



Naphthenic Acids in the Environment: State of the Union

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Geochemistry

Metallurgy

Mine Site

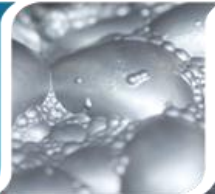
Inspection

Coal

Industrial

Tribology

Environmental Pharmaceutical



Why the Concern?



- The oil sands (OS) in northeastern Alberta are the second largest proven oil deposit on Earth (1.7 trillion barrels with 173 billion economically recoverable)
- Industrial production of crude oil from OS is estimated at more than 1.3 million barrels per day covering 530 km²
- Oil sands process-affected water (OSPW) take up ~20% of the area (130 km²)
- Production of crude oil from OS will reach 2.9 million barrels per day by 2020
- It is estimated that greater than 1 billion m³ of OSPW are currently stored on-site in various settling basins.

Why the Concern?

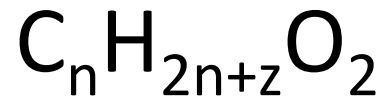


- The ponds will need to be reclaimed, however, they contain a recalcitrant group of compounds known as naphthenic acids (NAs) which are toxic.
- Natural half-lives of NAs in OSPW is 12.8-13.6 years
- OSPW is acutely and chronically toxic to aquatic organisms including fish. Endocrine effects have been observed (alterations T/E2 steroidogenesis)
- Comparison of estrogenicity and antiandrogenic response of NAs derived from Merrichem (petroleum derived) and OSPW reveal OSPW more estrogenic and antiandrogenic (cell line work)
- NAs have been the target of remediation efforts
- There is concern of off-site migration of NAs (dike seepage, groundwater intrusion, etc) and impact on the aquatic environment

Naphthenic Acids

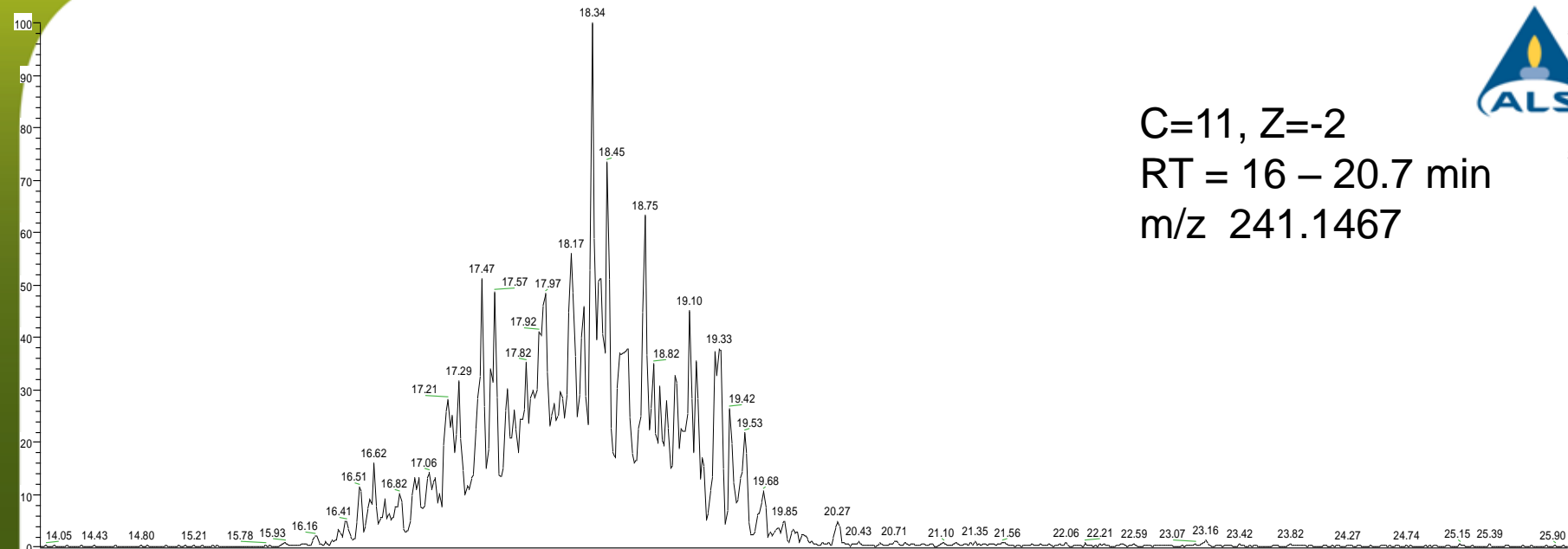


- Comprise a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids, with the general chemical formula

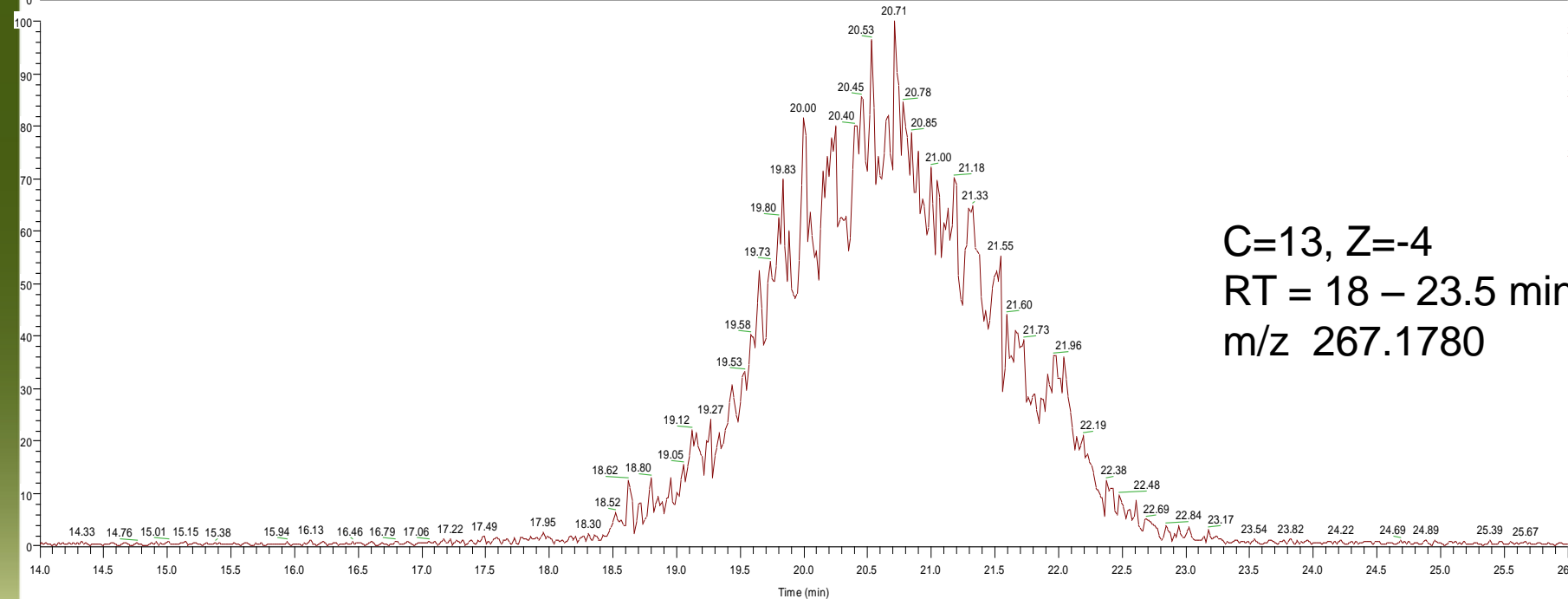


- Where, n = carbon number; Z is zero or a negative, even interger that specifies the hydrogen deficiency resulting from ring formation
- The rings may be fused or bridged
- For each n and Z combination there are numerous isomers of unknown molecular structure, thus complicating accurate characterization and quantification
- The acyclic components are highly branched
- pKa = 5-6
- Partition from an oil phase into an aqueous phase at neutral or alkaline pH
- Bioconcentration factor in fish is 2

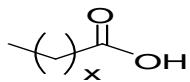
C=11, Z=-2
RT = 16 – 20.7 min
m/z 241.1467



C=13, Z=-4
RT = 18 – 23.5 min
m/z 267.1780

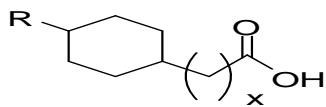
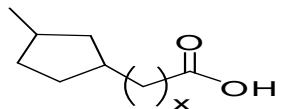


Z = 0

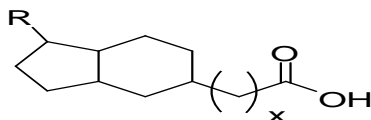
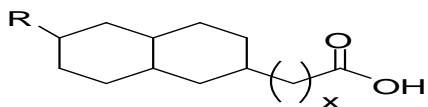


Strausz and Lowen, 2003 p 193

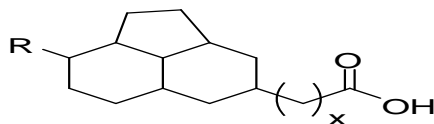
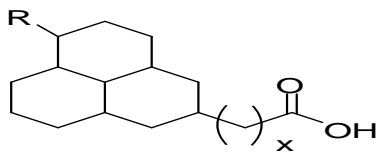
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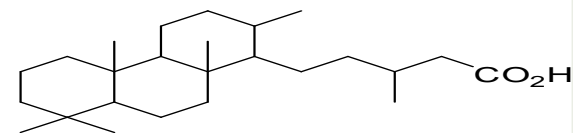
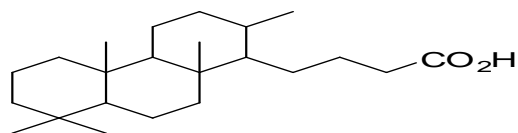
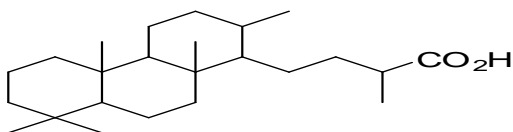
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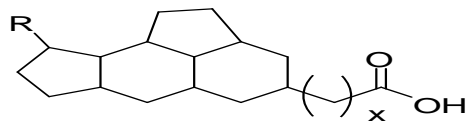
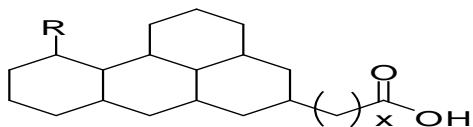
Z = -6



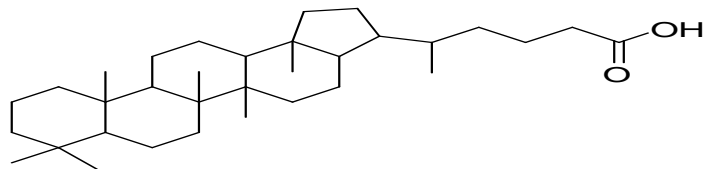
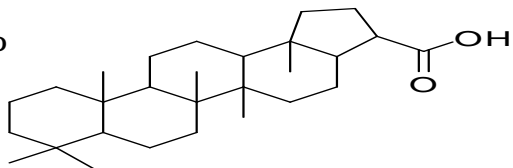
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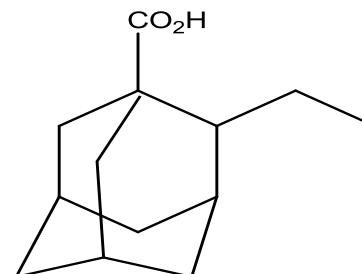
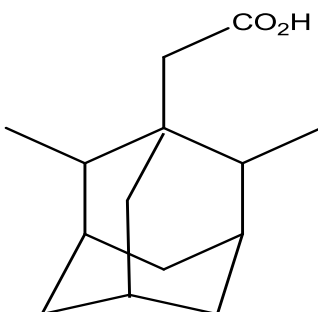
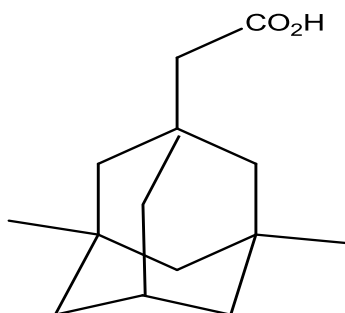
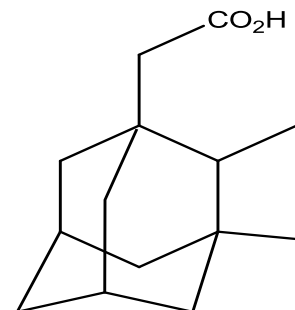
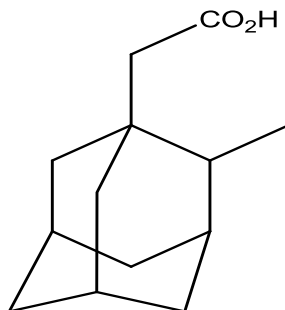
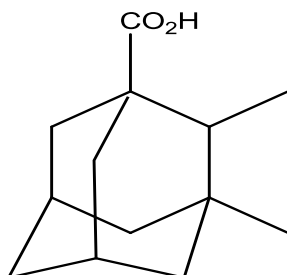
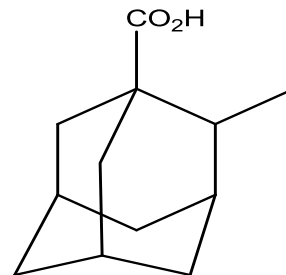
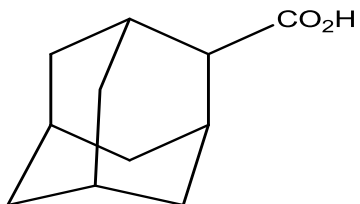
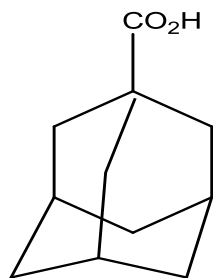


Z = -8



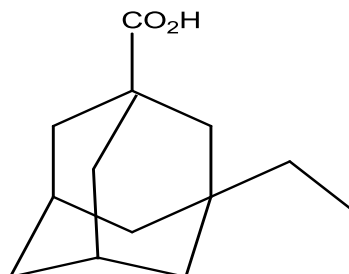
Z = -10

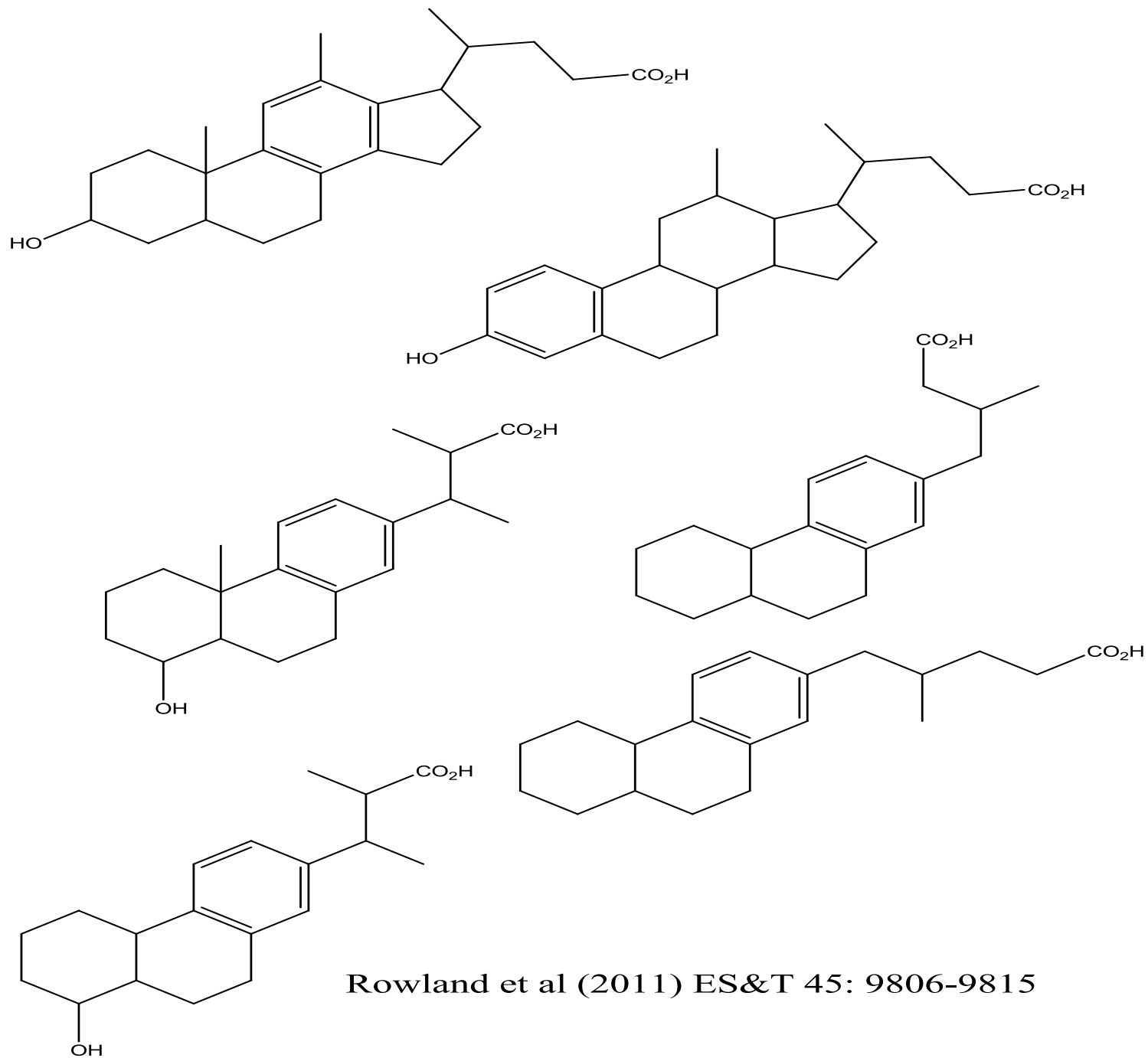




Rowland et al, 2011

GC*GC/TOF
1.6 billion theoretical plates





Rowland et al (2011) ES&T 45: 9806-9815

Sources of Naphthenic Acids



- Are natural components of petroleum
- Petroleum acids in crude oils range from undetectable to 3% by weight
- Average concentration in seven oil sands ore from Syncrude Canada Ltd (SCL) was 200 mg/kg
- Syncrude processes about 500,000 tonne of ore each day (SCL, 2000)
- There is the potential to release 100 tonne of naphthenic acids from the ore each day.
- Ref: Clemente and Fedorak (2005). Chemosphere, 60: 585-600

Tailings Ponds



- Tailing pond waters contain 20 – 120 mg/L of naphthenic acids
- The oil sands companies operate under a zero discharge policy, thus none of these waters can be intentionally released to the environment, and much of the water is recycled through the extraction process
- However, when the oil sands operations cease (in about 50 years), all of the disturbed land and the process-affected waters will have to be reclaimed, and the concentrations of naphthenic acids reduced to below toxic levels (< 0.15 mg/L)
- Decades of storage in tailings ponds under various conditions have not proven effective at decreasing NA concentrations to below 20 mg/L

Tailings Ponds



- Storage of tailings water represents a temporary solution but is a substantial cost to the industry, and the risk of large spills of NAs leaching into surrounding aquatic environments (detected in groundwater) grows with the size of the industry.
- Stores of OSPW already exceed 1 billion m³
- A more sustainable solution would be to reduce the toxicity of these aqueous tailings: thus, there is an urgent need to understand the fate of NAs under a variety of engineered scenarios

Toxicity of Naphthenic Acids



- Naphthenic acids are believed to be some of the most toxic components of refinery effluent and oil sands tailings water
- Concentrations > 2.5 – 5 mg/L in refinery effluent would be toxic to fish
- Naphthenic acids are quite soluble in neutral or slightly alkaline waters, thus aquatic organisms are readily exposed to the toxic effects of the dissolved naphthenates
- LC₅₀ 2-month-old chum salmon = 25 mg/L
- LC₅₀ 2-month-old kutum, roach fingerling and 2-year-old sturgeon = 50 mg/L
- LC₅₀ 2-year-old roach and Caspian round goby = 75 mg/L
- Physiological and biochemical parameters (leukocyte and glycogen levels) found to be impacted in fish exposed to 0.5 – 5 mg/L naphthenic acids
- Zooplankton (*Nephargoides maeoticus*) maximum allowable concentration = 0.15 mg/L
- Reference: Clemente and Fedorak (2005). Chemosphere ,60: 585-600

Toxicity of Tailings Water



- LD_{50} *Daphnia magna* = 2% v/v (EC₅₀ 2.4 mg/L (120 mg/L))
- LD_{50} rainbow trout = 7% v/v (EC₅₀ 8.4 mg/L (120 mg/L))
- IC₅₀ Microtox = 41.9 – 64.9 mg/L depending on MW
- IC₂₀ Microtox = 10% v/v – more reproducible than trout and *Daphnia magna*
- Because of these observations and its relatively low cost, Microtox (*Vibrio fischeri*) has commonly been used to monitor toxicity of the oil sands tailings water and naphthenic acid solutions.
- Reference Clemente and Fedorak (2005) Chemosphere 60: 585-600

Toxicity of Commercial Naphthenic Acids

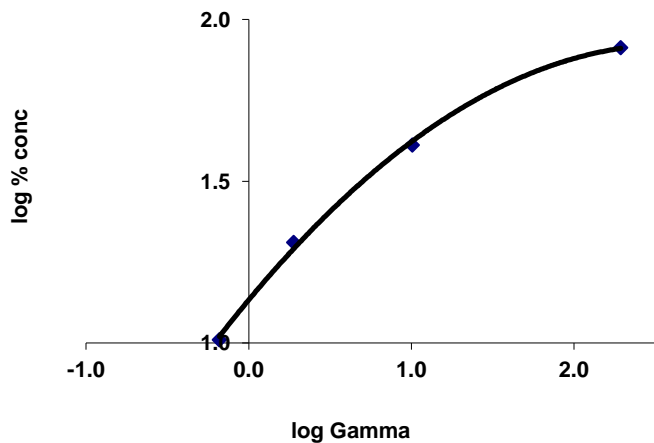


| Commercial Acid | EC ₅₀ – 15 min (conf. interval) | EC ₂₀ – 15 min |
|-------------------|--|---------------------------|
| #387 Merichem | 5.4 – 7.2 (3.4 – 10.6) | 2.7 |
| #388 Aldrich | 10.4 – 11.7 (8.3 – 13.0) | 5.1 |
| #389 Chem Service | 6.6 (5.8 – 7.6) | 3.1 |

Reference: ALS Data

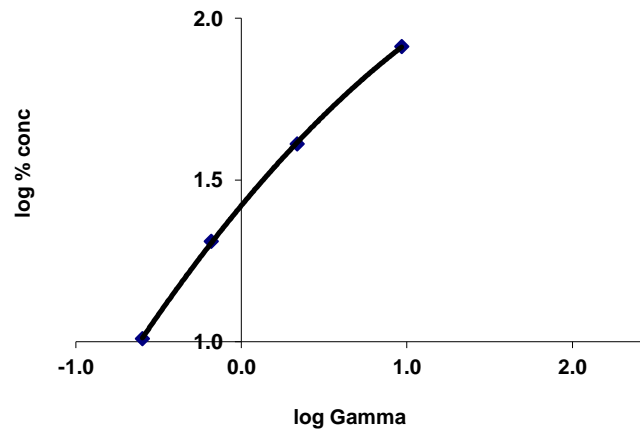


log/log Concentration vs. Gamma
 $y = -0.1154x^2 + 0.6041x + 1.1328$
 $R^2 = 0.9986$



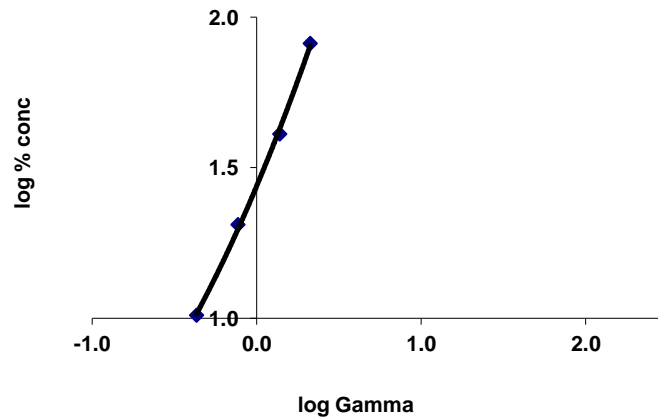
MERRICHEM

log/log Concentration vs. Gamma
 $y = -0.114x^2 + 0.6164x + 1.4213$
 $R^2 = 0.9999$



ALDRICH

log/log Concentration vs. Gamma
 $y = 0.3937x^2 + 1.3054x + 1.4394$
 $R^2 = 0.9986$



CHEM SERVICE

Biodegradation of Naphthenic Acids

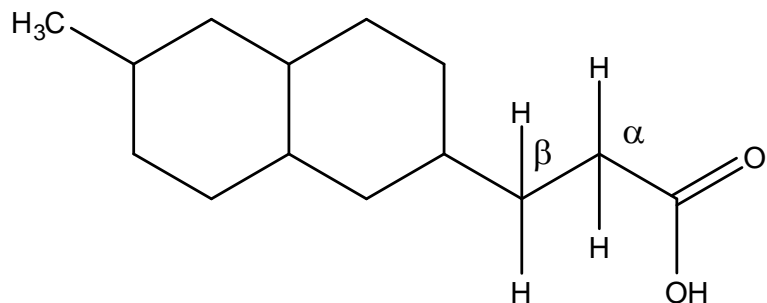


- Petroleum based (refined) naphthenic acids biodegrade differently than oil sands derived naphthenic acids
- Refined NAs degrade faster than oil sands derived naphthenic acids (e.g. Merichem $t_{50} = 1-8$ days)
- OSPW (oil sands process water – Syncrude) biodegradation proceeds much more slowly. $T_{50} = 44 - 240$ days
- Commercial naphthenic acids completely biodegrades completely with 14 days
- Only 25-30% of total NAs in OSPW were removed after 40-49 days
- The difference in the recalcitrance of commercial NAs and OSPW NAs is hypothesized to be a function of relatively high alkyl branching of OSPW NAs compared to petroleum derived (refined) naphthenic acids

Biodegradation



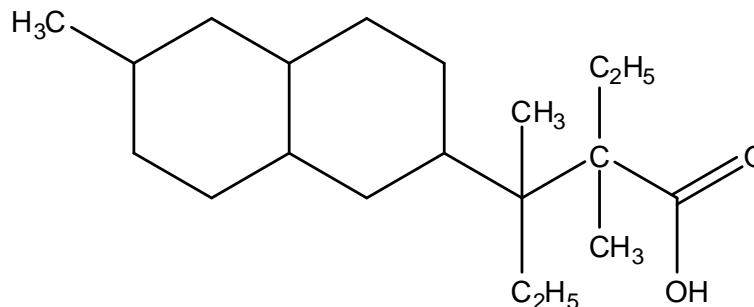
- Weight of evidence currently suggests that a high degree of alkyl branching is the principal factor that differentiates easily biodegradable commercial NAs from persistent OSPW NAs
- Among highly branched NAs, cyclization remains a major factor contributing to persistence: $Z=-2 < Z=-4 < < Z=-6 < Z=-8$
- β -oxidation is the preferred route by which most microorganisms degrade aliphatic and alicyclic carboxylic acids and, thus, is the most likely mechanism by which biodegradation occurs
- Other mechanisms include α -oxidation and aromatization



Chemical Formula: C₁₄H₂₄O₂
Exact Mass: 224.17763

n=14, Z=-4

Unbranched



Chemical Formula: C₂₀H₃₆O₂
Exact Mass: 308.27153

N=20 Z=-4

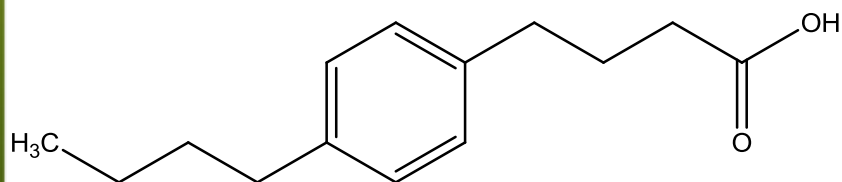
Branched

α

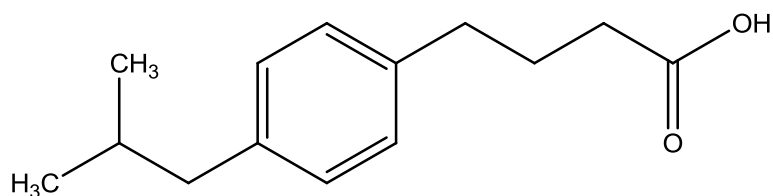


MICROTOX

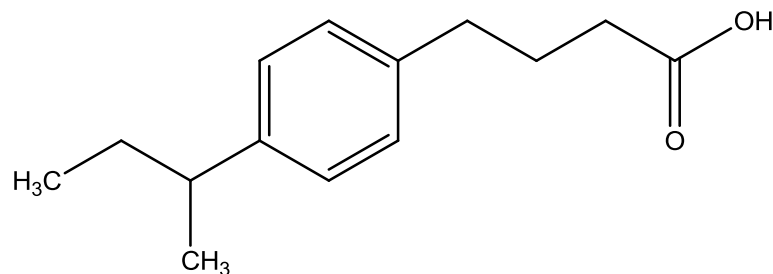
EC50 mg/L



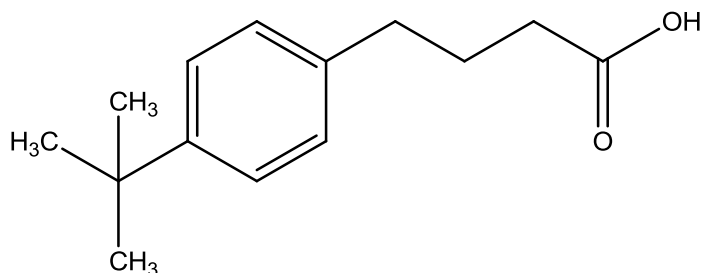
4'-n-butylphenyl-4-butanoic acid 18.8 ± 0.65



4'-iso-butylphenyl-4-butanoic acid 14.7 ± 0.68



4'-sec-butylphenyl-4-butanoic acid 39.6 ± 5.21



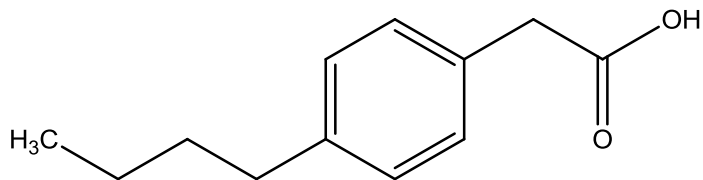
4'-tertbutylphenyl-4-butanoic acid 9.4 ± 0.66



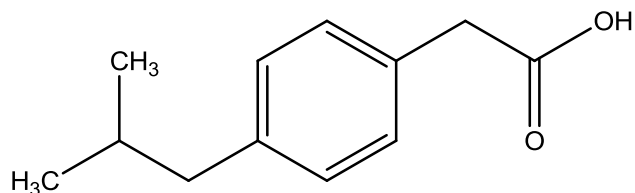
MICROTOX

EC50 mg/L

43.0 ± 0.75

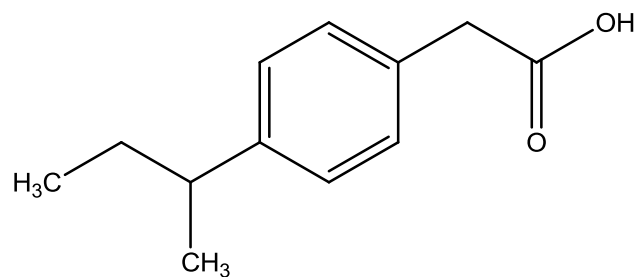


4'-n-butylphenylethanoic acid



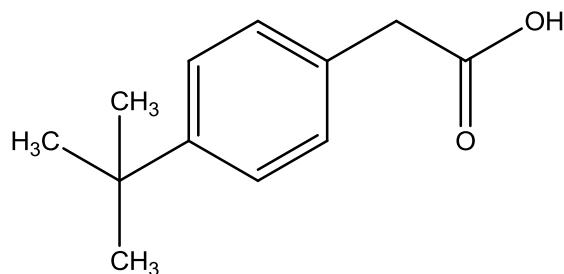
4'-iso-butylphenylethanoic acid

69.2 ± 1.04



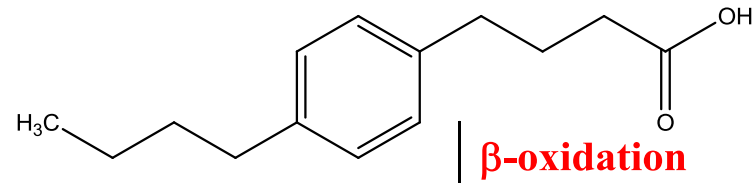
4'-sec-butylphenylethanoic acid

NA

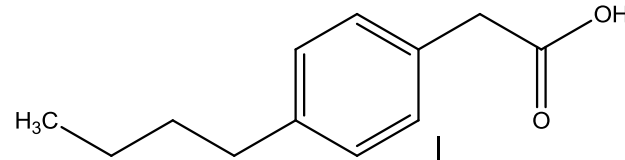


4'-tert-butylphenylethanoic acid

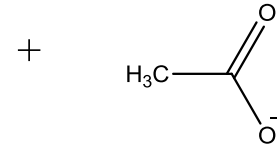
25.9 ± 0.71



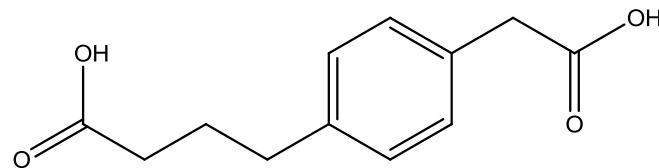
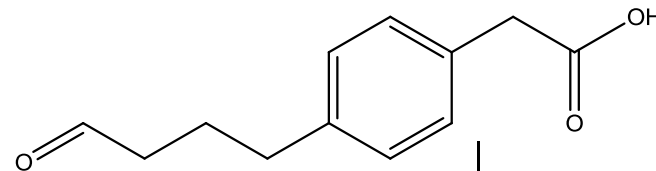
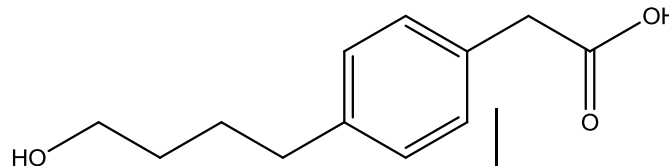
4'-n-butylphenyl-4-butanoic acid



4'-n-butylphenylethanoic acid



acetate



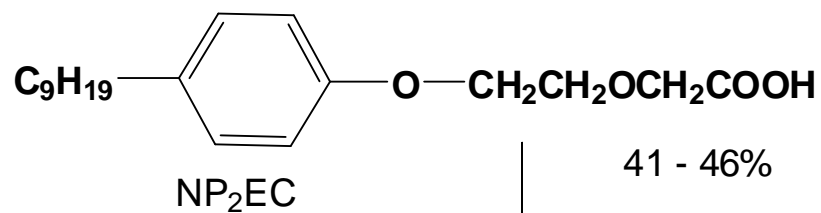
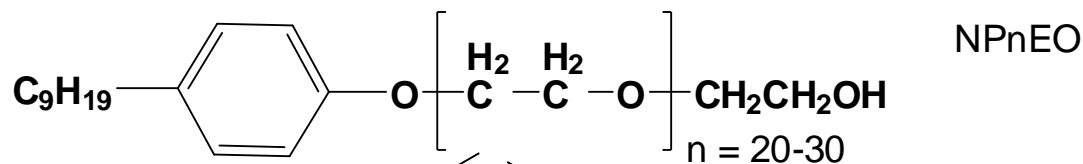
4'-carboxybutylphenylethanoic acid

Johnson et al, 2011

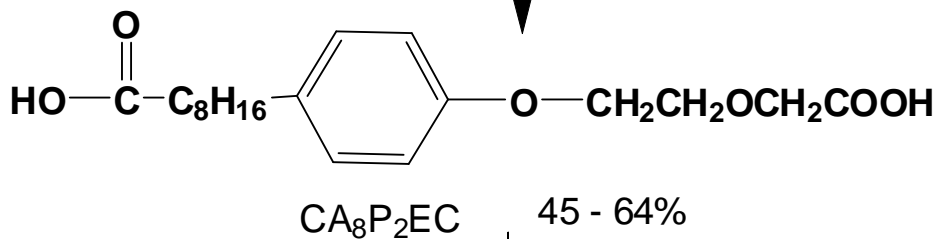
Biodegradation



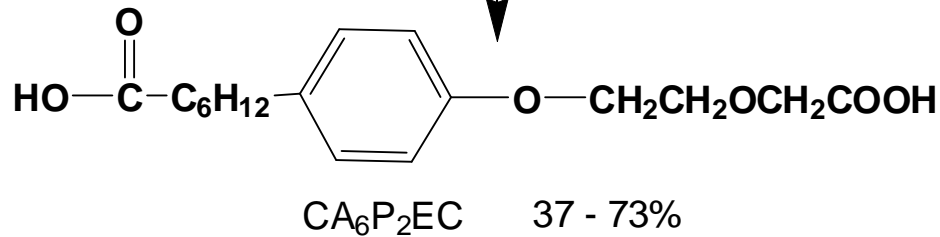
- Least branched n-BPBA completely degraded in 49 days
- More branched iso, sec, and tert-BPA isomers only metabolized as far as respective ethanoic acids by 49 days
- Increase in alkyl chain branching reduced biotransformation of BPBA
- Results suggest that the more refractory NAs found in OSPW may include branched alkyl phenylethanoic acids
- Tert-BPA was more toxic than n-, iso- and sec-BPBA
- Although the ethanoic acid metabolites produced during BPBA degradation were less toxic than the parent compounds, they were nonetheless toxic EC50 25-69 mg/L
- Our research on nonylphenol ethoxylates suggests that the di-carboxy naphthenic acids may be more endocrine disrupting



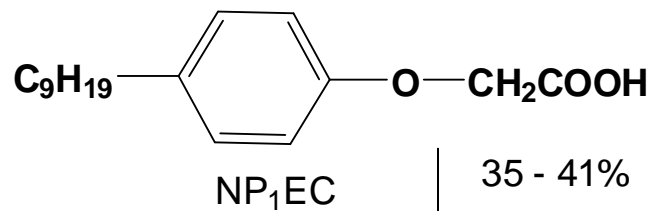
41 - 46%



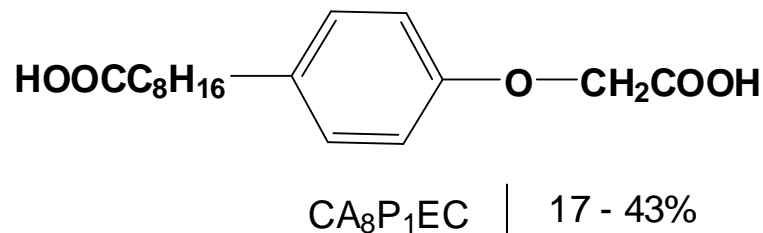
45 - 64%



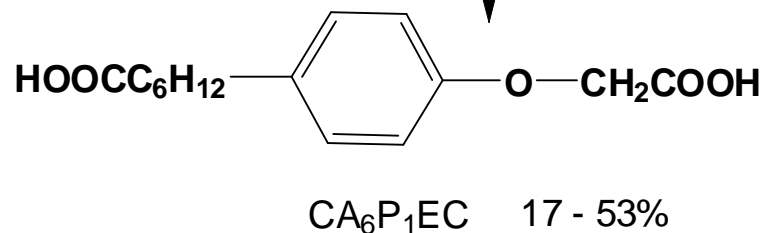
37 - 73%



35 - 41%



17 - 43%



17 - 53%



CAPECs (Carboxyl Alkyl Phenol Ethoxy Carboxylates)

- Laboratory biodegradation tests show that CAPECs with 3-8 carbons are recalcitrant. (Di Corcia et al (2000))
- Persisted in test liquor 5-months after their generation (Di Corcia et al (2000))
- Analysis of sewage treatment plant effluent showed CAPECs as a total accounted for 63% of the total A9PE breakdown products leaving the plant. (Di Corcia et al (2000))
- Very endocrine disrupting (YES assay)



Analytical Methods

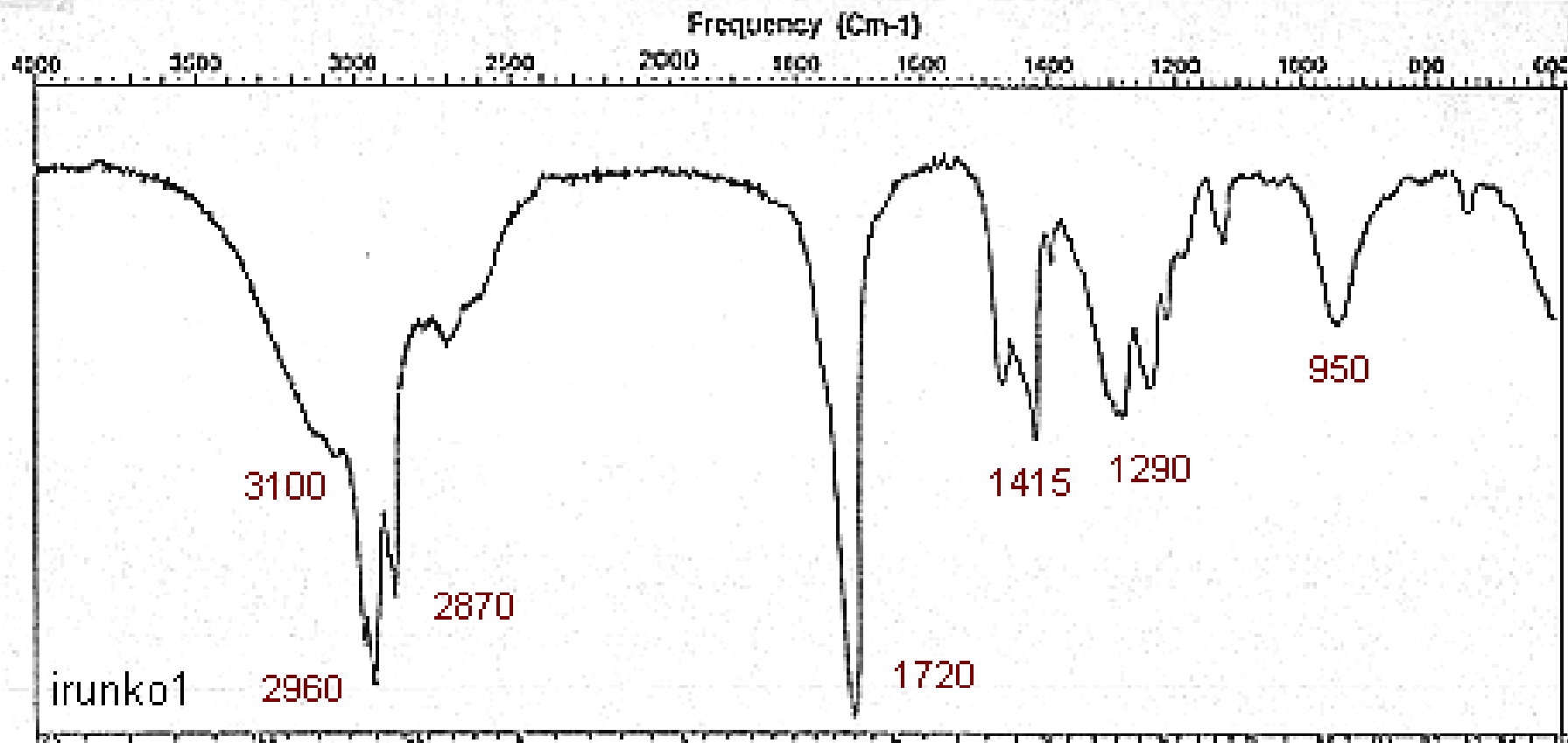
- There is currently no method that identifies or quantifies individual acids. This would be highly desirable.
- The complex nature of NA mixtures and the complex mixture of the associated organic compounds provide an analytical challenge.
- Thus, all presently used analytical methods treat these acids as a group, or as sub-groups based on carbon and Z numbers
- It is desirable to have a method that can tell us whether certain naphthenic acid groups (n and Z) are responding to a particular treatment and whether these changes are consistent with decreasing toxicity



Fourier Transform Infrared (FTIR) Spectroscopy

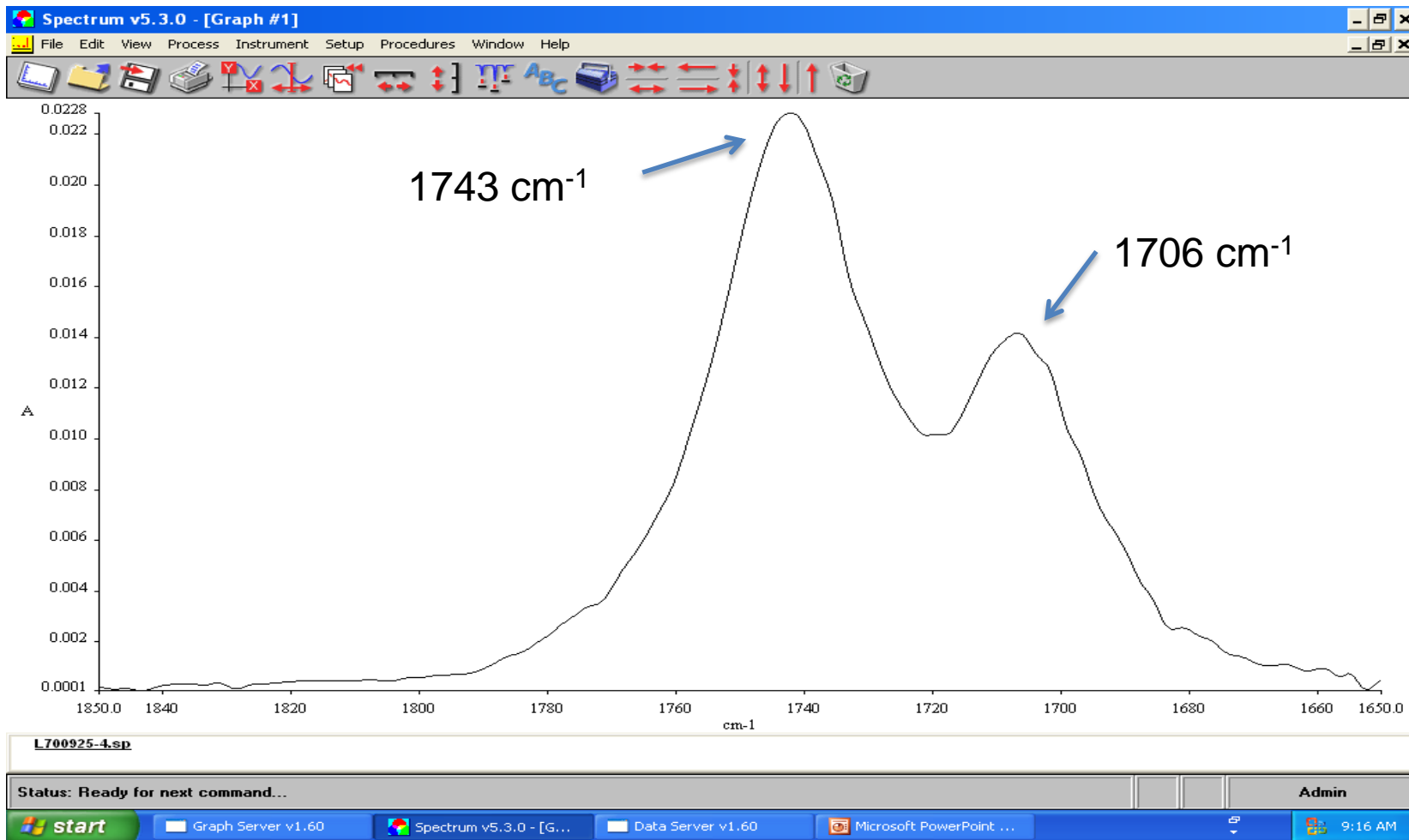
- Briefly, aqueous samples are acidified and the naphthenic acids are quantitatively extracted into dichloromethane.
- After concentrating the extract, the sample is analyzed by FTIR and the absorbances of the monomeric and dimeric forms of the carboxylic groups (at 1743 and 1706 cm^{-1} , respectively) are measured.
- The sum of these absorbances is compared to those in a calibration curve (commercial naphthenic acids) obtained from the FTIR analyses of solution prepared with a commercially available naphthenic acid preparation.
- Minimum detection limit is one to a few tenths of a milligram per liter.

Octanoic acid



the carbonyl (C=O) absorption between 1690-1760 cm^{-1} ; this strong band indicates either an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide.

FTIR Method (Syncrude Canada, 1995) Merrichem NAs



FTIR Spectra

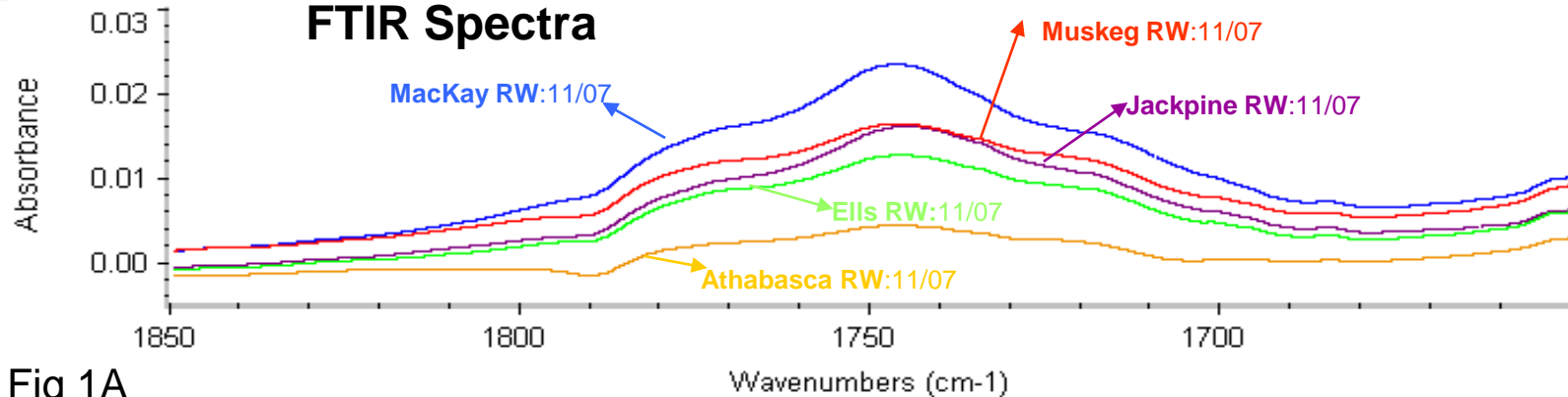


Fig 1A

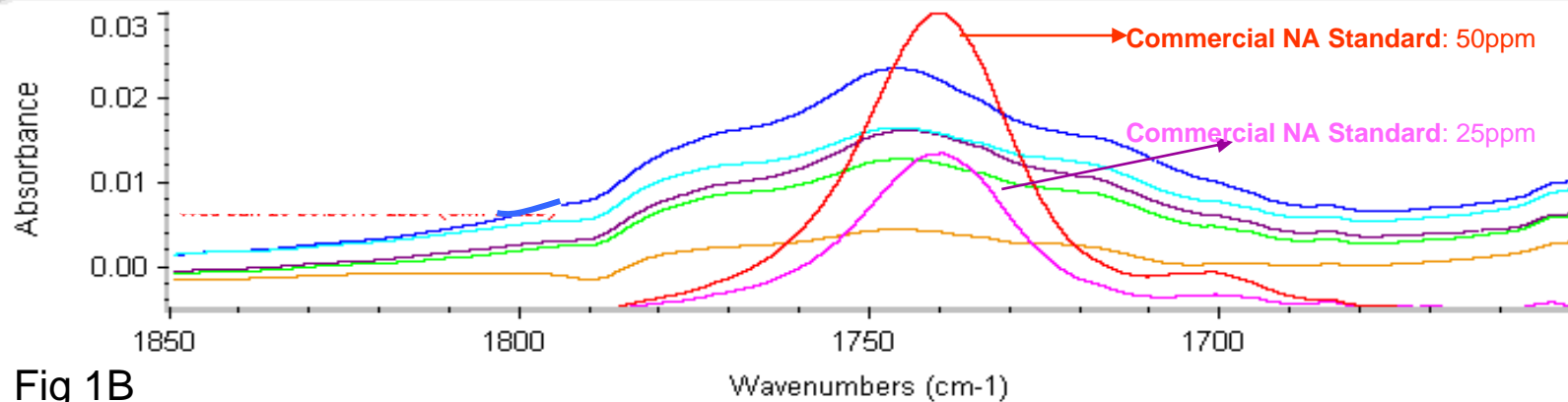


Fig 1B

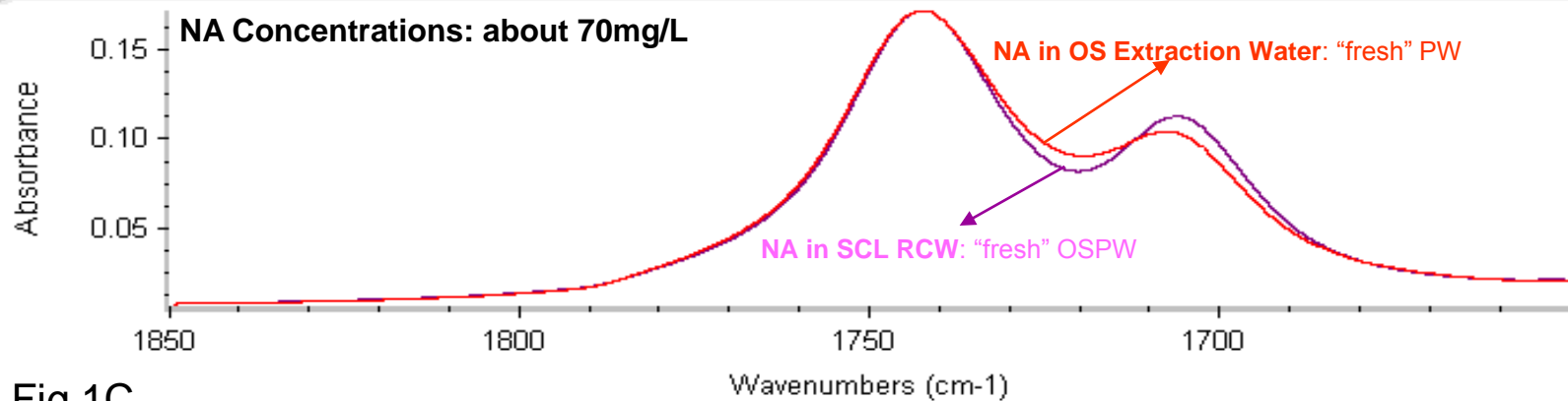


Fig 1C

FTIR vs GC/MS



| Sample | Naphthenic Acids GC/MS (mg/L) | Naphthenic Acids FTIR (mg/L) | Ratio: FTIR/GC-MS |
|--------------------------|-------------------------------|------------------------------|-------------------|
| North Saskatchewan River | <0.01 | 0.14 | >14 |
| Athabasca River | <0.01 | 0.29±0.08 | >29 |
| Domestic Well #12 | 0.13±0.05 | 0.99±0.3 | 7.6 |
| Domestic Well #13 | 0.025±0.007 | 0.3 | 12 |
| Fresh Water Reservoir | 0.099±0.045 | 0.53±0.06 | 5.4 |
| Tailings Pond | 17 | 45 | 2.6 |
| Tailings Pond | 4.0 | 17 | 4.2 |
| SAGD | 21 | 120 | 5.7 |
| SAGD | 110±57 | 100 | 0.91 |

Reference: Scott et al (2008) Chemosphere 73: 1258-1264



FTIR

- Is a good and inexpensive quantitative method for OSPW, but appears to overestimate the naphthenic acids in river waters (not useful for RAMP)
- Current FTIR method gets DLs in the order of 1 mg/L
- For lower levels suggest using the GC/LRMS method
- This method is not appropriate for forensics



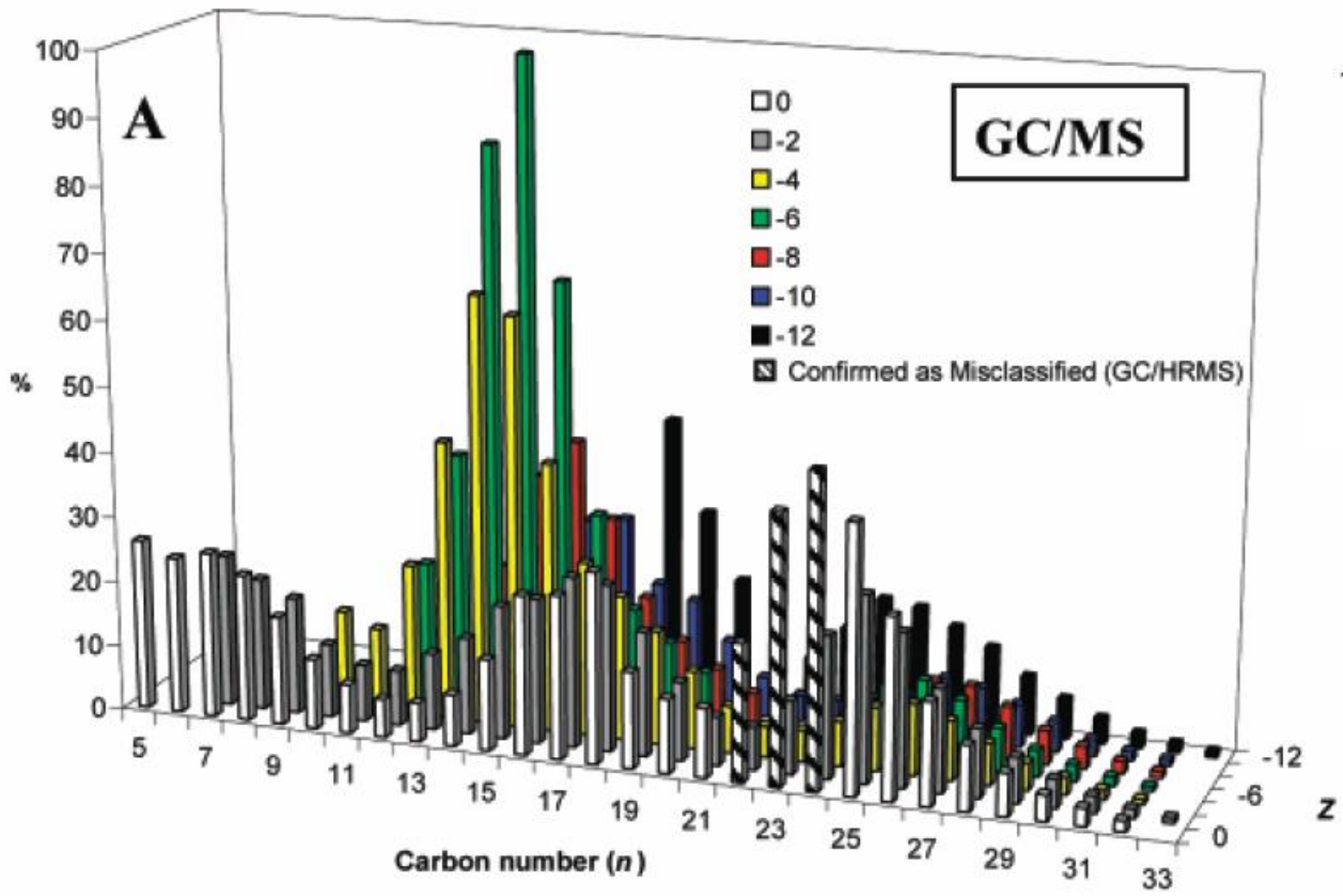
Mass Spectrometry Method of Choice

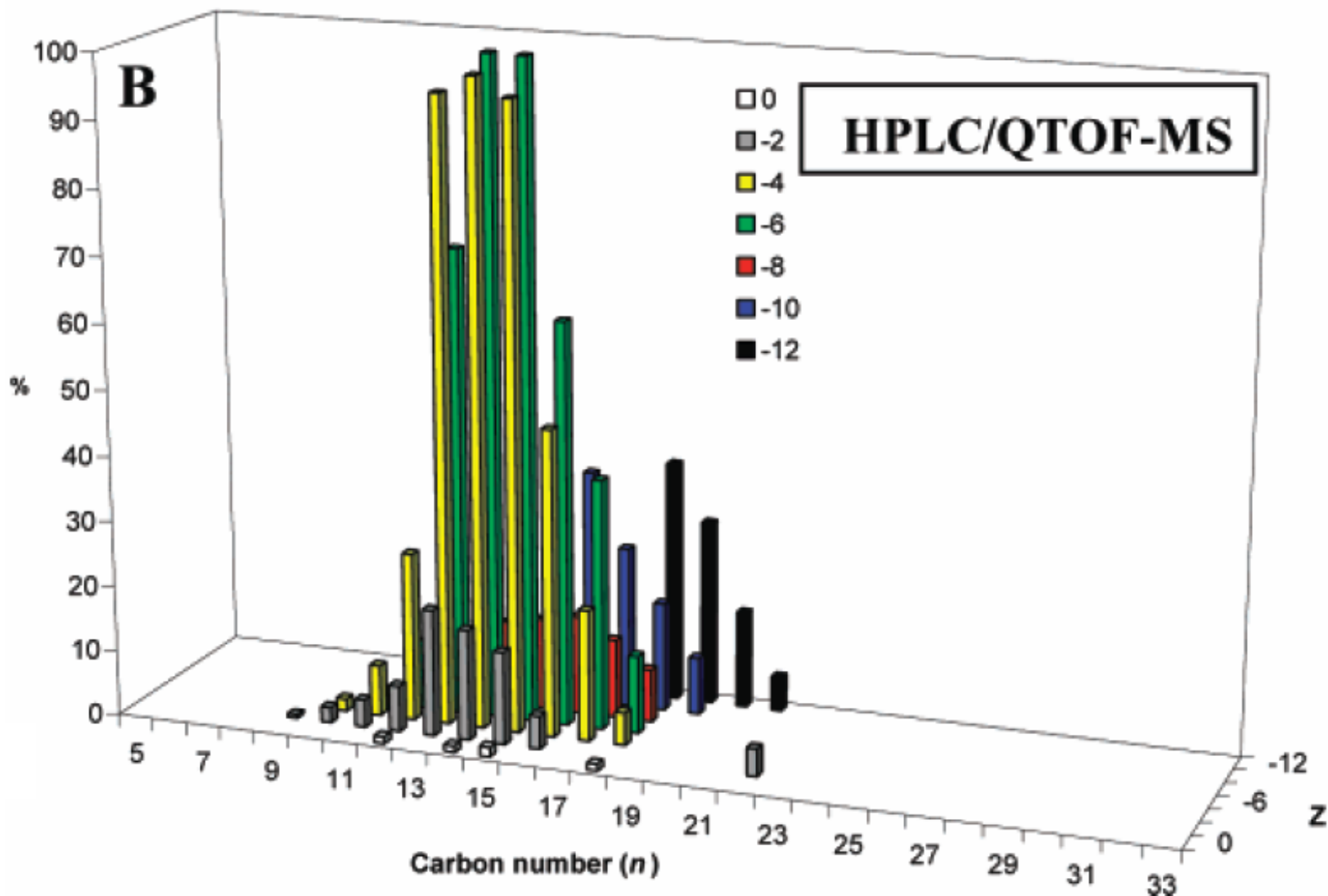
- Negative ion electrospray mass spectrometry ESI-LRMS and ESI-HRMS (TOF and Orbitrap)
- Gas chromatography – mass spectrometry – dimethyl-butyl-silyl-esters
- The formation of the t-butyldimethylsilyl esters was chosen because when subjected to electron impact the esters predominantly yield $(M+57)^+$ ions where M is the mass of the underivatized naphthenic acid.
- GC/LRMS is used because can scan for 167 ions. GC/HRMS is used for selected ions only



Mass Spectrometry Methods

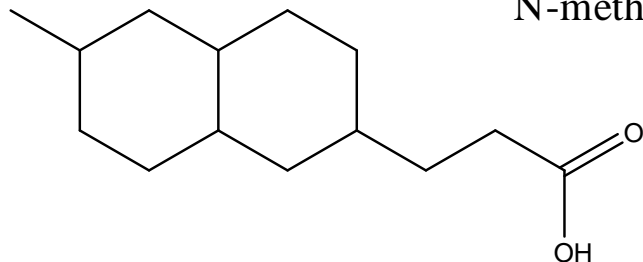
- Give similar forensic profiles for petroleum (refined) naphthenic acids – irrespective of method
- Low resolution methods (GC/MS and or LC-ESI-LRMS) give profoundly different profiles when compared against high resolution methods (LC-ESI-HRMS and GC-HRMS) for OSPW samples
- This observation raises a question as to what low resolution methods are measuring besides naphthenic acids?







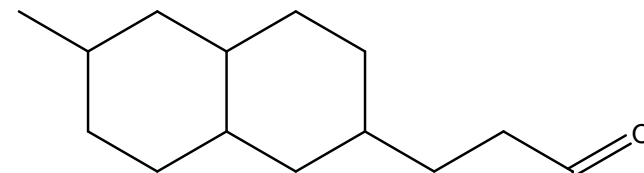
N-methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide



Chemical Formula: $C_{14}H_{24}O_2$

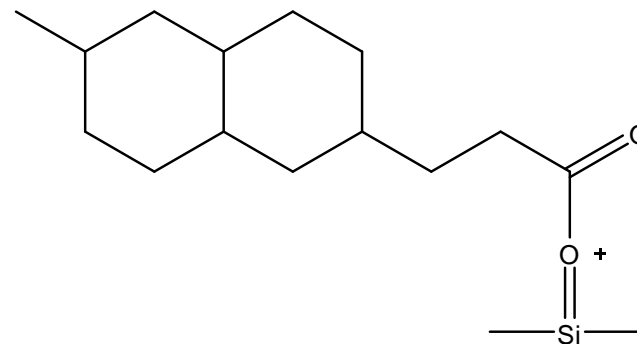
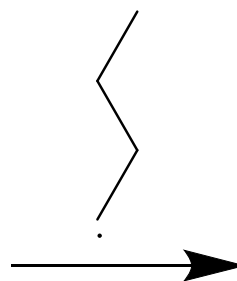
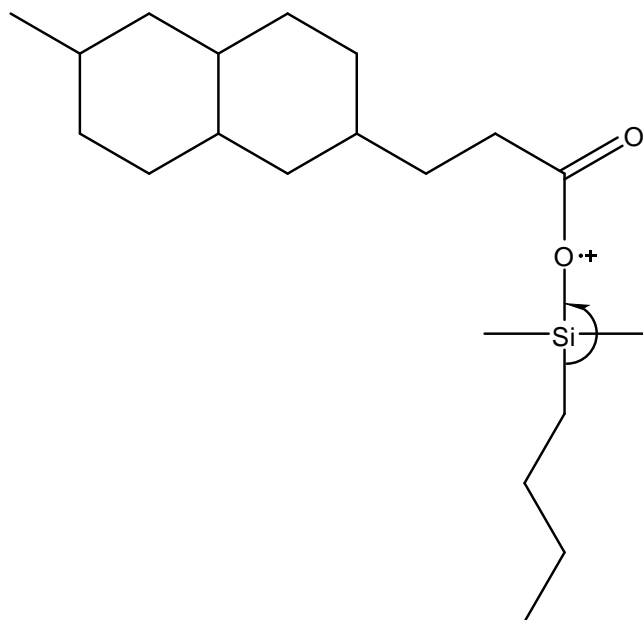
Exact Mass: 224.17763

n=14, Z=-4



Chemical Formula: $C_{20}H_{38}O_2Si$

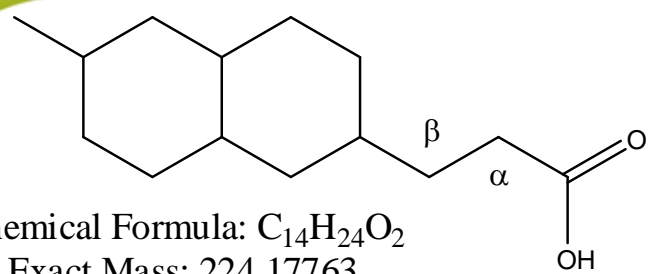
Exact Mass: 338.26411



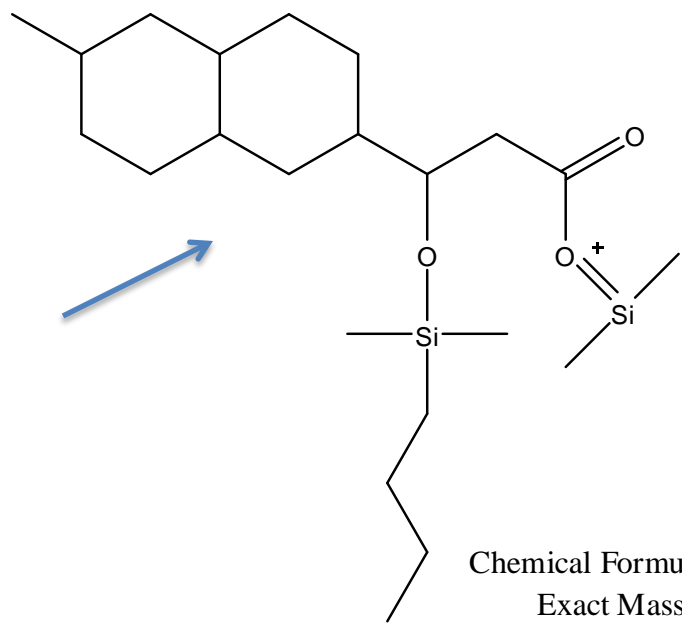
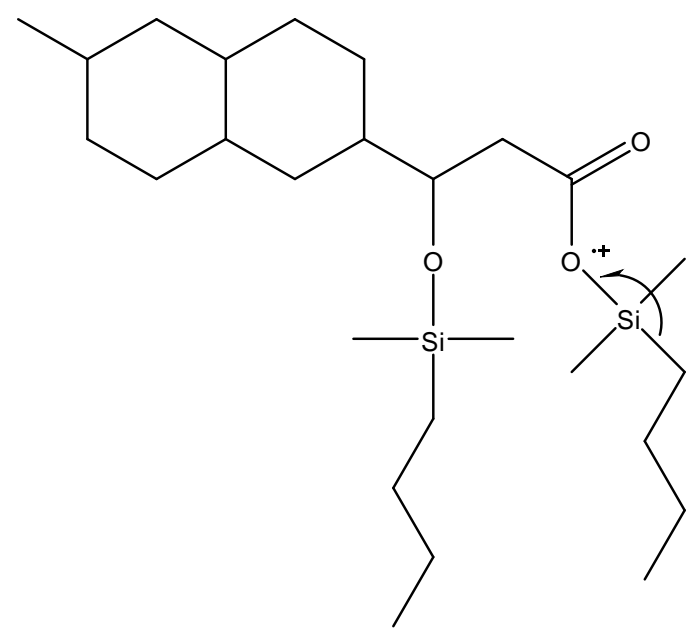
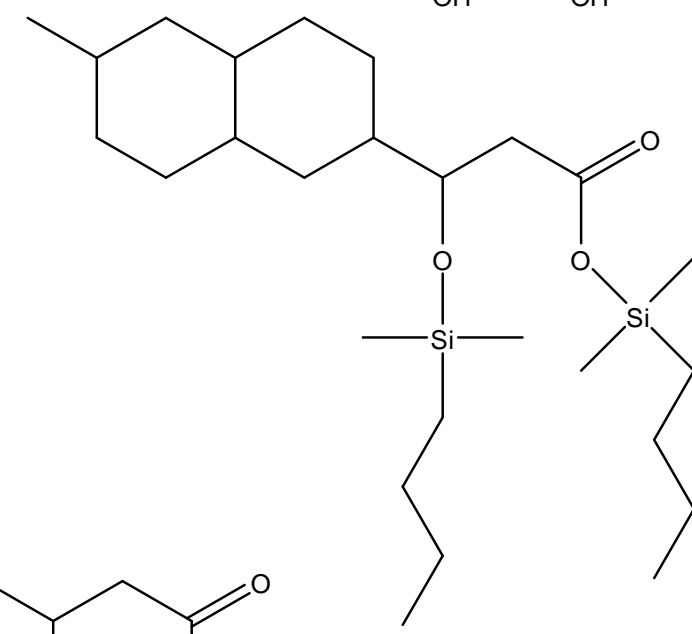
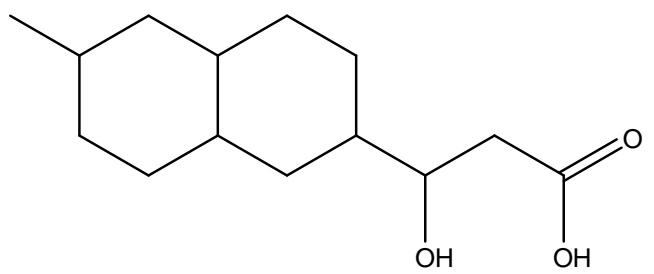
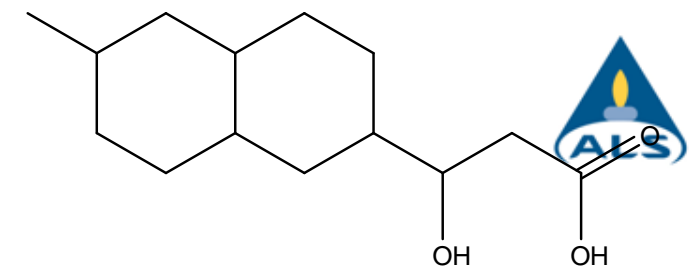
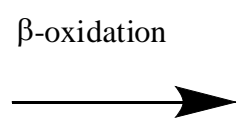
Chemical Formula: $C_{16}H_{29}O_2Si^+$

Exact Mass: 281.19313

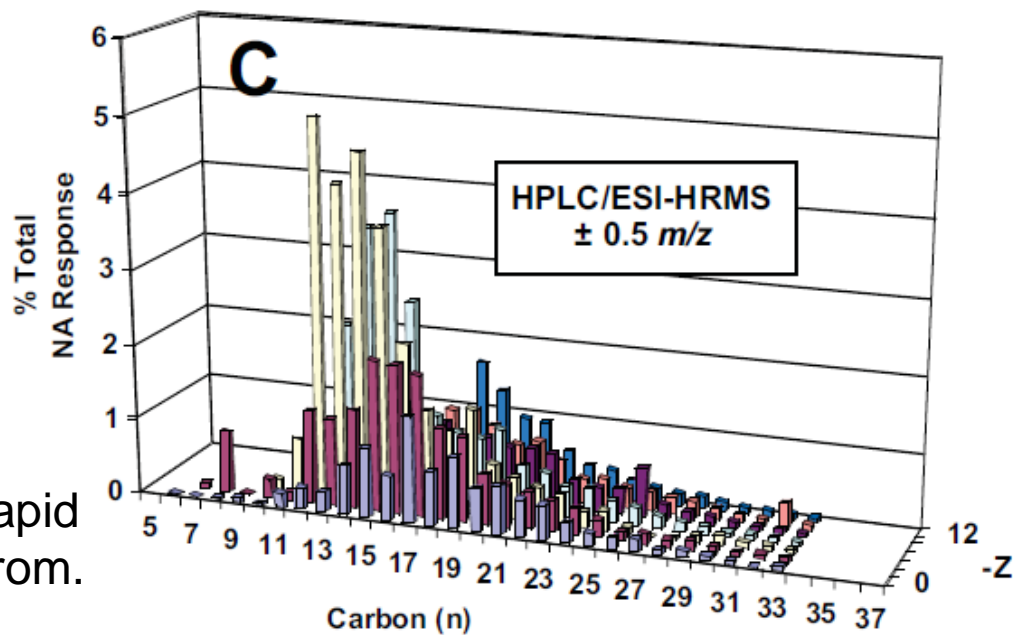
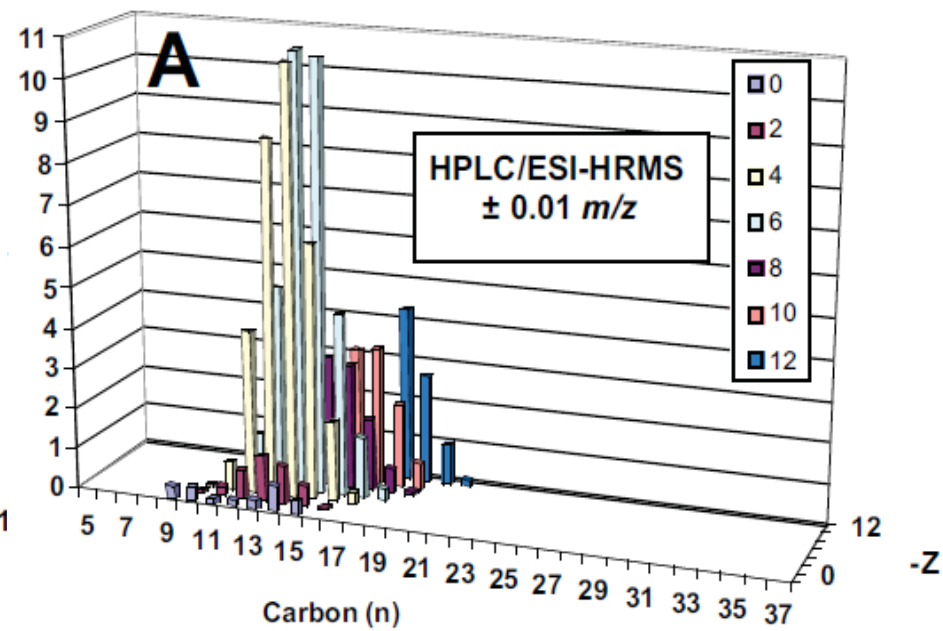
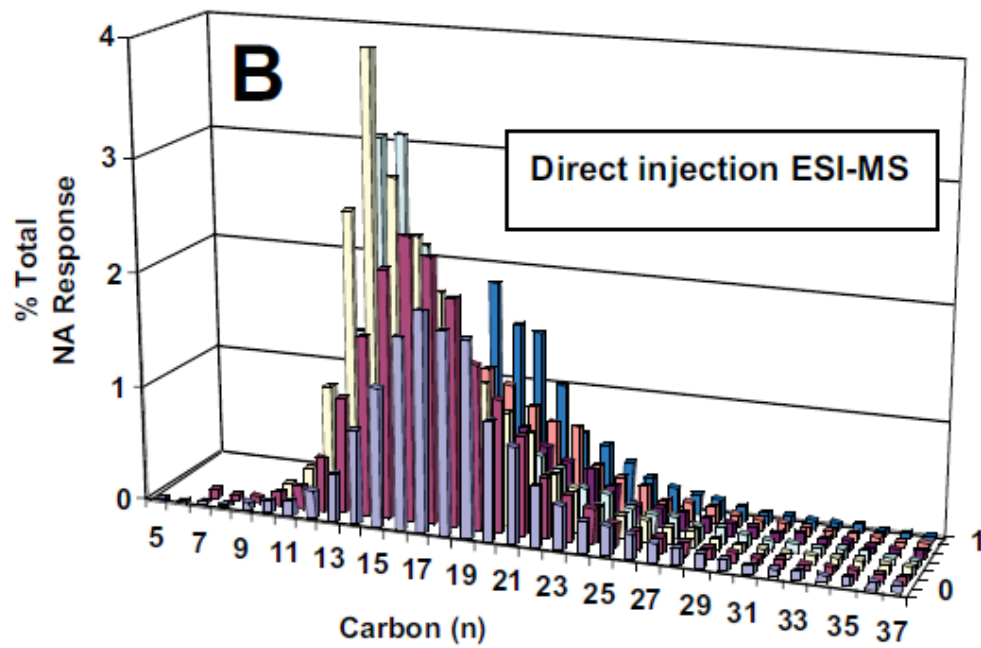
n=14, Z=-4



Chemical Formula: $C_{14}H_{24}O_2$
Exact Mass: 224.17763
 $n=14, Z=-4$

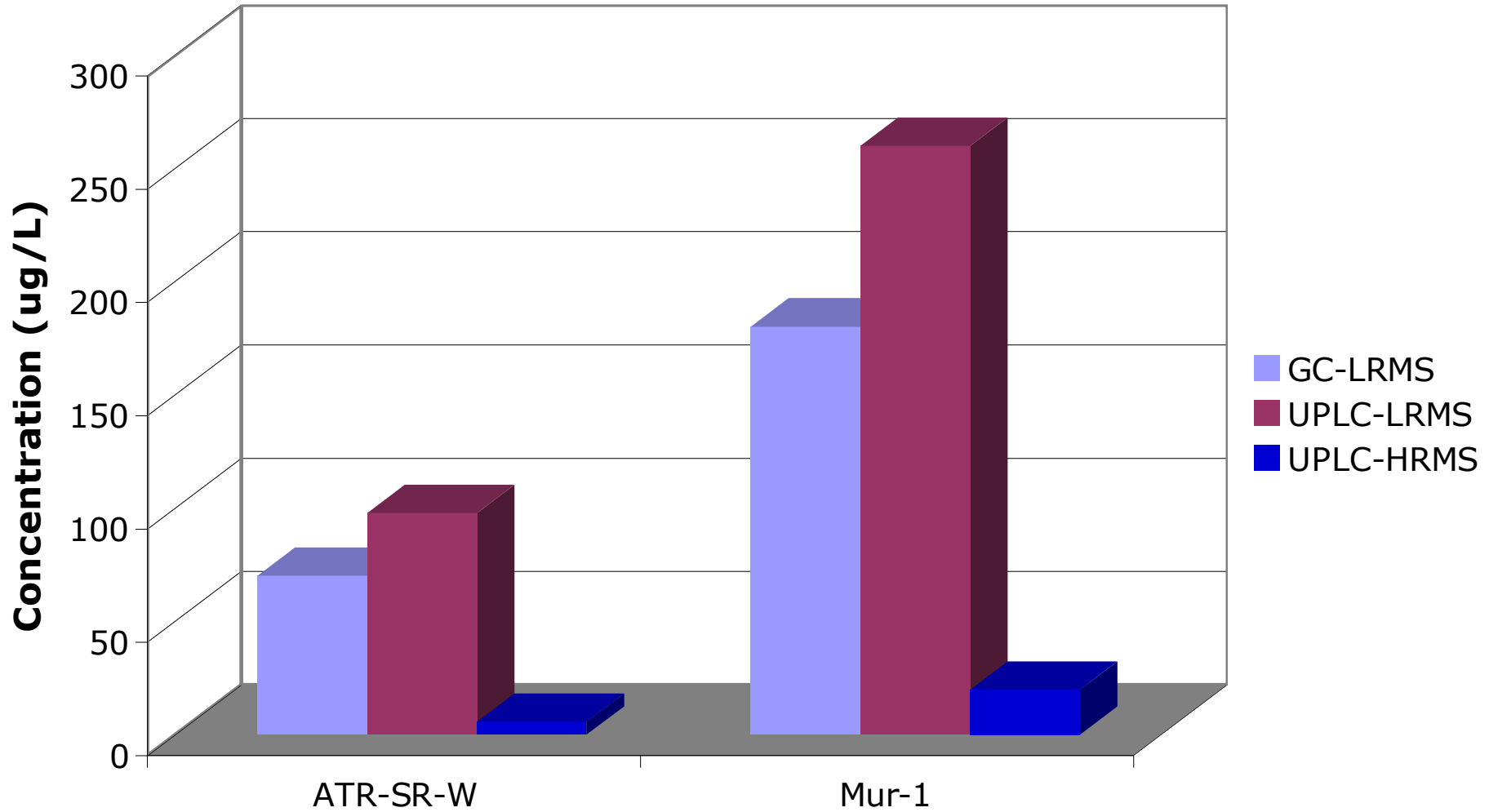


Chemical Formula: $C_{22}H_{43}O_3Si_2^+$
Exact Mass: 411.27452
 $n=23, Z=0$



Martin et al, 2008, Rapid
Comm. Mass. Spectrom.
22: 1919-1924

Comparison of Methods



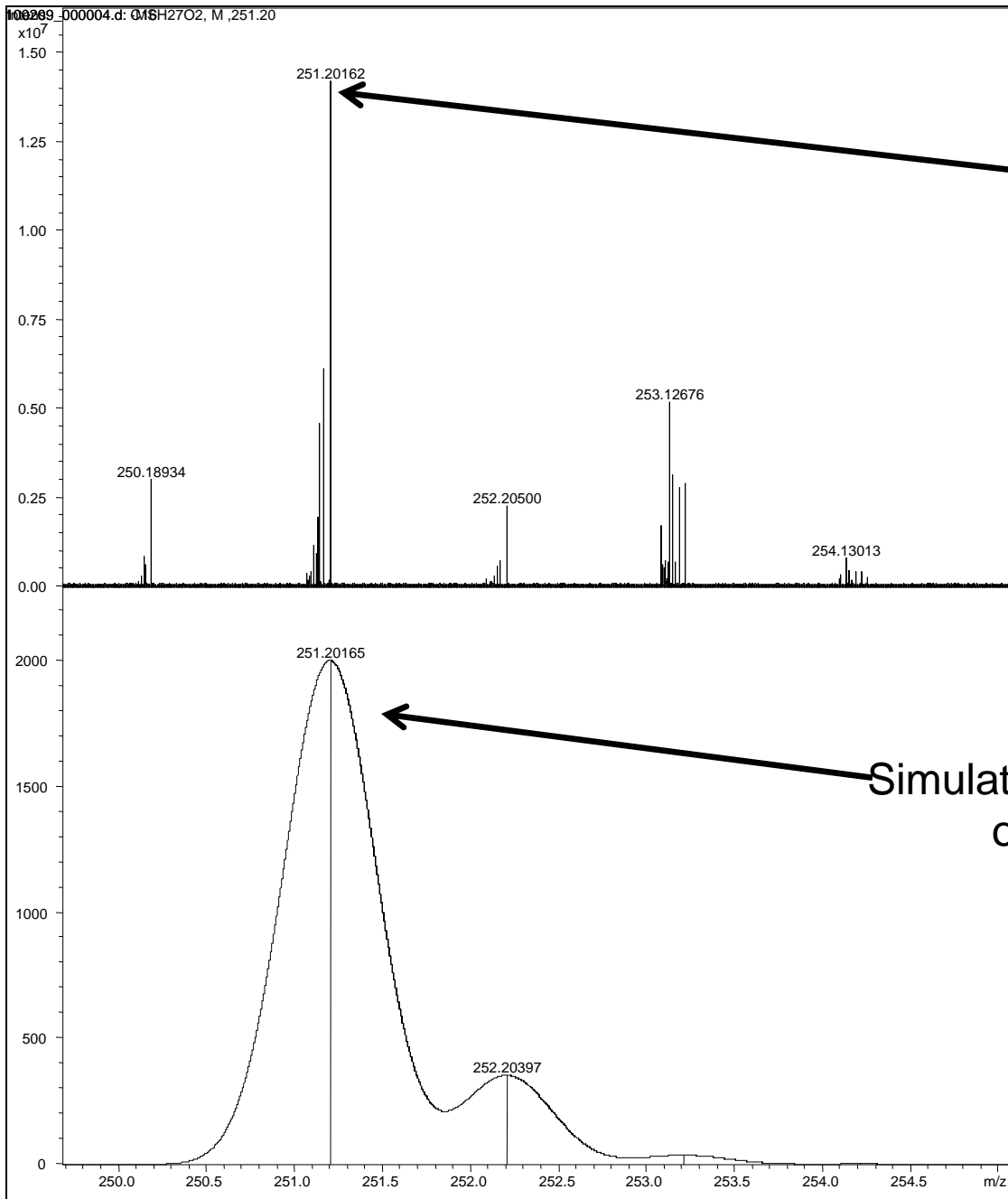
Negative ion ES

extract of tailings pond water



Compound of formula $C_{16}H_{27}O_2$

$C=16, Z=-4$



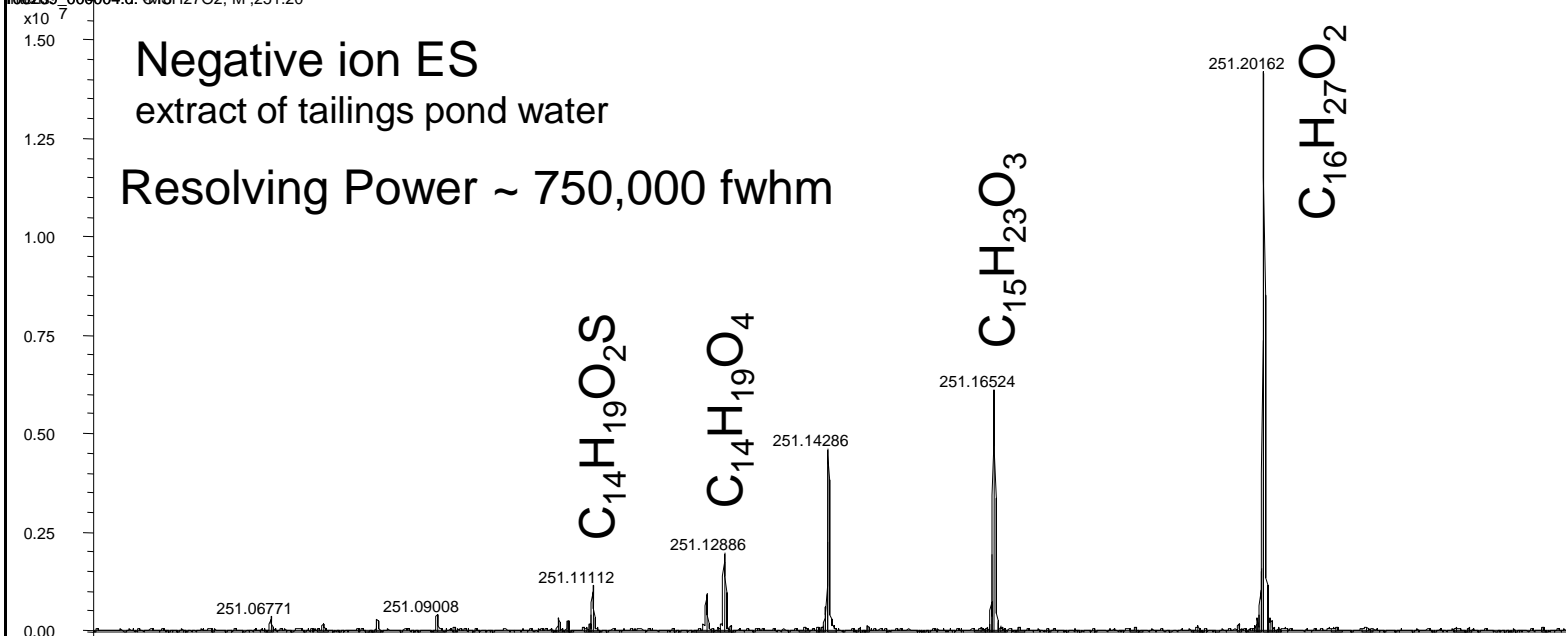
Simulation of isotope pattern for $C_{16}H_{27}O_2$ on low resolution instrument

Electrospray ionization
Fourier transform ion
cyclotron resonance
mass spectrometry
FTICR-MS

00289_000004.d: 018H27O2, M, 251.20

Negative ion ES
extract of tailings pond water

Resolving Power ~ 750,000 fwhm



Resolving Power ~ 400 fwhm

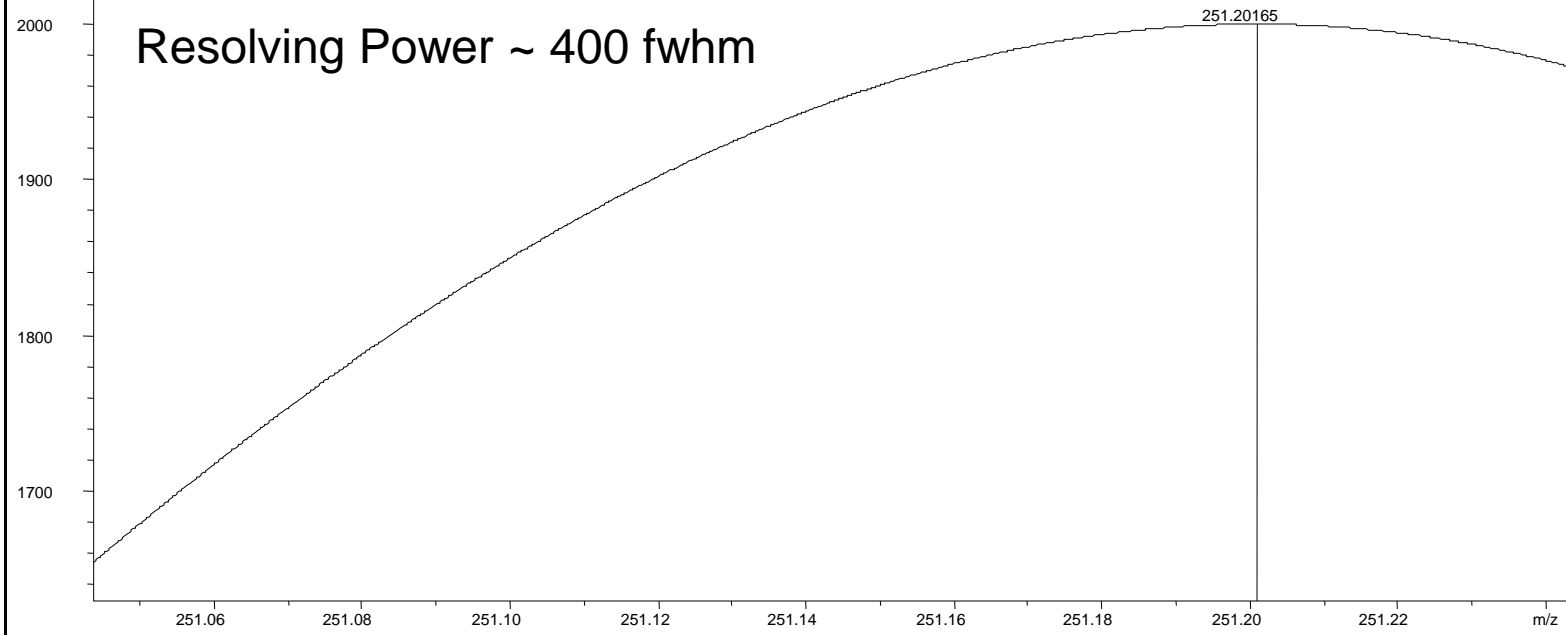


Table 3. Summary of peak counts from ESI-FT-ICR MS analyses for formula $C_nH_{2n+Z}O_x$ $x = 2$ to 5 and for sodium dimers. Acids containing the ^{13}C isotope are included.

| Sample | Total number of peaks | $C_nH_{2n+Z}O_x$ | | | | Percent of Total number of peaks ^a | Sodium dimers | |
|-----------------|-----------------------|--------------------------|--------------------------|--------------------------|--------------------------|---|-----------------|--|
| | | x = 2 Number of peaks | x = 3 Number of peaks | x = 4 Number of peaks | x = 5 Number of peaks | | Number of peaks | Cumulative Percent of Total number of peaks ^b |
| Merichem | 1597 | 91 | 13 | 16 | 1 | 8 | 74 | 12 |
| Acros | 303 | 58 | 0 | 6 | 0 | 21 | 41 | 35 |
| Kodak | 886 | 86 | 8 | 18 | 5 | 13 | 56 | 20 |
| MLSB | 1849 | 102 | 73 | 65 | 23 | 14 | 53 | 17 |
| WIP | 1312 | 83 | 55 | 47 | 19 | 16 | 28 | 18 |
| Pond 9 | 1680 | 75 | 61 | 57 | 40 | 14 | 32 | 16 |
| Demo Pond | 1691 | 95 | 76 | 67 | 42 | 17 | 39 | 19 |
| Pond 2/3 | 1416 | 98 | 67 | 54 | 12 | 16 | 59 | 20 |
| Pond 5 | 1873 | 95 | 84 | 73 | 44 | 16 | 38 | 18 |
| SAGD | 1883 | 83 | 75 | 101 | 26 | 15 | 23 | 16 |
| Albian pond | 1497 | 89 | 67 | 53 | 23 | 15 | 32 | 18 |
| Athabasca River | 1605 | 65 | 71 | 69 | 46 | 16 | 15 | 17 |
| Gregoire Lake | 1771 | 50 | 59 | 63 | 54 | 13 | 9 | 13 |
| N. Sask. River | 1316 | 19 | 26 | 51 | 43 | 11 | 0 | 11 |
| Red Deer River | 1687 | 57 | 71 | 74 | 56 | 15 | 19 | 16 |
| Bow River | 1624 | 66 | 73 | 73 | 55 | 16 | 24 | 18 |
| S. Sask. River | 1601 | 60 | 73 | 75 | 60 | 17 | 14 | 18 |

^a Based on sum of peaks with $x = 2$ to 5.

^b Based on sum of peaks with $x = 2$ to 5 plus number of sodium dimers.



Table 4. Relative abundance of peaks with formula $C_nH_{2n+Z}O_x$, $x = 2$ to 5 and of sodium dimers from ESI-FT-ICR MS analyses. Acids containing the ^{13}C isotope are included.

| Sample | Total Abund. of peaks ($\times 10^6$) | $C_nH_{2n+Z}O_x$ | | | | Sum ^a of (%) of Total Abundance | Sodium dimers | |
|-----------------|---|------------------------------|------------------------------|------------------------------|------------------------------|--|------------------------|---|
| | | x = 2 (%) of Total Abundance | x = 3 (%) of Total Abundance | x = 4 (%) of Total Abundance | x = 5 (%) of Total Abundance | | (%) of Total Abundance | Cumulative sum ^b of (%) of Total Abundance |
| Merichem | 2232 | 43.5 | 0.1 | 0.2 | 0.0 | 43.9 | 3.2 | 47.1 |
| Acros | 215 | 33.2 | 0.0 | 0.9 | 0.0 | 34.1 | 22.1 | 56.2 |
| Kodak | 759 | 41.8 | 0.3 | 0.9 | 0.1 | 43.1 | 4.3 | 47.4 |
| MLSB | 2032 | 28.6 | 7.5 | 3.8 | 0.4 | 40.3 | 2.2 | 42.5 |
| WIP | 951 | 24.4 | 7.4 | 3.8 | 0.5 | 36.1 | 1.9 | 38.0 |
| Pond 9 | 1782 | 10.7 | 16.3 | 9.1 | 1.7 | 37.7 | 1.0 | 38.7 |
| Demo Pond | 1743 | 17.0 | 17.2 | 11.2 | 2.0 | 47.4 | 1.6 | 49.0 |
| Pond 2/3 | 1165 | 35.6 | 6.9 | 3.1 | 0.3 | 45.9 | 2.2 | 48.1 |
| Pond 5 | 2033 | 19.8 | 13.8 | 7.7 | 1.4 | 42.7 | 1.6 | 44.3 |
| SAGD | 1866 | 14.2 | 6.8 | 8.4 | 0.5 | 29.9 | 0.6 | 30.5 |
| Albian pond | 1295 | 19.5 | 10.3 | 5.8 | 0.6 | 36.2 | 1.5 | 37.7 |
| Athabasca River | 1362 | 10.6 | 4.5 | 7.6 | 6.9 | 29.7 | 0.8 | 30.5 |
| Gregoire Lake | 1727 | 5.5 | 3.3 | 7.4 | 7.7 | 23.9 | 0.3 | 24.2 |
| N. Sask. River | 876 | 2.3 | 0.9 | 3.2 | 3.9 | 10.2 | 0.0 | 10.2 |
| Red Deer River | 1304 | 16.0 | 4.7 | 5.8 | 3.9 | 30.5 | 1.3 | 31.8 |
| Bow River | 1344 | 17.7 | 5.9 | 6.5 | 4.9 | 35.0 | 1.8 | 36.8 |
| S. Sask. River | 1308 | 14.7 | 5.5 | 7.2 | 5.3 | 32.7 | 1.2 | 33.9 |

^a Based on sum of peaks with $x = 2$ to 5.

^b Based on sum of peaks with $x = 2$ to 5 plus number of sodium dimers.

Recommendations



- Grewer et al (2010)
- HPLC-HRMS (Martin et al, 2008) clearly demonstrated that HRMS is superior to unit mass, low-resolution MS for accurate assignment of congeners to classical naphthenic acids
- HPLC/HRMS may be the best compromise between cost and accessibility for monitoring naphthenic acids in the environment.
- With use of Thermo Orbitrap can achieve 200,000 resolution of naphthenic acids

Why Not GC/HRMS



- GCxGC/TOF (1.6 billion theoretical plates of separation) provided the best data to date on structures of naphthenic acids.
- ESA scanning the best option for accurate mass but limited mass range requiring several runs. There are cost and TAT implications – Not a good option
- Selected ion-monitoring is a best option but need to decide on which ions to use



| Carbon number | Z - family | | | | | | |
|---------------|------------|------------|------------|------------|------------|-----|-----|
| | 0 | -2 | -4 | -6 | -8 | -10 | -12 |
| 5 | 159 | | | | | | |
| 6 | 173 | | | | | | |
| 7 | 187 | 185 | | | | | |
| 8 | 201 | 199 | | | | | |
| 9 | 215 | 213 | | | | | |
| 10 | 229 | 227 | 225 | | | | |
| 11 | 243 | 241 | 239 | | | | |
| 12 | 257 | 255 | 253 | 251 | | | |
| 13 | 271 | 269 | 267 | 265 | 263 | | |
| 14 | 285 | 283 | 281 | 279 | 277 | | |
| 15 | 299 | 297 | 295 | 293 | 291 | | |
| 16 | 313 | 311 | 309 | 307 | 305 | 303 | |
| 17 | 327 | 325 | 323 | 321 | 319 | 317 | |
| 18 | 341 | 339 | 337 | 335 | 333 | 331 | 329 |
| 19 | 355 | 353 | 351 | 349 | 347 | 345 | 343 |
| 20 | 369 | 367 | 365 | 363 | 361 | 359 | 357 |
| 21 | 383 | 381 | 379 | 377 | 375 | 373 | 371 |
| 22 | 397 | 395 | 393 | 391 | 389 | 387 | 385 |
| 23 | 411 | 409 | 407 | 405 | 403 | 401 | 399 |
| 24 | 425 | 423 | 421 | 419 | 417 | 415 | 413 |
| 25 | 439 | 437 | 435 | 433 | 431 | 429 | 427 |
| 26 | 453 | 451 | 449 | 447 | 445 | 443 | 441 |
| 27 | 467 | 465 | 463 | 461 | 459 | 457 | 455 |
| 28 | 481 | 479 | 477 | 475 | 473 | 471 | 469 |
| 29 | 495 | 493 | 491 | 489 | 487 | 485 | 483 |
| 30 | 509 | 507 | 505 | 503 | 501 | 499 | 497 |
| 31 | 523 | 521 | 519 | 517 | 515 | 513 | 511 |
| 32 | 537 | 535 | 533 | 531 | 529 | 527 | 525 |
| 33 | 551 | 549 | 547 | 545 | 543 | 541 | 539 |



Semi-Quantitative Analysis for Naphthenic Acids – GC/HRMS

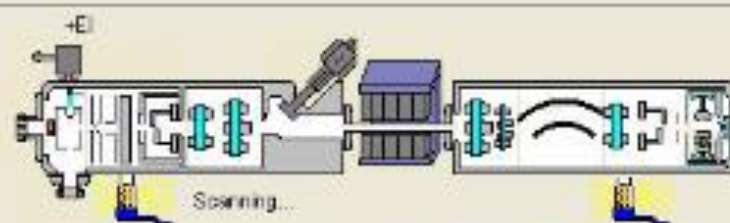


- Surrogate is added to an aliquot
- Acidify (pH<2) and add 150 g NaCl
- Extract with dichloromethane
- OR Solid Phase Extract Using HLB-Oasis RAMP
- Surrogate is added
- Derivatize using MTBSTFA
- Add internal standard
- Analyze by GC/HRMS
- Detection limit 1 – 10 ug/L

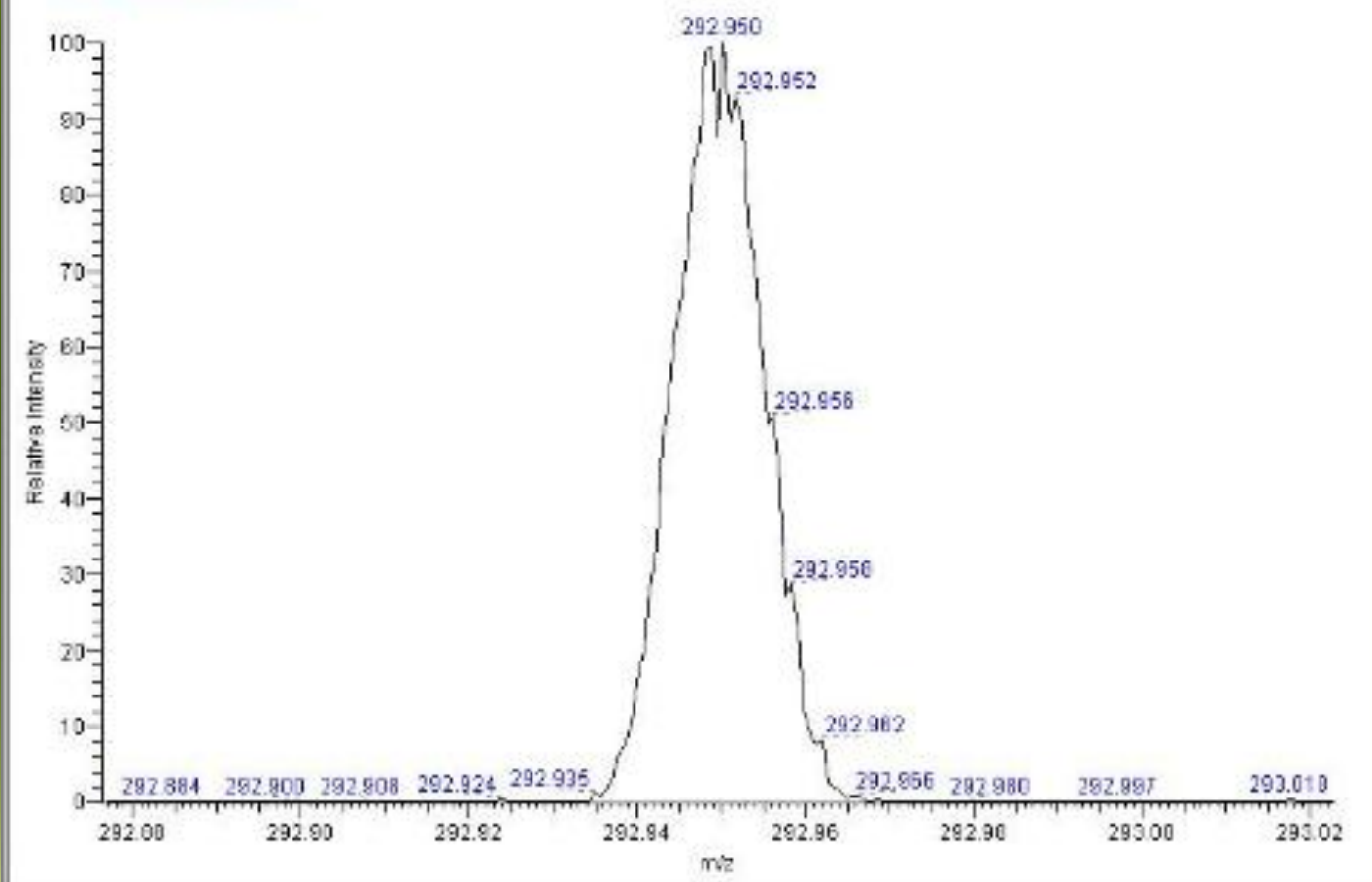


Mass Resolution

- LC-ESI-QTOF can analyze at 10,000 resolution. Newer models can operate at 15,000 resolution
- Newer Agilent and AB Sciex claims 40,000 resolution
- Thermo Orbitrap claims 200,000 resolution
- The way resolution is determined on the QTOF vs GC/HRMS is very different – which may explain any differences we observe



#152 R: 12637 ST: 0.50 NL: 4.35E5
 F: +p EIMS [292.43-293.57]

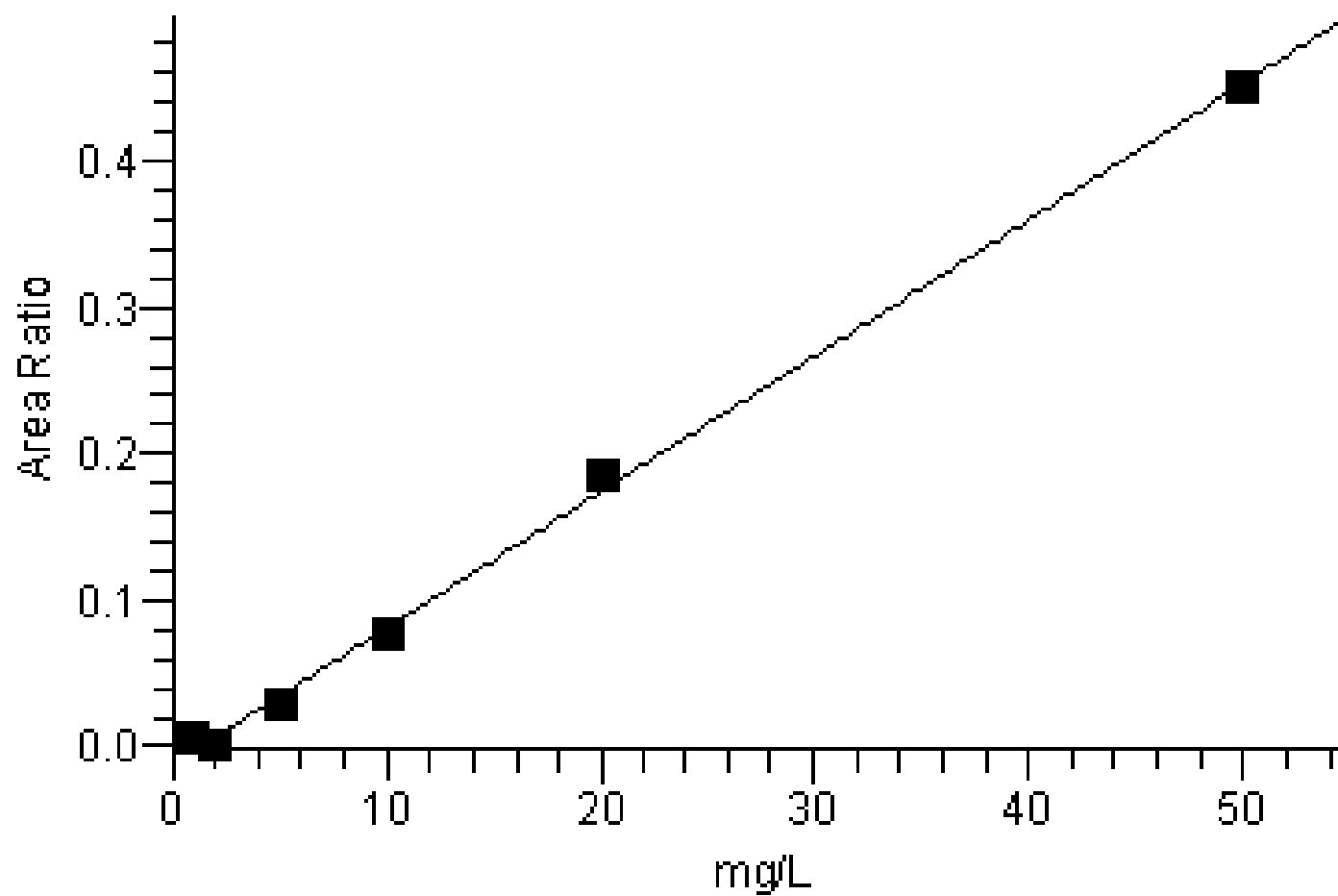


| Label | Value |
|--------------------------|------------|
| Acc On: | On |
| Acc Voltage: | 4780.3 ... |
| Resolution @ 5% height: | 12637 |
| Resolution @ 10% height: | 13270 |
| Resolution FWHM: | 23582 |
| Multiplier Voltage: | 2023 V |
| Faraday Current: | 0.1 pA |
| Source Gauge: | 2.1e5 ... |
| Electron Energy: | -39.9 eV |
| Emission Current: | 0.55 mA |
| Source Temperature: | 260 °C |
| Filament Current: | 3.59 A |
| Box Current: | 0.05 mA |
| Trap Current: | 0.61 mA |
| Temp Mag: | 24 °C |
| Uesa outer plate: | 324 V |
| Uesa inner plate: | -355 V |
| Polarity: | Positive |
| EDAC Zero: | 0.0000 ... |
| EDAC Gain: | 1.0000 ... |
| ECORR: | 0.9999 ... |

Ion 267 curve at 10,000 resolution

Ion_267

$$Y = -0.0116432 + 0.00929992 * X \quad R^2 = 0.9984 \quad W: \text{Equal}$$

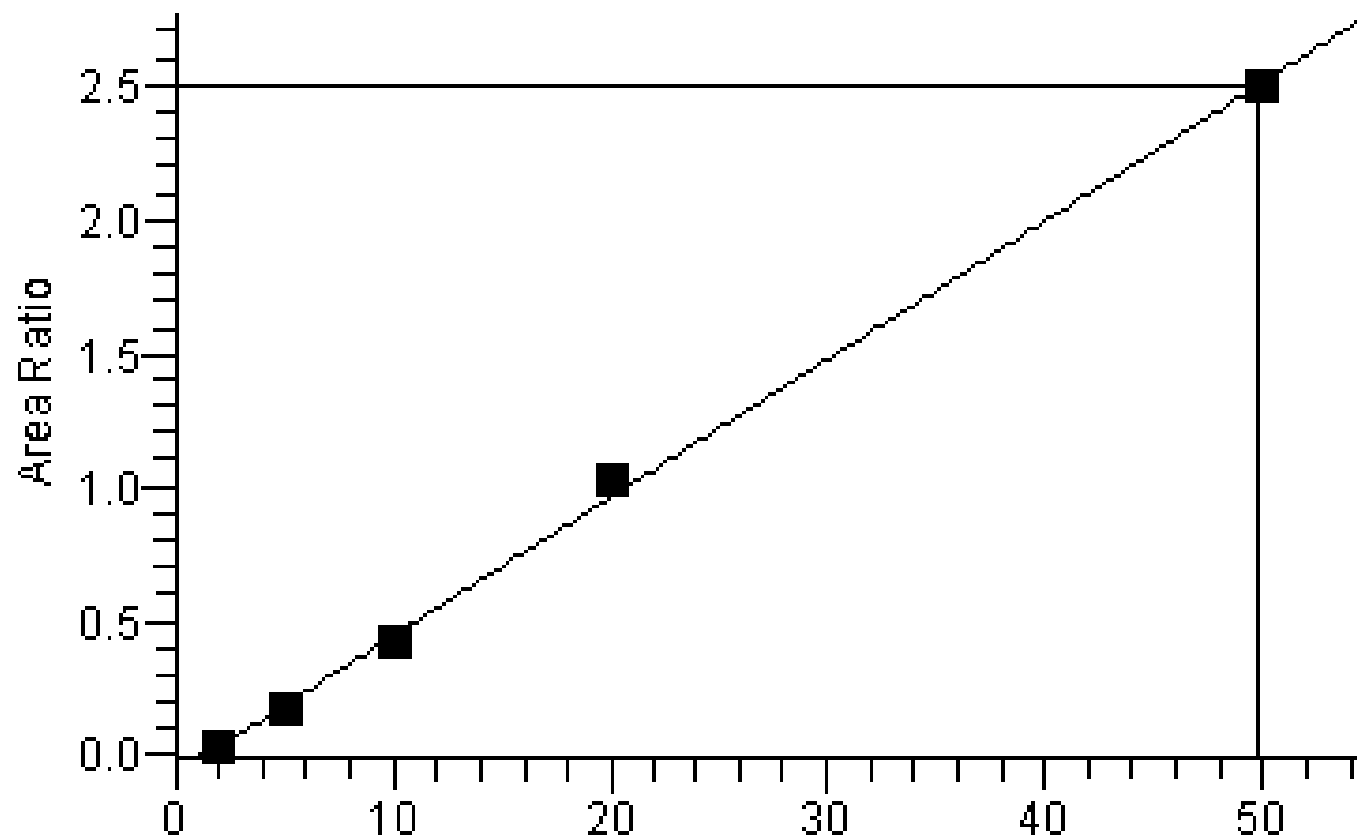




Sum of Ion curve at 10,000 resolution

Sum_of_Ions

$$Y = -0.0677901 + 0.0515785 * X \quad R^2 = 0.9988 \quad W: \text{Equal}$$



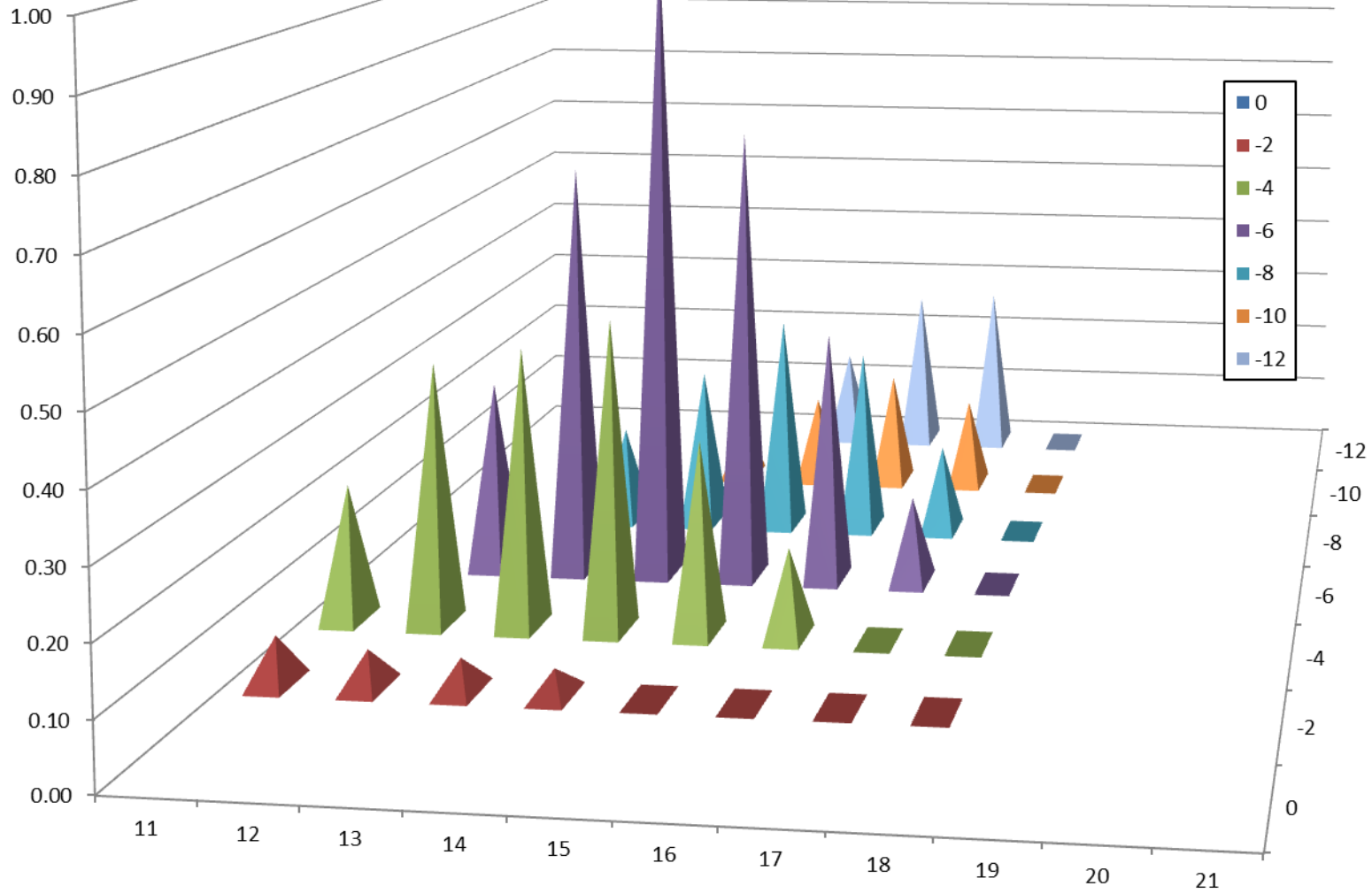
GC/HRMS vs FTIR



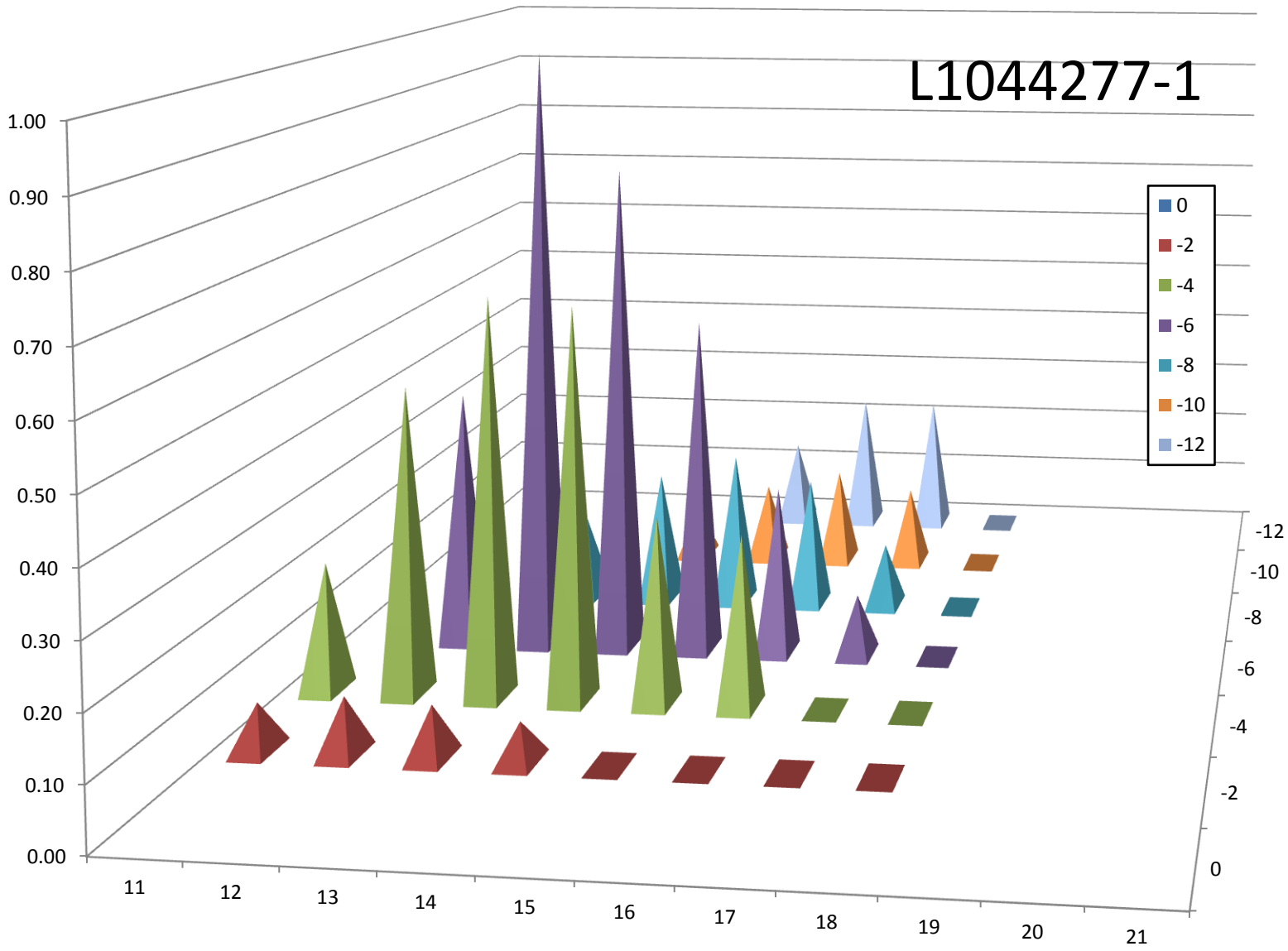
| Sample I.D. | Sum of ions mg/L | m/z 267 mg/L | FTIR mg/L |
|-------------|---------------------|-----------------|--------------|
| L1074277-1 | 23.6 | 21.7 | 42.0 |
| L1074277-2 | 26.4 | 25.2 | 37.2 |
| L1074283-6 | 15.2 | 16.5 | 26.7 |
| L1074995-6 | 14.9 | 12.1 | 16.1 |
| OSPW | 34.3 | 31.1 | |

m/z 267 n=13, Z=-4

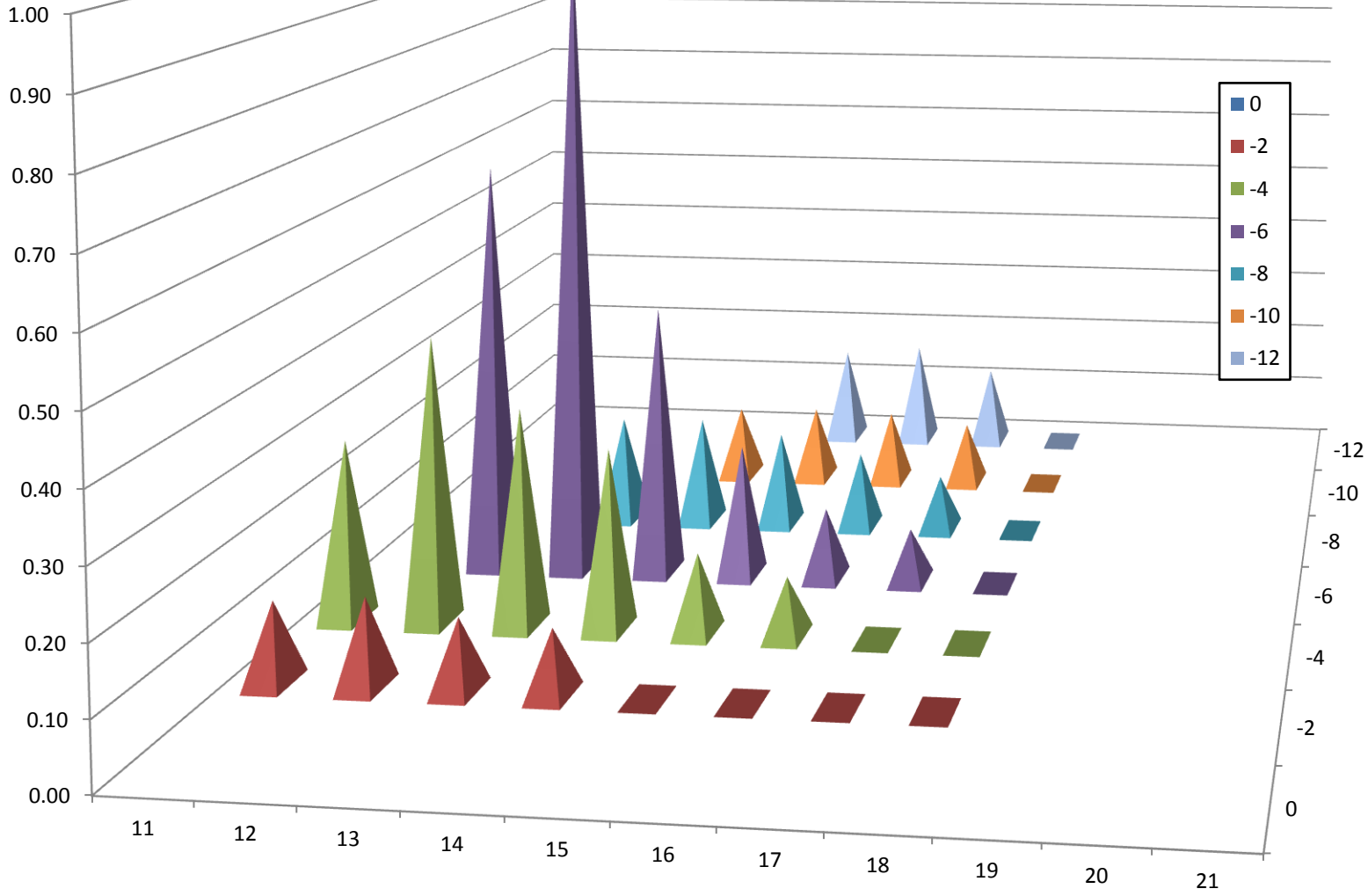
OSPW-2



L1044277-1



L1074995-6



Industries View



- Validated and accepted method (used by monitoring laboratories)
- Validated and accepted method to fingerprint sources “forensics” in the case of detection
- From an impact assessment perspective, data is meaningless without toxicology to tell us what the numbers mean, i.e. is there going to be an adverse impact?
- Proof that the method is related to oilsands by analyzing municipal effluent, pulp and paper effluent, etc.
- If we are going to sample rivers the industry wants to be convinced that the method is unique to oilsands operations.

Where Do We Go From Here



- Workshop held and analytical chemistry and toxicity discussed
- Proceedings and short papers will be published
- Common reference standard for calibration (chemistry and toxicity) was agreed upon
- Round robin samples are being prepared and labs have been invited to participate
- Results will be published
- More workshops to be held to glean a consensus on appropriate analytical methods
- KEEP TUNED!



ALS Laboratory Group

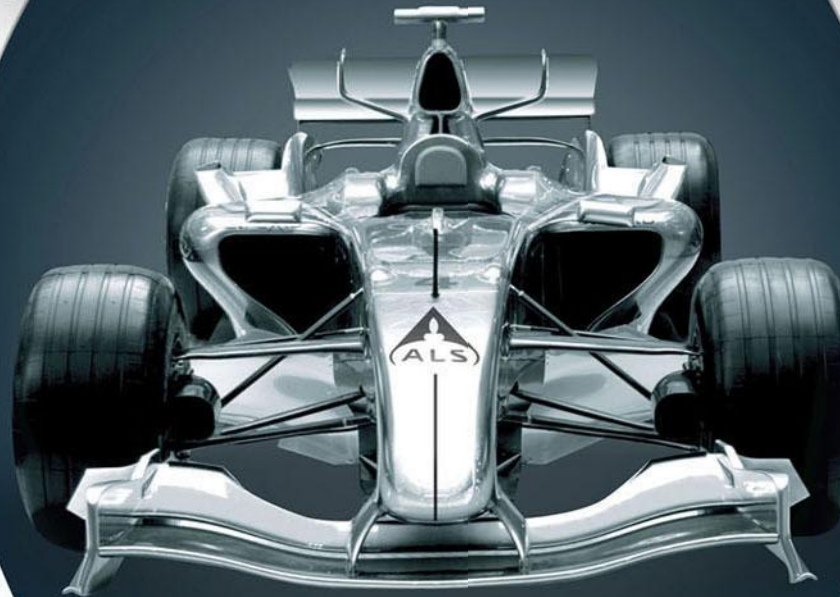
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