Ali Mirhosseini, Norwegian Public Roads Administration (Statens Vegvesen), Oct. 2024

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Norwegian Public Roads Administration

Measuring bio-oil content and understanding chemical interactions in bio-bitumen

Introduction

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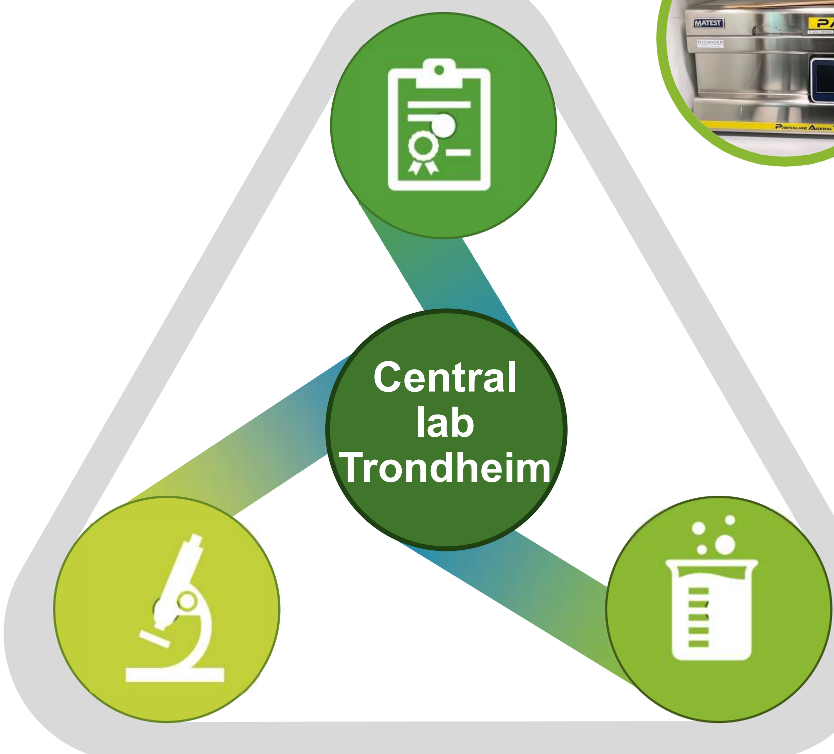


Research and Development

Both long-term strategics and short-term projects, tied with the NPRA main goals

Performance and quality control

- Samples from different contracts / contractors / road owners
- Routine testing

Standards and handbooks

Continuous work with standard committees, improving and updating regulations and test methods

EPD – Environmental Product Declaration

- A document showing the environmental impacts (CO_2 emission) for the product (asphalt).
- The A and C modules in an EPD represent the environmental impacts during the <u>product's production **(A)**</u> and its <u>end-of-life phase **(C)**</u>

epd-norge.no
The Norwegian EPD Foundation

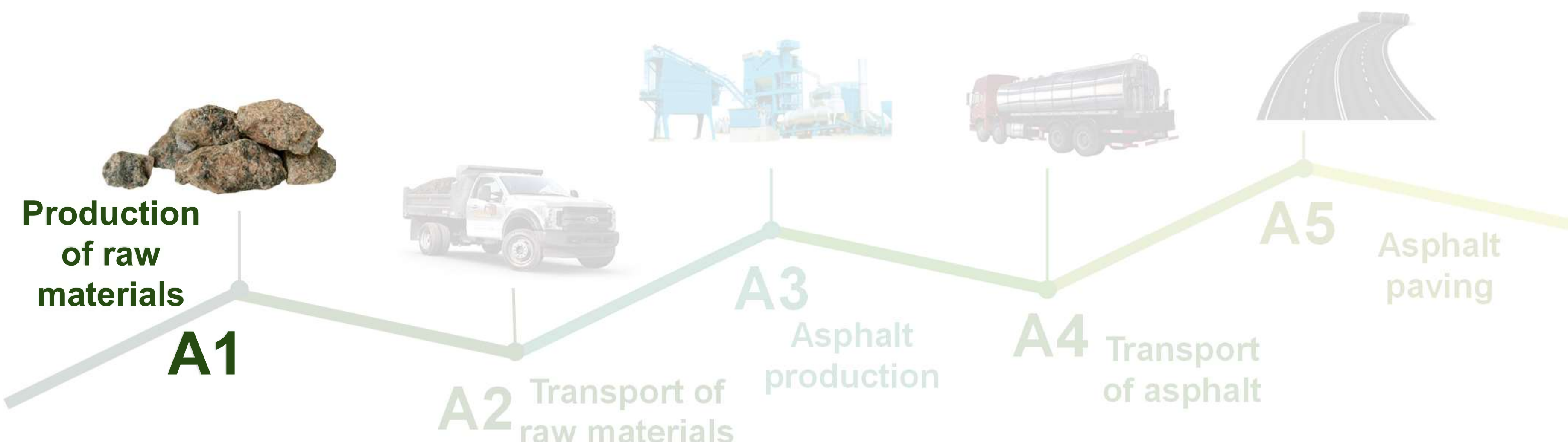
ENVIRONMENTAL PRODUCT DECLARATION

In accordance with ISO 14025, ISO 21930 and EN 15804

Eier av deklarasjonen:	EBA
Programoperatør:	Næringslivets Stiftelse for Miljødeklarasjoner
Utgiver:	Næringslivets Stiftelse for Miljødeklarasjoner
Deklarasjonsnummer:	NEPD-1391-456-NO
Publiseringssnummer:	NEPD-1391-456-NO
ECO Platform registreringsnummer:	-
Godkjent dato:	14.09.2017
Gyldig til:	14.09.2022

Ska 11 PmB. Asfalt (slitelag)

EBA



Reduction in A1 by using …

- Recycled Asphalt Pavement (RAP)
- Bio-based additives in bitumen (replacement for neat bitumen, additive while blending with RAP etc.)

- How much bio-oil is there..?
- How has it blended with bitumen?
- Interactions with recycled asphalt..?
- What happens if we recycle and add bio-oil again..?

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- How has it blended with bitumen?
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- What happens if we recycle and add bio-oil again..?

How much bio-oil is there..?

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Project and funding

Main project: **Asfaltdekkers Funksjonsegenskaper**

Long-term strategic Research and Development project with focus on **climate**, **contract strategy**, and **quality**

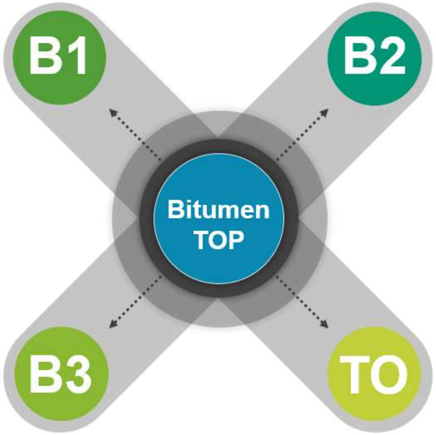
Sub-projects: **Biobitumen** and **Levetids effekt**

Project leader:
Thor Asbjørn Lunaas

Sample preparation

Pure bitumen

Bitumen + 9.5% TOP



Bitumen + 5% TOP

Pure Tall Oil Pitch

Gas Chromatography-Mass Spectrometry (GC-MS)

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- GC-MS is a technique that combines gas chromatography (GC) and mass spectrometry (MS) to analyze complex mixtures.
- Gas chromatography separates the different components of the sample by passing it through a column using an inert gas.
- Mass spectrometry then identifies and quantifies the separated components by measuring their mass-to-charge ratio.

Two main steps:

1. To extract fatty acids present in the various samples and determine their concentration
2. Quantification of fatty acids in the various samples should be correlated with their content in tall oil

- ~0.5 g sample (B1, B2, B3, TO) mixed with 20 mL toluene/chloroform and 20 mL 0.1 M NaOH solution.
- Mixtures were shaken overnight and centrifuged the next day.
- Fatty acids were extracted using chloroform, HCl 0.5 M, and shaken overnight.
- Solution was mixed with tridecanoic acid (internal standard), solvent removed with nitrogen, and acids dissolved in BF_3/methanol.
- After heating at 60°C for 1 hour, hexane and Milli-Q water were added, and the oil phase was extracted.
- Analyzed by Gas Chromatography (Agilent GC 7890) with flame ionization (FID) and mass spectrometry detectors (MSD).

GC MS – Step 1: Extraction of Fatty acids

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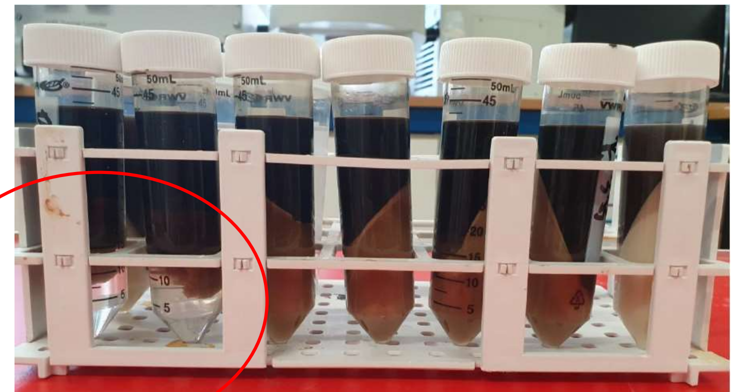
- Putting the samples in contact with a basic aqueous solution.
- As a result, the fatty acids are ionized and partition into the aqueous phase.
- Centrifugation in order to separate the aqueous and the organic phases

Centrifugated at 9000 rpm for 10 minutes



Partial separation

Choice of the solvent:

1. Toluene

2. Chloroform

Full separation
No polyaromatic compounds in the aqueous phase

B1 B2 B3 TO

GC MS – Step 2: Determination of fatty acid content

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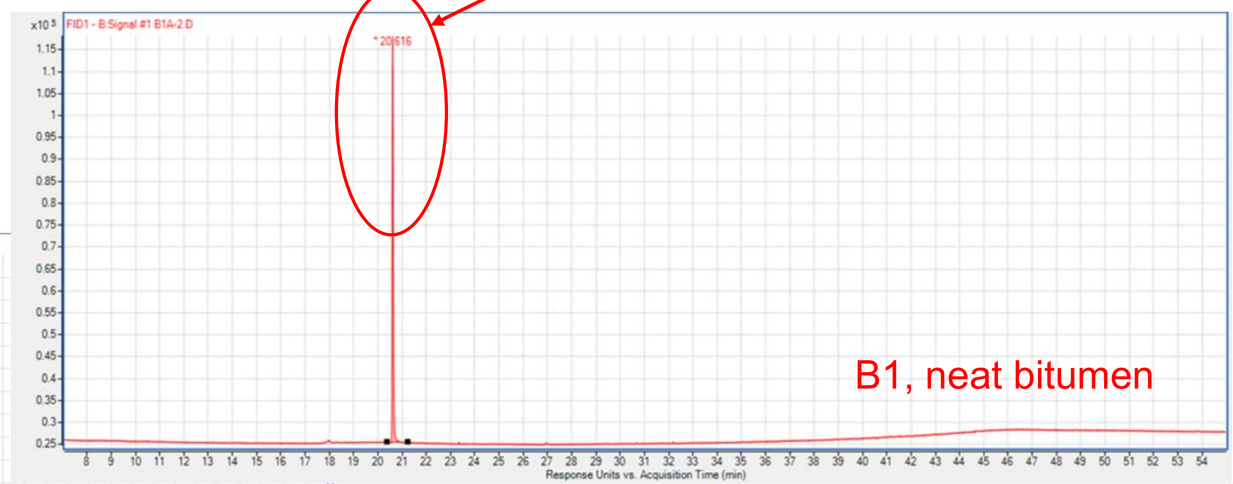
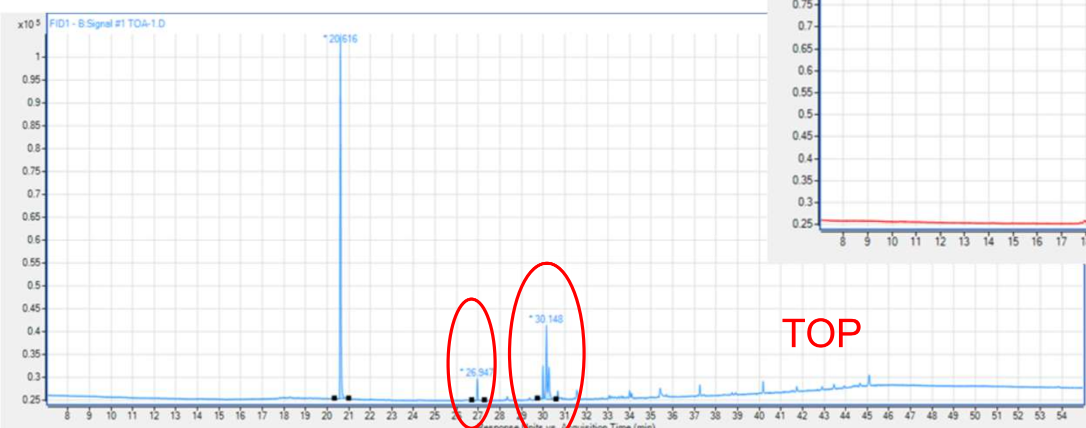
- Back-extraction of the ionized fatty acids into chloroform.
- Reacidification (tridecanoic acid)
- Extraction and evaporation of the chloroform
- Fatty acids are methylated and solubilized into hexane
- Ready to be analyzed

Esterified internal standard (tridecanoic acid)



Retention time



Retention time

GC MS – Step 2: Determination of fatty acid content

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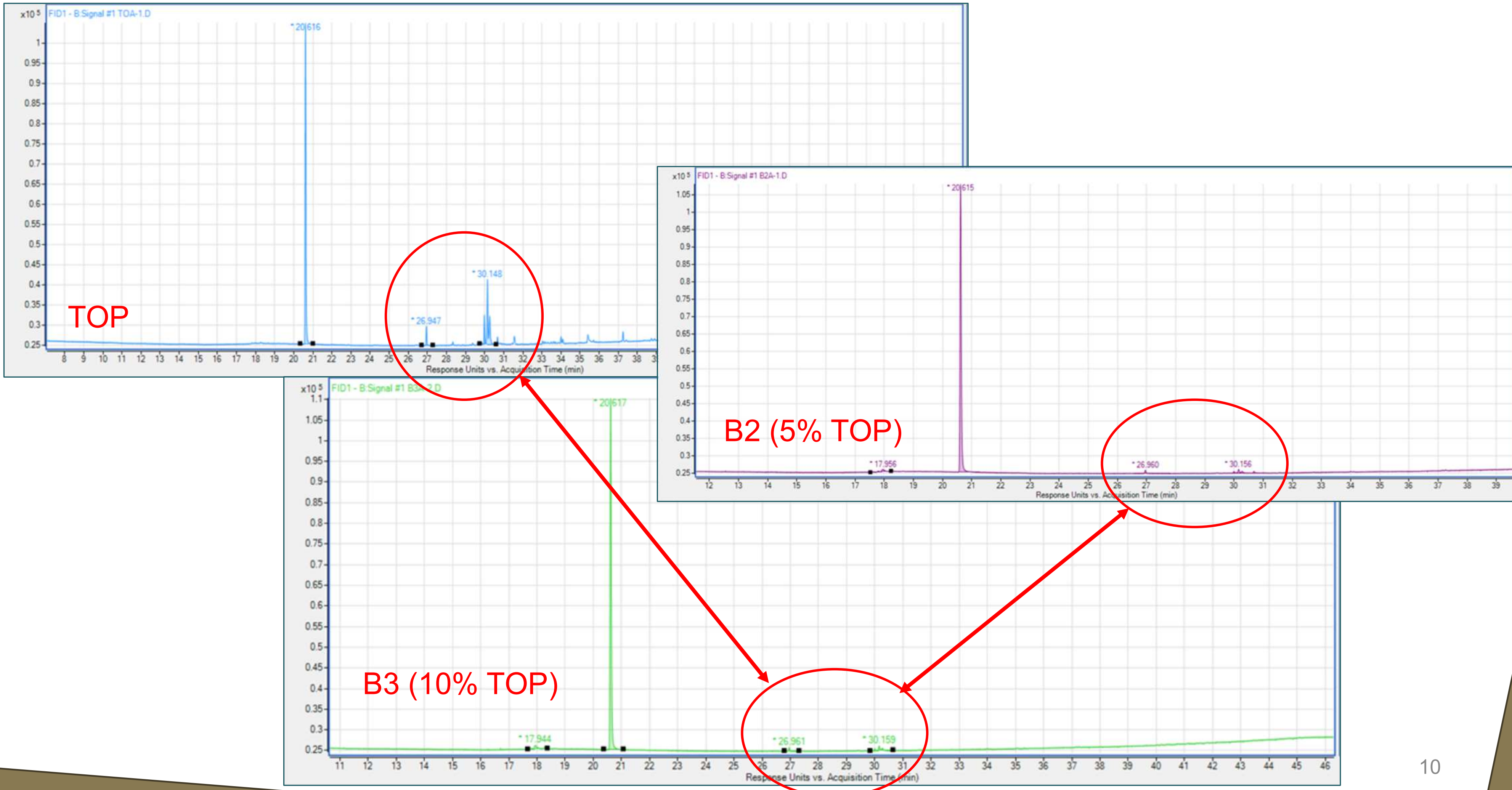

GC MS – Step 2: Determination of fatty acid content

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Sample	Parallel	ϕ_m (%)	
B1	1	0	
	2	0	
B2	1	11.6	5% ✗
	2	4.7	5% ✓
B3	1	10.3	9.5% ✓
	2	11.9	9.5% !
TO	1	102	
	2	97.9	

Carbon-14 dating

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Radiocarbon dating, or carbon-14 dating, is a scientific method that can accurately determine the age of organic materials as old as approximately 60,000 years.

- It is used to determine the age of carbon-containing materials by measuring the amount of radioactive carbon-14 isotope remaining in the sample.
- This test can be used to distinguish between **bio-based carbon** (recently absorbed by plants from the atmosphere) and **fossil-based carbon** (millions of years old).
- The amount of C-14 present in a sample helps confirm the percentage of bio-oil in the bitumen by identifying how much of the carbon comes from recent biological sources

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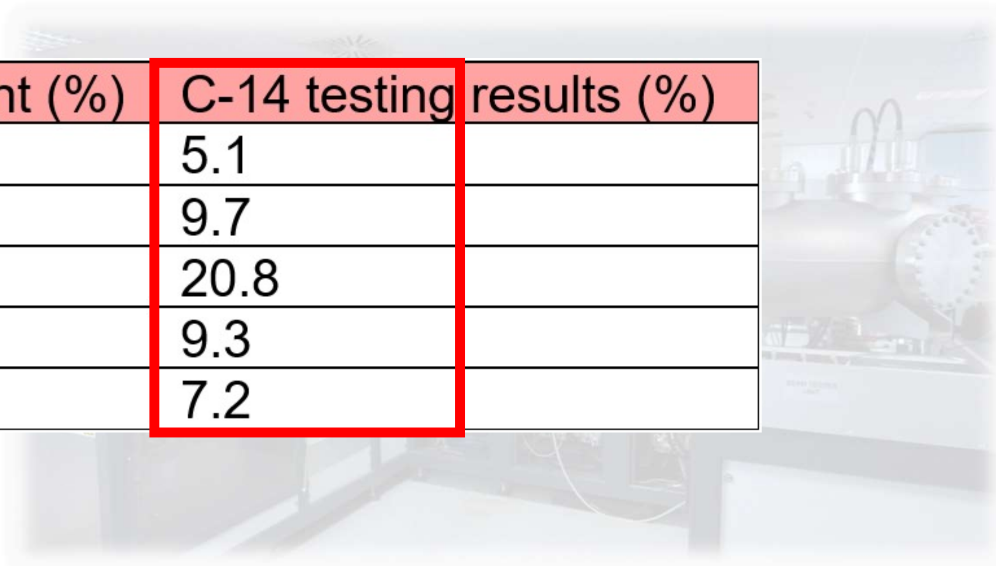
- It is used to determine the age of carbon-containing materials by measuring the amount of radioac… the sampl…
- This test c… **bio-base…** from the a… (millions c…

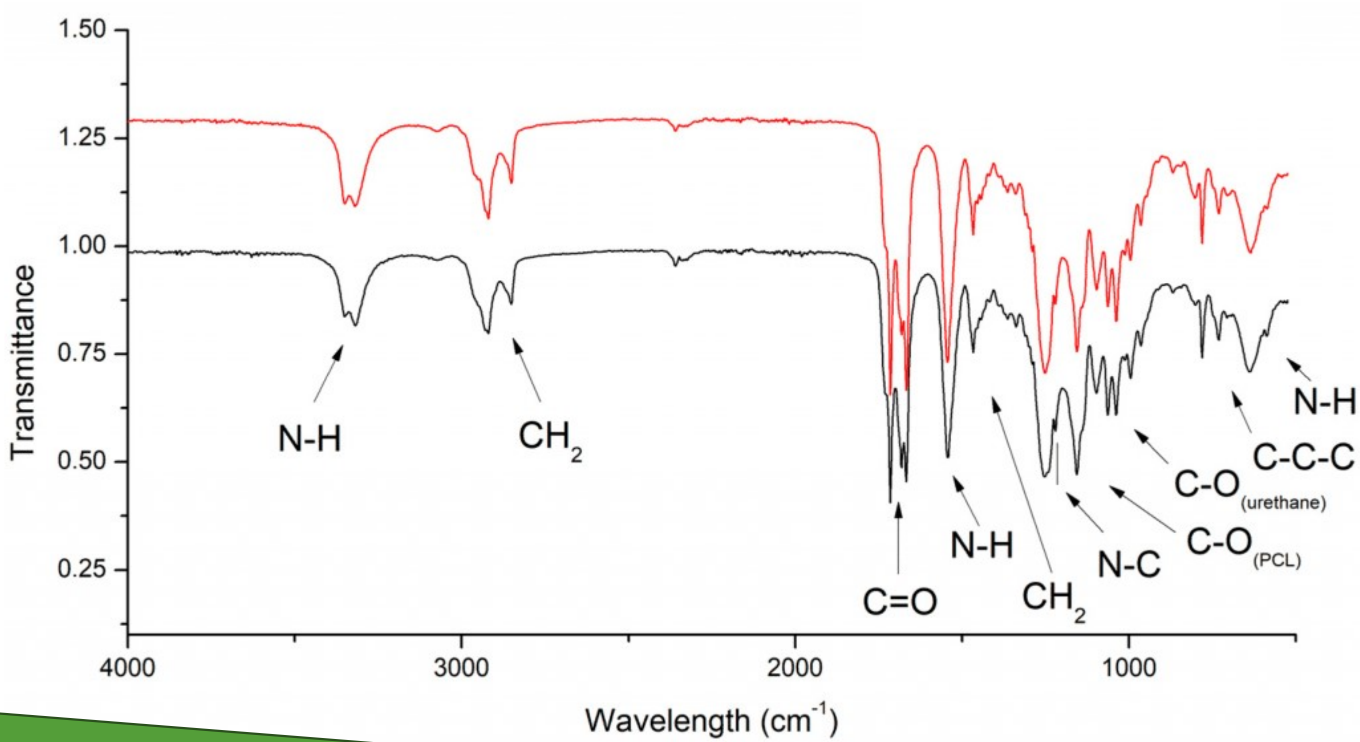
Sample	Actual TOP content (%)	C-14 testing results (%)
B2	5	5.1
B3	9.5	9.7
A60	25	20.8
A61	11	9.3
Ent. 1	8	7.2



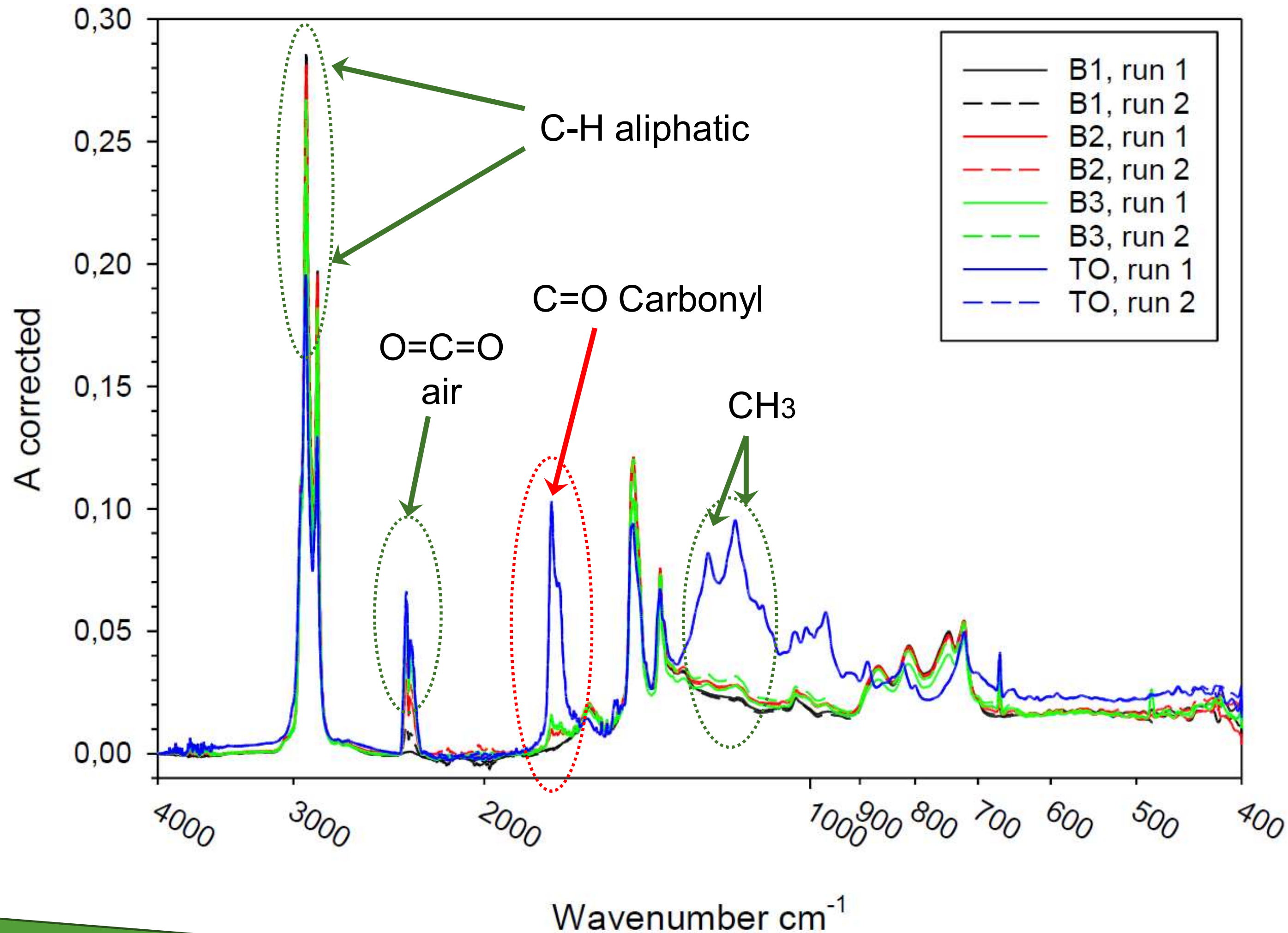
- The amount of C-14 present in a sample helps confirm the percentage of bio-oil in the bitumen by identifying how much of the carbon comes from recent biological sources

Fourier transform infrared spectroscopy (FTIR)

A technique used to analyze the molecular composition of materials by measuring how they absorb infrared light. When infrared light passes through a sample, the molecules in the sample vibrate at specific frequencies depending on their chemical bonds. FTIR captures these vibrations, producing a spectrum that provides a ‘fingerprint’ of the material’s molecular structure.



FTIR – testing results (1st round)



Sample	Content
B1	Neat bitumen
B2	5% TOP
B3	9.5% TOP
TO(P)	TOP

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FTIR – testing results (1st round)

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Determining TOP content

TOP absorbance

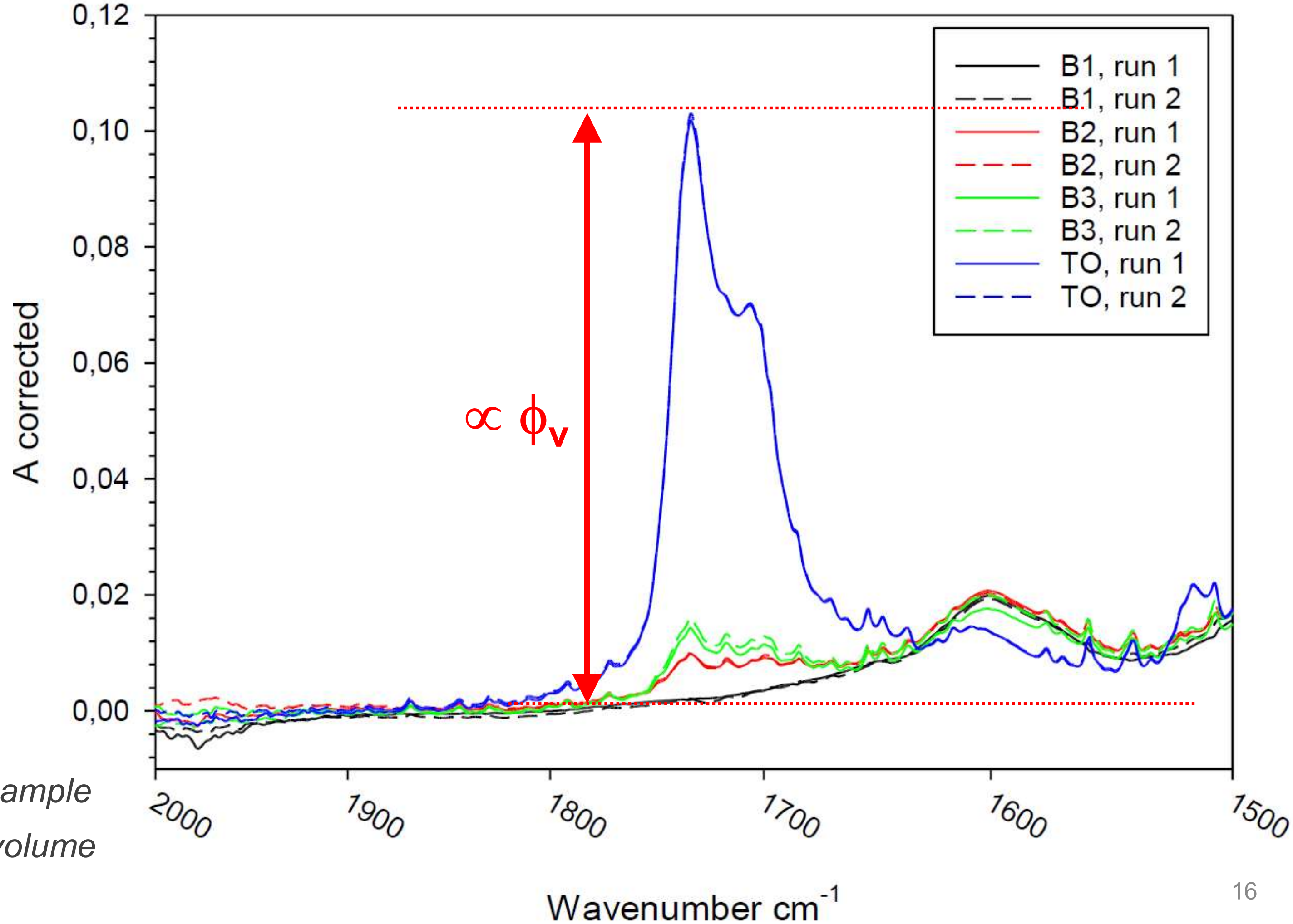
$$\phi_V = \frac{A_X - A_{B1}}{A_{TO} - A_{B1}}$$

Mass fraction

$$\phi_m = \frac{\phi_V \cdot d_{TO}}{\phi_V \cdot (d_{TO} - d_B) + d_B}$$

A_X: Absorbance of analyzed sample

Absorbance is proportional to volume concentrration



FTIR – testing results (1st round)

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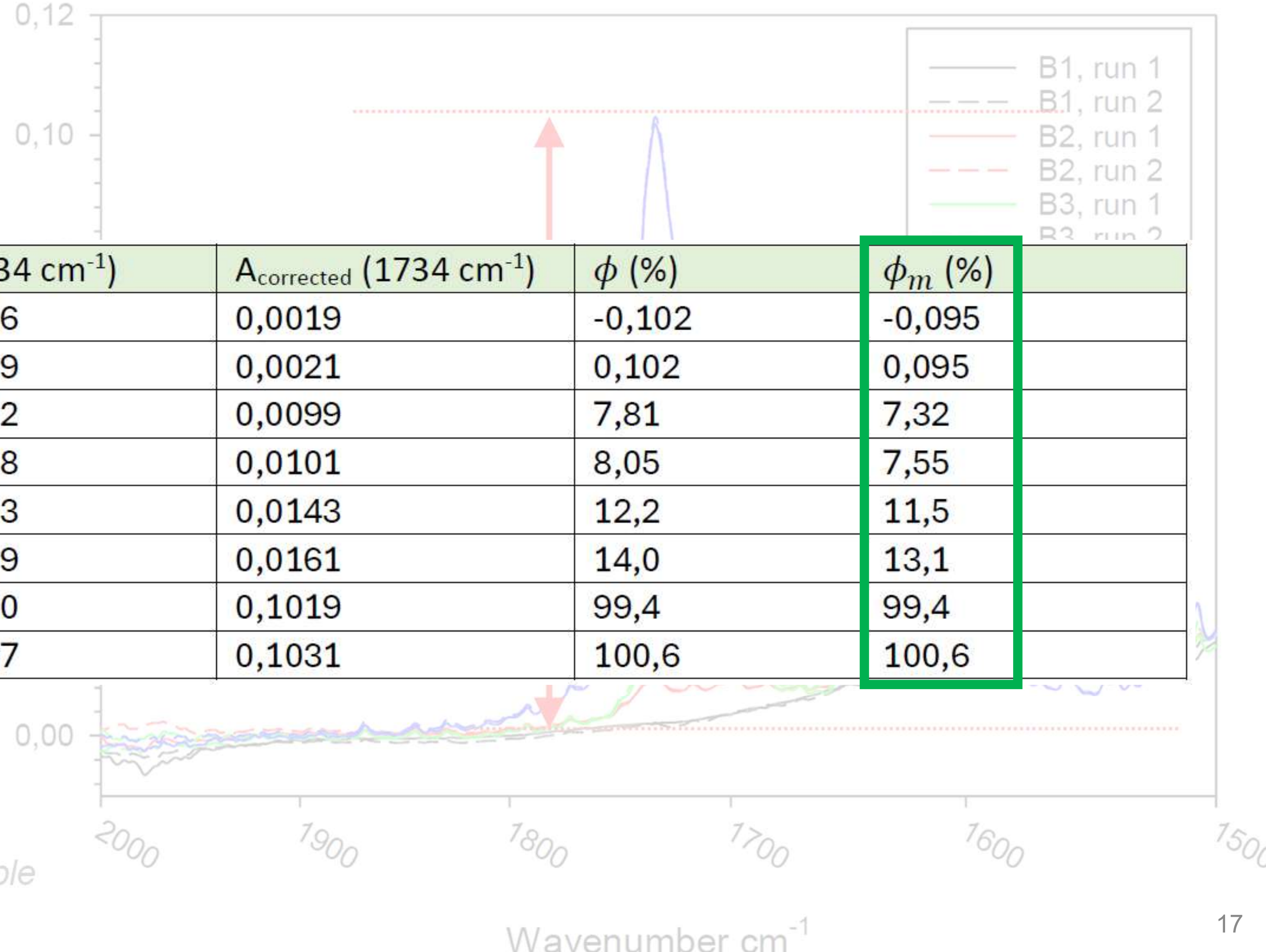
Determining TOP content



Sample	A (1734 cm^{-1})	$A_{corrected}$ (1734 cm^{-1})	ϕ (%)	ϕ_m (%)
B1 run 1	0,0046	0,0019	-0,102	-0,095
B1 run 2	0,0069	0,0021	0,102	0,095
B2 run 1	0,0122	0,0099	7,81	7,32
B2 run 2	0,0128	0,0101	8,05	7,55
B3 run 1	0,0183	0,0143	12,2	11,5
B3 run 2	0,0199	0,0161	14,0	13,1
TO run 1	0,1060	0,1019	99,4	99,4
TO run 2	0,1067	0,1031	100,6	100,6

TOP

ϕ_V =

Mass

$$\phi_m = \phi_V \cdot (d_{TO} - d_B) + d_B$$

A_X: *Absorbance of analyzed sample*

FTIR – testing results (2nd round)

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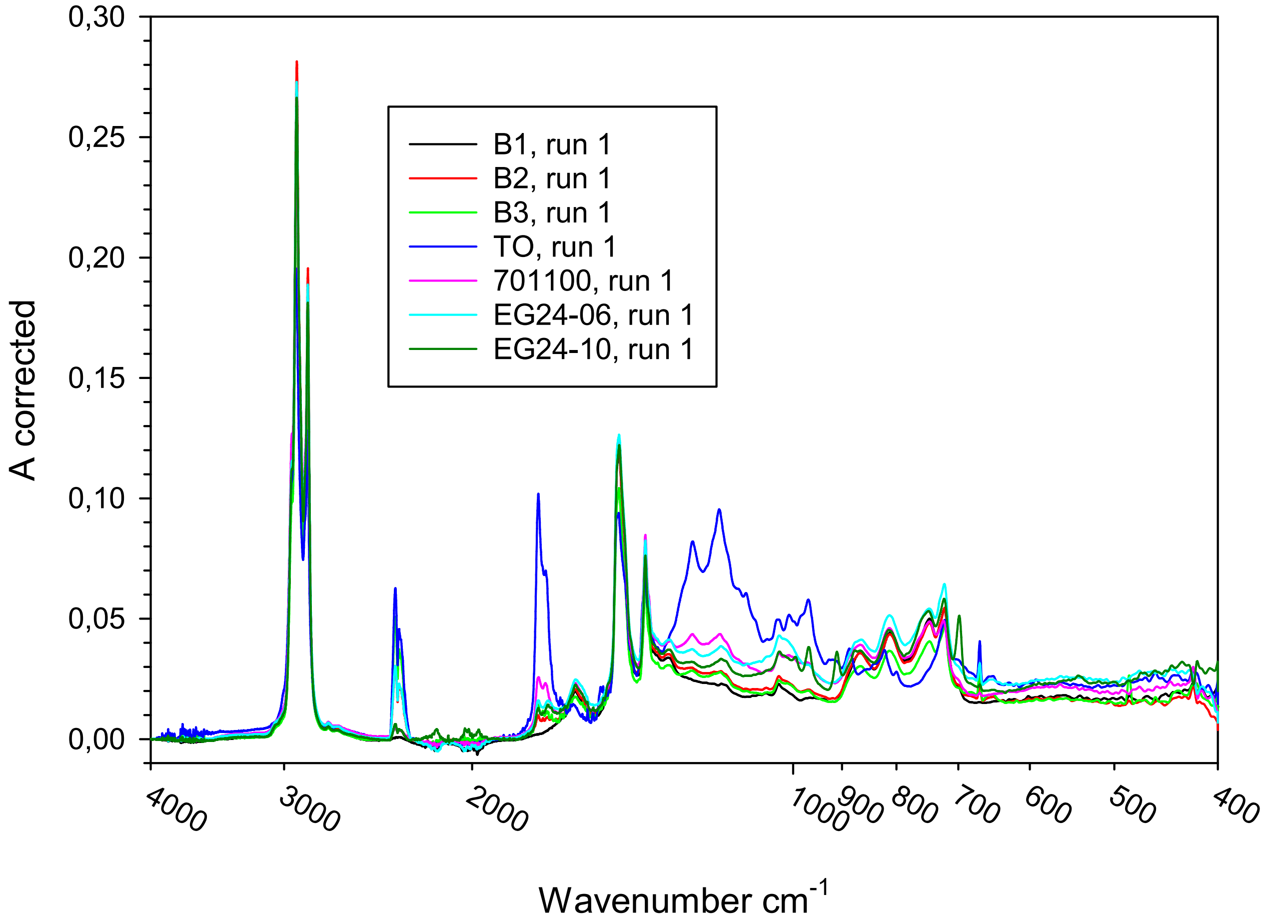
Same samples (after 3 months) + 3 new samples

Sample	Content
B1	Neat bitumen
B2	5% TOP
B3	9.5% TOP
EG24-06	8%
EG24-10	?
70/100	17.5%
TO(P)	TOP



FTIR – testing results (2nd round)

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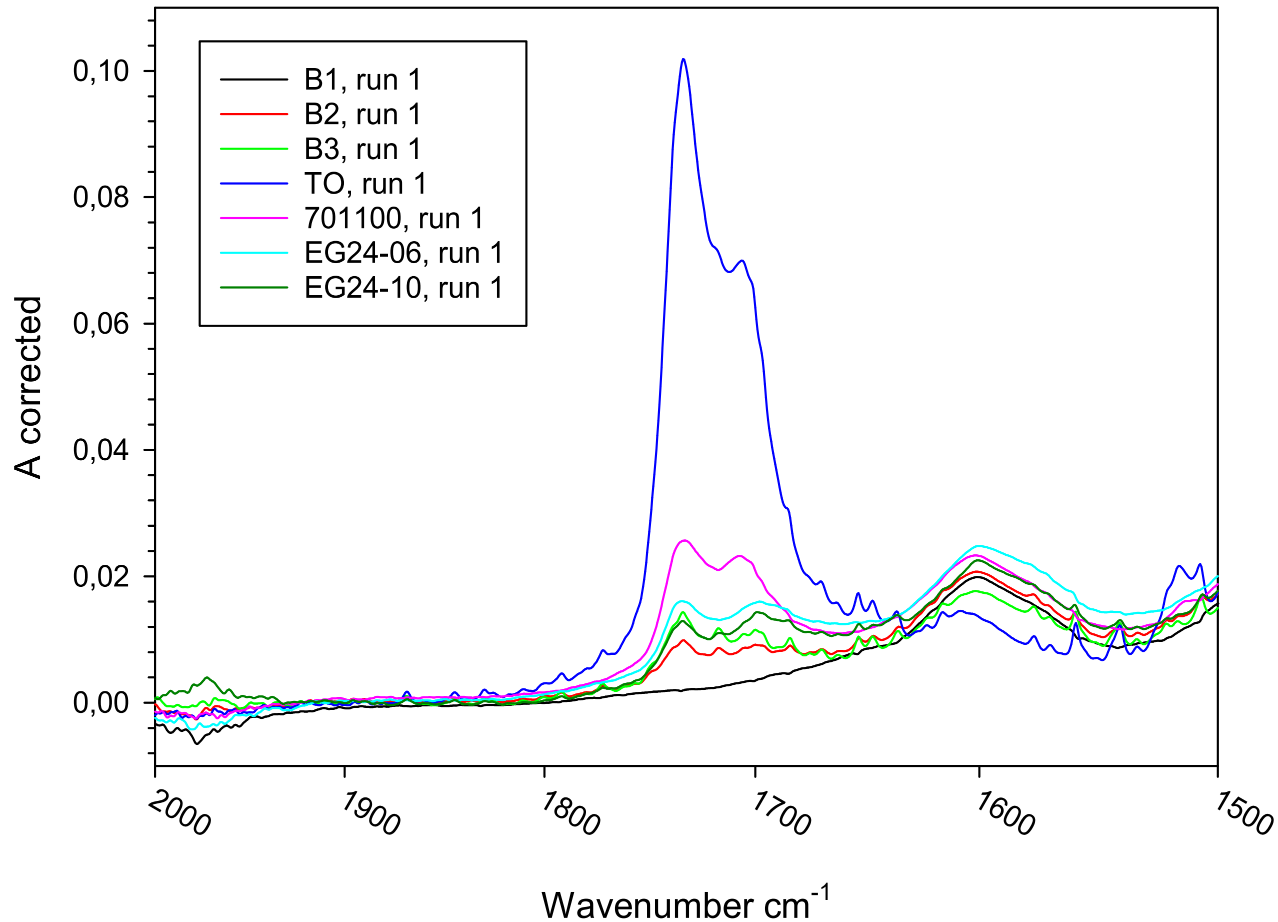
Sample	Content	Results
B1	Neat bitumen	
B2	5% TOP	9%
B3	9.5% TOP	15.6%
EG24-06	8%	13.5%
EG24-10	?	5.5%
70/100	17.5%	21.9%
TO(P)	TOP	TOP



FTIR – testing results (1st and 2nd round)

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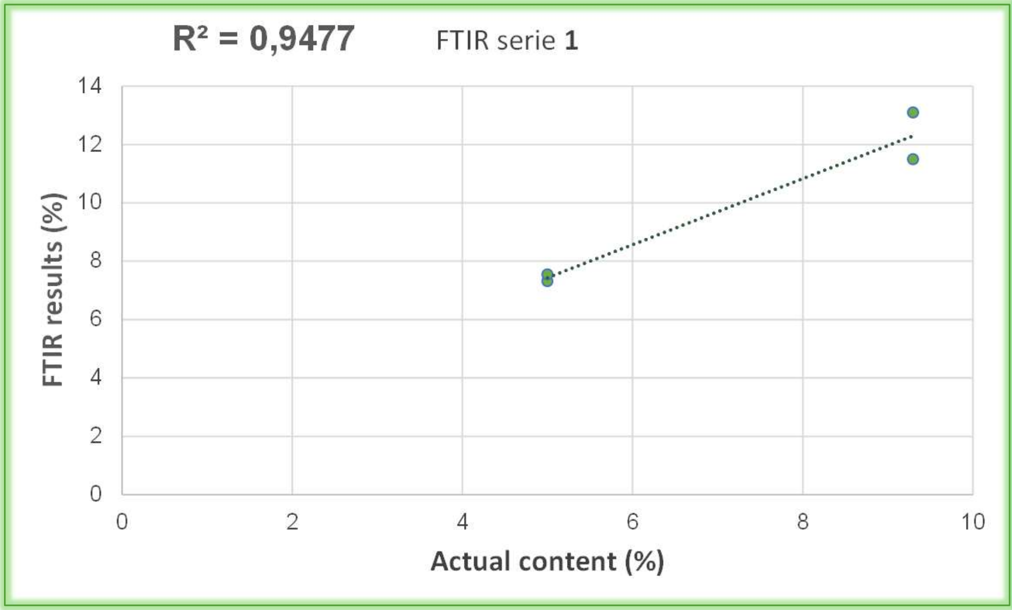

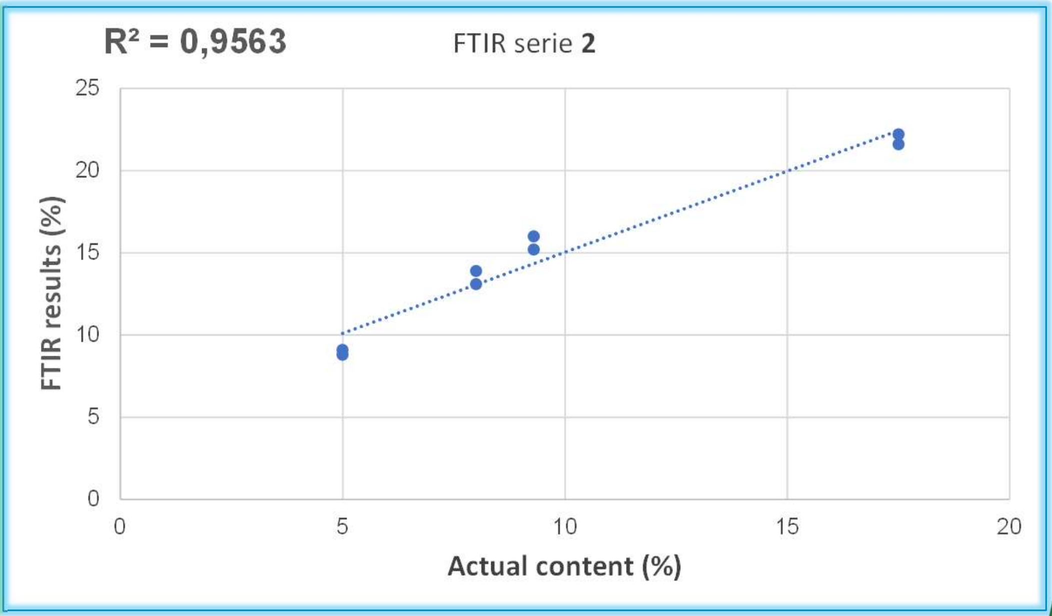

FTIR – testing results (1st and 2nd round)

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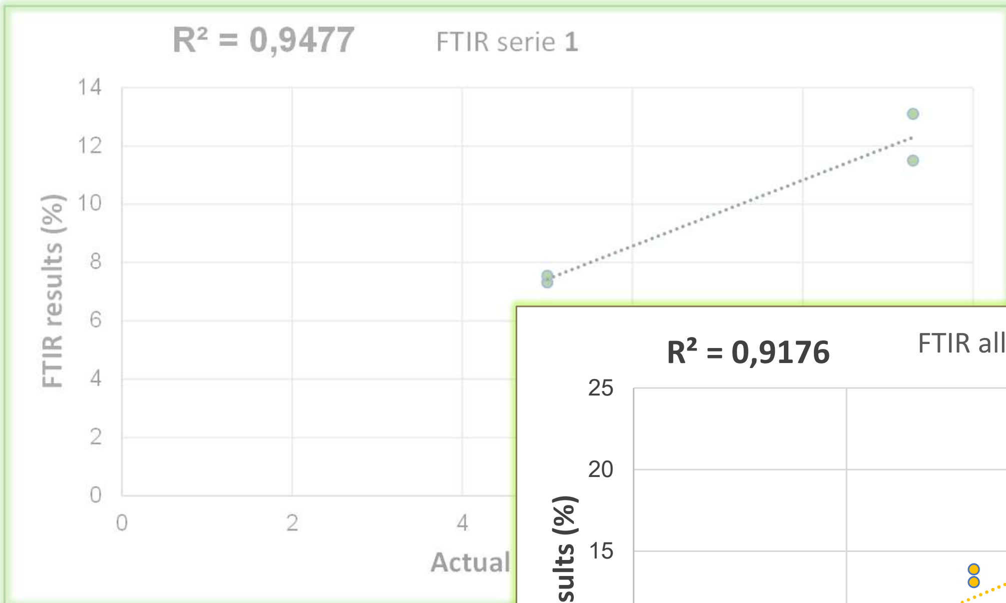

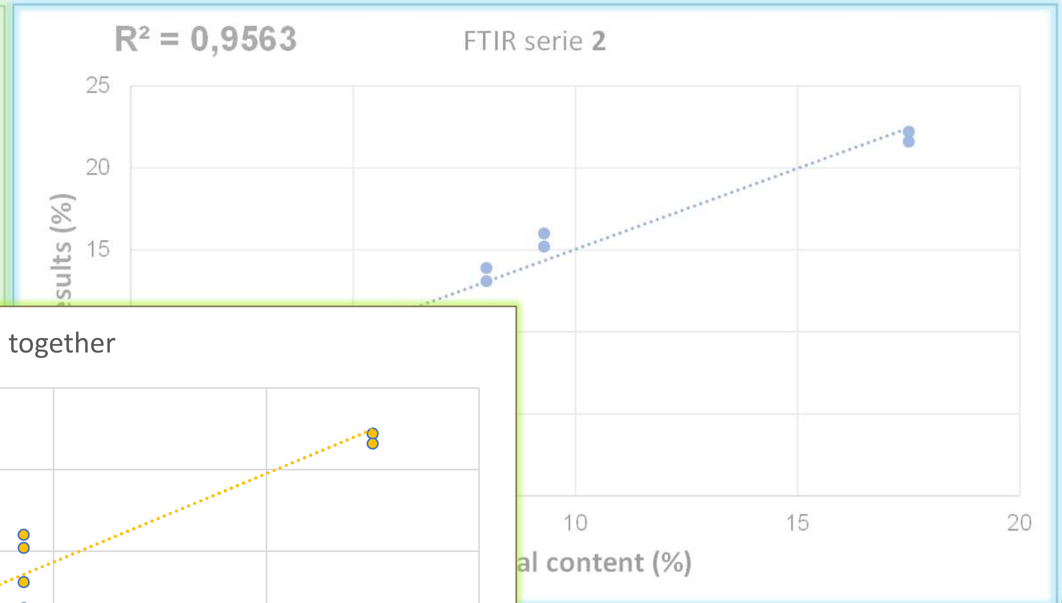

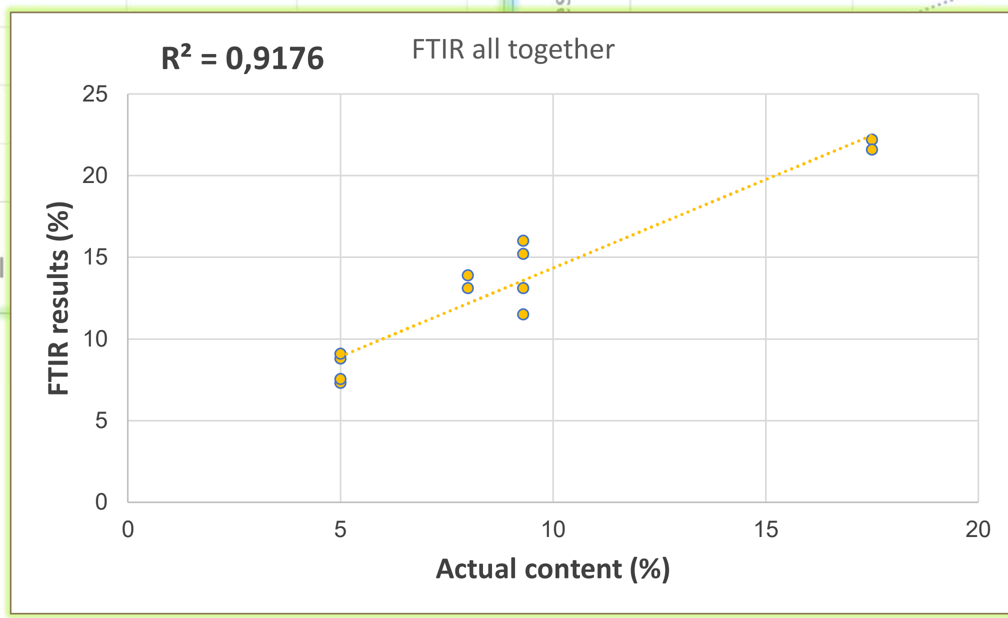

Ageing (time) has a significant impact on fatty acid content and therefore on the results

Calibration should be done everytime before testing

Conclusions

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Reducing emissions while maintaining or enhancing quality is a top priority for NPRA. As a result, the introduction of new materials into the asphalt industry requires further research, robust quality assurance systems, and potentially new regulations.

Bio-binders are gaining significant traction due to their potential to lower CO2 emissions and conserve raw materials. A systematic evaluation of these materials is essential to ensure their performance and sustainability.

Tests such as **FTIR** and **C-14 dating** have shown promise in identifying and quantifying bio-additives. FTIR, in particular, offers valuable insights into the chemical composition of these materials, but more research is needed to fully explore its potential.

The impact of **ageing** on the chemical properties of bio-based binders requires further investigation to ensure long-term performance.

Recycling bio-based binders after several years presents challenges, particularly when it comes to blending with new additives. More research is needed to address these challenges effectively.

Recommendations / Future work

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Develop guidelines for bio-binders: As bio-based binders gain prominence, it would be beneficial to develop specific guidelines and testing protocols to ensure they meet performance standards, particularly regarding long-term durability and environmental impact.

Establish collaboration between industry and research institutions: Collaboration will be key to accelerating innovation. By working closely with universities and research centers, we can further explore advanced testing methods, such as FTIR and C-14, and improve their accuracy and application.

Pilot projects for real-world testing: Implement more pilot projects using bio-binders in various road conditions and climates. This will provide valuable data on performance, recyclability, and any unforeseen challenges during practical use.

Consider life-cycle assessments: To fully understand the environmental benefits of bio-binders, conduct comprehensive life-cycle assessments that measure their impact from production to disposal or recycling. This will provide clear data on their potential to reduce CO2 emissions.


THANK YOU
Measuring bio-oil content and understanding chemical interactions in bio-bitumen

Nuclear Magnetic Resonance (NMR)

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- A technique is used to analyze the molecular structure of a sample by detecting hydrogen atoms (protons) in a compound.
- It works by applying a magnetic field to the sample, causing the hydrogen nuclei to resonate at specific frequencies depending on their chemical environment.
- These resonances provide information about the number of hydrogen atoms in different environments and their bonding structure within the compound
- NMR helps identify and quantify the specific hydrogen atoms from bio-oil components, allowing us to determine the percentage of bio-oil in the bitumen mixture

- The experiments were conducted using a 400 MHz NMR (400neo) from Bruker at the NMR Laboratory, NTNU.
- Samples were preheated at 100°C to ensure proper conditions for testing.~0.2 g of sample was diluted in 1 mL of deuterated chloroform ($CDCl_3$) and left to mix overnight.
- Each solution was inspected under an optical microscope to confirm complete solubilization.
- Samples were placed in 5 mm NMR tubes before undergoing NMR analysis for further characterization.

Nuclear Magnetic Resonance (NMR)

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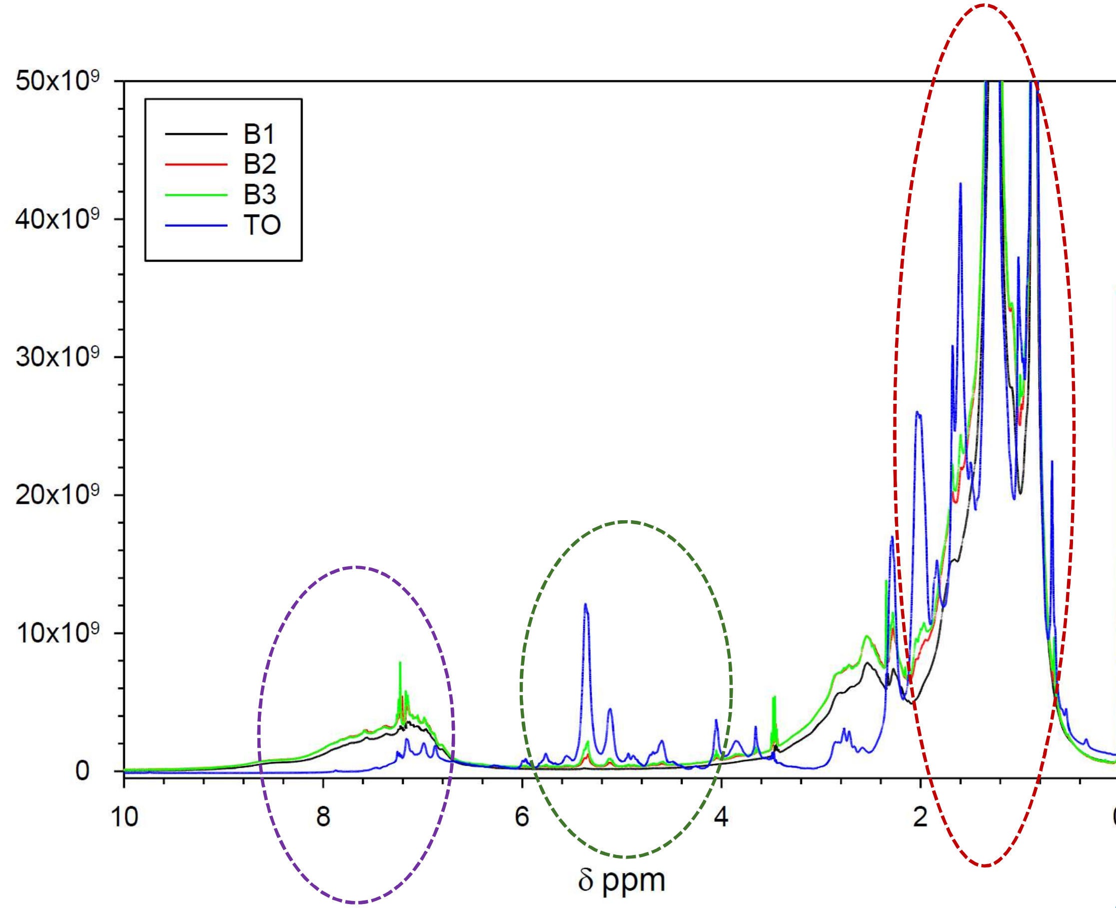
Aliphatic hydrogens with chemicals shift comprised between ca. 0.5-2 ppm.

Hydrogens in β of electronegative atoms with chemicals shifts comprised between ca. 4-6 ppm

Aromatic hydrogens with chemicals shift comprised between ca. 7-9 ppm

In order to be able to quantify the concentration of tall oil in bitumen, regions where only tall oil or bitumen resonate must be identified.



Nuclear Magnetic Resonance (NMR)

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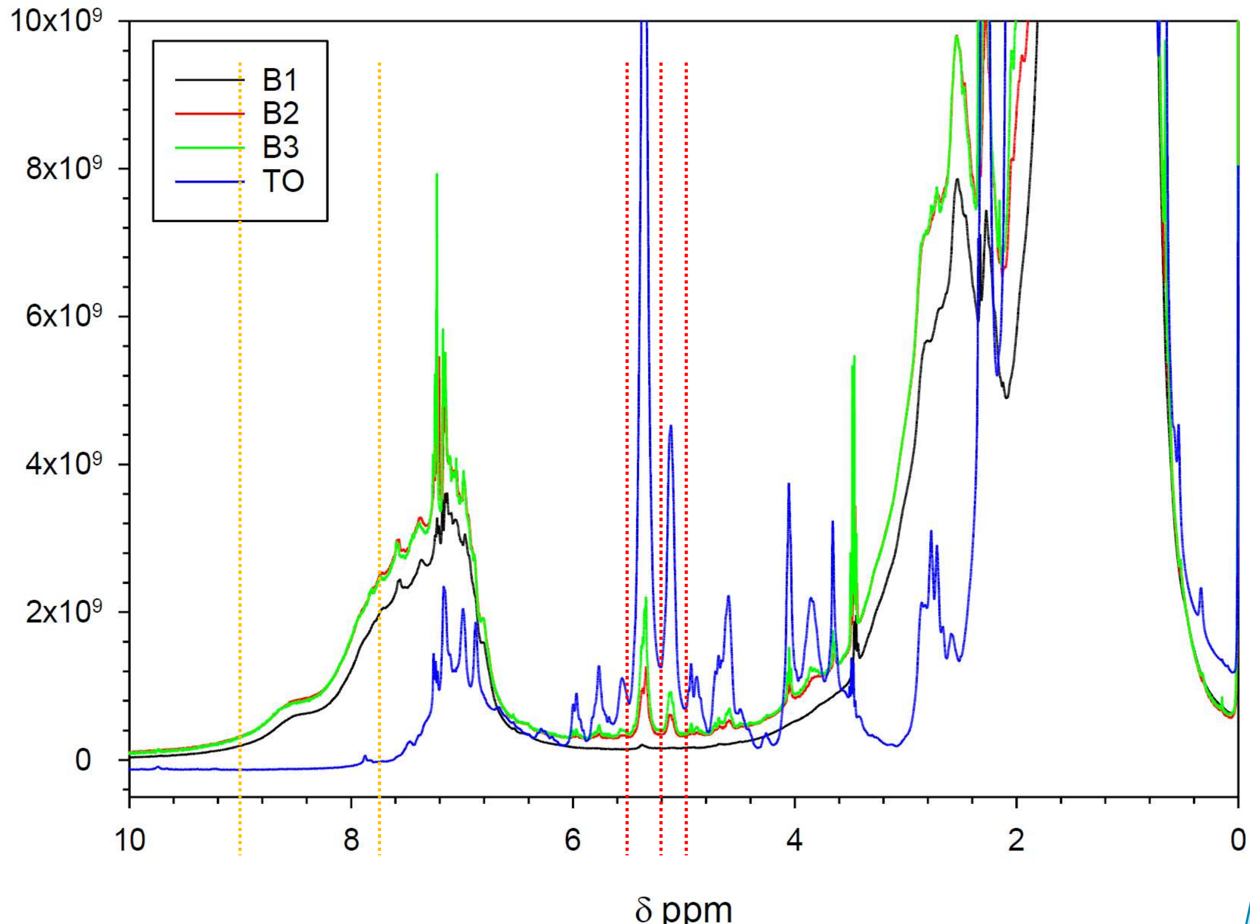
The signal in these two regions will allow to quantify the content of tall oil in bitumen. However, a direct determination of the mass fraction of tall oil in bitumen is not possible, since the signal in NMR is proportional to proton density.

Consequently, the quantification of the signal in the two regions would only allow to determine the mass fraction of tall oil in bitumen after calibration with samples of known tall oil mass fractions.

$$SR_{5.2-5.49} = \frac{A_{5.2-5.49\_corr}}{A_{7.8-9}}$$

$$SR_{5.0-5.2} = \frac{A_{5.0-5.2\_corr}}{A_{7.8-9}}$$



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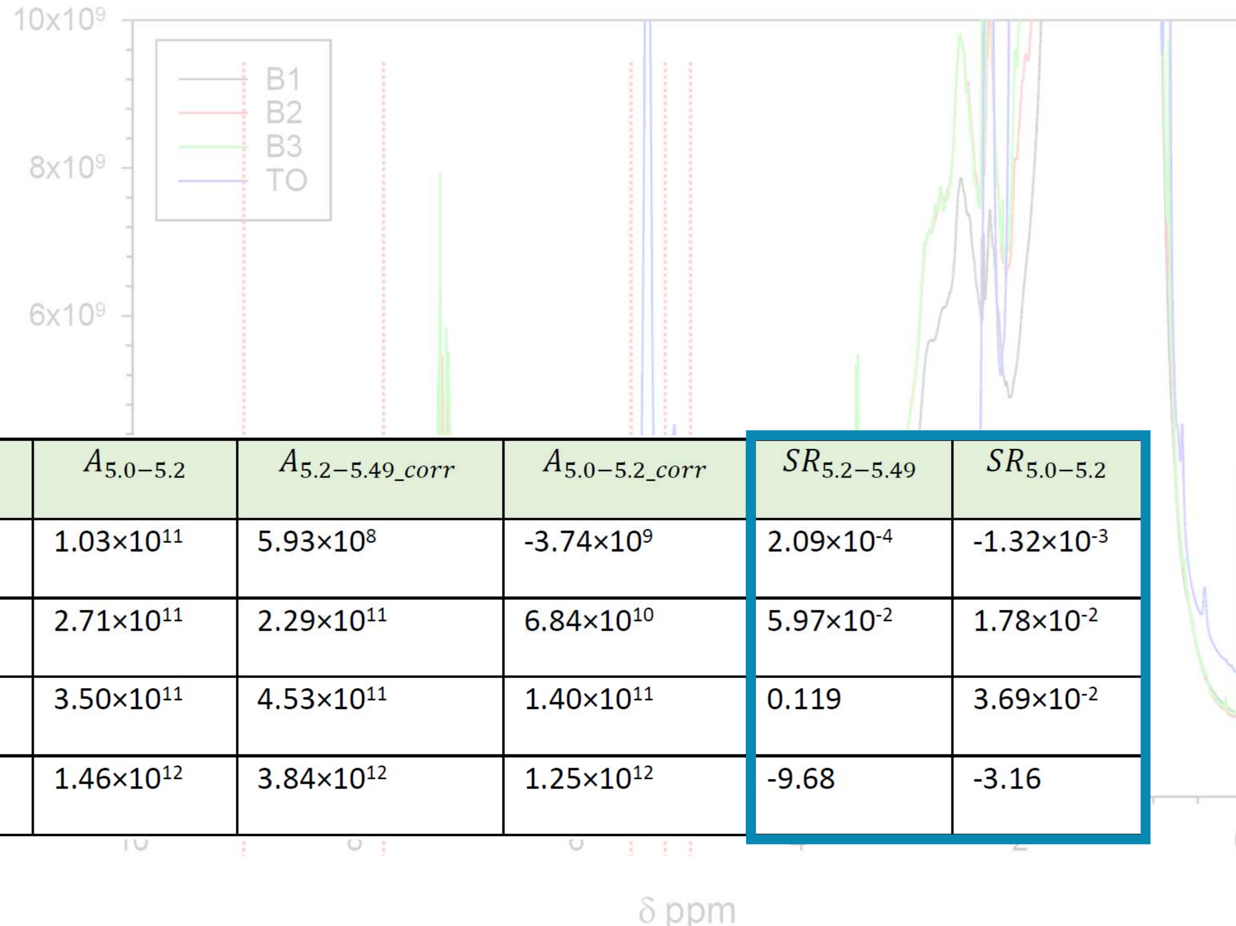

Sample	$A_{7.8-9}$	$A_{5.2-5.49}$	$A_{5.0-5.2}$	$A_{5.2-5.49\_corr}$	$A_{5.0-5.2\_corr}$	$SR_{5.2-5.49}$	$SR_{5.0-5.2}$
B1	2.83×10^{12}	1.55×10^{11}	1.03×10^{11}	5.93×10^{8}	-3.74×10^{9}	2.09×10^{-4}	-1.32×10^{-3}
B2	3.83×10^{12}	2.94×10^{11}	2.71×10^{11}	2.29×10^{11}	6.84×10^{10}	5.97×10^{-2}	1.78×10^{-2}
B3	3.80×10^{12}	3.04×10^{11}	3.50×10^{11}	4.53×10^{11}	1.40×10^{11}	0.119	3.69×10^{-2}
TO	-3.97×10^{11}	2.99×10^{11}	1.46×10^{12}	3.84×10^{12}	1.25×10^{12}	-9.68	-3.16

Nuclear Magnetic Resonance (NMR)

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- Using results from FTIR to build up calibration curve
- Linear (3 points…)
  - Results consistent with FTIR
- Simple method
  - More data treatment than FTIR