Tracer Measurement by LC-MS

- Chemical Tracers such as Fluorobenzoic Acids (FBA) are used in reservoir fluids produced from the oil well being tested.
- Measurement of FBAs as tracers allows informed decision-making as to continue clean-up or begin production.
- FBAs are compatible in both aqueous fluid as salts and in organic base fluids as acids.
- Techniques such as GC, GC-MS, LC-UV, FTIR have been employed for the measurement of these tracers.
- Researchers continue to look for optimal methodologies with reduced sample preparation time, analysis time, multiplexing ability in newer technologies.
- LC-MS/MS using a QQQ system presents the ability to improvise the analytical method over existing technologies

"Method for Determining the Extent of Recovery of Materials Injected in Oil Wells During Oil and Gas Exploration and Production" – *Malone et.al*., US 6, 659, 175 B2, **2003**

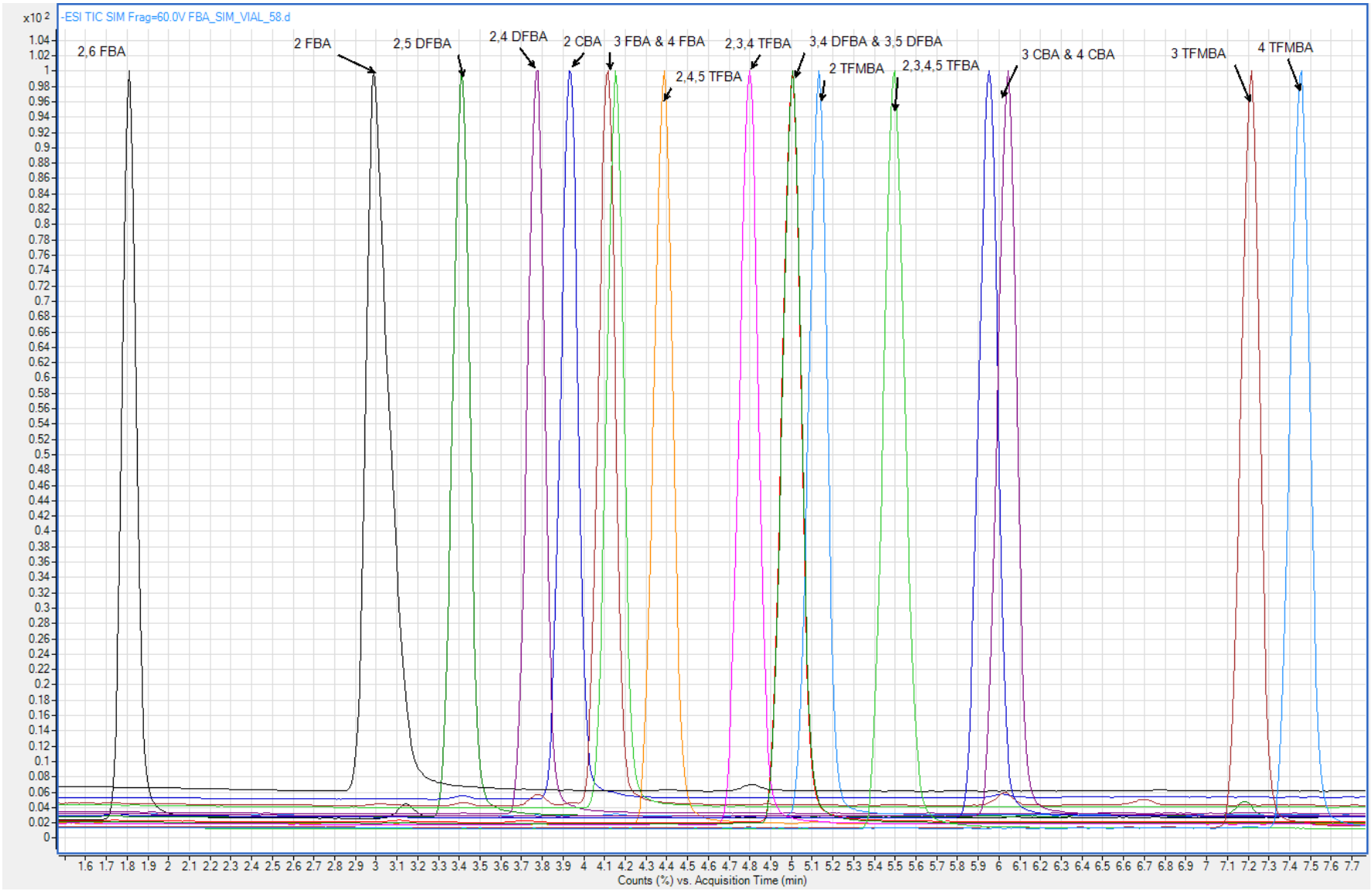
LC-MS/MS method for analysis of FBAs

- **Many of the FBAs are positional isomers hence they are isobaric. MS Resolving Power on its own is insufficient.**
- Challenge is to provide adequate resolution in the LC dimension for at least the critical FBAs (10-14 analytes).
- Sensitivity required in the low ppb to upper ppt for all analytes.
- Sample matrix is high in salt content.

List of FBA Tracers
MS/MS- Dynamic MRM Conditions

Time	Name	Transition	CE	Fragmentor
1.78	2,6 DFBA	157-113	3	60
3.05	2 FBA	139-95	6	60
3.41	2,5 DFBA	157-113	6	60
3.77	2,4 DFBA	157-113	6	68
3.93	2 CBA	155-111	2	68
4.14	3 FBA & 4 FBA	139-95	10	88
4.41	2,4,5 TFBA	175-131	6	70
4.82	2,3,4 TFBA	175-131	6	58
5.02	3,4 FBA & 3,5 FBA	157-113	10	72
5.35	2 TFMBA	189-145	10	64
5.77	2,3,4,5 TFBA	193-149	6	64
5.96	3 CBA & 4 CBA	155-111	6	70
7.22	3 TFMBA	189-145	10	88
7.73	4 TFMBA	189-145	10	88

LC-MS/MS of FBA Tracers
10 uL injection of a 1 ppb standard mixture



Results

- Chromatographic Separation of most critical tracers achieved using as UHPLC column. Requires Fast Acquisition rates in the MS – well suited to QQQ.
- Sensitivity limits of 10 ppt was achieved on tracers by using MRM analysis conditions on the QQQ MS.
- The samples were prepared by simple dilution and the LC-flow was diverted to waste for up to 1.5 min to eliminate the salt plug from the samples.
- Since samples are highly salty the source is cleaned more often than other methods – Cleaning the source on an Agilent LC-MS is practical and user-friendly.

Conclusion

- A simple, sensitive, fast LC-MS/MS method with very little sample preparation has been developed for the analysis of tracers such as FBAs,
- The current analysis time is only **7 min** long in comparison to GC-MS or LC-UV methods that are ~ 20-30 min long/sample.
- Sample preparation for the LC-MS method involves simple dilution as opposed to GC-MS methods that require multi-step SPE and derivatization.