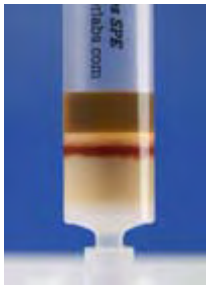


Solid Phase Extraction (SPE) and Quantification of Naphthenic Acid in Milli-Q, Simulated Groundwater and River Waters

John Headley, Jing-Long Du, Kerry Peru, Arash Janfada

Aquatic Ecosystem Protection Research Division
Water Science and Technology Directorate
Environment Canada

Outline of the Presentation

What are Naphthenic Acids?

Quantification of Naphthenic acids

Merits of Solid Phase Extraction

Analysis by –ve ESI/MS

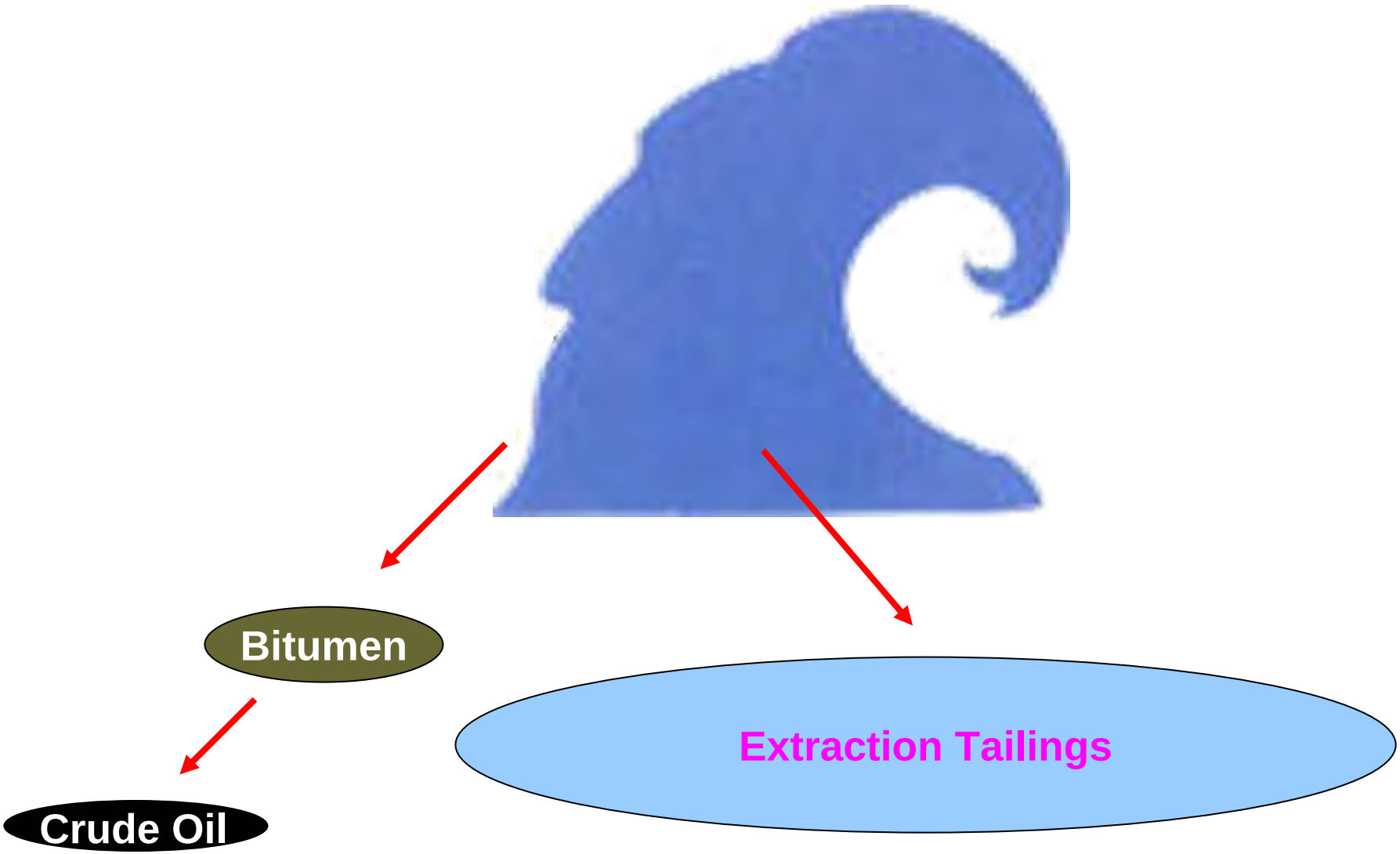
Results and Discussion

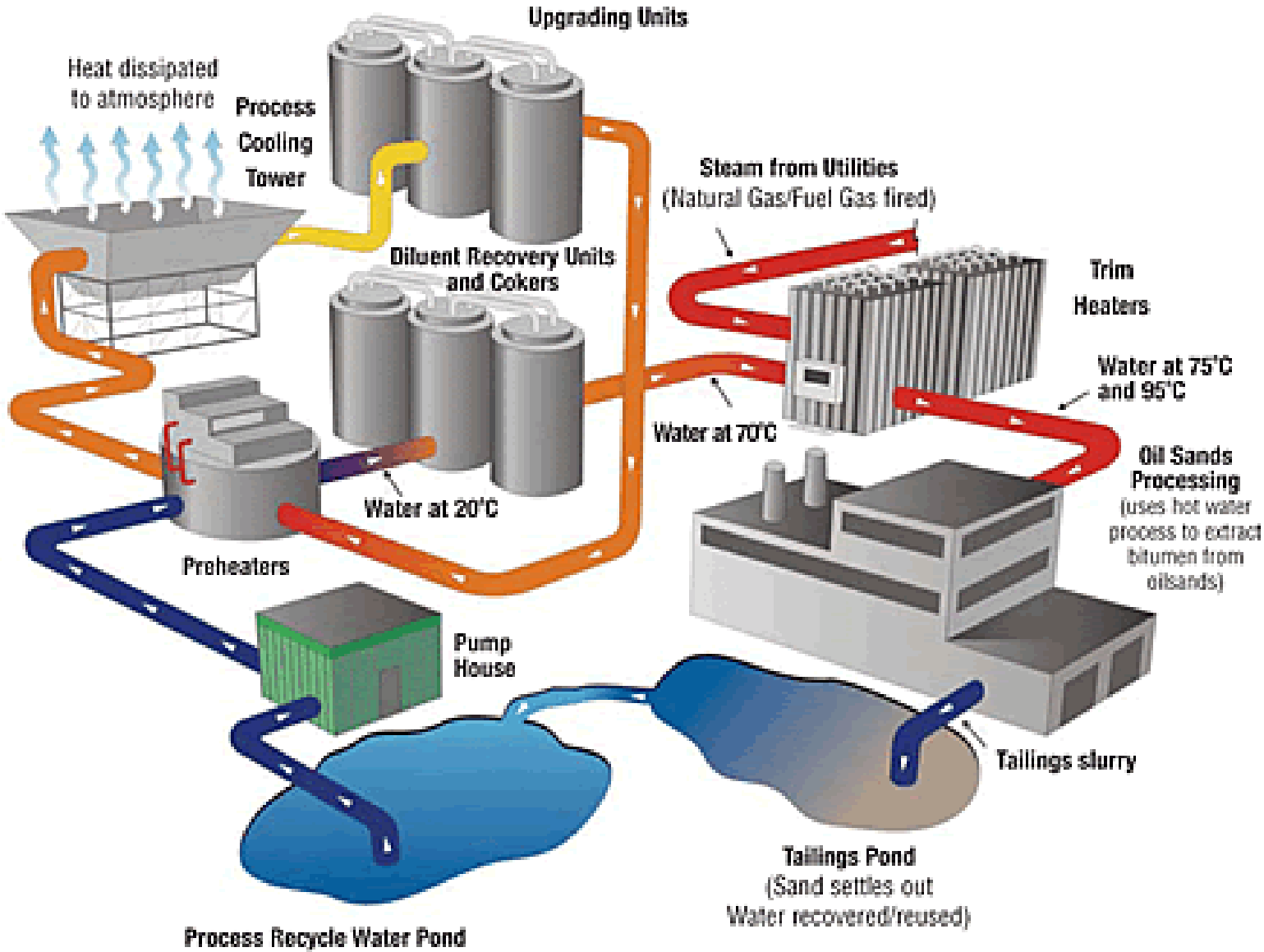
Conclusions

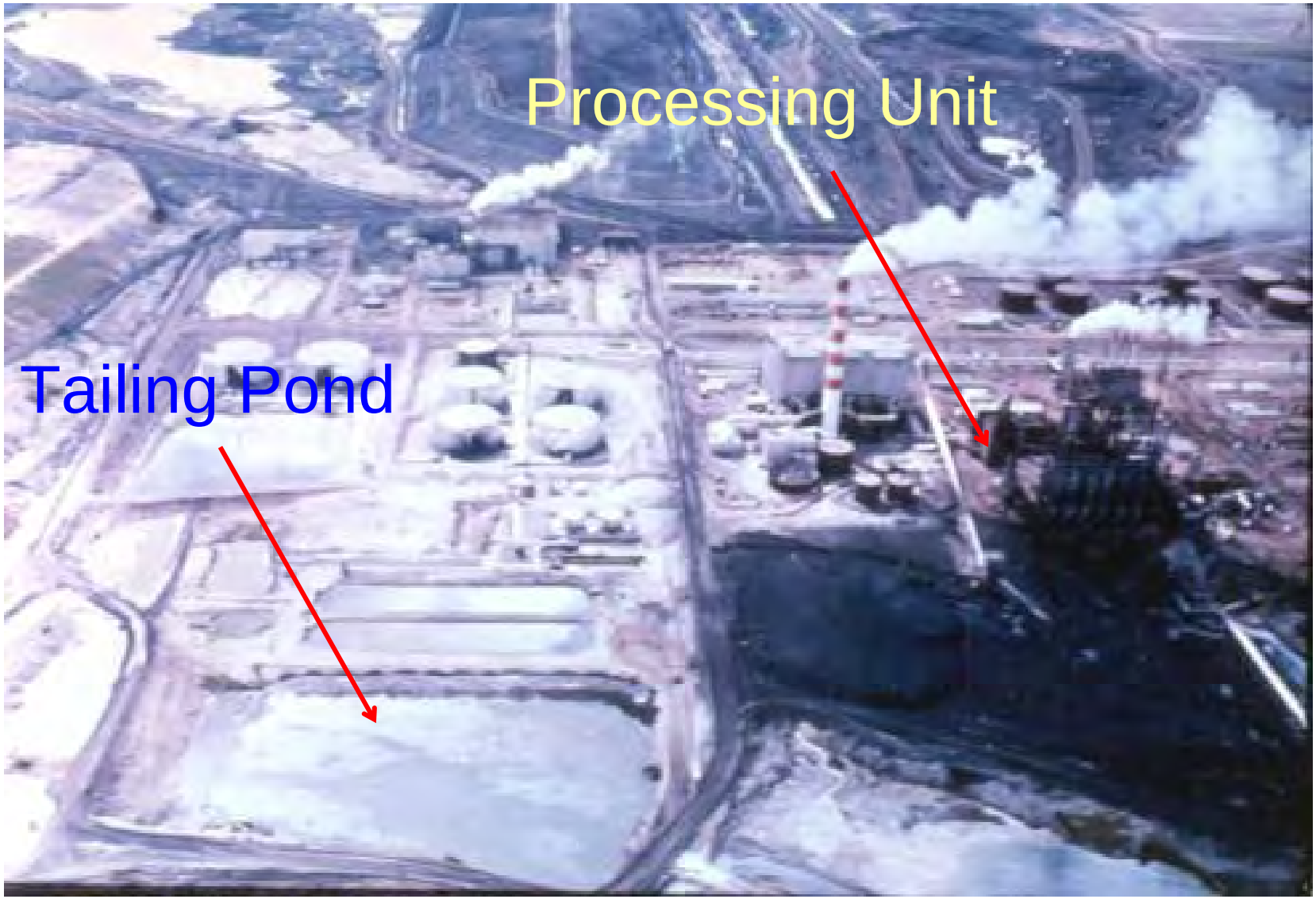

NORTHWEST TERRITORIES
Athabasca
Oil Sands
SASKATCHEWAN
ALBERTA
BRITISH
COLUMBIA
Edmonton
Calgary
Lethbridge
United States
MONTANA

Oil Sands

Oil Sand Extraction Process




Upgrading Units
Heat dissipated to atmosphere
Process Cooling Tower
Steam from Utilities (Natural Gas/Fuel Gas fired)
Diluent Recovery Units and Cokers
Trim Heaters
Water at 75°C and 95°C
Water at 70°C
Oil Sands Processing (uses hot water process to extract bitumen from oilsands)
Water at 20°C
Preheaters
Pump House
Tailings slurry
Tailings Pond (Sand settles out Water recovered/reused)
Process Recycle Water Pond


Processing Unit
Tailing Pond

What are Naphthenic Acids?

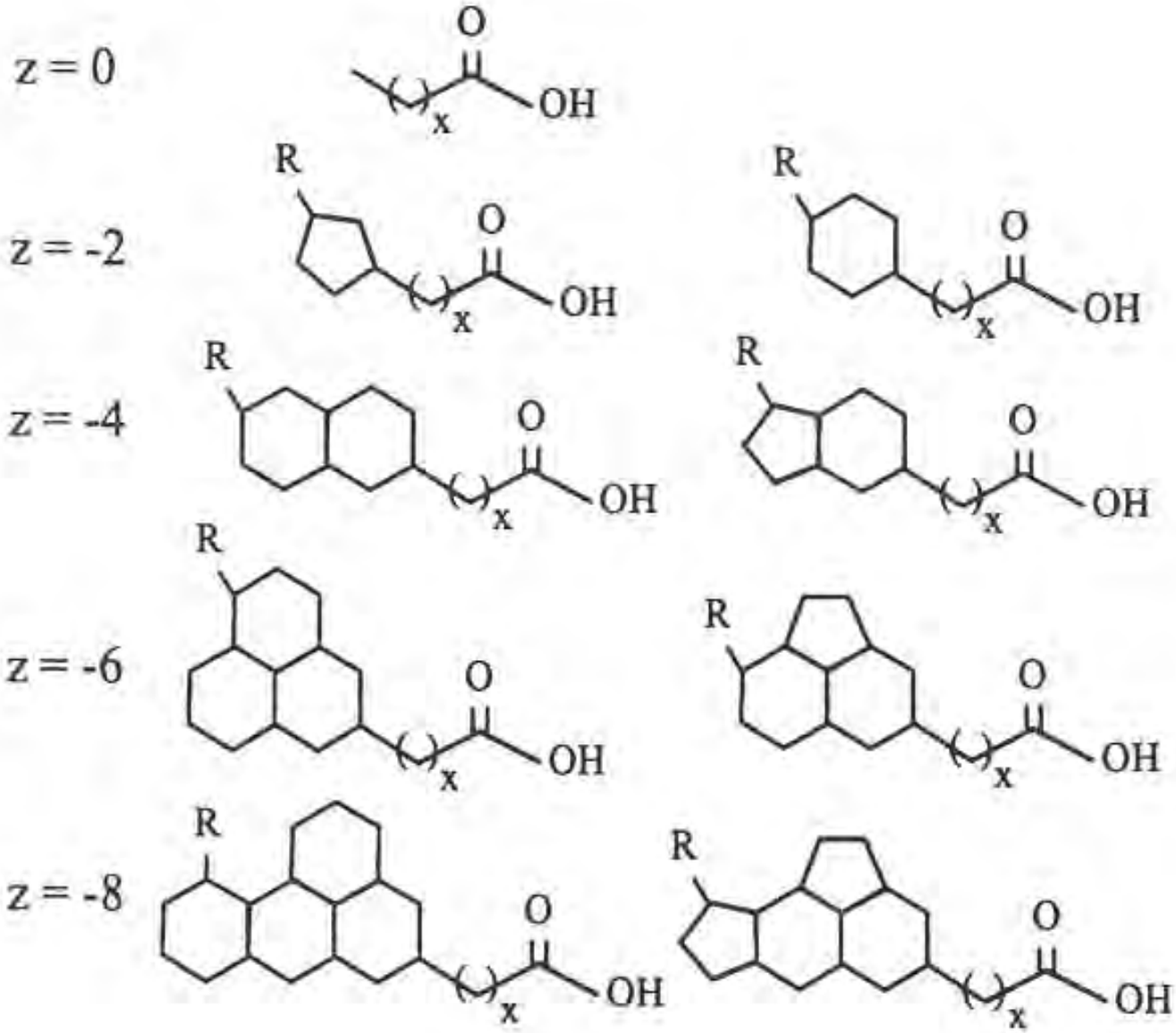
Naphthenic acids are carboxylic acids which include linear and/or saturated ring structures.

$$C_nH_{2n+Z}O_2$$

N --- the carbon number

Z --- number of hydrogen atoms that are lost as the structure becomes more compact

General Structure of Naphthenic Acids



H. L. LOCHTE

Petroleum Acids and Bases

H. L. LOCHTE
The University of Texas, Austin, Tex.

This review of petroleum acids and bases is presented in a single paper since most operations in the study of both classes of compounds are identical or analogous. The acidic compounds in petroleum consist of a mixture of phenols and carboxylic acids which are of aliphatic and cyclic types. The cyclic acids consist of ones containing the cyclopentane and those with a cyclohexane ring along with traces of aromatic acids. The carboxyl group is sometimes attached directly to the ring and sometimes one or more CH_2 groups lie between carboxyl and ring. In addition to the monocyclic acids, those with 10 or more carbons include some with two or more rings but practically nothing is known in regard to their structure. The nitrogen compounds in petroleum are known to consist of nearly equal amounts of compounds that can be extracted from refinery products with dilute acids and those that cannot be so extracted. The so-called nonbasic compounds are thought to include pyrroles and similar compounds that can be removed by treatment with solid potassium hydroxide but very little is known in regard to these compounds. The basic compounds are known to include alkylated and cyclic substituted pyridines and alkylated quinolines and probably isoquinolines. The alkyls in the quinolines have so far been shown to be located at positions 2, 3, 4, and 8 with alkyls higher than ethyl only at position 8. In addition to industrial interest in these compounds, they should be considered in connection with theories on the origin of petroleum.

◆ ◆ ◆ ◆ ◆

AS WILL become apparent later, there are so many points of similarity between petroleum acids and bases and their study, that the presentation of both subjects in a single paper appears to be desirable for logical reasons as well as to conserve space.

While a single case does not establish this as a fact, there may be a genetic relationship between these acids and bases since, in the case of California petroleum it has been found that 2,4-dimethyl-5-(2,2,6-trimethylcyclohexyl)pyridine and what may be considered as an oxidation product of the base, namely, 2,2,6-trimethylcyclohexanecarboxylic acid, have been isolated among the most abundant bases and acids, respectively.

Finally, any theory or theories in regard to the origin of petroleum cannot ignore these classes of compounds.

ISOLATION

Petroleum acids and bases have both been isolated from crude oil and from natural gas but the concentration of these compounds in viscous crude oil is so low that it is difficult to isolate considerable amounts of either class in this way. The bases can be extracted from crude oil by means of concentrated sulfuric acid or by liquid sulfur dioxide (Edeleanu process) while the acids can be extracted with aqueous or alcoholic sodium hydroxide solution, but the procedure is unsatisfactory and, in practice, both classes of compounds are isolated by extracting the proper refinery fraction with acid or alkali.

In both cases the compounds are then fractionated by distillation of the free acids or their methyl or ethyl esters and as the free base. Modern efficient columns are used to avoid the tedious redistillations formerly required.

Fractional distillation may or may not yield cuts containing individual compounds in such high concentration that crystalline salts or derivatives can be obtained, but the yield of pure compound that can be obtained in this way is so low that it is almost always advisable to use some other physical method of separation before attempting to isolate pure compounds by recrystallization of salts or derivatives. Fractional neutralization or liberation of acids or bases has been most commonly applied to effect further separations, since these methods used with modern countercurrent equipment lead to numerous fractions from which crystalline derivatives can be obtained and recrystallized to a state of purity. Determination of structure then follows the usual methods of organic chemistry.

PETROLEUM ACIDS

By 1930 after half a century of tedious and often discouraging study of mixtures of acids isolated from refinery products and, in some cases, from crude oil, chemists were able to state that:

1. Phenols and carboxylic acids are found in all acidic mixtures.
2. The carboxylic acids consist of a mixture of the lower liquid and a few higher solid aliphatic acids and alicyclic acids which are known as naphthenic acids.
3. The naphthenic acids range from 6 to more than 20 carbon atoms, show no unsaturation, and appear to contain normally only minor concentrations of cyclohexyl acids.
4. While rings with 4 carbon atoms and with 7 or more such atoms are not excluded they are considered to be unlikely; consequently, the naphthenic acids consist predominatingly of cyclopentyl acids.

In 1928 von Braun (*5*) began a long series of studies in the chemistry of the naphthenic acids. These gave more information on the reactions of these acids than had been obtained in all previous work, but, since he separated almost entirely by distillation, as had been done in vain by earlier workers, he was not able to isolate a single pure naphthenic acid.

Von Braun concluded as a result of his research that:

1. Acids with less than 8 carbons are almost entirely aliphatic in nature.
2. Monocyclic acids start at C_8 and predominate between C_9 and C_{15}.
3. Bicyclic acids start at C_{13} and predominate above C_{18} except in cases of the Galician acids in which no bicyclic acids were detected.
4. His "chlorine number" determinations (*4*) showed that most fractions of naphthenic acids had two alpha hydrogen atoms (chlorine number, 200) and so must have at least one CH_2 group between the ring and the carboxyl group.
5. In a few cases he was able to form a lactone after converting the acid to one with beta-gamma unsaturation and so concluded that in these the carboxyl group had at least three carbons between it and the ring. He concluded, however, that in most cases there was only one carbon between the ring and carboxyl.
6. The amines formed in good yield by the K. F. Schmidt degradation of the acids appear to be more easily separated by distillation or by recrystallization of the oxalates than the parent acids.

November 1952 INDUSTRIAL AND ENGINEERING CHEMISTR

Naphthenic acid characteristics

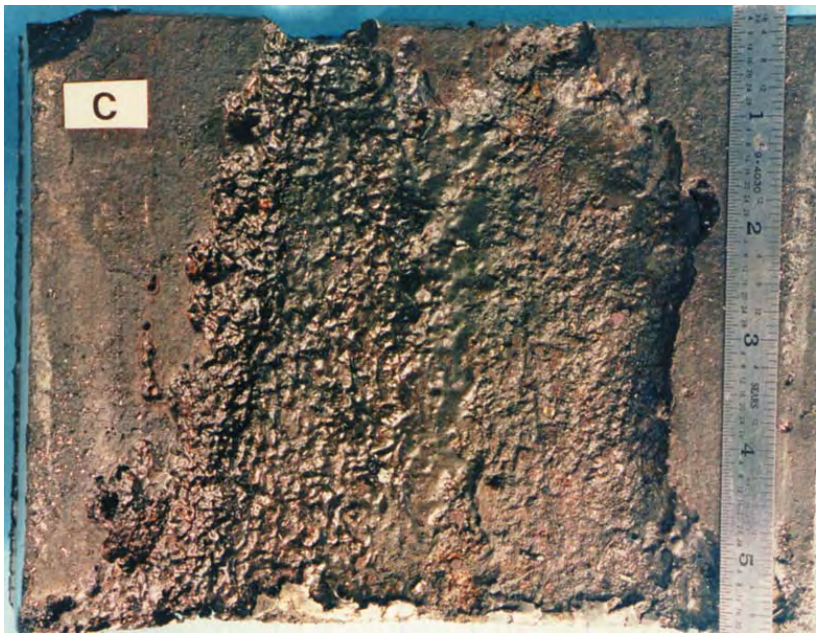
Negative

- Naphthenic acids are the main organic toxic constituents of Oil Sands process-water
- Corrosive

Positive

- Wood preservative
- Detergent

Corrosion



Refinery units

Pipelines

Toxicity

Aquatic creatures

Animals

Quantification of Naphthenic Acids

Gas Chromatography/Mass Spectrometry (GC/MS)

Seifert, W.K., *et. al. Anal. Chem. 41, 1638, 1969*

Infrared Spectroscopy (IR)

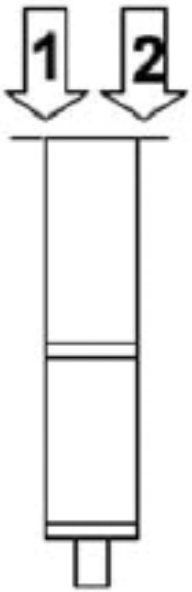
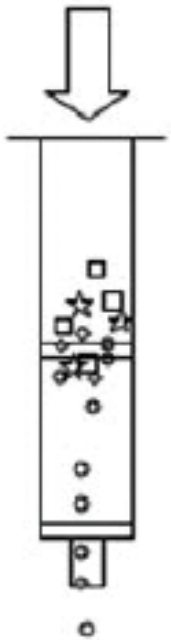
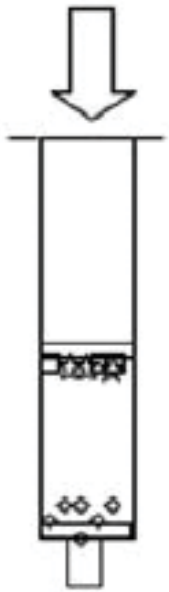
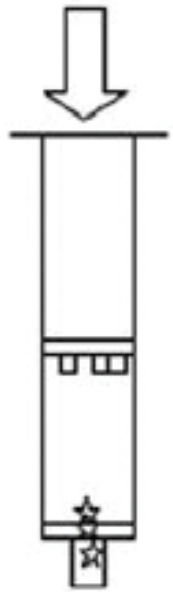
Fan, T.P., *Energy & Fuel*, 5, 371, 1991.

Fast Atom Bombardment/Mass Spectrometry (FAB/MS)

CEATAG, Naphthenic *Acids Background Information Discussion Report*, 1998.

Negative-Ion Electrospray Mass Spectrometry

John V. Headley, Kerry M. Peru, Dena W. McMartin and Marcus Winkler, *AOAC*, 85, 1, 2002.

Precondition	Load	Wash	Elute
Prepare cartridge to accept sample	Load sample and rinse reservoir(s)	Wash with solvent that won't elute analyte	Elute analyte in smallest volume possible
			
1. Methanol or acetonitrile 2. Weak solvent (water, buffer)	Weakly retained matrix compounds are eluted	Analyte and other matrix compounds retained	Elute analyte leaving highly retained compounds

Water sample description

Milli-Q

Simulated Ground Water

Composition	Composition (mg/L)
CaSO4 (DBH, DBH Chemicals, Poole, UK)	1013
MgSO4 (DBH, DBH Chemicals, Toronto, Ont.)	938
NaN3(DBH, DBH Chemicals, Toronto, Ont.)	525

South Saskatchewan River water

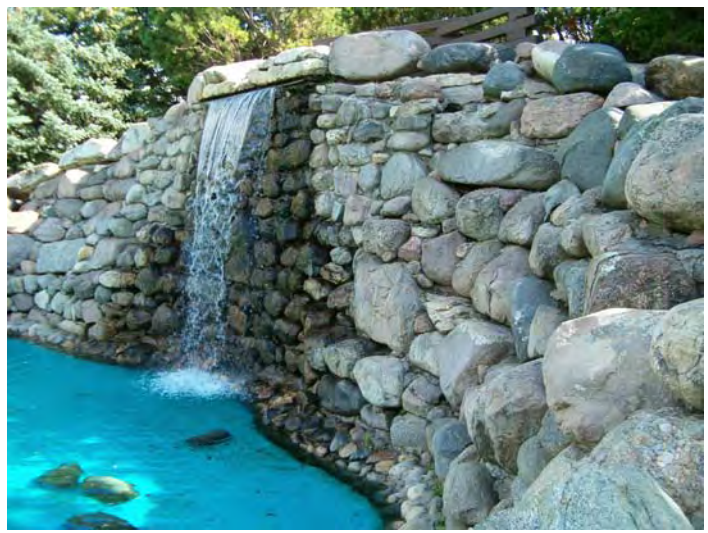
Experimental

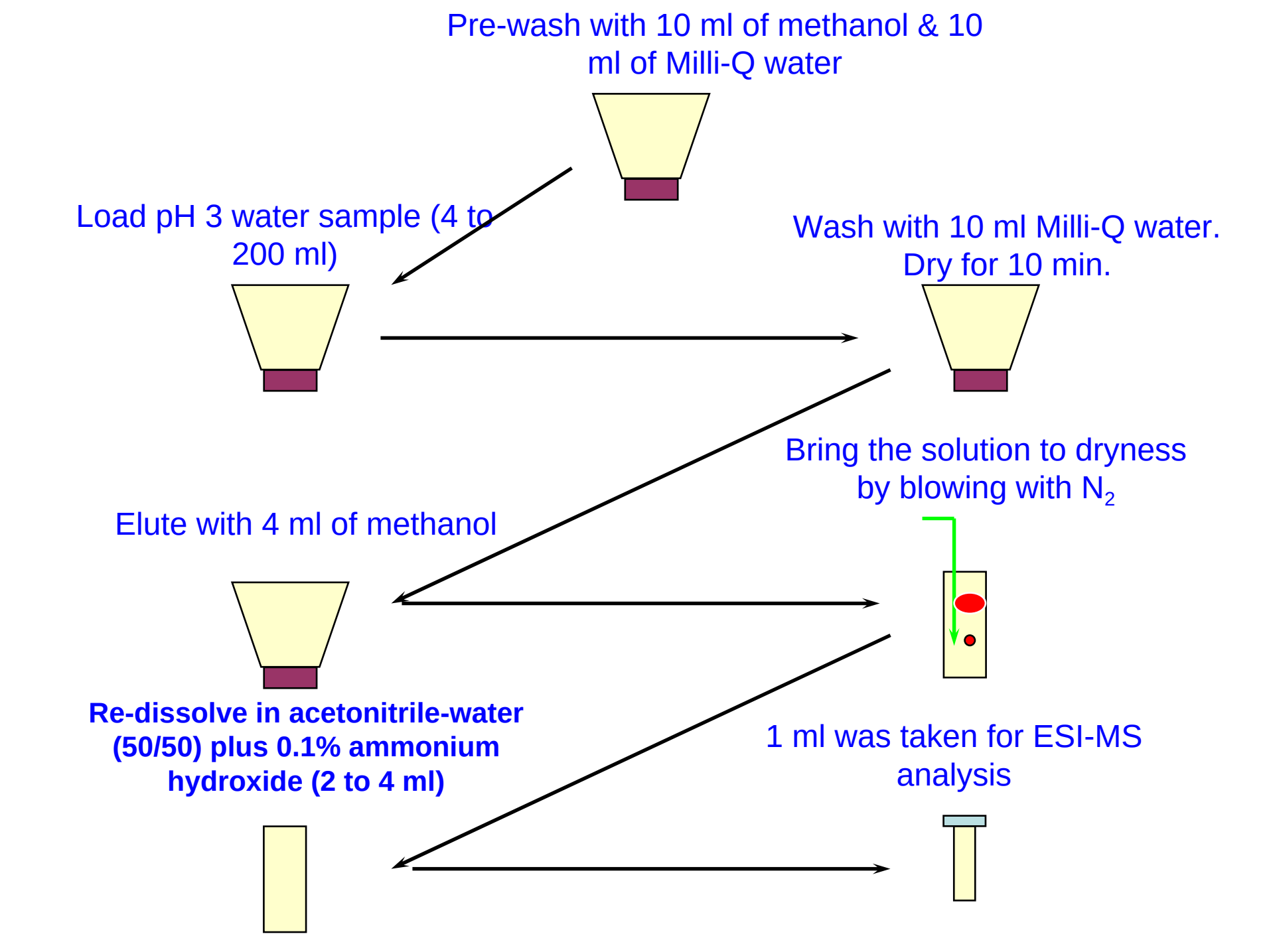
Stock NA: Obtained from Athabasca Oilsands tailing pond water ($pK_{a:}$ 5 -6)

Cartridges: ENV+ (crosslinked polystyrene-based polymer)(Biotage); C18 and Oasis.

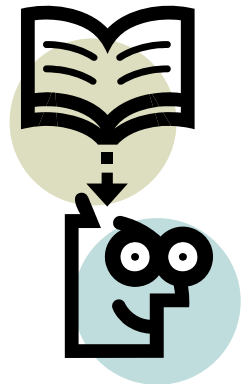
Elution: Methanol

Mass Spectrometry: Electrospray (negative-ion mode)




Pre-wash with 10 ml of methanol & 10 ml of Milli-Q water
Load pH 3 water sample (4 to 200 ml)
Wash with 10 ml Milli-Q water. Dry for 10 min.
Bring the solution to dryness by blowing with N_2
Elute with 4 ml of methanol
Re-dissolve in acetonitrile-water (50/50) plus 0.1% ammonium hydroxide (2 to 4 ml)
1 ml was taken for ESI-MS analysis

Henderson-Hasselbalch Equation



$$pH = pK_a + \log \frac{A^-}{HA}$$

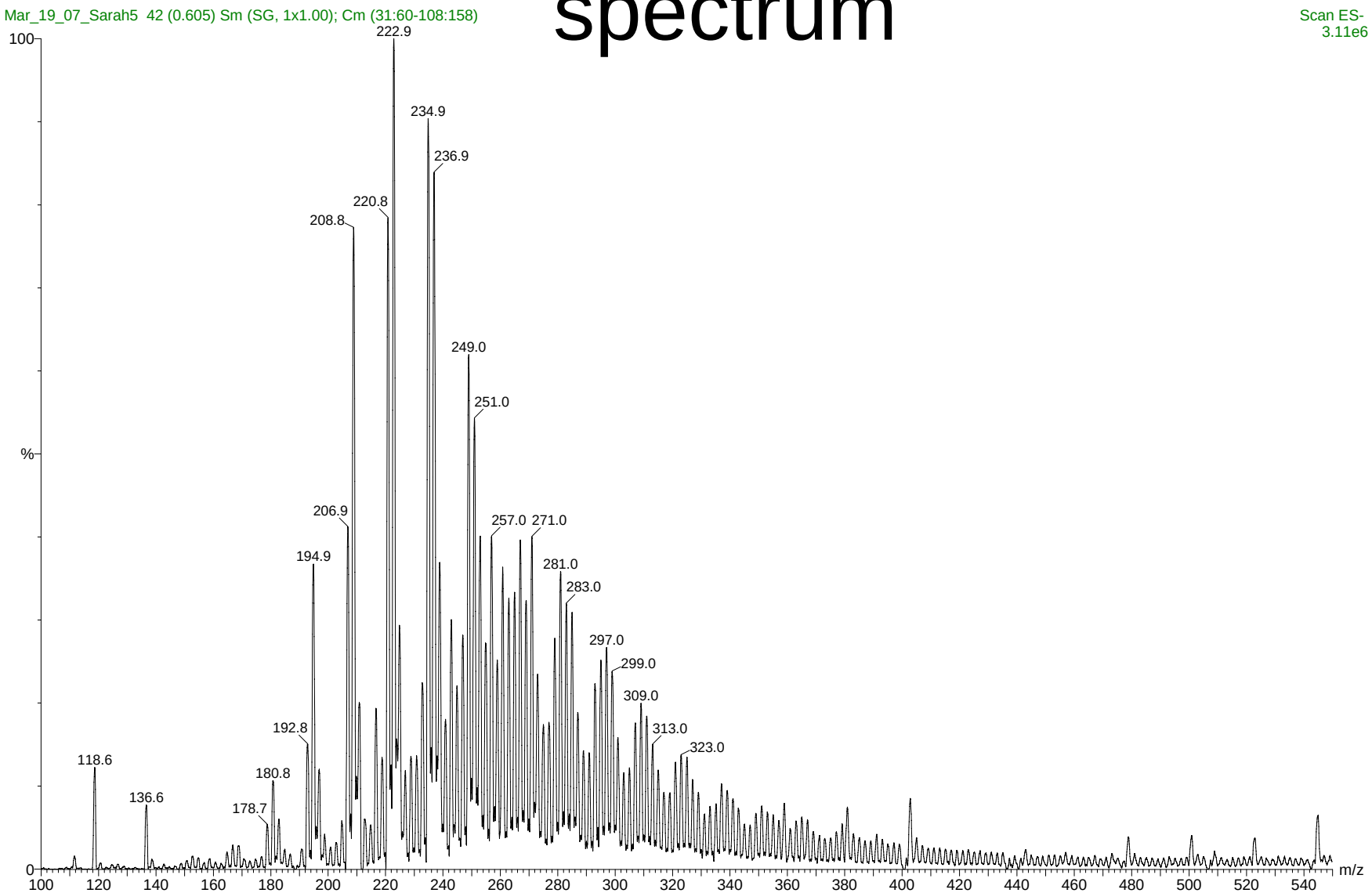
Or

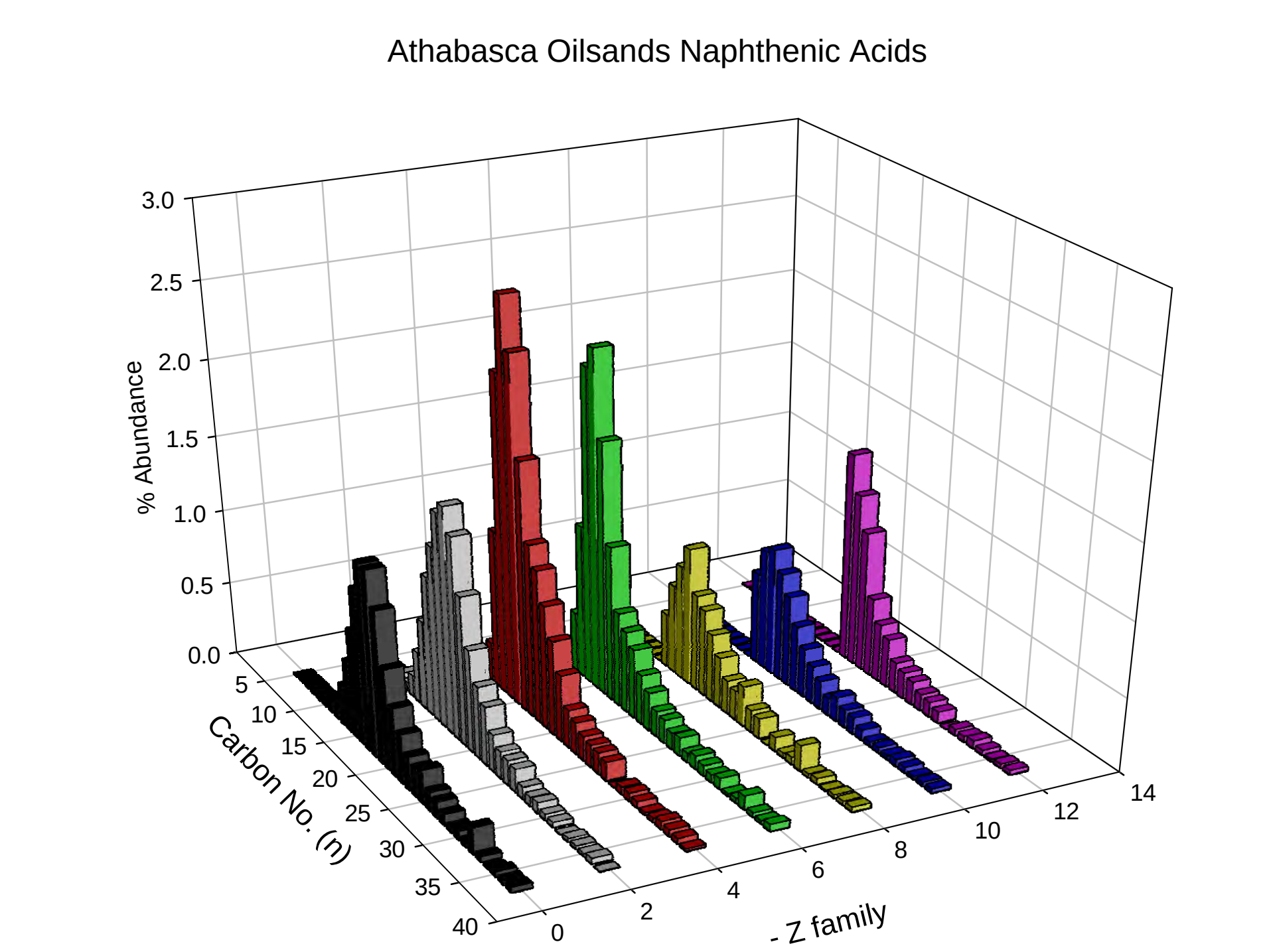
$$pK_a = pH + \log \frac{HA}{A^-}$$

At pH = 3 and pKa = 5

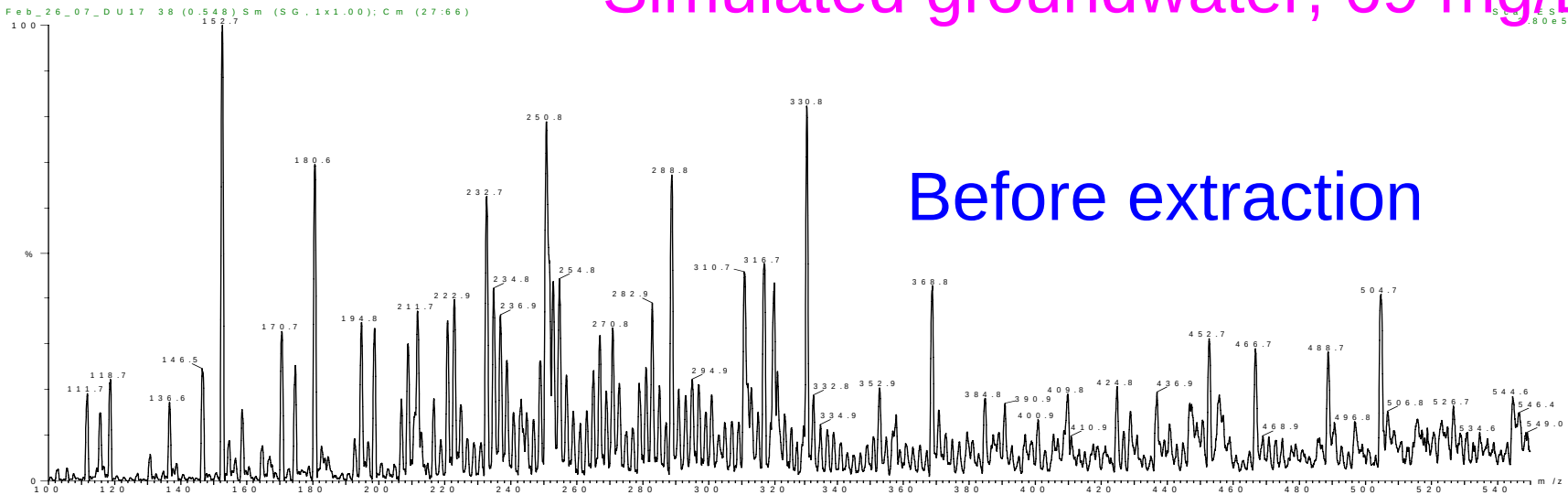
$$\frac{HA}{A^-} = 100$$

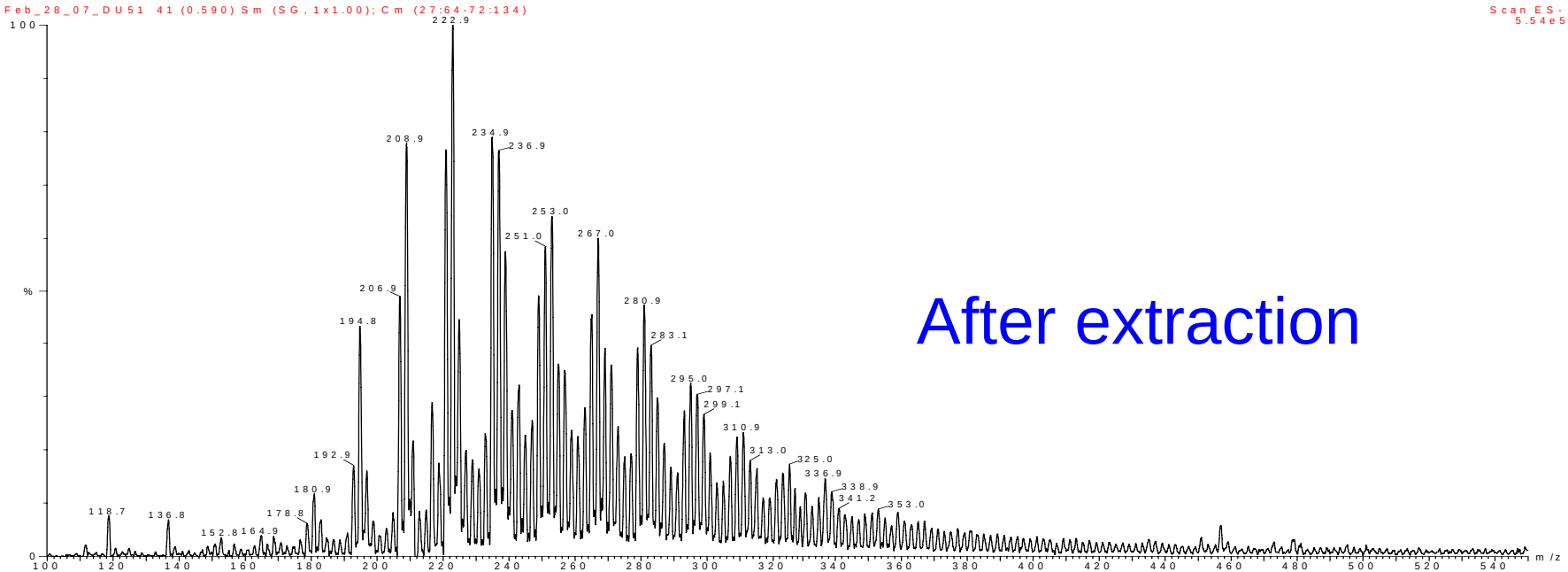
NA (Syncude standard) mass spectrum




Athabasca Oilsands Naphthenic Acids
% Abundance
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Carbon No. (n)
5
10
15
20
25
30
35
40
0
2
4
6
8
10
12
14
- Z family

Simulated groundwater, 69 mg/L

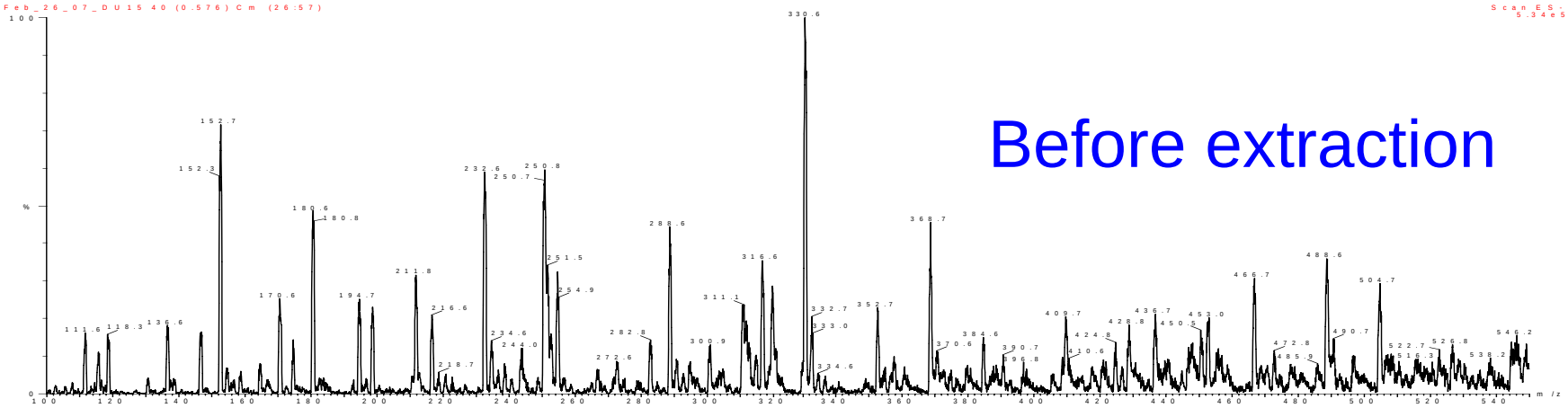




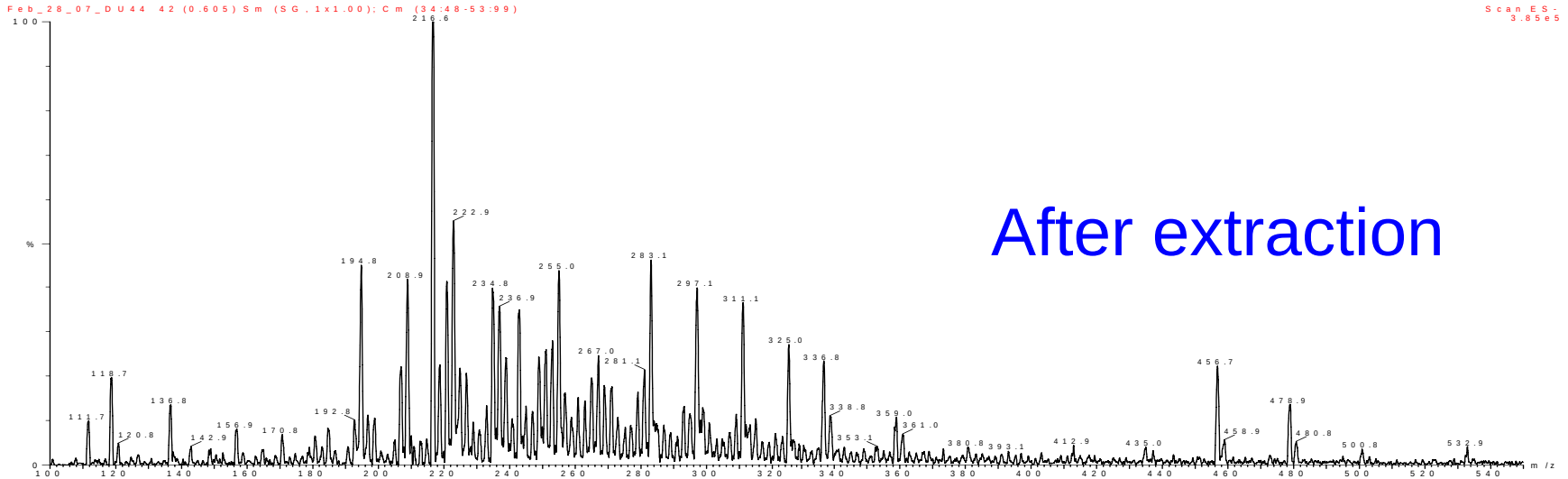
Before extraction

After extraction

Simulated groundwater, 0.069 mg/L

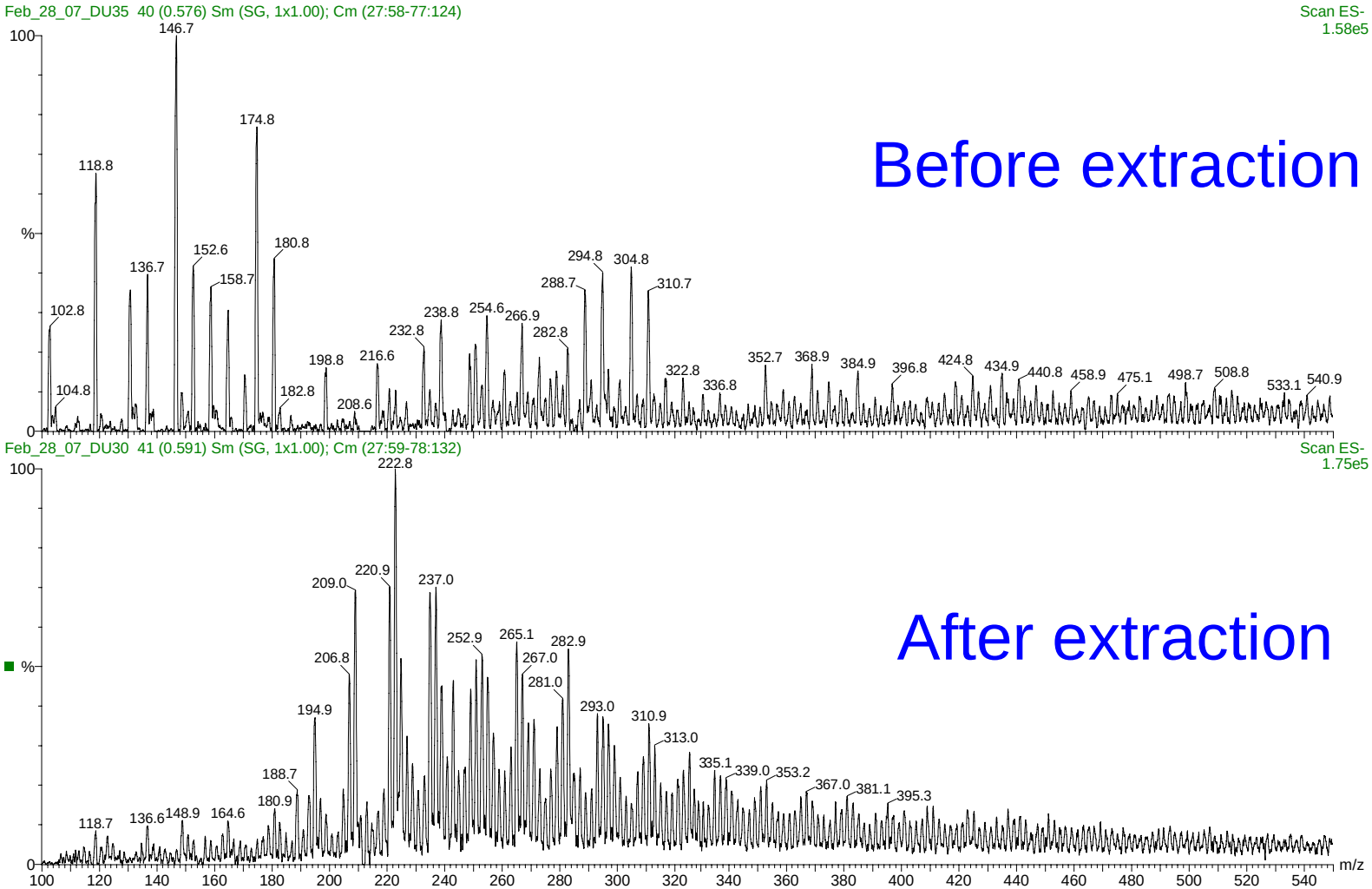


Before extraction

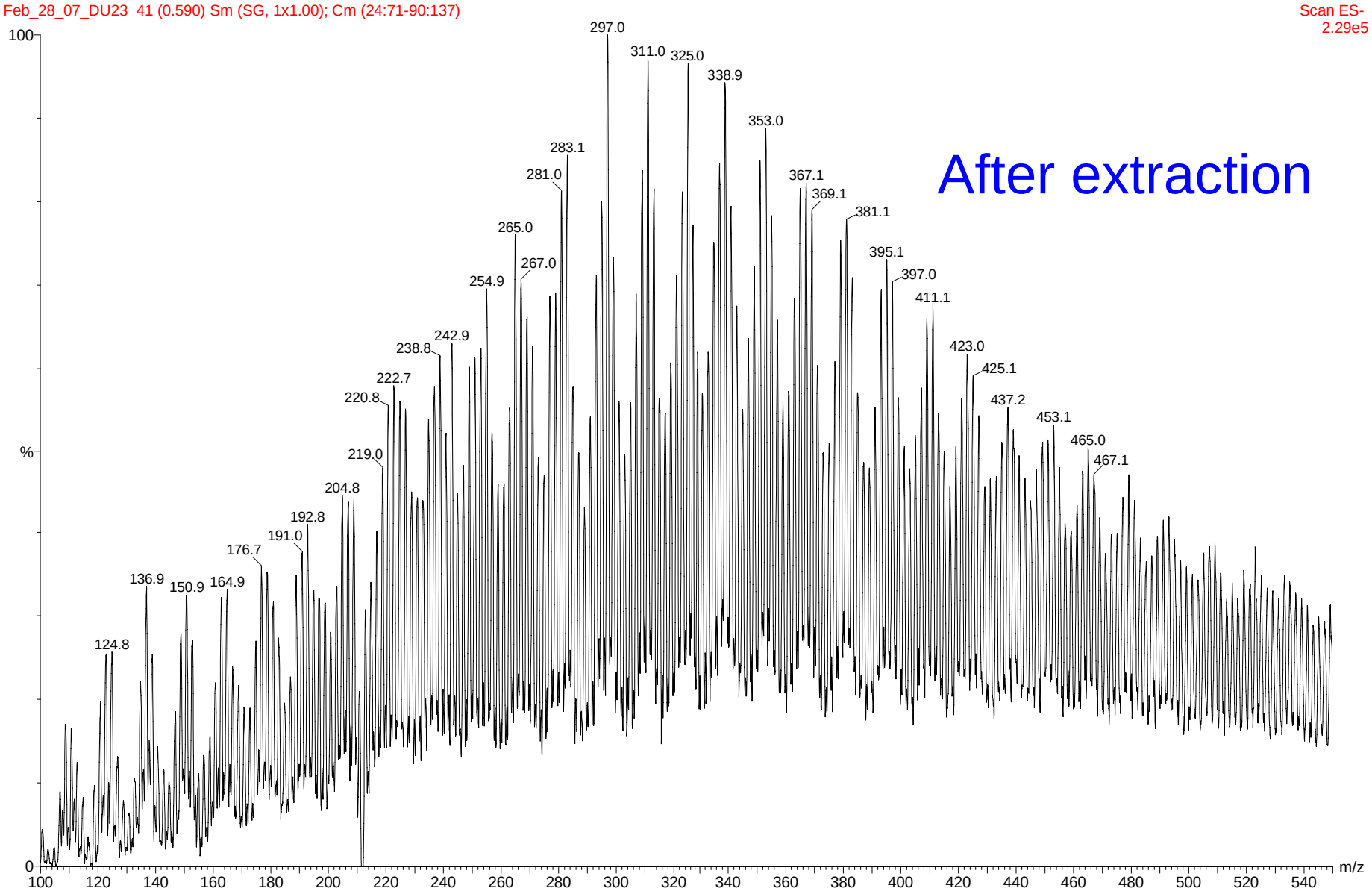


After extraction

River water, 6.9 mg/L



River water, 0.069 mg/L



Simulated Groundwater

Sample	mg/L	Recovery	Mean recovery	RSD
200 mL blank	0.0			
4 mL blank	0.0			
S 0.069-1	0.060	86.7		
S 0.069-2	0.057	82.8	85.3	2
S 0.069-3	0.060	86.3		
S 6.9-1	3.7	53.2		
S 6.9-2	4.4	63.1	55.9	18
S 6.9-3	3.5	67.7		
S 69-1	44.2	64.1		
S 69-2	46.4	67.2	66.3	3
S 69-3	46.7	67.7		

S = Simulated ground water

River Water

Sample	mg/L	Corr. Conc.	Recovery	Mean recovery	RSD
200 mL blank	69.3				
4 mL blank	2.0				
R 0.069-1	69.8	0.005	7.6		
R 0.069-2	71.4	0.021	30.4	30.5	75
R 0.069-3	73.0	0.037	53.6		
R 6.9-1	7.6	5.6	81.2		
R 6.9-2	7.3	5.3	76.8	83.1	9
R 6.9-3	8.3	6.3	91.3		
R 69-1	46.8	44.8	64.9		
R 69-2	46.4	44.4	64.3	61.2	10
R 69-3	39.6	37.6	54.4		

R = South Saskatchewan River water

Milli-Q Water

Sample	mg/L	Recovery	Mean recovery	RSD
200 mL blank	0.0			
4 mL blank	0.0			
M 0.069-1	0.050	72.2		
M 0.069-2	0.041	60.0	65.5	5
M 0.069-3	0.045	64.9		
M 6.9-1	4.2	60.9		
M 6.9-2	4.0	57.4	61.4	7
M 6.9-3	4.6	66.0		
M 69-1	43.8	63.5		
M 69-2	46.1	66.8	63.5	5
M 69-3	41.6	60.3		

M =Milli-Q water

Conclusions:

ENV+ is more efficient than Oasis and C_{18} cartridges in extraction of NAs.

ENV+ cartridge efficiently extracts the non-dissociated naphthenic acid and desalts the final extract.

There is a significant matrix effect in the river water samples due to natural carboxylic acids (humic, fulvic etc.) in the natural river water systems.

The described SPE procedure significantly reduced the ion suppression during ESI caused by matrix interference.

Thank you!