1,4-Dioxane in Alcohol Ethoxylates: Concentration, Measurement Methods and Mechanism of Formation

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Outline

- 1,4-Dioxane legislation
- Measurement of 1,4-Dioxane in Shell's Alcohol Ethoxylates
- Level of 1,4-Dioxane in other Alcohol Ethoxylates
- Mechanism of formation in Alcohol Ethoxylates
- Conclusions

1,4-Dioxane (1,4-D) legislation

- NY:
  - Household Cleaning Products & Personal Care Products:
    - 2 ppm by 31 December 2022
    - 1 ppm by 31 December 2023
  - Cosmetic Products:
    - 10 ppm by 31 December 2022
  - 2025: Department of Environmental Consultation, in consultation with Department of Health, shall determine by rule if the trace concentration threshold shall be lowered
- CA and NJ: Have similar regulations, either in committee or proposed
  - CA requires all producers of chemicals sold to list 1,4-D content on their website
- European Union: 1,4-D proposed to be a SVHC – substance of very high concern
- Background:
  - EPA has concluded that 1,4-D is "likely to be carcinogenic to humans"*

*EPA and 2016 report by Dept of Health and Human Services National Toxicology Program

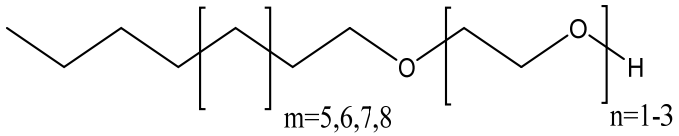
History of 1,4-D measurement in Shell's alcohol ethoxylates

- Variety of testing methods are available for 1,4-D
  - Typically GC-FID or GC-MS preferred, GC-MS giving higher sensitivity
- Shell achieved early success using GC-FID for Alcohol Ethoxylates
  - In 1979, a lower detection limit reported[1]
    - Direct injection technique with a backflush: Minimum Detection Limit (MDL) of 0.5 mg/kg
    - Gave faster, simpler technique c.f. alternative Birkel method
  - Applied to Shell Alcohol Ethoxylates:
    - Yielded no quantifiable 1,4-D
    - Covered range of ethoxylates with EO mol range (>2 to 11)
    - Alcohols C9 to C15

[1]**Stafford, Guin, Johnson, Sanders, Rockey, *J. Soc. Cosmet. Chem.* 1980, (31), 281-287.**

Current 1,4-D measurement at production QC support laboratory

- GC-FID work started in 2019 for Shell's Alcohol Ethoxylates
  - FID Chosen for its robustness
    - Adaptation of USP method for analysis of 1,4-D in EO derived products[2] and the ISO 17280 methods[3]
      - Using headspace unit with no special handling – sample simply dissolved in polar solvent
    - Initial minimum Detection Limit (MDL) of 0.3 mg/kg, Minimum Quantifiable Limit (MQL) of 1 mg/kg
    - 1,4-D concentration by GC-FID is part of the Certificate of Analysis (COA)
- Results across Shell's Alcohol Ethoxylates: 1,4-D found to be less than MDL (= not detectable)
  - Low mole: C12-15 alcohol range, 1-3 EO range
  - High mole: C9-15 alcohol range, 7-8 EO range

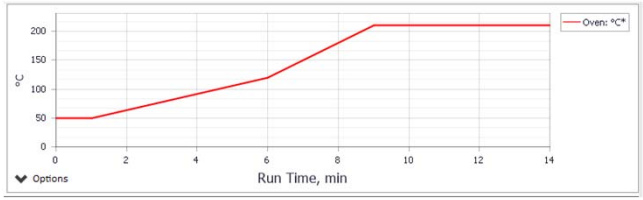


[2] United States Pharmacopeia (USP) Monograph 35, Chemical Test 228 (Ethylene Oxide and Dioxane), pp 143.

[3] International Standard (ISO 17280) – Surface Active Agents – Determination of 1,4-Dioxan residues in surfactants obtained from epoxyethane by gas chromatography – 2015.

GC/MS method for 1,4-D

- Motivation: ability to peer deeper into the mechanism of formation
  - Affords entry toward a lowering of reporting limits to customers
- GC/MS with single-ion monitoring (SIM)
  - Dates to 1982[4] and a variety of adaptations made since then
  - Method suited to an R&D setting. Less practicable as a QC method at a manufacturing plant
- Shell method uses static GC-MS and SIM with deuterated 1,4-Dioxane as internal standard with headspace injection
  - Chromatographic conditions
    - Ramped program on DB-624, 60mx0.25mmx1.40 um column at 1.5 split



  - Mass Detector Conditions
    - Temps: Source – 230 C, Quadropole 150 C
    - SIM ions 58.00, 64.00, 88.00, 96.00

[4] Bruce Waldman, *J. Soc. Cosmet. Chem.* 1982, (33), 19-25.

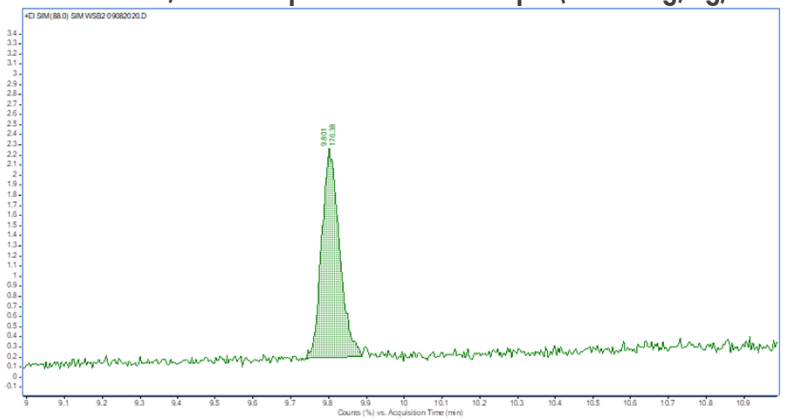
GC/MS-SIM method results

- Method Validation Results (based on a 0.006 mg/kg standard sample)
  - Samples introduced in dimethylformamide (DMF) as solvent
  - Detection limit of 0.003 mg/kg and Quantitation at 0.011 mg/kg

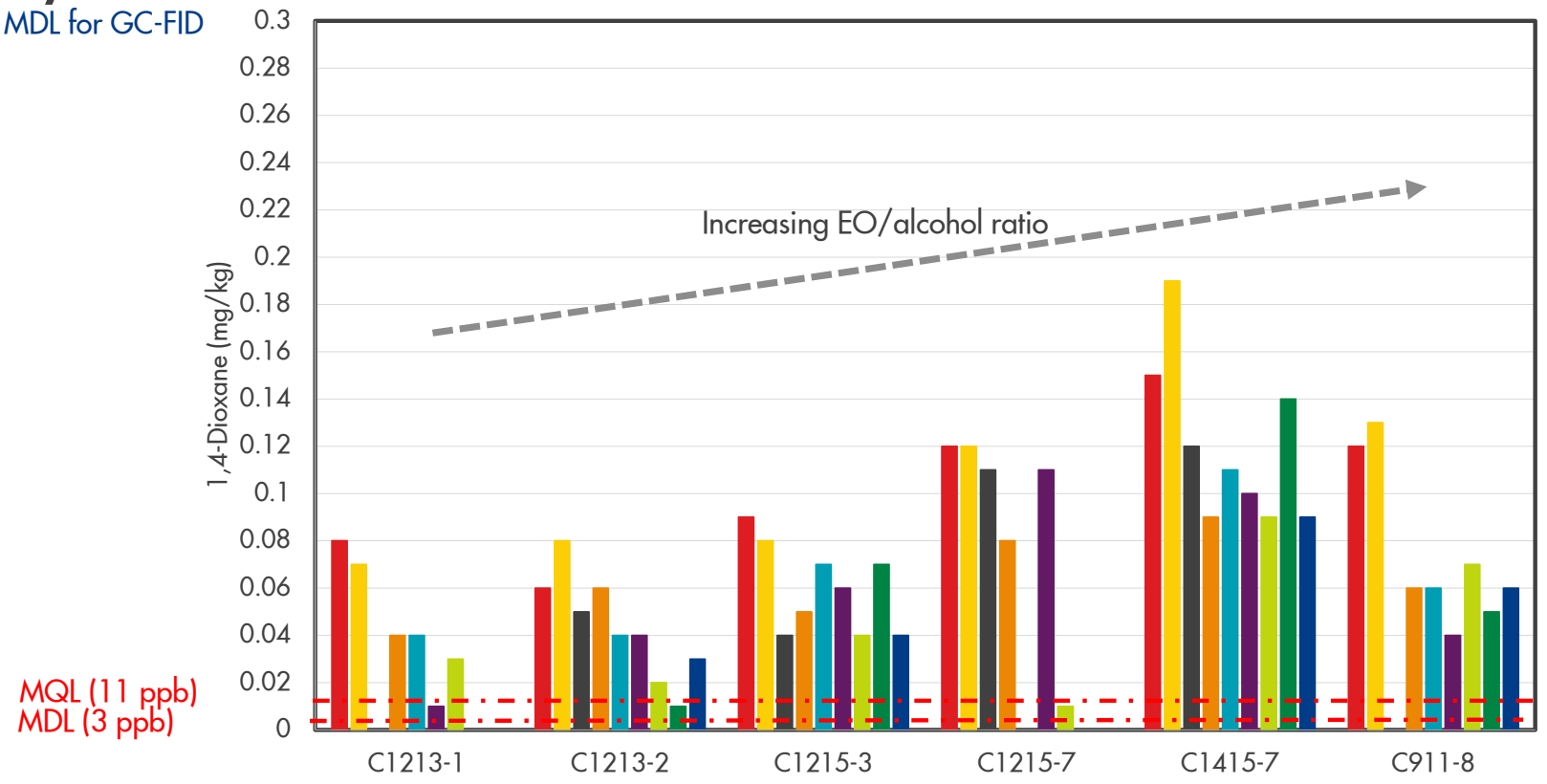
Instrument DL = 3 * [Cal Std]/(S/N) (S/N = m/z 88 peak height/ noise height)
Instrument QL = 10 * [Cal Std]/(S/N)
Sample DL = 5 * Instrument DL
Sample QL = 5 * Instrument QL

- Recovery based on a C1213-1 sample = 105%
- Repeatability based on high (0.17 mg/kg) and low (0.10 mg/kg) stds
  - Analyzed 5 times over 3 days
  - 2.3% and 0.8%, respectively

Resolution/Peak Shape of Standard Sample (0.006 mg/kg)

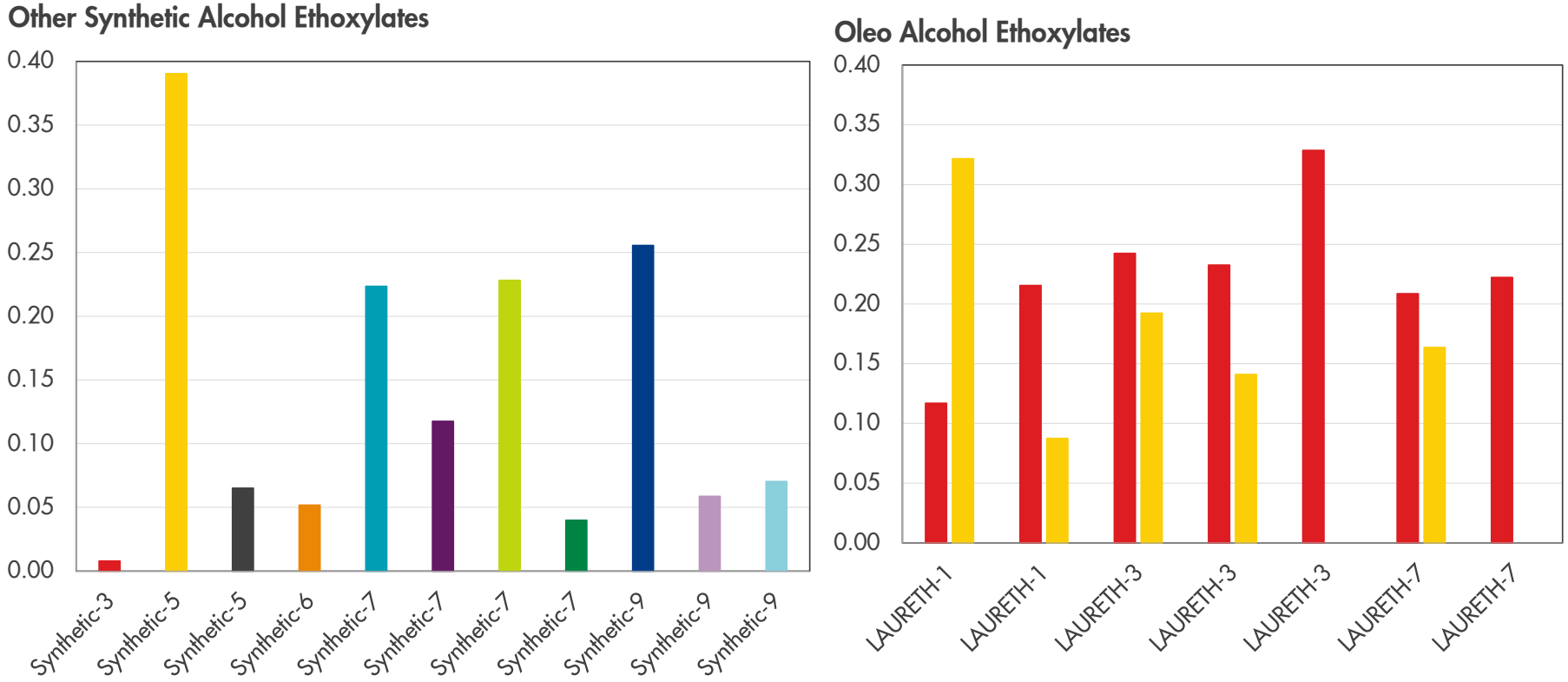


1,4-D in Shell's Alcohol Ethoxylates produced in USA, measured by GC/MS - SIM



- Results for different batches at different times are shown (shown by colours).
- Results are <0.2 mg/kg, many <0.1 mg/kg

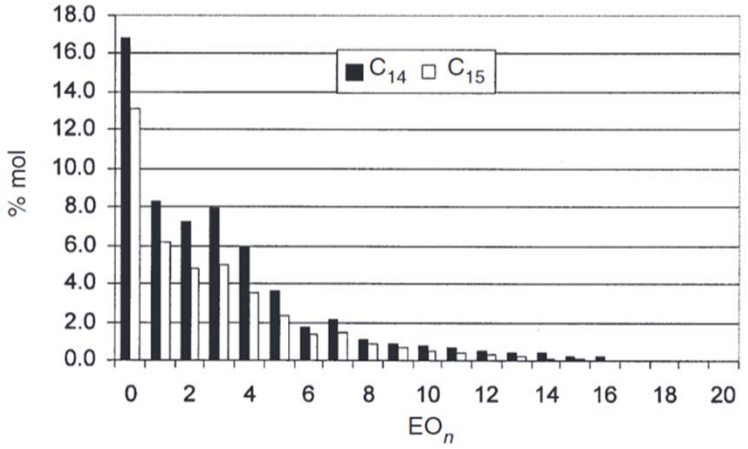
Levels of 1,4-D (mg/kg) in other Alcohol Ethoxylate grades

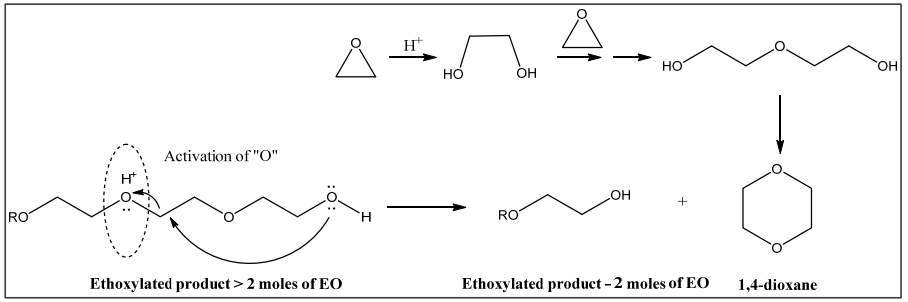


Results for different products and suppliers are shown. Right hand side chart also shows results for different batches. Synthetic and oleo alcohol ethoxylates have comparable levels, 0.05 – 0.4 mg/kg

1,4-D formation in Alcohol Ethoxylate

- Base catalysis (with KOH) ethoxylation is widely used in the industry[5,6]
- Two plausible reaction schemes for formation of 1,4-D:
  1. Back-biting from formed Ethoxylate
     - >2 EO-mol addition to alcohol follows a distribution (EO/alcohol ratio is a average value)[7]. See chart for a representative 3 EO-mol
     - Terminal alcohol backbiting within the chain can occur to a limited extent. Releases 1,4-D, reaction below
     - Longer chains have higher mobility and generate 1,4-D more readily
     - Reaction likely catalysed by adventitious water: provides a proton to catalyse cyclization of terminal hydroxyl to internal ether oxygen, via a 6-membered transition state
  2. Direct reaction of EO at reactor inlet
     - Catalyzed by trace water in alcohol
     - Would occur at front of reaction since EO is very dry
     - Similar to mechanism to PEG formation in system

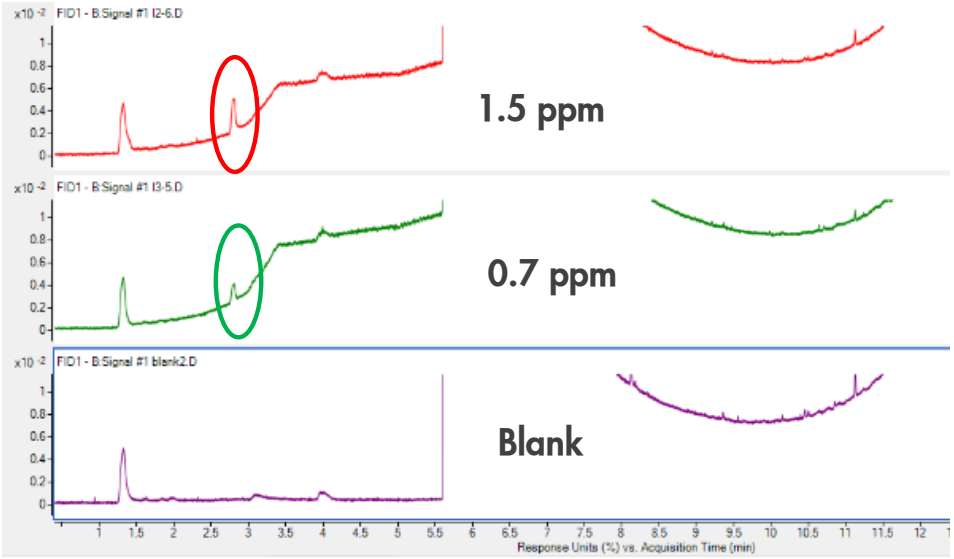


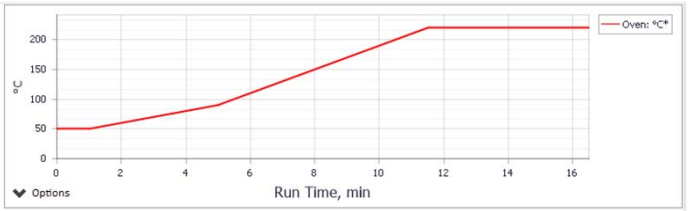


[5]L. Matheson, G. Russell, B. MacArthur, W. B. Sheats. *100th AOCS Annual Meeting 6 May 2009.* "1,4-dioxane is not easily formed under conditions of alkaline catalysis". [6]J. G. Lawrence. *Surfactants III-Chromatography, pp 4326.* [7] G. Cassani, C. Pratesi, L. Faccetti, S. Pravettoni, G. Nucci, N.Andriollo, L. Valtorta, L. Matheson, *J. Surfactants and Detergents*, 2004, *7* (2) 195-204)

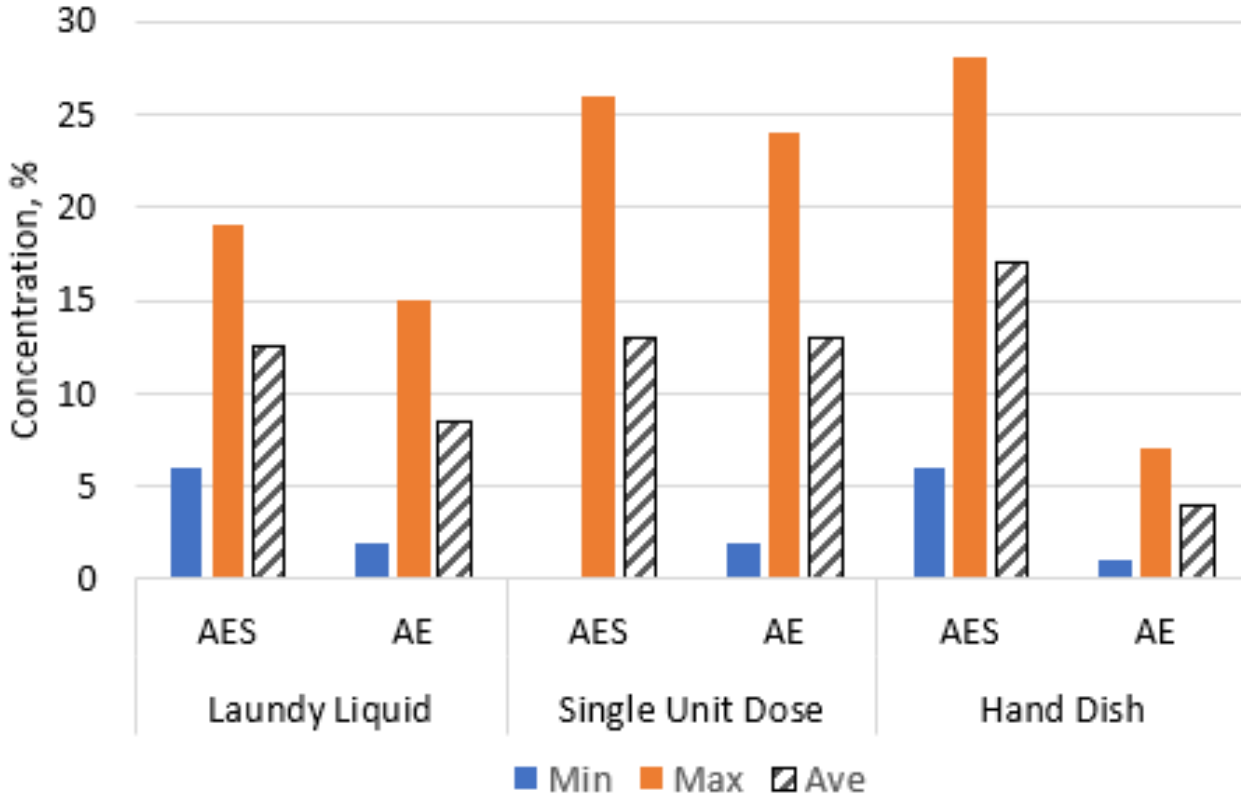
Development of routine QC method for production environment

- Requirements
  - Adaptable to standard GC-FID w/ headspace
  - No special sample handling
  - No need for deuterated internal standards ($$$$)
  - MDL of < 0.2 mg/kg
- Results
  - DMF afforded adequate solubility across family of products
    - No matrix effect considerations required
  - Isolated chromatographic conditions
    - Headspace Conditions
      - 85 C oven, loop 90 C and line at 150 C with 20 min equil time
      - Injection time 1 min
    - FFAP Column (30mx320umx0.25 um) 1:10 split with ramped profile
    - Afforded 0.1 mg/kg MDL for 1,4-D in our products
- Method now pushed to production environment





Meeting the future challenges of 1,4-D in final products: % concentration of AES and AE surfactants



- Data taken from Battelle Detergent Analysis Program. For several products within each category, 2018 and earlier
- Data based on selection of on-the-shelf products in USA

Conclusions from this study

- To measure 1,4-D:
  - GC-FID is used as a process QC method with MDL of 0.1 mg/kg
  - GC/MS is used as an R&D lab-based method to measure to a very low level (MDL 0.003 mg/kg) – offers insight to its formation/selectivity
- Shell Alcohol Ethoxylates produced in USA have <0.2 mg/kg
- Mechanism of formation: we postulate that trace levels of water provide the proton to give back-biting of the ethoxylate chain to form the low level of 1,4-D detected
- 1,4-D levels are comparable for synthetic vs oleo alcohol ethoxylates