continued)

Method	Analyte	PQL,ug/L
EPA 625	4-Nitrophenol	25
EPA 625	Acenaphthene	5
EPA 625	Acenaphthylene	5
EPA 625	Anthracene	5
EPA 625	Atrazine	5
EPA 625	Benz(a)anthracene	5
EPA 625	Benzidine	20
EPA 625	Benzo(a)pyrene	5
EPA 625	Benzo(b)fluoranthene	5
EPA 625	Benzo(g,h,i)perylene	5
EPA 625	Benzo(k)fluoranthene	5
EPA 625	Bis(2-chloroethoxy)methane	5
EPA 625	Bis(2-chloroethyl)ether	5
EPA 625	Bis(2-chloroisopropyl)ether	5
EPA 625	Bis(2-ethylhexyl)phthalate	5
EPA 625	Butyl benzyl phthalate	5
EPA 625	Chrysene	5
EPA 625	Di-n-butyl phthalate	5
EPA 625	Di-n-octyl phthalate	5
EPA 625	Dibenz(a,h)anthracene	5
EPA 625	Diethyl phthalate	5
EPA 625	Dimethyl phthalate	5

Fracturing Fluid Analyses Parameters 600 Series (continued)

Method	Analyte	PQL,ug/L
EPA 625	Fluorene	5
EPA 625	Hexachlorobenzene	5
EPA 625	Hexachlorobutadiene	5
EPA 625	Hexachlorocyclopentadiene	10
EPA 625	Hexachloroethane	5
EPA 625	Indeno(1,2,3-cd)pyrene	5
EPA 625	Isophorone	5
EPA 625	N-Nitrosodi-n-propylamine	5
EPA 625	N-Nitrosodimethylamine	5
EPA 625	N-Nitrosodiphenylamine	5
EPA 625	Naphthalene	5
EPA 625	Nitrobenzene	5
EPA 625	Pentachlorobenzene	5
EPA 625	Pentachlorophenol	25
EPA 625	Phenanthrene	5
EPA 625	Phenol	5
EPA 625	Pyrene	5
EPA 625	2-Methylphenol	5
EPA 625	3 & 4-Methylphenol	5
Method	Analyte	PQL,pg/L
EPA 1613B	2,3,7,8 TCDD	10.2

Fracturing Fluid Analyses Parameters Inorganic

Method	Analyte	PQL,mg/L
EPA 200.8	Antimony	0.005
EPA 200.8	Arsenic	0.005
EPA 200.8	Barium	0.005
EPA 200.8	Beryllium	0.004
EPA 200.8	Cadmium	0.005
EPA 200.8	Chromium	0.005
EPA 200.8	Copper	0.005
EPA 200.8	Lead	0.005
EPA 200.8	Nickel	0.005
EPA 200.8	Selenium	0.005
EPA 200.8	Silver	0.005
EPA 200.8	Thallium	0.005
EPA 200.8	Zinc	0.005
EPA 245.1	Mercury	0.005
SM4500 CN E	Cyanide	0.005
SM45000 CN I	Cyanide, Weak and dissociable	0.005
Method	Analyte	PQL,colonies/100 mL
SM9222 D	Coliform,Fecal	1
SM9222 B	Coliform, Total	1
Method	Analyte	PQL,mg/L
EPA 300.0	Nitrogen,Nitrate (As N)	0.5
EPA 300.0	Nitrogen,Nitrite (As N)	0.5
EPA 300.0	Fluoride	0.5
EPA 420.1	Phenolics,Total Recoverable	0.005
SM 4500 Cl G	Residual Chlorine,Total	0.1

Fracturing Fluid Analyses Parameters SW846

Method	Analyte	PQL, ug/L
EPA 8316	Acrylamide	80
EPA 8151A	2,4,5-TP (Silvex)	1
EPA 8151A	2,4-D	0.94
EPA 8151A	Dinoseb	0.47
EPA 8151A	Dalapon	1.1

PQL's and MDL's

- The PQL's were achieved for most of the Frac Fluids except for the highly viscous samples.
- The target PQL's listed in the individual methods were utilized.
- The MDL's used for the study were those obtained for waters.

PQL's and MDL's

Recommendations for highly viscous Frac fluids

- Use of Liquid/Liquid extraction techniques.
- Use GPC cleanup techniques (although samples are liquids).
- Use of above techniques may or may not influence the interactions on chromatographic columns.

Interferences and Dilution Challenges

Matrix Spike/ Surrogate Spike interactions:

- Spiking viscous liquids does not yield much information due to dilutions that are required.
- Spikes performed on non viscous matrices yielded adequate recoveries.
- Acid Surrogate recoveries in the SVOA analyses are affected even though the base surrogate recoveries are acceptable.

Interferences and Dilution Challenges

Issues encountered due to viscosity:

- Chromatographic columns were affected (SVOA's).
- GC/MS Ion sources were affected.
- Ion Chromatographic columns were clogged and their phases were altered.
- Even though matrix effects are inevitable, Tentatively identified compounds may or may not be detected in these samples.
- Metals analyses were not affected due to digestions performed using acids.

Interferences and Dilution Challenges

- Dilution factors ranged from 2 to 50 fold for the viscous fluids depending on their viscosity.
- Interference effects are due to the viscous nature or composition of the fluids.
- Example MS/MSD recoveries would be affected – an example is in the VOA analysis, the gases recovered at almost 100 percent, but the mid range compounds recovered at less than 50 percent and the higher boiling compounds recovered at around 60 percent.

Interferences and Dilution Challenges

- Chromatographic columns would experience active surfaces wherein continuing calibrations would not pass QC criteria.
- Required injection port maintenance after each sequence.
- Ion Chromatographic columns would have to be replaced if appropriate dilutions are not made before analysis.
- Some fluids would exhibit foaming and the samples would have to be handled appropriately.

Summary

- Not all frac fluids are made equal.
- Care should be exercised during analysis to manage viscous samples.
- Sample preservations are not a problem.
- Analytical parameters must be predefined.
- Expectations must be defined.
- If constituents of frac fluids must be determined, then, other methodologies must be developed.

Practical Quantitation, Method Detection Limits, Interferences and Dilution Challenges

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

The matrices of fracturing fluids vary significantly in consistency and viscosity prior to fracturing. Hence, the analytical challenges increase with the viscosity of the samples provided for analyses. The samples on their own merits are generally representative. The flow back water samples are representative and uniform in nature unless the amount of sediment collected is a significant quantity.

Samples should be collected before fracturing and after fracturing to understand the contaminants present before fracturing and after fracturing. This would yield valuable information in terms of the transformations occurring during the fracturing process and comingling of components from the host materials or the extracted materials. Another suggested step would be collection of a sample of the host material if available or possible, to assess the material balance or source of components detected. One recommendation is that gas samples be collected at the point of exposure as the flow back water is discharged to determine if gaseous components are being emitted and account for any emissions. A suggested method for determining gaseous components in backflow water samples flowing from the wells would be the use of GPA 2174-93. (GPA=Gas Processors Association)(Constant pressure sampling method) This method allows for the samples to be captured at the same conditions as the stream of water.

Sample Preservation

Preservation of the samples of fracturing fluids for the various analytical processes does not pose any issues. Preservation of the Backflow waters generally does not pose issues. Volatile components in both the fracturing fluids and the backflow waters need not be preserved with acid and analyzed within 7 days of collection of samples thus satisfying the regulatory guidelines on holding times prescribed in the various methodologies.

Practical Quantitation Limits (PQLs) and Method Detection Limits (MDLs)

Methods employed for the analyses of the fracturing fluids include US EPA 500 and 600 series methods and Standard Methods for Water and Wastewater in combination with SW846 methods. The typical methods utilized are listed in Table 10. The components of the analytical suite are presented in Table 11 through Table 14. The practical quantitation limits are also listed in the aforementioned tables. However, depending on the viscosity of the frac fluids and the interferences present in the various samples, the PQLs may be affected. The MDLs utilized are those determined for liquid samples. The MDLs are statistically derived, as outlined in the method requirements for each of the analytes.

Interferences and Dilution Challenges

The PQLs are affected when dilutions are performed due to the matrix interferences. Dilutions are generally performed to alleviate the viscosity issues or the interferences. Based on analyses performed, flow back waters do not pose the same challenges as the fracturing fluid matrices. Matrix interferences, specially, with respect to samples which are highly viscous are handled by dilutions. Surrogates and internal standards and its behavior in the matrix vary based on the samples. In some cases matrix spike compounds behave differently. For example, in a VOA analysis the gases may recover fine yet the rest of the compounds may not recover at the same level as the gaseous components. In a semi volatile analysis the acid surrogates may not recover where as in the same sample the base surrogate recoveries may be adequately recovered. Based on our experience, approximately 10 % of the fracturing fluid matrices pose analytical challenges for the parameters analyzed.

Table 10. Typical Methods

- Acrylamide – SW846 – 8316
- Metals – Method 200.8 / 245.1
- Cyanide/ Weak and dissociable, Total – SM 4500 CN E & I
- Fecal and Total Coliform – SM 9222D & B
- Total Phenolics – EPA Method 420.1
- Herbicides – SW846 – 8151
- Ion Chromatography – EPA Method 300
- Residual Chlorine – SM 4500 CL G
- VOA's – EPA Method 624
- SVOA's – EPA Method 625
- Pesticides/ PCB's – EPA Method 608
- 2,3,7,8 – TCDD – EPA Method 1613B
- Halo Acetic Acids – EPA Method 552.3
- 1, 2 – Dibromoethane – EPA Method 504.1

Table 11. 500 Series Methods

Method	Analyte	PQL, ug/L
EPA 552.3	Dibromoacetic Acid	0.8
EPA 552.3	Dichloroacetic Acid	0.8
EPA 552.3	Monobromoacetic Acid	1.6
EPA 552.3	Monochloroacetic Acid	0.8
EPA 552.3	Trichloroacetic Acid	0.8
EPA 552.3	Haloacetic Acid	0.8
EPA 504.1	1,2-Dibromoethane	0.025

Table 12. 600 Series Methods

Method	Analyte	PQL,ug/L
EPA 608	4,4´-DDD	0.05
EPA 608	4,4´-DDE	0.05
EPA 608	4,4´-DDT	0.05
EPA 608	Aldrin	0.05
EPA 608	alpha-BHC	0.05
EPA 608	Aroclor 1016	1
EPA 608	Aroclor 1221	1
EPA 608	Aroclor 1232	1
EPA 608	Aroclor 1242	1
EPA 608	Aroclor 1248	1
EPA 608	Aroclor 1254	1
EPA 608	Aroclor 1260	1
EPA 608	beta-BHC	0.05
EPA 608	Chlordane	0.5
EPA 608	delta-BHC	0.05
EPA 608	Dieldrin	0.05
EPA 608	Endosulfan I	0.05
EPA 608	Endosulfan II	0.05
EPA 608	Endosulfan sulfate	0.05
EPA 608	Endrin	0.05
EPA 608	Endrin aldehyde	0.05
EPA 608	gamma-BHC	0.05
EPA 608	Heptachlor	0.05
EPA 608	Heptachlor epoxide	0.05
EPA 608	Methoxychlor	0.05
EPA 608	Toxaphene	1
EPA 624	1,1,1-Trichloroethane	1
EPA 624	1,1,2,2-Tetrachloroethane	1
EPA 624	1,1,2-Trichloroethane	1
EPA 624	1,1-Dichloroethane	1
EPA 624	1,1-Dichloroethene	1
EPA 624	1,2,4-Trichlorobenzene	1
EPA 624	1,2-Dibromo-3-chloropropane	5
EPA 624	1,2-Dichlorobenzene	1
EPA 624	1,2-Dichloroethane	1
EPA 624	1,2-Dichloropropane	1
EPA 624	1,3-Dichlorobenzene	1
EPA 624	1,4-Dichlorobenzene	1
EPA 624	2-Chloroethyl vinyl ether	5
EPA 624	Acrolein	50
EPA 624	Acrylonitrile	5

Method	Analyte	PQL,ug/L
EPA 624	Benzene	1
EPA 624	Bromodichloromethane	1
EPA 624	Bromoform	1
EPA 624	Bromomethane	1
EPA 624	Carbon tetrachloride	1
EPA 624	Chlorobenzene	1
EPA 624	Chloroethane	1
EPA 624	Chloroform	1
EPA 624	Chloromethane	1
EPA 624	Dibromochloromethane	1
EPA 624	Dibromomethane	1
EPA 624	Epichlorohydrin	10
EPA 624	Ethylbenzene	1
EPA 624	Methylene chloride	1
EPA 624	Styrene	1
EPA 624	Tetrachloroethene	1
EPA 624	Toluene	1
EPA 624	Trichloroethene	1
EPA 624	Vinyl chloride	1
EPA 624	cis-1,2-Dichloroethene	1
EPA 624	cis-1,3-Dichloropropene	1
EPA 624	m,p-Xylene	2
EPA 624	o-Xylene	1
EPA 624	trans-1,2-Dichloroethene	1
EPA 624	trans-1,3-Dichloropropene	1
EPA 624	1,3-Dichloropropylene	1
EPA 624	Trihalomethane, Total	1
EPA 624	Xylenes,Total	1
EPA 624	Epichlorohydrin	25
EPA 625	1,2,4-Trichlorobenzene	5
EPA 625	1,2-Diphenylhydrazine	5
EPA 625	2,4,6-Trichlorophenol	5
EPA 625	2,4-Dichlorophenol	5
EPA 625	2,4-Dimethylphenol	5
EPA 625	2,4-Dinitrophenol	25
EPA 625	2,4-Dinitrotoluene	5
EPA 625	2,6-Dinitrotoluene	5
EPA 625	2-Chloronaphthalene	5
EPA 625	2-Chlorophenol	5
EPA 625	2-Nitrophenol	5
EPA 625	3,3´-Dichlorobenzidine	10
EPA 625	4,6-Dinitro-2-methylphenol	25

Method		PQL,ug/L
EPA 625	4-Bromophenyl phenyl ether	5
EPA 625	4-Chlorophenyl phenyl ether	5
EPA 625	4-Nitrophenol	25
EPA 625	Acenaphthene	5
EPA 625	Acenaphthylene	5
EPA 625	Anthracene	5
EPA 625	Atrazine	5
EPA 625	Benz(a)anthracene	5
EPA 625	Benzidine	20
EPA 625	Benzo(a)pyrene	5
EPA 625	Benzo(b)fluoranthene	5
EPA 625	Benzo(g,h,i)perylene	5
EPA 625	Benzo(k)fluoranthene	5
EPA 625	Bis(2-chloroethoxy)methane	5
EPA 625	Bis(2-chloroethyl)ether	5
EPA 625	Bis(2-chloroisopropyl)ether	5
EPA 625	Bis(2-ethylhexyl)phthalate	5
EPA 625	Butyl benzyl phthalate	5
EPA 625	Chrysene	5
EPA 625	Di-n-butyl phthalate	5
EPA 625	Di-n-octyl phthalate	5
EPA 625	Dibenz(a,h)anthracene	5
EPA 625	Diethyl phthalate	5
EPA 625	Dimethyl phthalate	5
EPA 625	Fluoranthene	5
EPA 625	Fluorene	5
EPA 625	Hexachlorobenzene	5
EPA 625	Hexachlorobutadiene	5
EPA 625	Hexachlorocyclopentadiene	10
EPA 625	Hexachloroethane	5
EPA 625	Indeno(1,2,3-cd)pyrene	5
EPA 625	Isophorone	5
EPA 625	N-Nitrosodi-n-propylamine	5
EPA 625	N-Nitrosodimethylamine	5
EPA 625	N-Nitrosodiphenylamine	5
EPA 625	Naphthalene	5
EPA 625	Nitrobenzene	5
EPA 625	Pentachlorobenzene	5
EPA 625	Pentachlorophenol	25
EPA 625	Phenanthrene	5
EPA 625	Phenol	5
EPA 625	Pyrene	5

Method	Analyte	PQL,ug/L
EPA 625	2-Methylphenol	5
EPA 625	3 & 4-Methylphenol	5

Table 13. SW846 Series

Method	Analyte	PQL, ug/L
EPA 8316	Acrylamide	80
EPA 8270	Atrazine	50
EPA 8151A	2,4,5-TP (Silvex)	1
EPA 8151A	2,4-D	0.94
EPA 8151A	Dinoseb	0.47
EPA 8151A	Dalapon	1.1

Table 14. Inorganic Parameters

Method	Analyte	PQL,mg/L
EPA 200.8	Antimony	0.005
EPA 200.8	Arsenic	0.005
EPA 200.8	Barium	0.005
EPA 200.8	Beryllium	0.004
EPA 200.8	Cadmium	0.005
EPA 200.8	Chromium	0.005
EPA 200.8	Copper	0.005
EPA 200.8	Lead	0.005
EPA 200.8	Nickel	0.005
EPA 200.8	Selenium	0.005
EPA 200.8	Silver	0.005
EPA 200.8	Thallium	0.005
EPA 200.8	Zinc	0.005
EPA 245.1	Mercury	0.005
SM4500 CN E	Cyanide	0.005
SM45000 CN I	Cyanide, Weak and dissociable	0.005
Method	Analyte	PQL,colonies/100 mL
SM9222 D	Coliform,Fecal	1
SM9222 B	Coliform, Total	1
Method	Analyte	PQL,mg/L
EPA 300.0	Nitrogen,Nitrate (As N)	0.5
EPA 300.0	Nitrogen,Nitrite (As N)	0.5
EPA 300.0	Fluoride	0.5
EPA 420.1	Phenolics,Total Recoverable	0.005
SM 4500 Cl G	Residual Chlorine,Total	0.1