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FACULTY OF ENVIRONMENTAL ENGINEERING
ROAD RESEARCH INSTITUTE

Queen's University

Queen's Chemistry

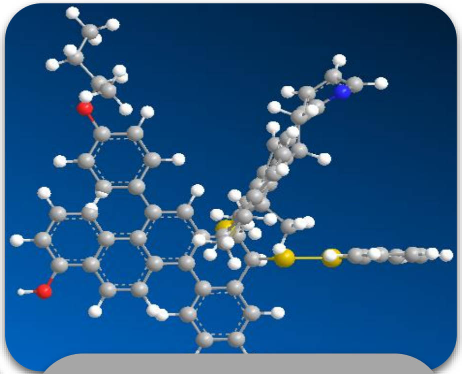
BITUMEN CONFERENCE

19th of February, 2015

Results of bitumen research in Lithuania and on-going study in Ontario (Canada)

Miglė Paliukaitė, PhD

OUTLINE



BACKGROUND

PROBLEM

RRI RESEARCH ACTIVITIES

BITUMEN RESEARCH

STUDY IN ONTARIO

CONCLUSIONS

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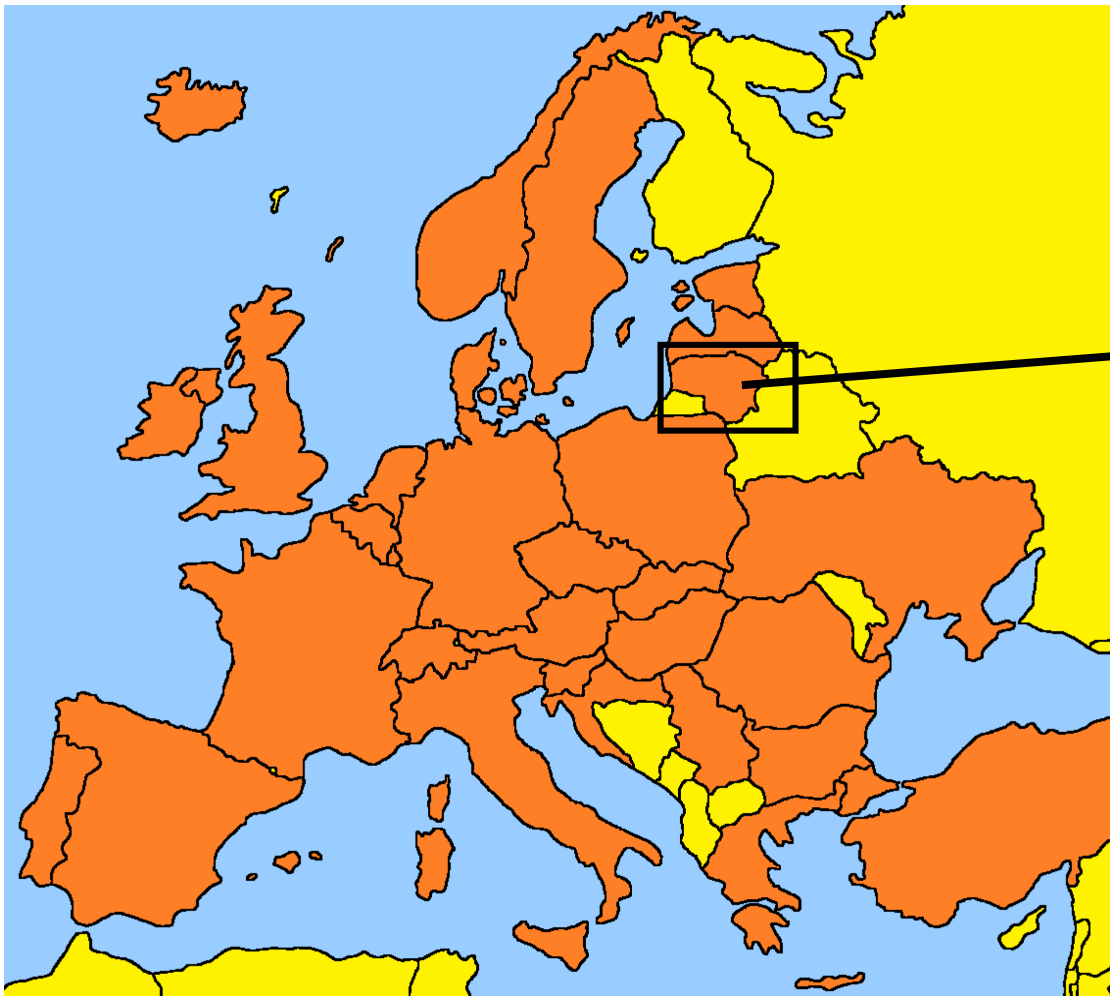
LITHUANIA



Area	65,300 km^2
Population	~2.944 million
Density	50.3/km^2

LITHUANIAN ROAD NETWORK

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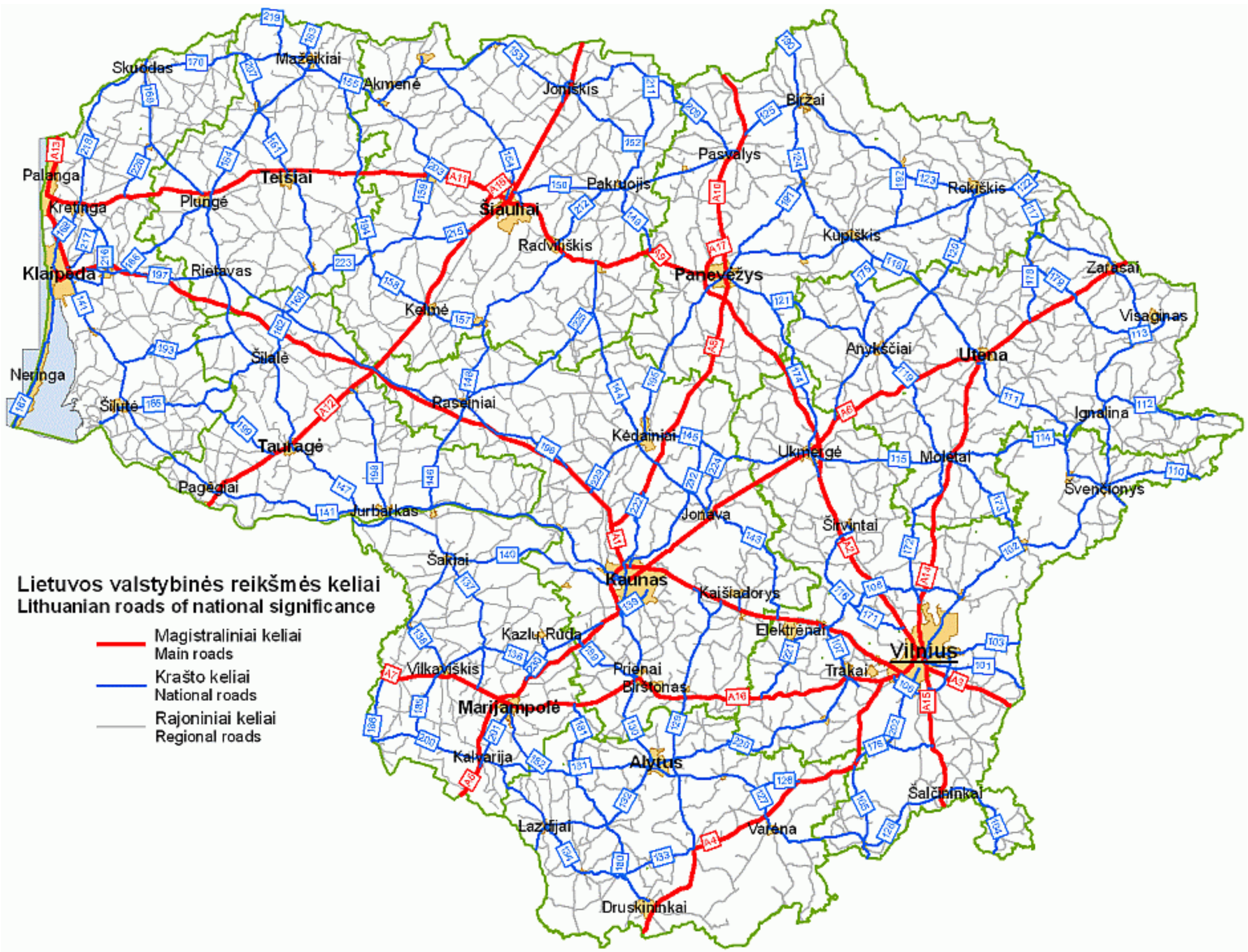
LITHUANIAN ROAD NETWORK



I TEN-T corridor
IX TEN-T corridor

Main roads: 1 745 km
National roads: 4 936 km
Regional roads: 14 573 km
Total: 21 254 km

328.4 km/1000 km^2
7.28 km/1000 inhab.

E category roads: 1499 km
Motorways: 309 km
Bridges: 54 km

Asphalt: 13 584 km
Concrete: 72 km
Gravel: 7 604 km

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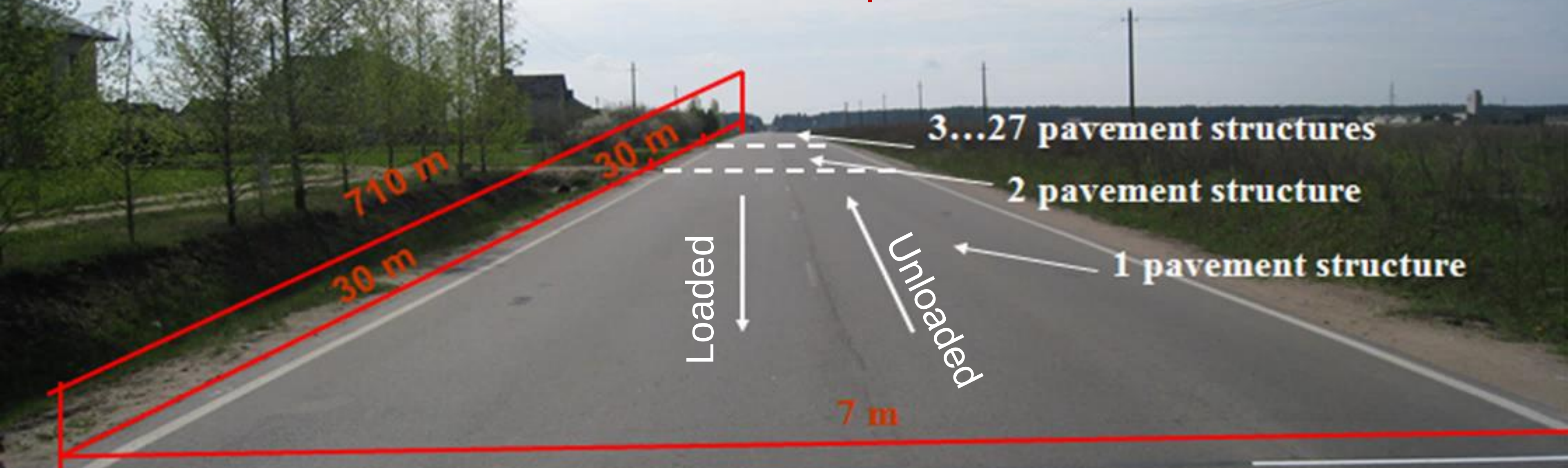
ABOUT ROAD RESEARCH INSTITUTE (RRI)

- Vilnius Gediminas Technical University (11 000 students; 940 employees)
- Department of Roads (established over 90 years ago)
- Road Research Laboratory established in 1999
- Road Research Institute founded in 2009
- Personnel of 35-40 people (incl. Laboratory), 5 PhDs, 7 PhD students
- Accredited Road Research Laboratory

Test Road – road of experimental pavement structures

- 27 short sections
- Same traffic loading conditions
- Same environmental conditions
- Different materials in same type pavement structures



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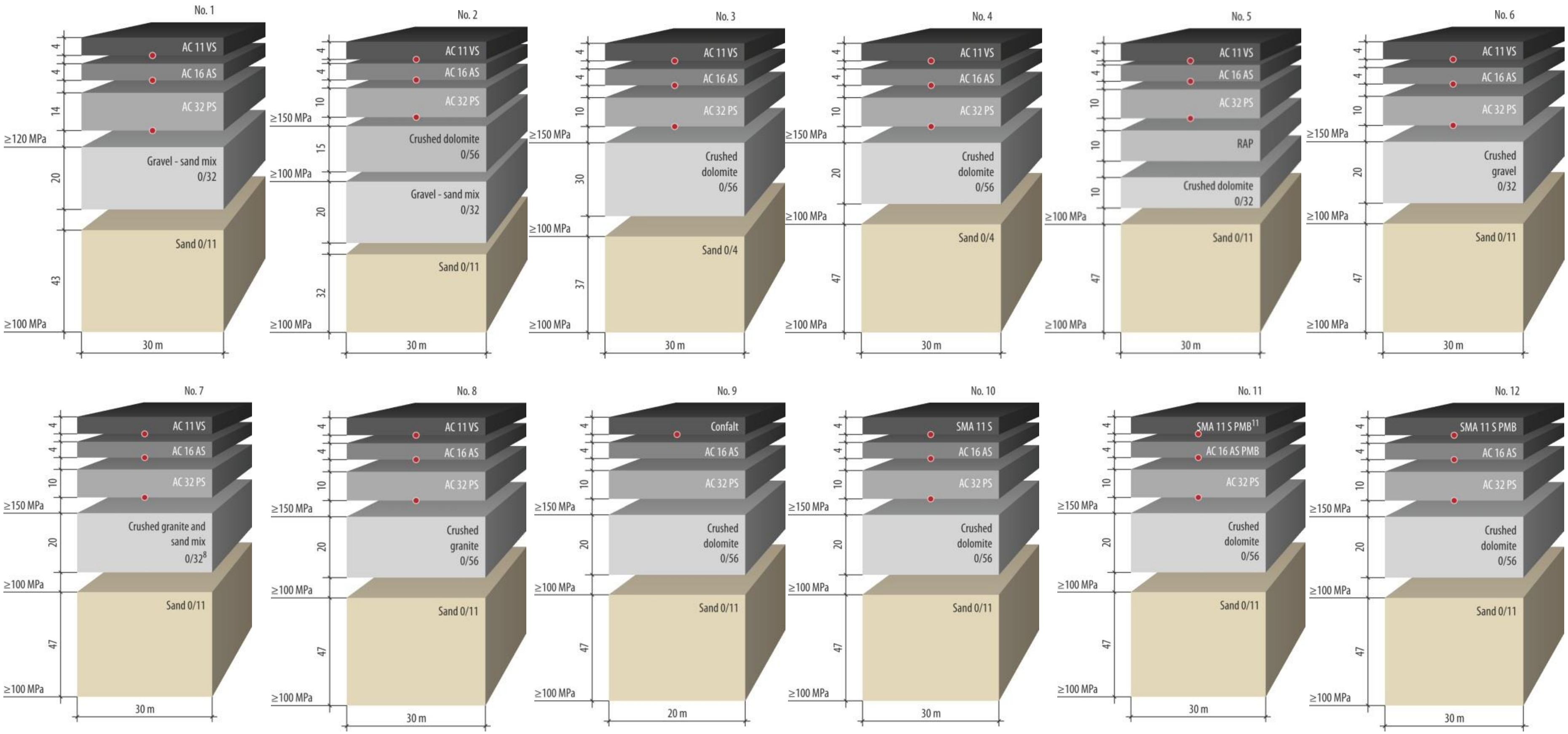
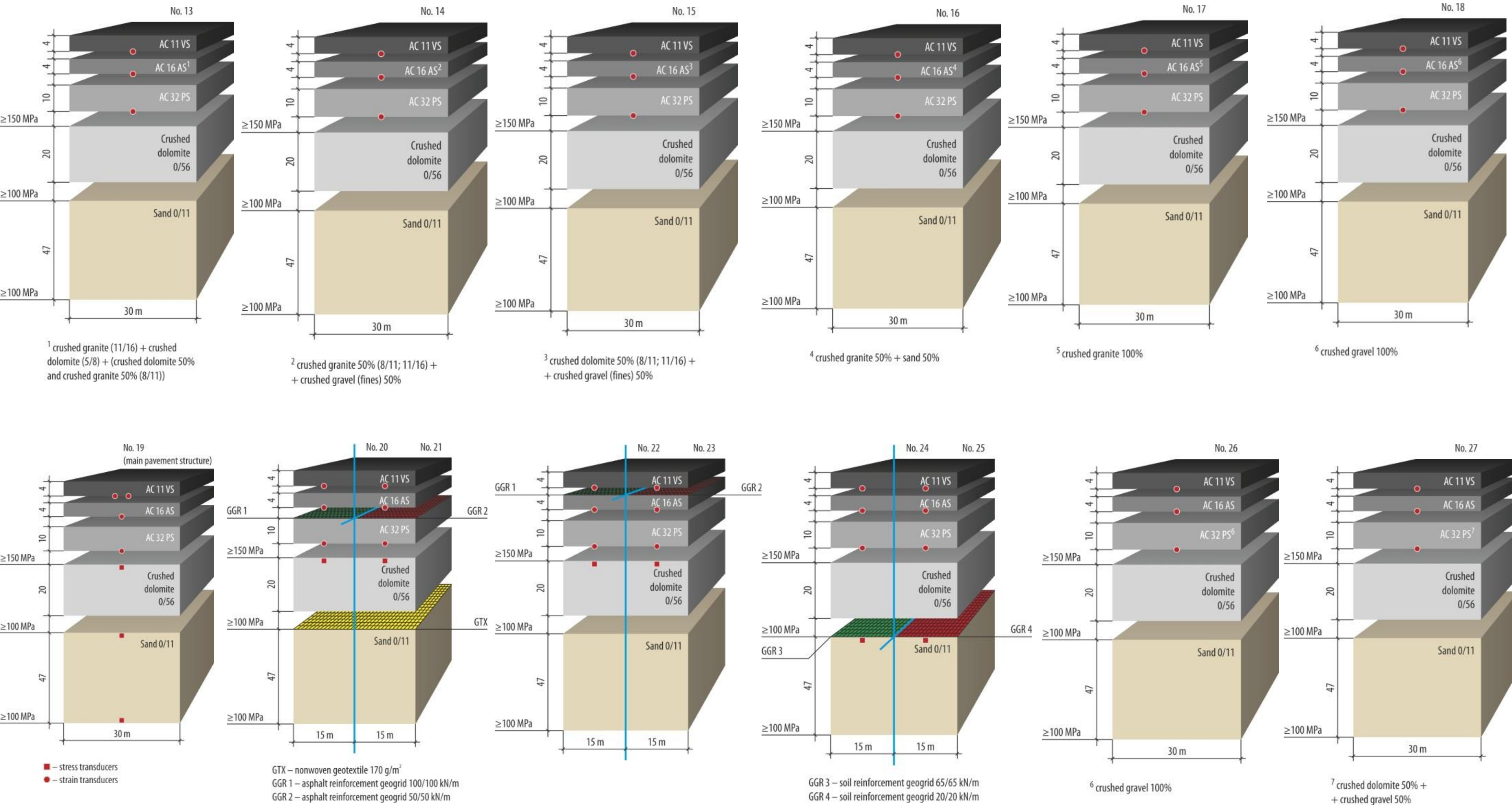
TEST ROAD – ROAD OF EXPERIMENTAL PAVEMENT STRUCTURES



[8] crushed granite 50% + sand and gravel mix 50%

[11] PMB – polymer modified bitumen

TEST ROAD – ROAD OF EXPERIMENTAL PAVEMENT STRUCTURES



ANNUAL MEASUREMENTS

- traffic flow
- temperature and moisture
- visual assessment of pavement distress
- performance with mobile laboratory RST-28
- pavement equivalent modulus with Falling Weight Deflectometer (FWD)
- pavement deflection with Benkelman Beam
- skid resistance in asphalt wearing layer with pendulum device

RRI RECENT PROJECTS

- Traffic safety evaluation and prediction
- Analysis of the effectiveness of traffic calming measures and assessment of vertical traffic calming measures impact on environment
- Traffic monitoring and weigh-in-motion system for Lithuanian road network
- Optimization of pavement surface characteristics
- Implementation of Mechanistic Empirical Pavement Structure Design in Lithuania

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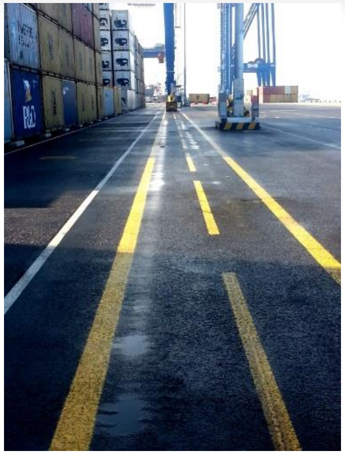
RRI RECENT PROJECTS

- Experimental research of soft asphalt and double Otta Seal at low volume roads
- Study of effective winter road maintenance
- Development of pavement structure resistant to static and impact loading

- BITUMEN RESEARCH



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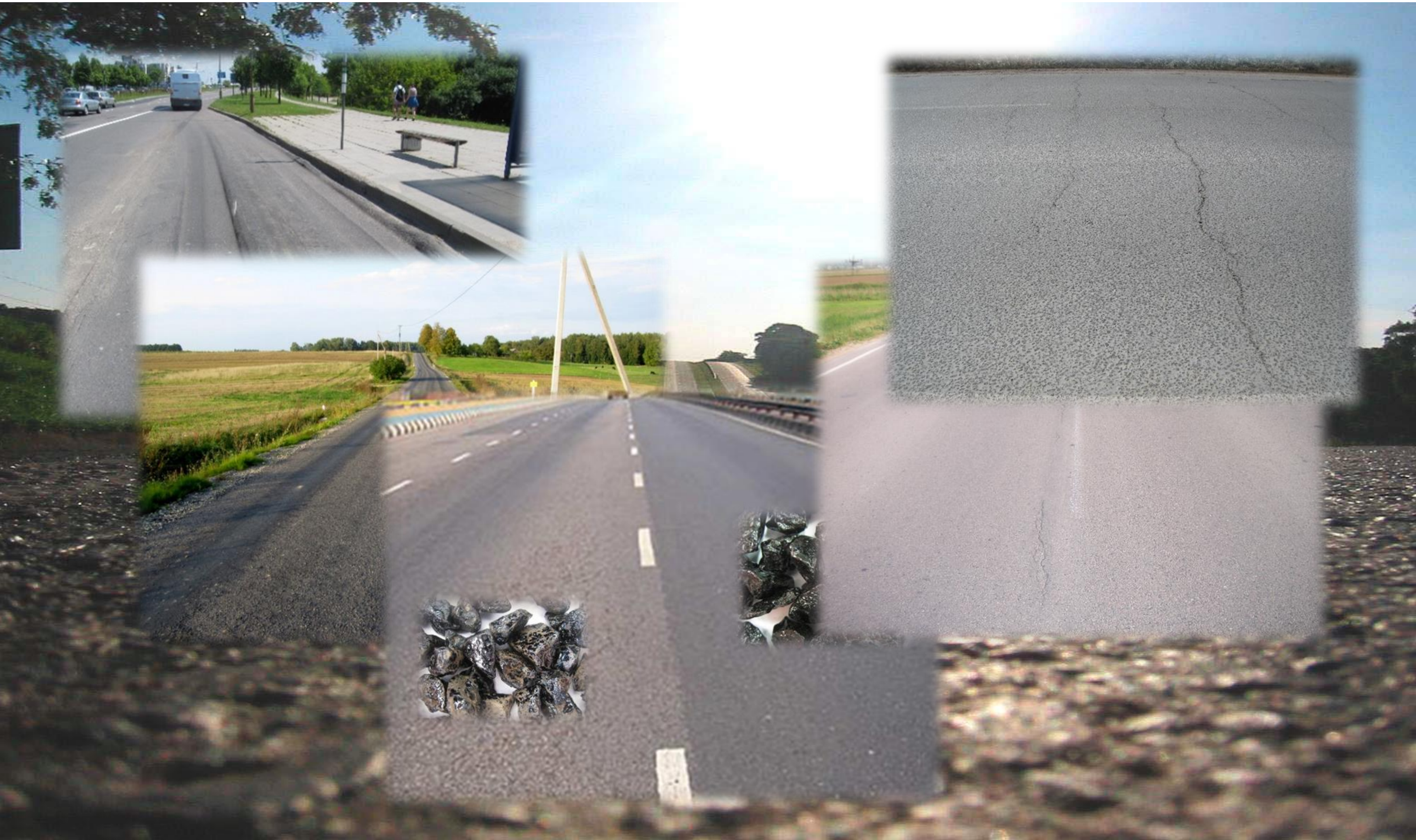
PROBLEM (1)



PROBLEM (2)

- bitumen is more liquid
- less sticky at a laying temperature
- reduced cohesion
- increased cracking during compaction
- reduced adhesion between bitumen and mineral aggregates
- changes in perceptible properties (odour, colour)

PROBLEM (3)

Light Medium Heavy

Bitumen refinery process

Bitumen

Chemical composition

Polar molecules → Molecular association

Nonpolar molecules → Molecular association

Molecular association → Physical properties

?

Chemical composition → Asphalt pavement performance

Physical properties → Asphalt pavement performance

Asphalt pavement performance

BITUMEN RESEARCH

- Bitumen chemical composition depends on the crude oil type and production technology
- Bitumen chemical composition influences asphalt pavement performance
- An effective test method for bitumen adhesion properties
- Bitumen performance during aging process

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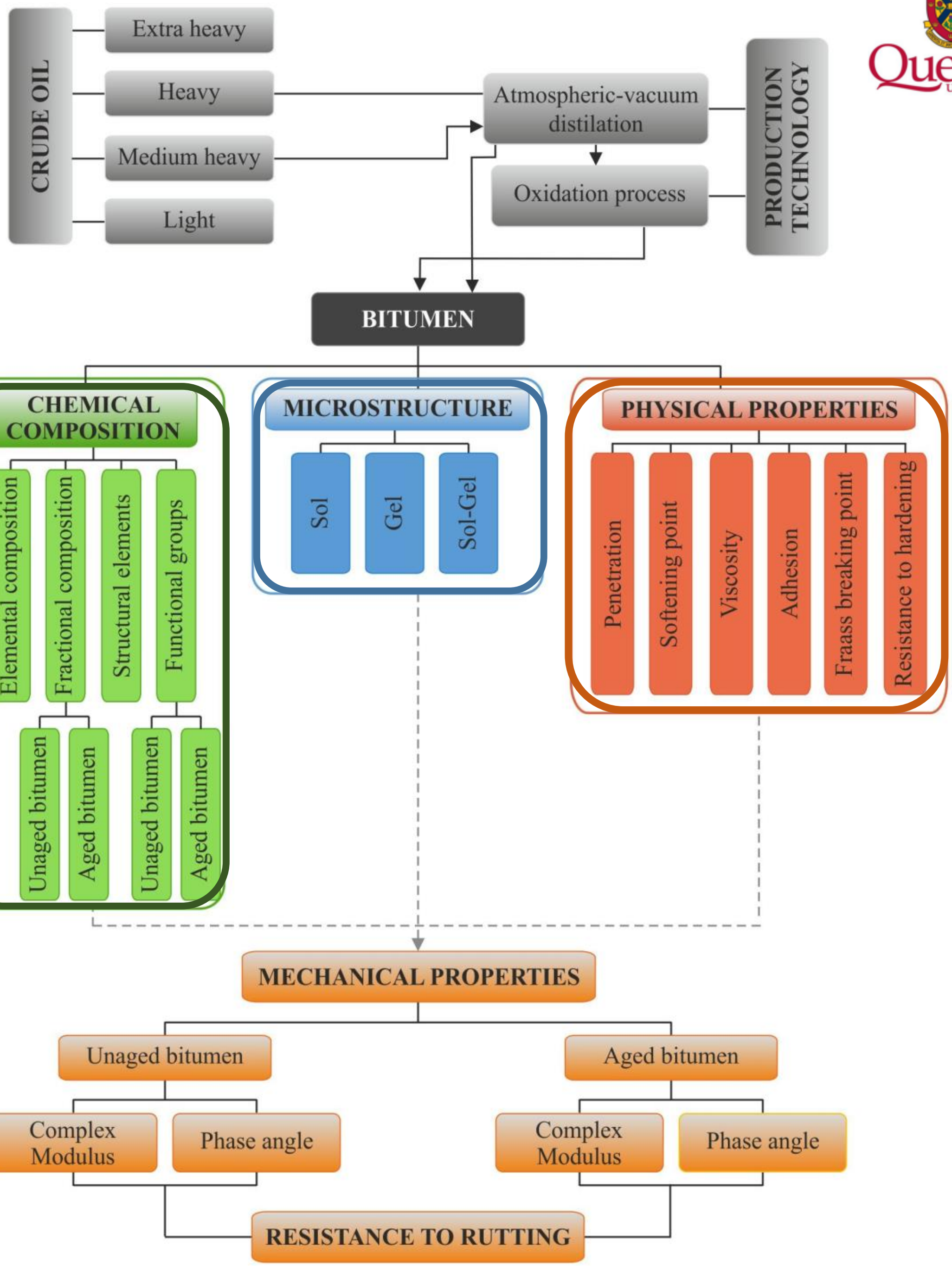
A SCHEME OF EXPERIMENTAL RESEARCH



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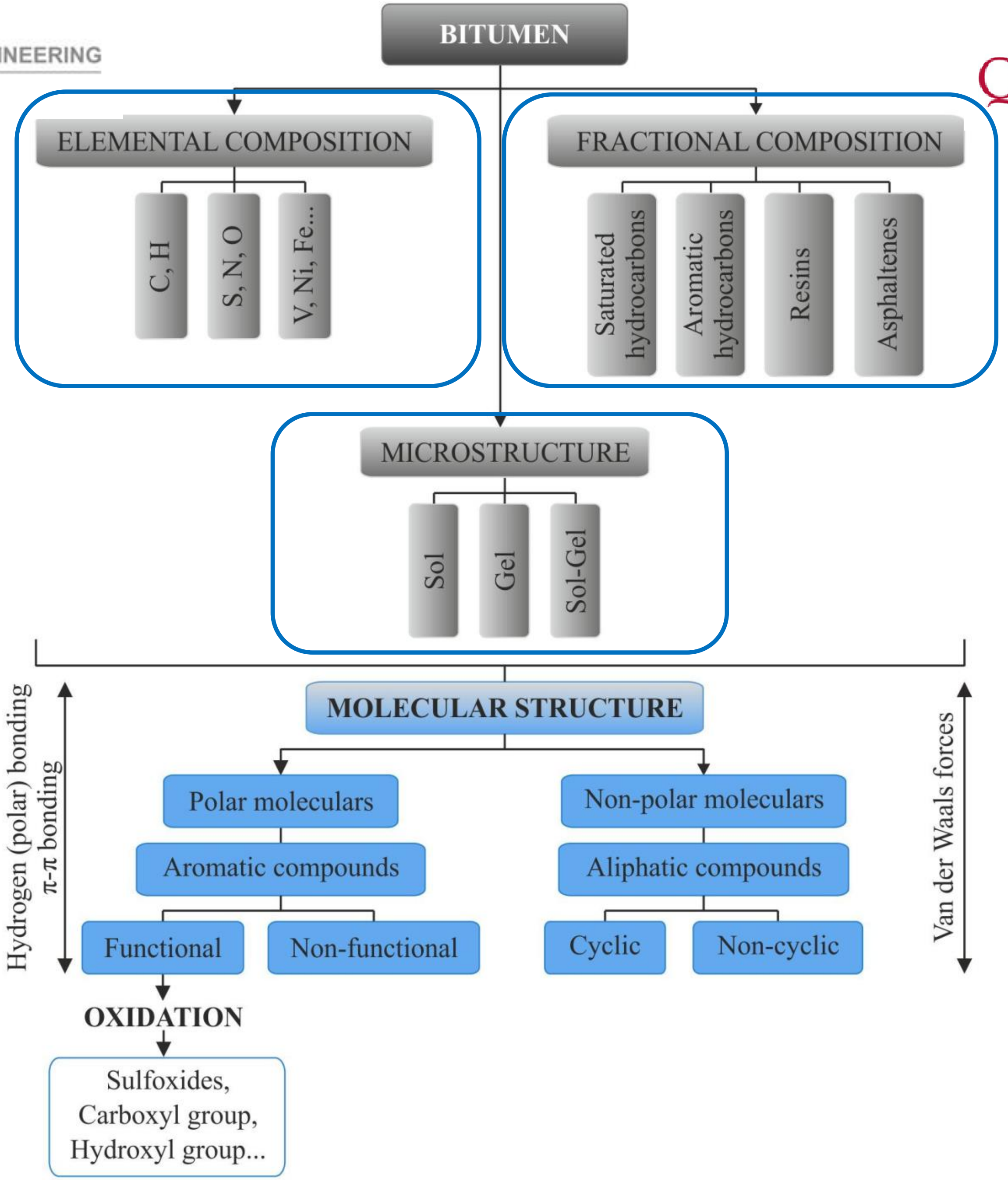
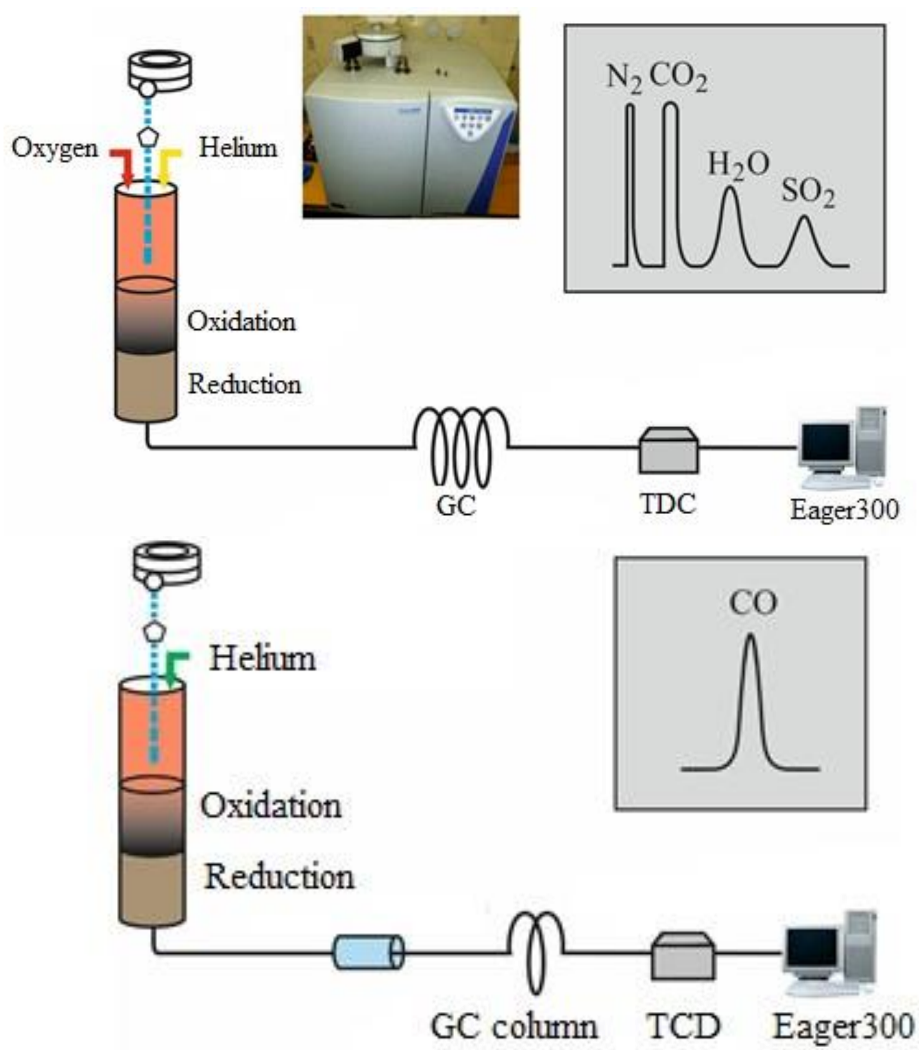
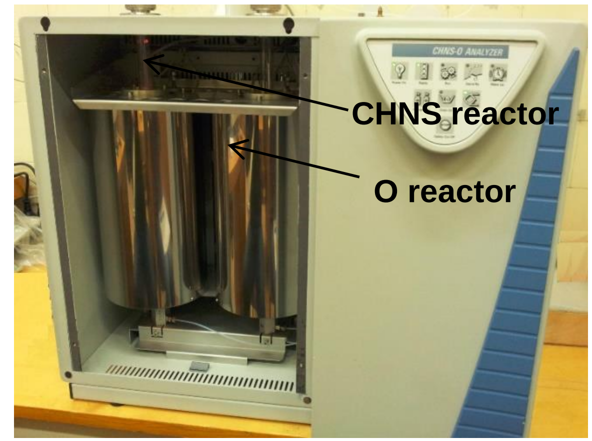
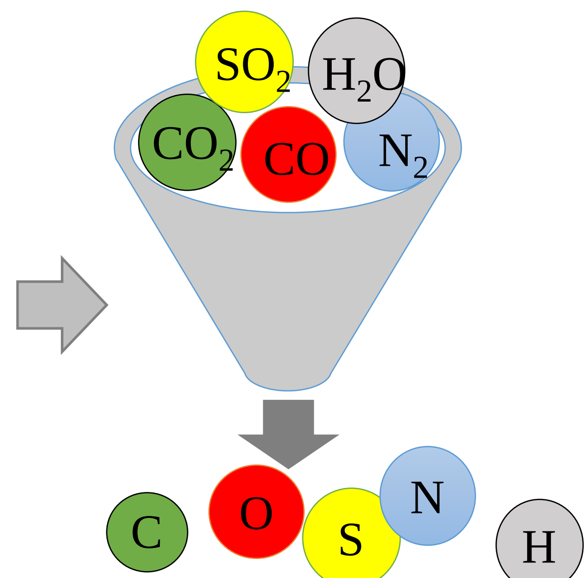
A BASIC SCHEME OF THE CONSTITUTION OF BITUMEN



BITUMEN ELEMENTAL COMPOSITION







RESULTS OF BITUMEN ELEMENTAL COMPOSITION

Producer	Bitumen	Elemental composition, %						C/H
		N	C	H	S	$O_{calcul.}$	$O_{determ.}$	
A	50/70	0,76	84,53	10,41	3,12	1,18	0,62	0,68
B	50/70	0,78	84,53	10,34	3,36	0,99	0,99	0,68
C	50/70	0,79	84,20	10,09	4,01	0,90	0,80	0,70
D	50/70	0,79	84,49	10,13	3,44	1,15	0,92	0,70
E	50/70	0,72	84,32	10,36	3,75	0,84	0,93	0,68
E (PMB)	PMB 45/80-55	0,68	84,58	10,45	3,26	1,03	0,93	0,67

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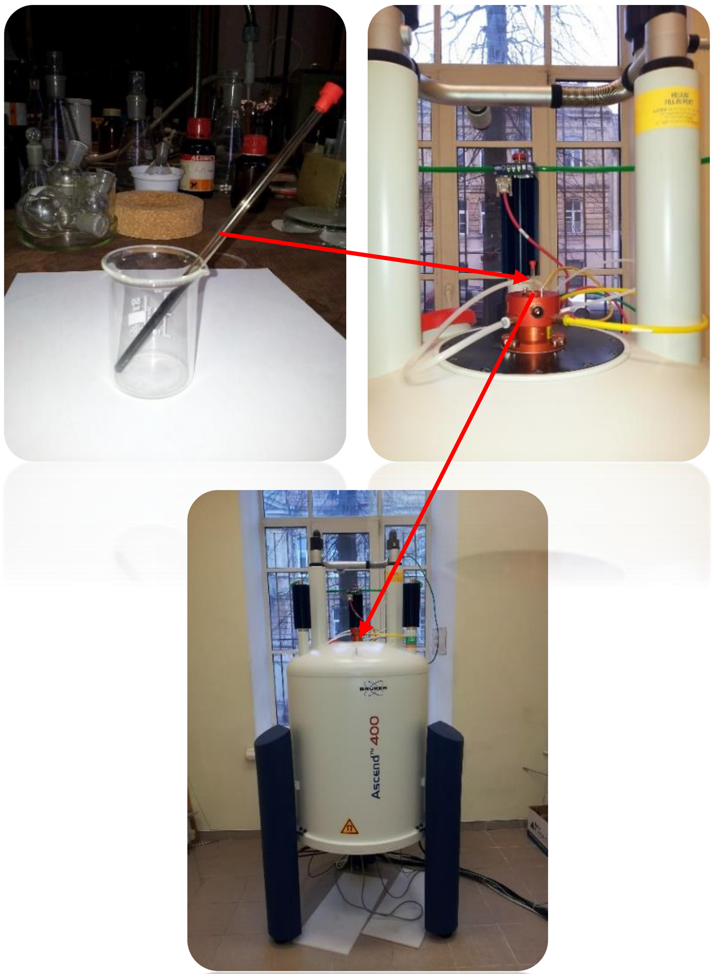
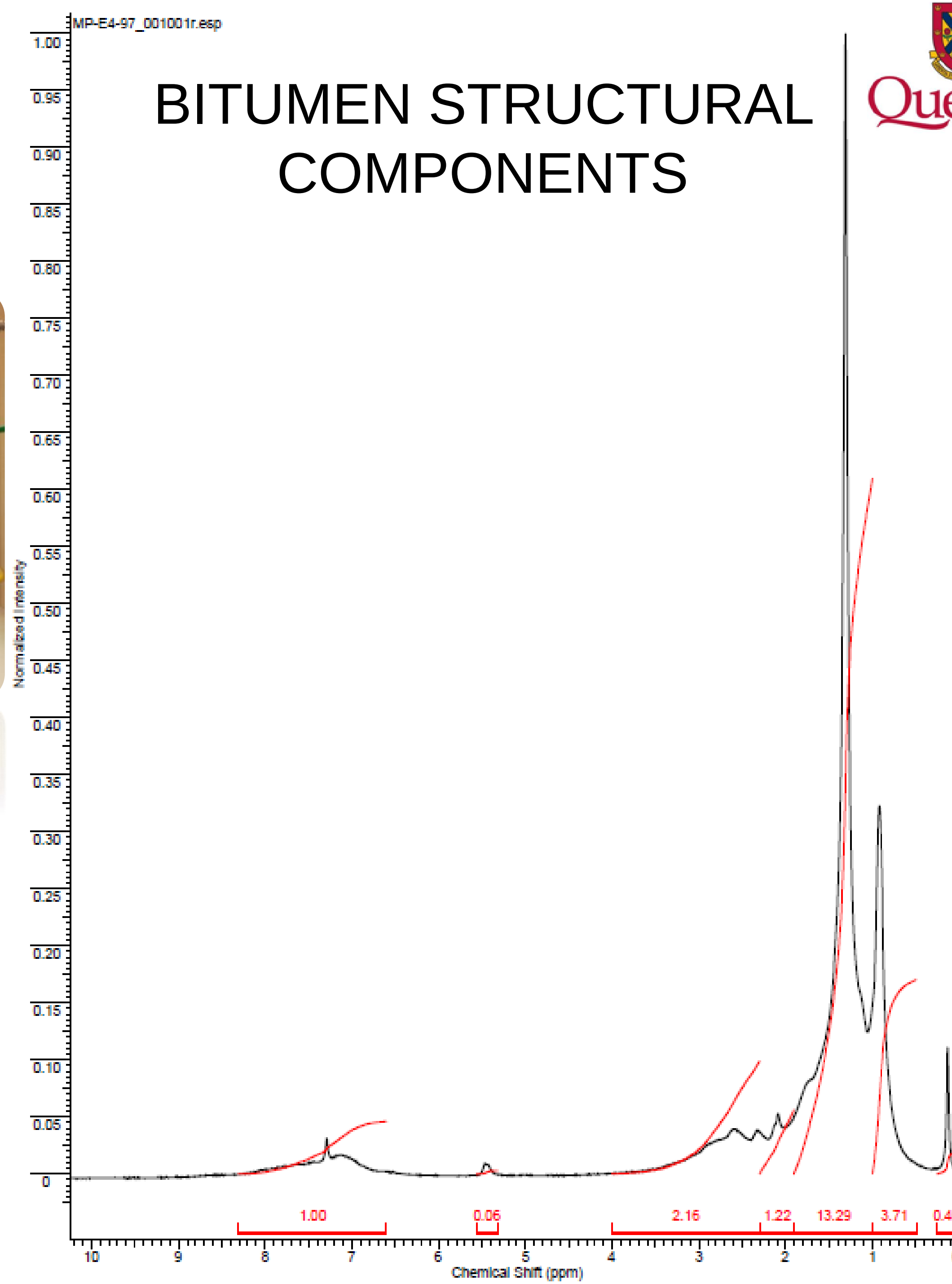
BITUMEN STRUCTURAL COMPONENTS



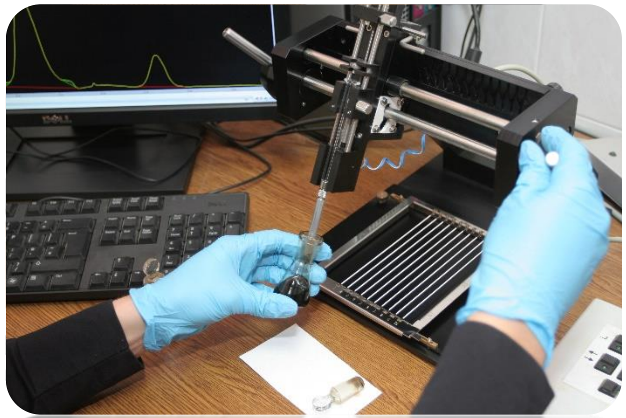
^{1}H NMR spectroscopy

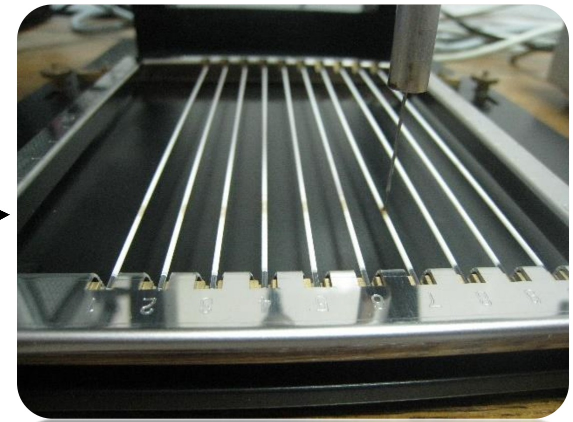


RESULTS OF ^{1}H NMR SPECTROSCOPY

Structural elements	Peak Position, ppm	Bitumen from different producers					
		A	B	C	D	E	E (PMB)
H^{α}_{ar}	8,3–6,6	0,99	0,77	1,66	1,11	1,17	1,68
H_b^{ol}	6,0–4,0						0,10
$H_{\alpha CH2}$	4,0–2,3	2,01	1,69	4,17	2,12	2,32	3,64
$H_{\alpha CH3}$	2,3–1,9	0,90	0,81	1,86	0,88	1,00	2,05
H_{CH2}	1,9–2,3	12,74	11,63	22,24	11,24	12,99	22,38
H_{CH3}	1,0–0,5	3,38	3,25	9,26	2,85	3,47	6,24
H_{α}/H_{ar}		2,91	2,50	6,03	3,00	3,47	5,69
$H_{(CH2+CH3)}/H_{ar}$		16,03	14,88	31,51	14,10	16,25	28,63
$H_{\alpha CH2}/H_{\alpha CH3}$		2,20	1,61	3,72	2,69	2,69	2,98
H_{CH2}/H_{CH3}		3,72	2,77	3,98	4,37	4,36	6,03
$(H_{\alpha CH2}/2+H_{\alpha CH3}/3)+H_{\alpha ar}$		2,30	1,89	4,36	2,46	2,66	4,19

BITUMEN FRACTIONAL COMPOSITION

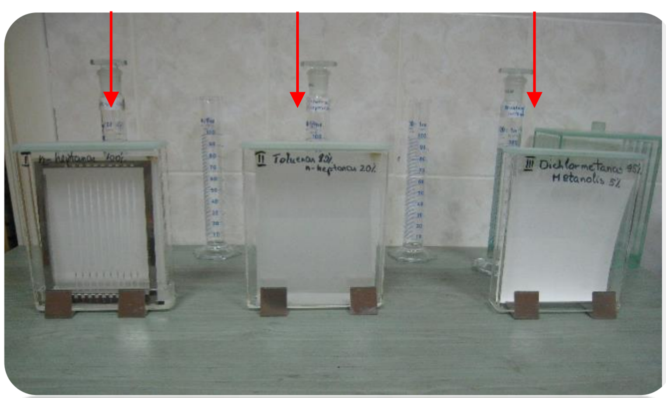


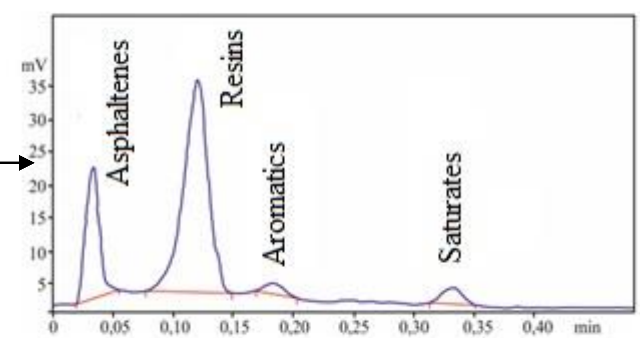


n-heptan 100 %

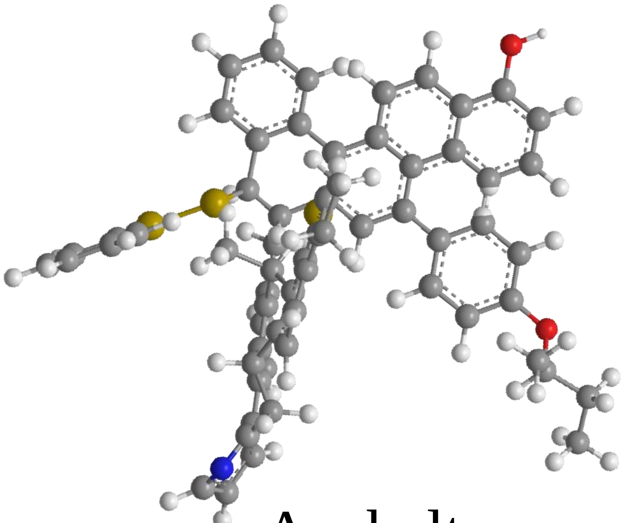
toluene 100 %

dichloromethane/ metanol 95/5 %

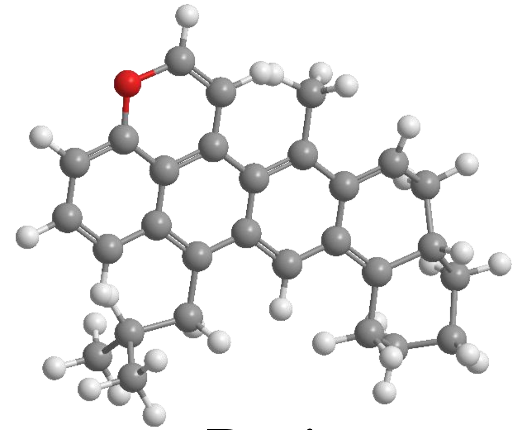




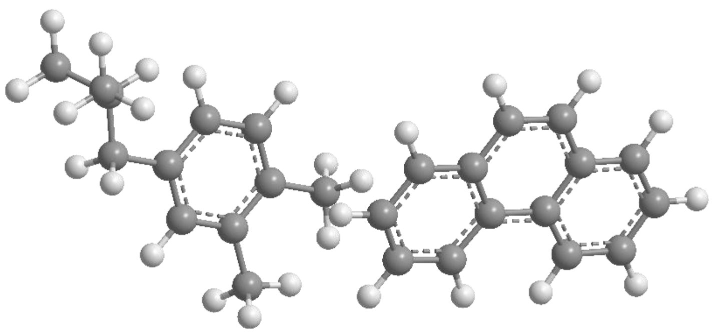
BITUMEN FRACTIONAL COMPOSITION



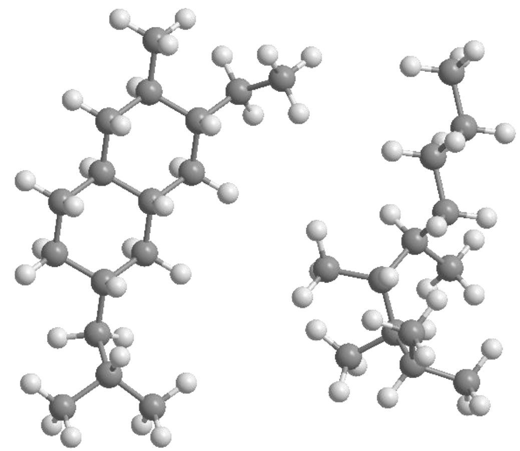
Asphaltenes



Resins



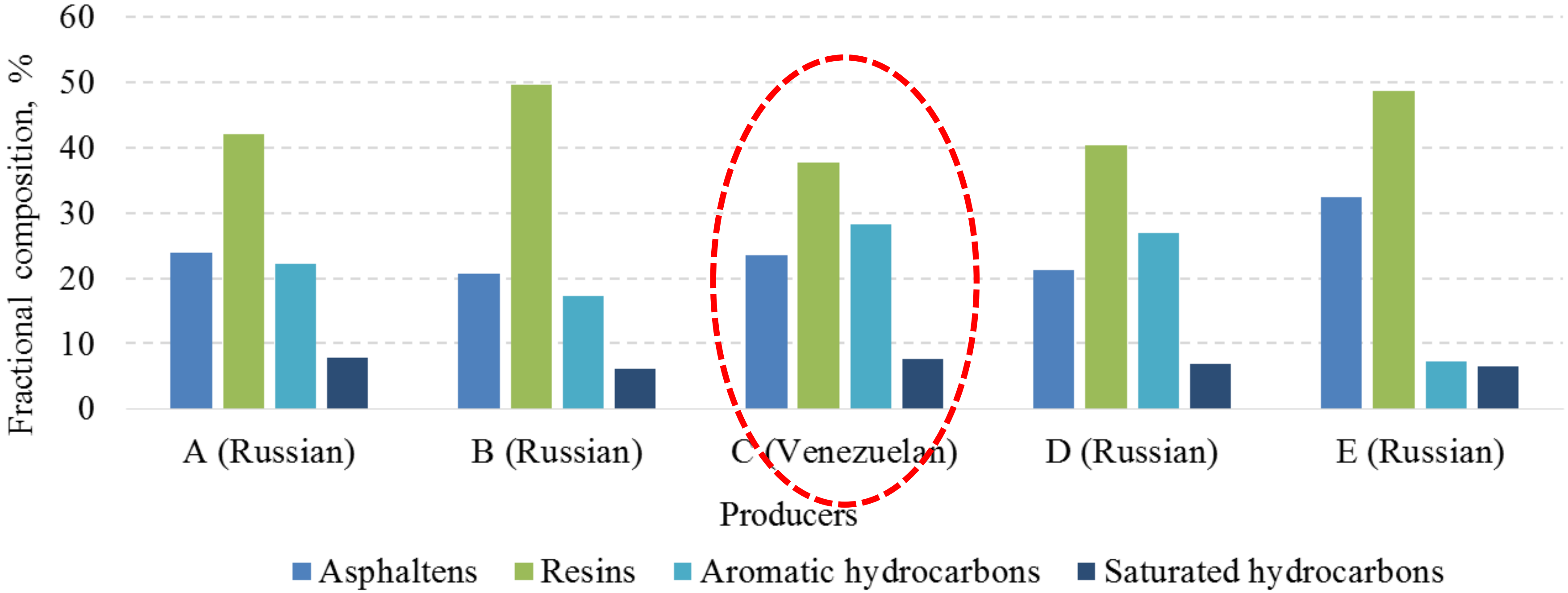
Aromatics



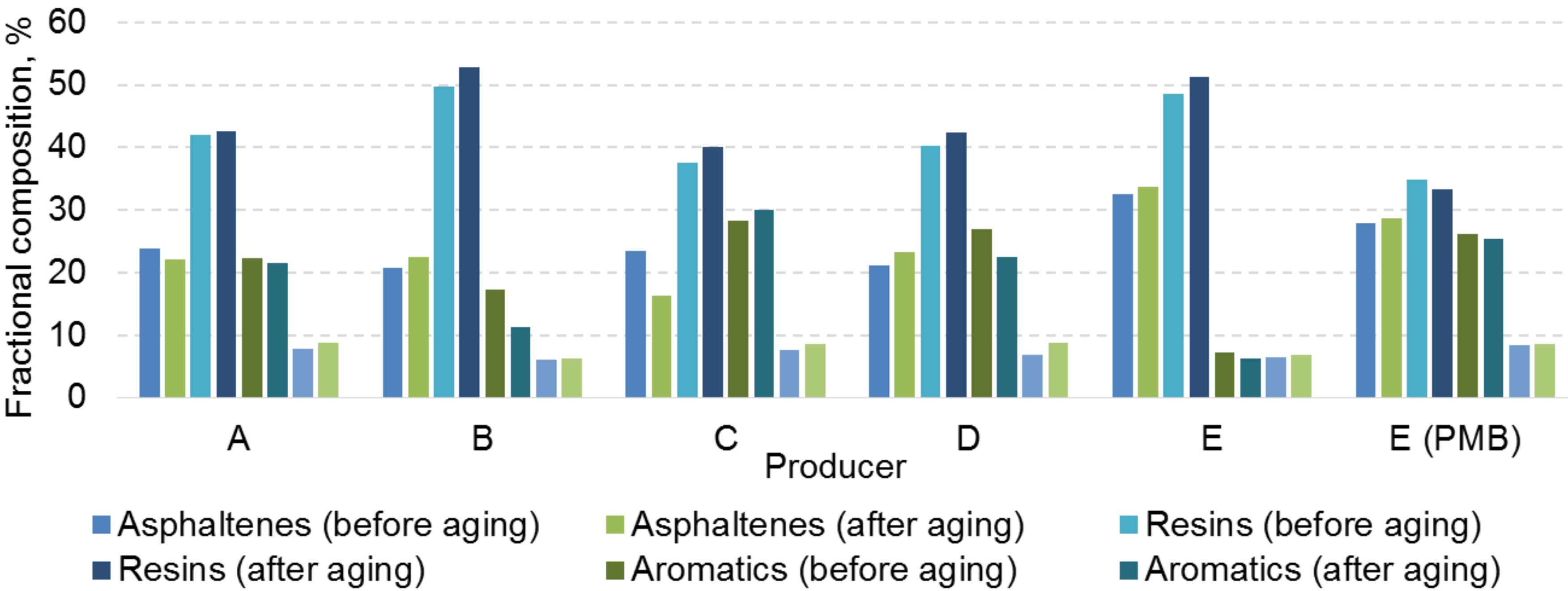
Saturates

H C O S

BITUMEN FRACTIONAL COMPOSITION BEFORE AGING



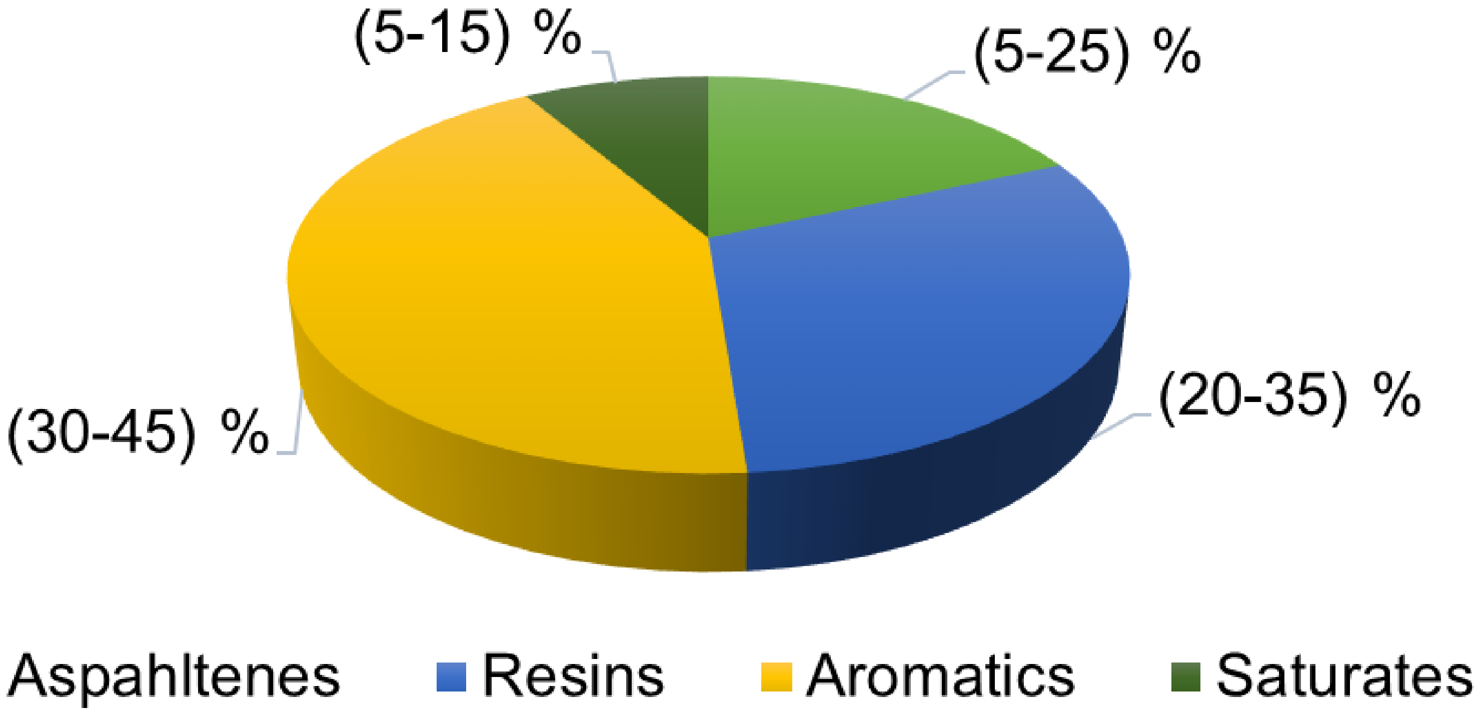
BITUMEN FRACTIONAL COMPOSITION AFTER AGING



LIMITS OF BITUMEN FRACTIONAL COMPOSITION

Country	**Bitumen fraction composition**			
	Asphaltenes, %	Resins, %	Aromatics, %	Saturates, %
USA	5–25	15–25	45–60	5–20
Great Britain	5–25	15–25	40–65	5–20
Rumania	15–35	18–48	40–60	
Spain	5–20	30–45	30–45	5–15
Russia	10–25	20–40	40–60	
Belarus	19–21	32–34	45–49	

LIMITS OF BITUMEN FRACTIONAL COMPOSITION

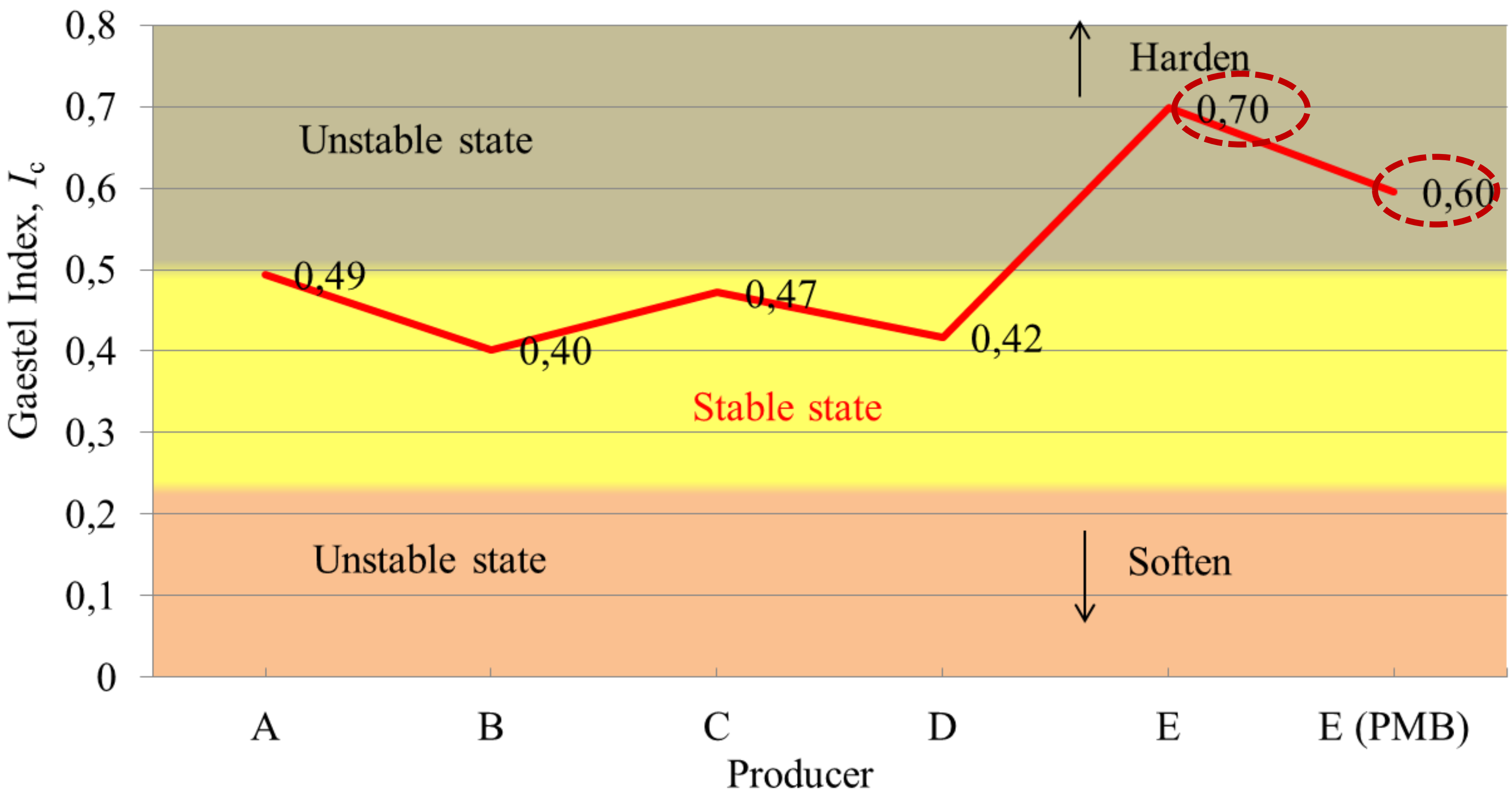


STABILITY OF BITUMEN

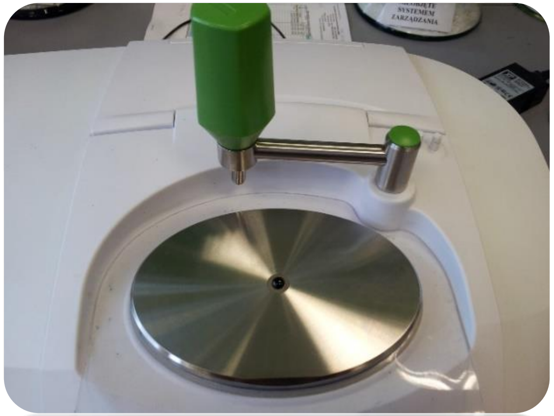
Gaestel's index: $I_c = \frac{Saturates + Aspahletens}{Resins + Aromatics}$

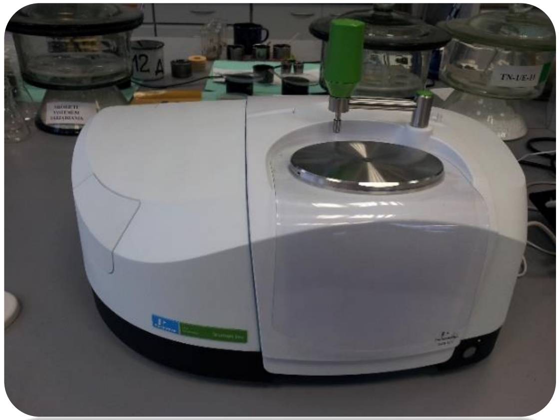
I_c	0,5–2,2	$I_c > 0{,}5$	$I_c < 0{,}22$
State of bitumen	Colloidal system is stable	Bitumen becomes more harder	Bitumen becomes more softer

BITUMEN COLLOIDAL STABILITY



BITUMEN FUNCTIONAL GROUPS



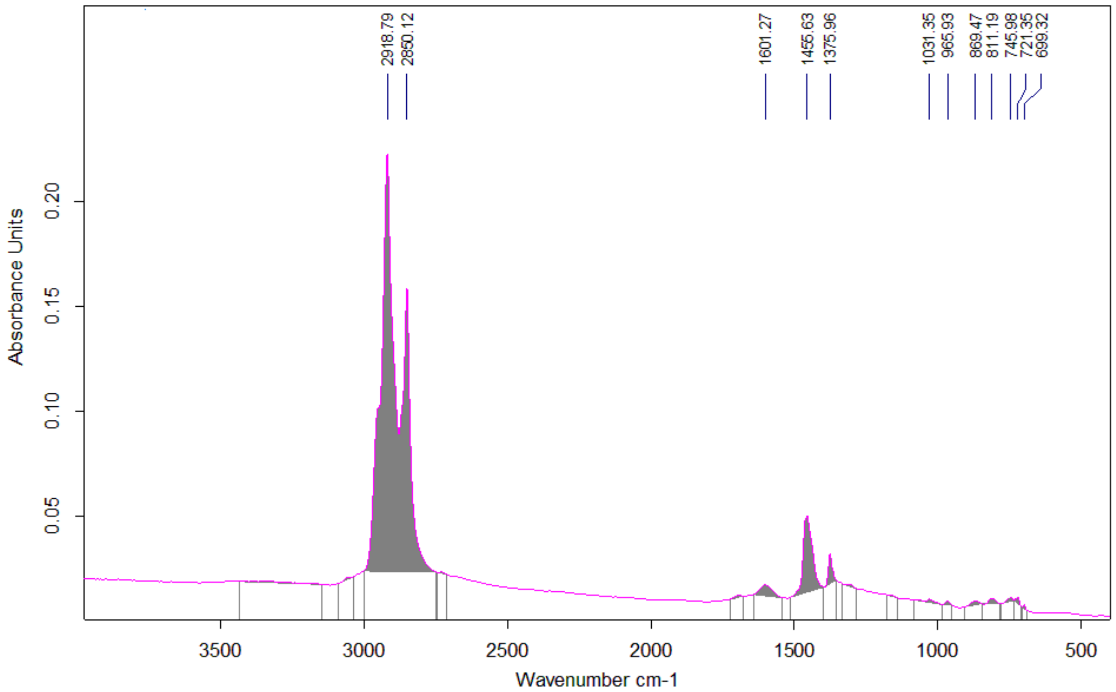


Sulfoxide index:

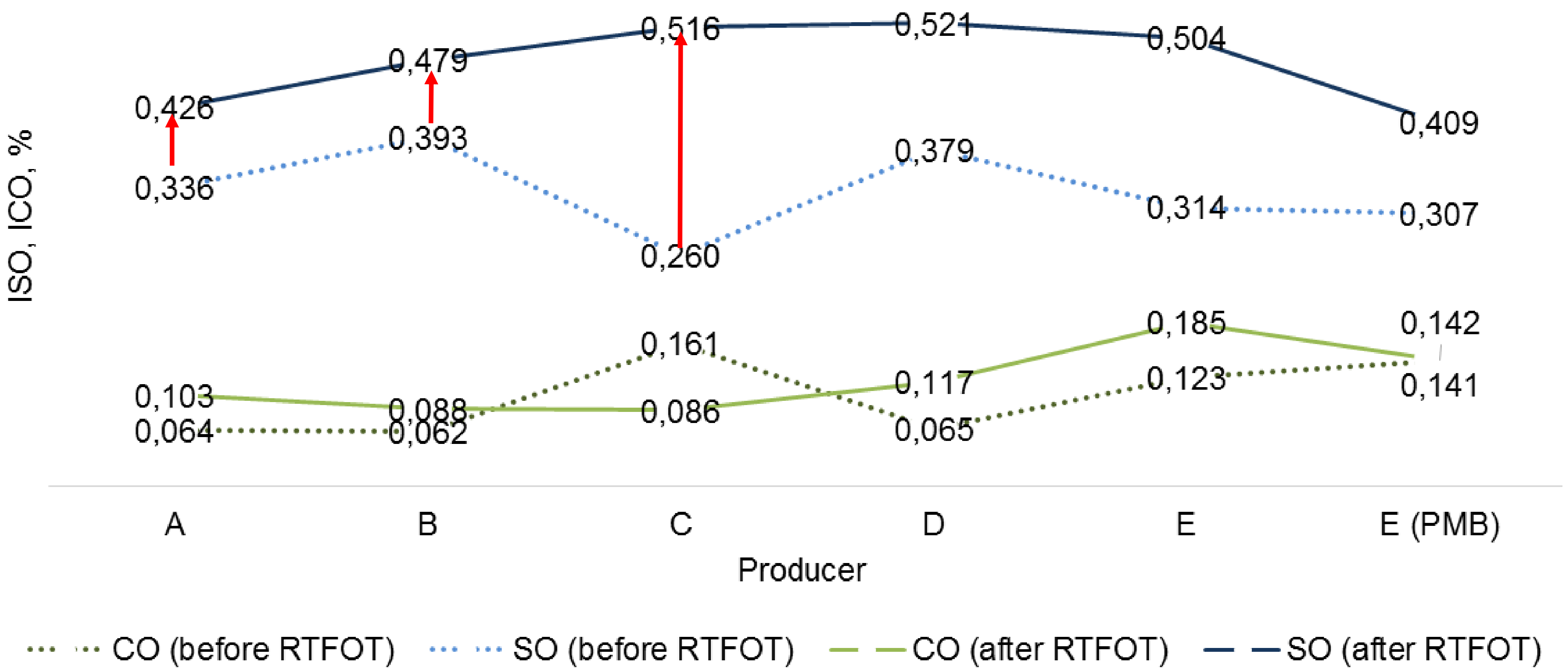
$$I_{SO} = AR_{1030} / \sum AR_{\tilde{v}}$$

Carbonyl index:

$$I_{CO} = AR_{1700} / \sum AR_{\tilde{v}}$$



RESULTS OF FTIR SPECTROSCOPY



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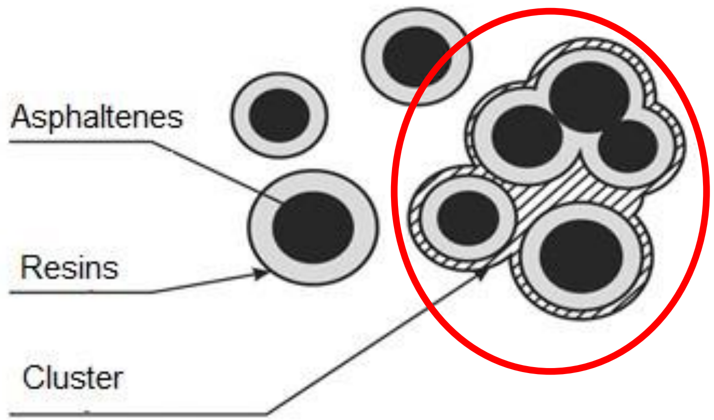
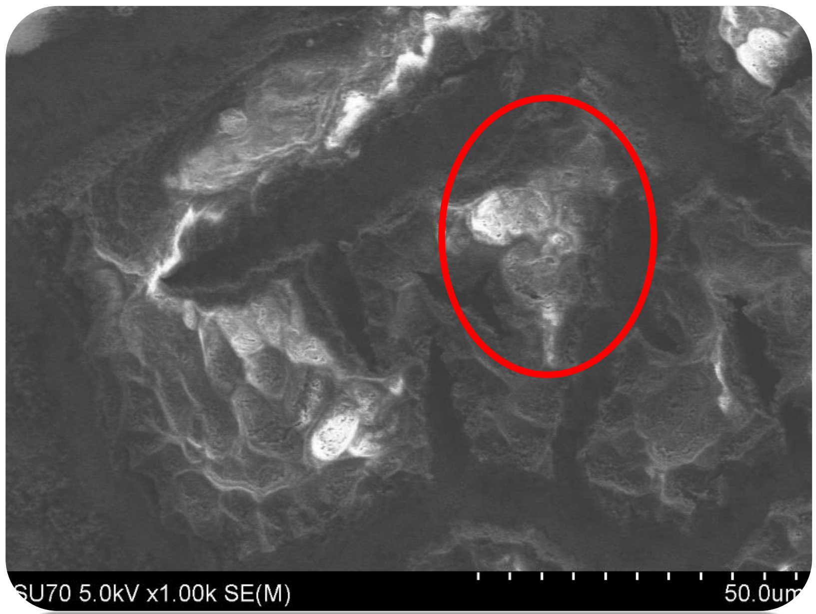
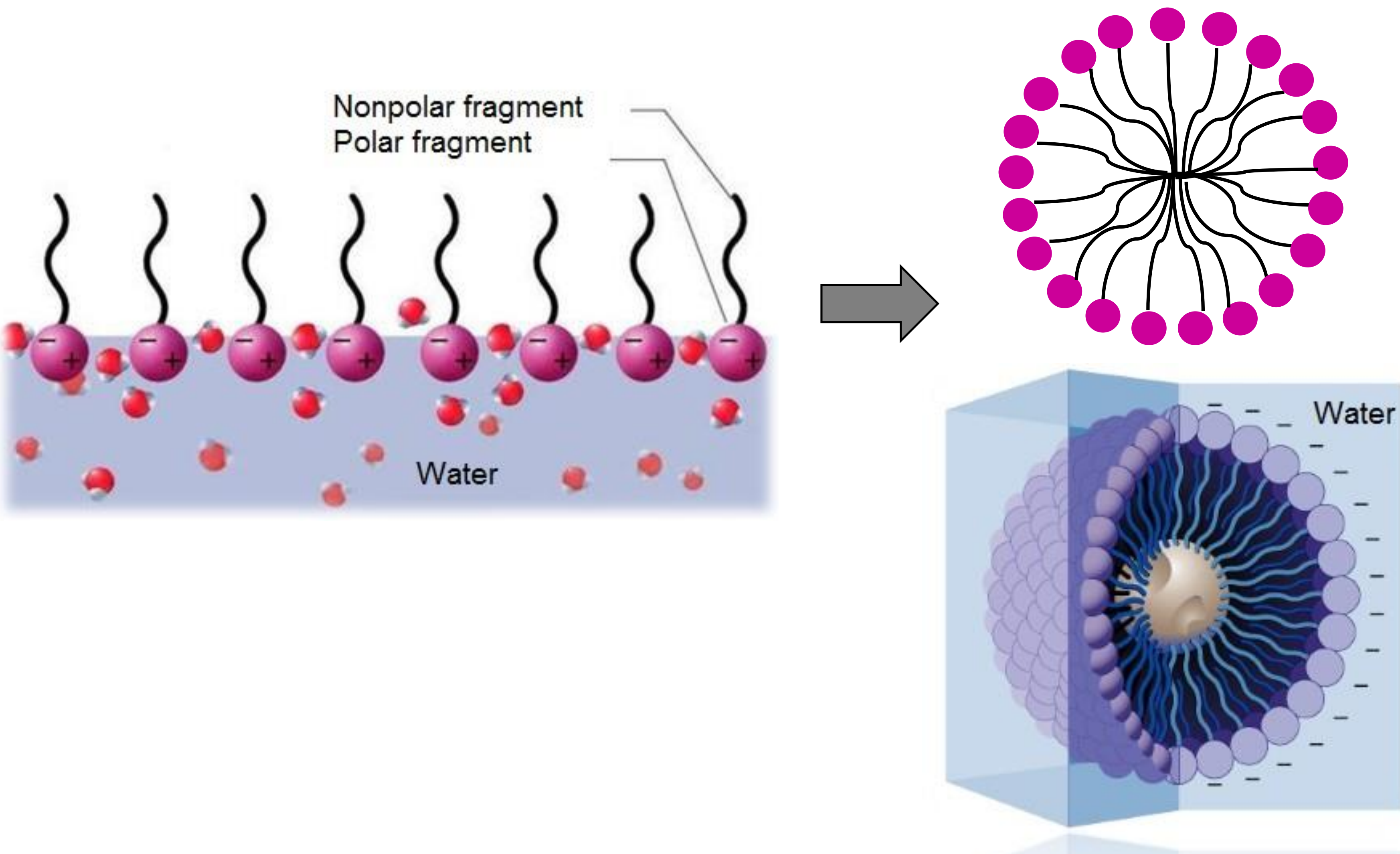
BITUMEN MICROSTRUCTURE

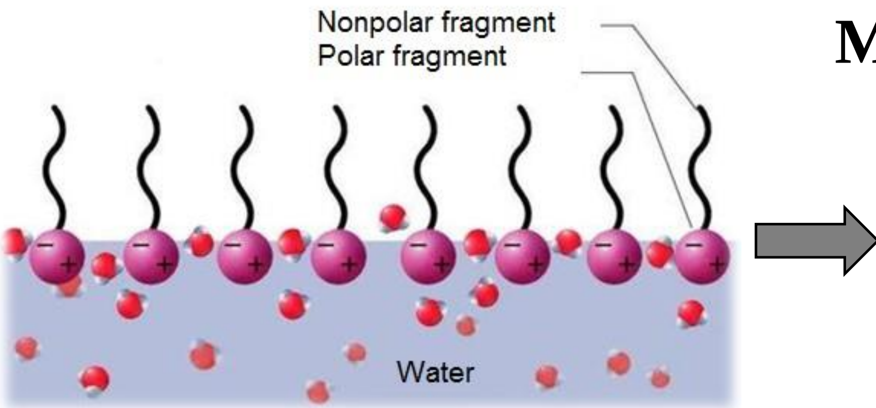




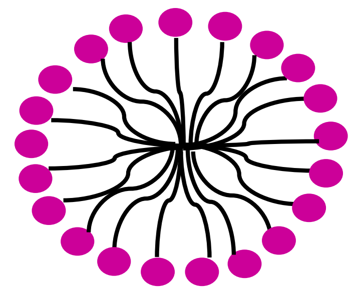
MICELLE IN THE NATURE



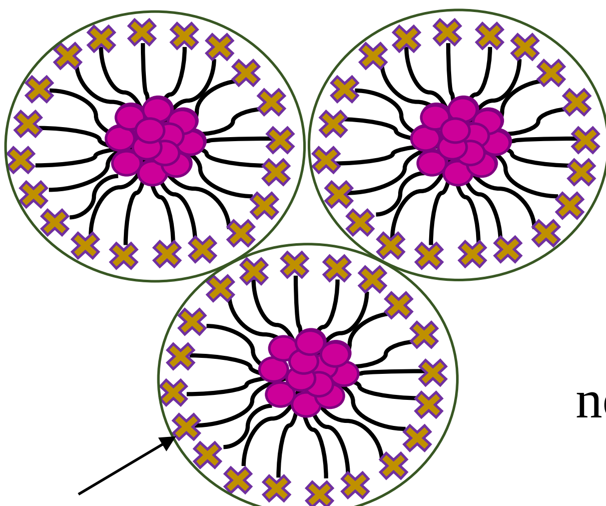
REVERSE BITUMEN MICELLE



Micelle in the water



Bitumen micelle *(Gel type)*

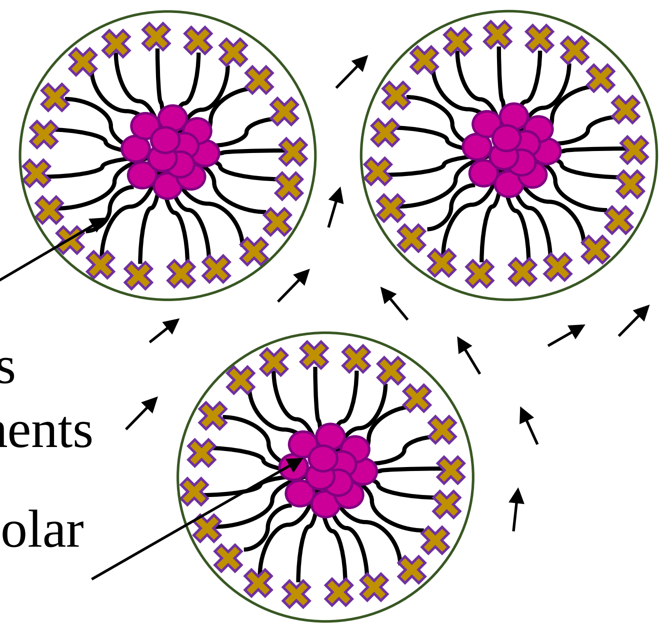


Resins nonpolar fragments

Bitumen micelle (*Sol type*)

Asphaltenes nonpolar fragments

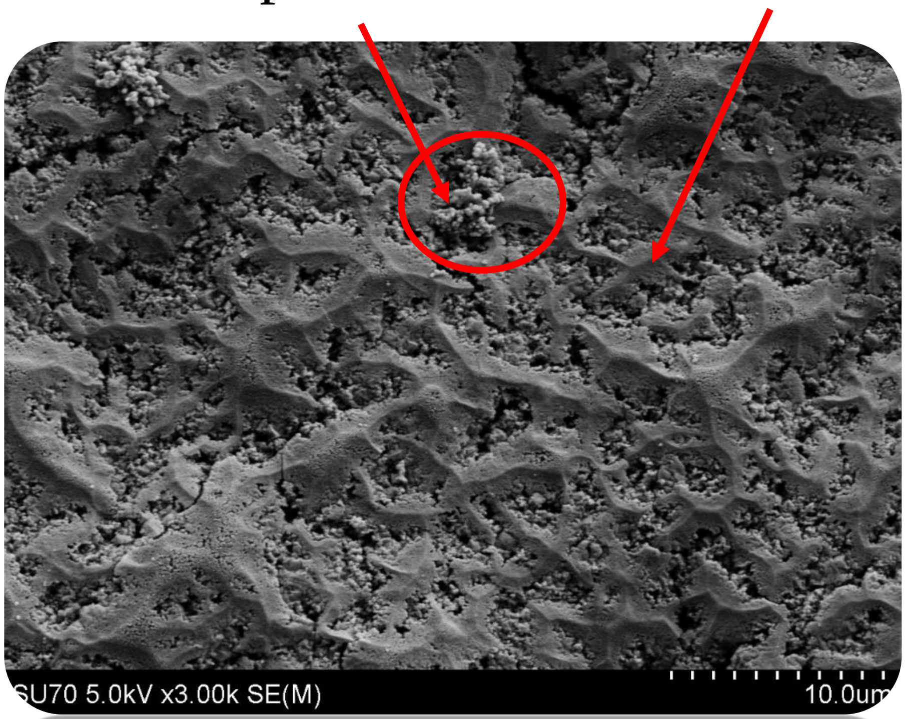
Asphaltenes polar fragments



RESULTS OF BITUMEN MICROSTRUCTURE

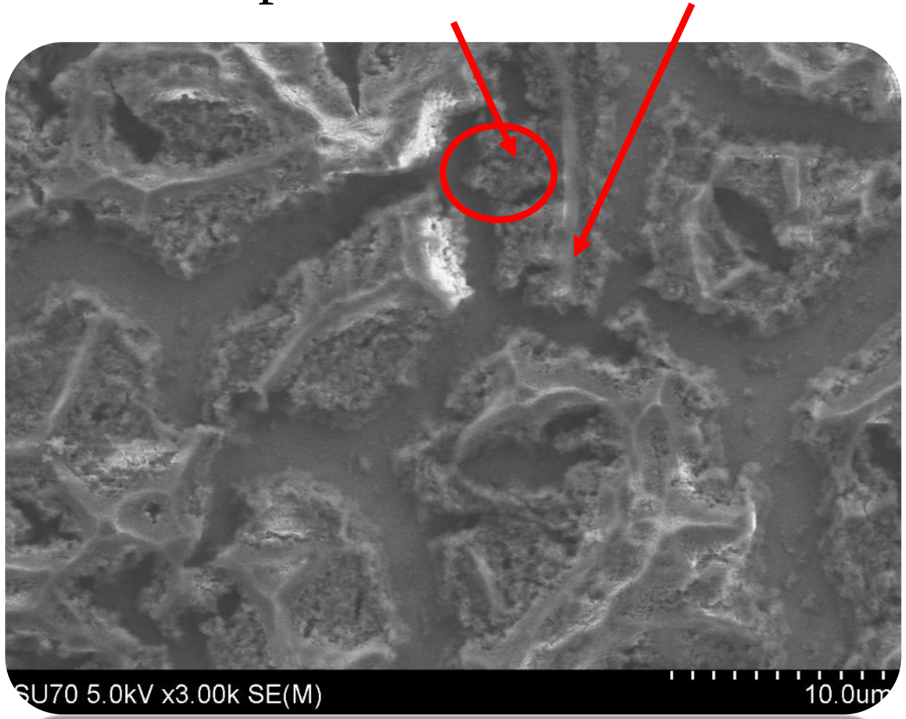
Gel type
(Venezuelan crude oil)

Asphaltenes Resins



Sol type
(Russian crude oil)

Asphaltenes Resins



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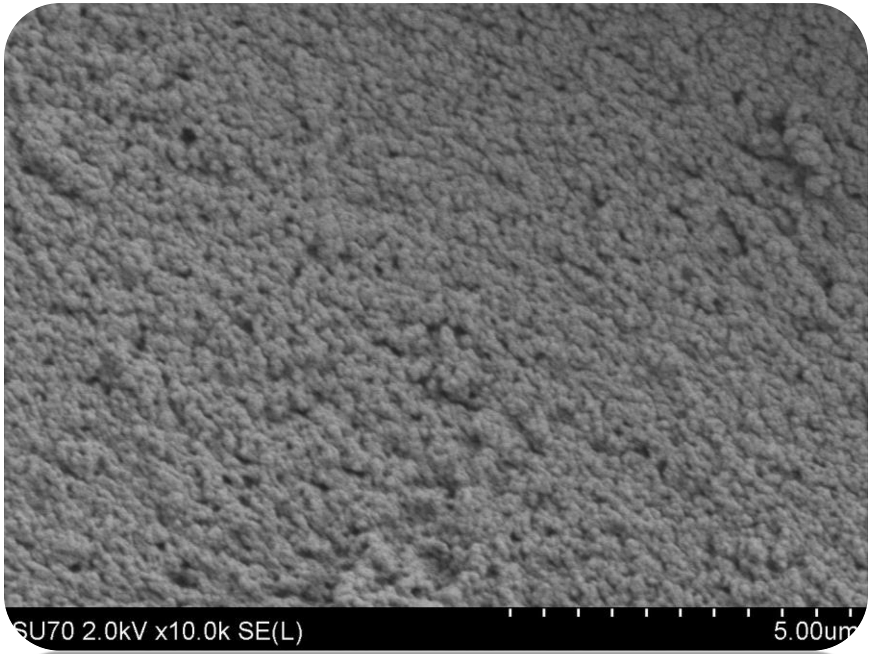
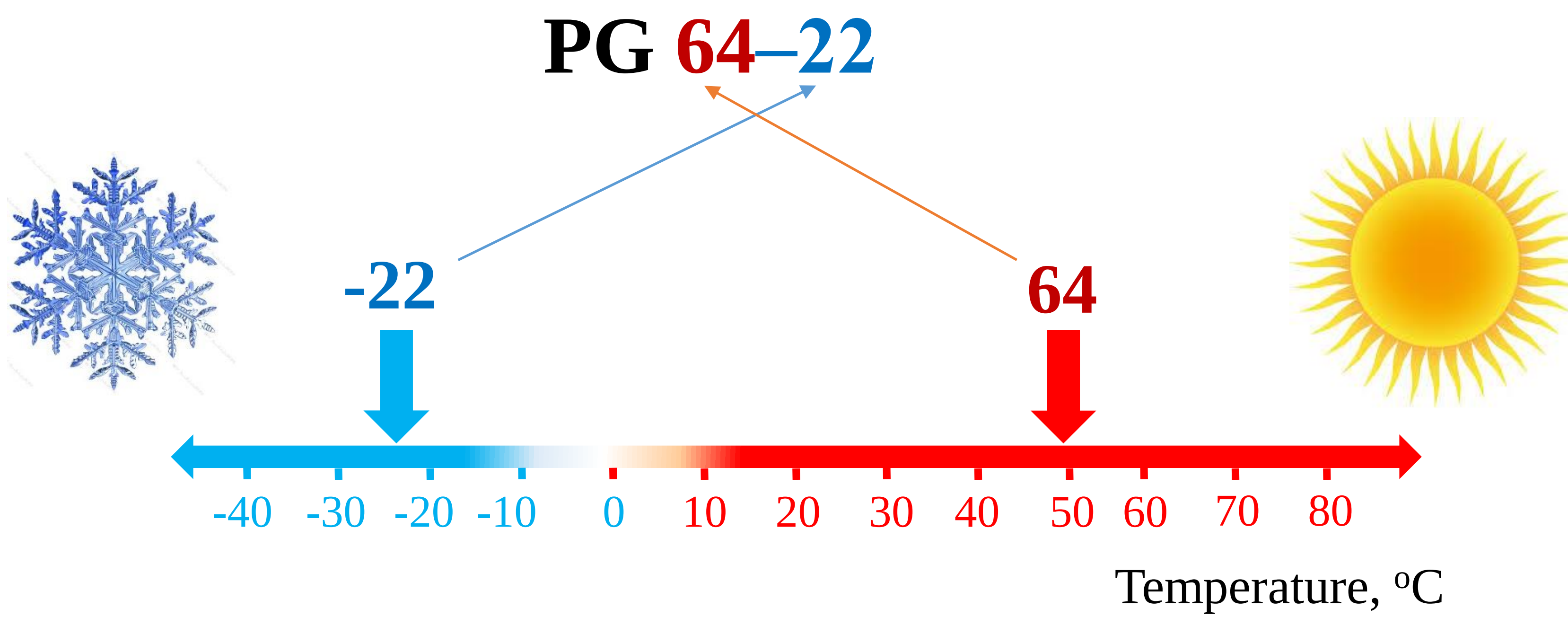
RESULTS OF BITUMEN MICROSTRUCTURE

Modified bitumen from producer E (Russian Crude oil)

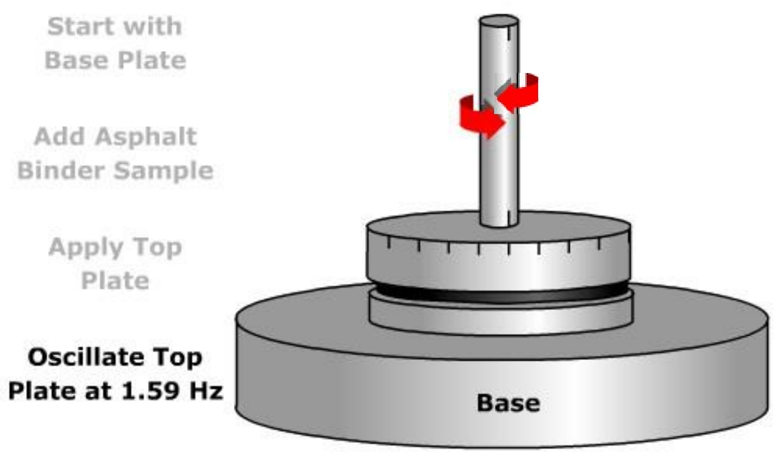


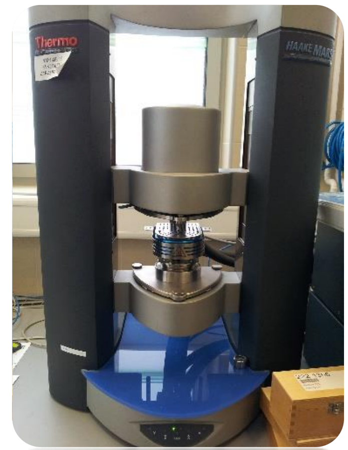
PERFORMANCE GRADE (PG)

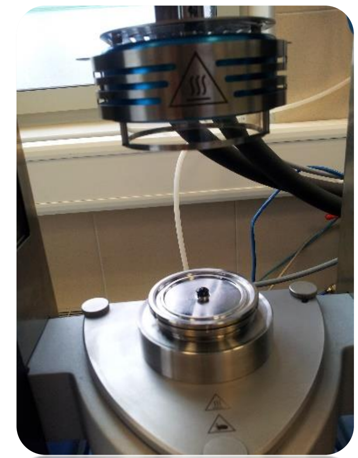


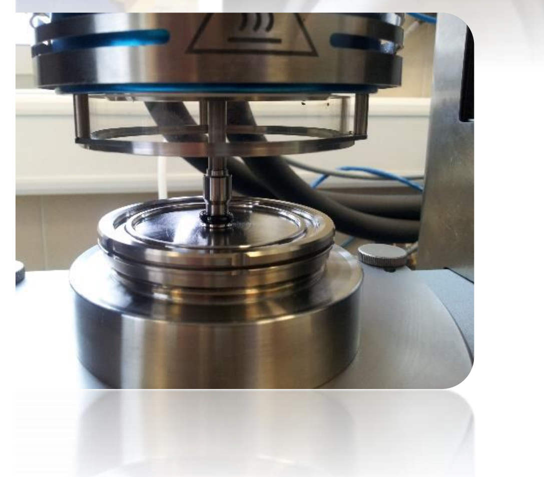
Bitumen	Value	Limit values, kPa
Original	$G^*/\sin\delta$	≥ 1,0
After short-term aging	$G^*/\sin\delta$	≥ 2,2

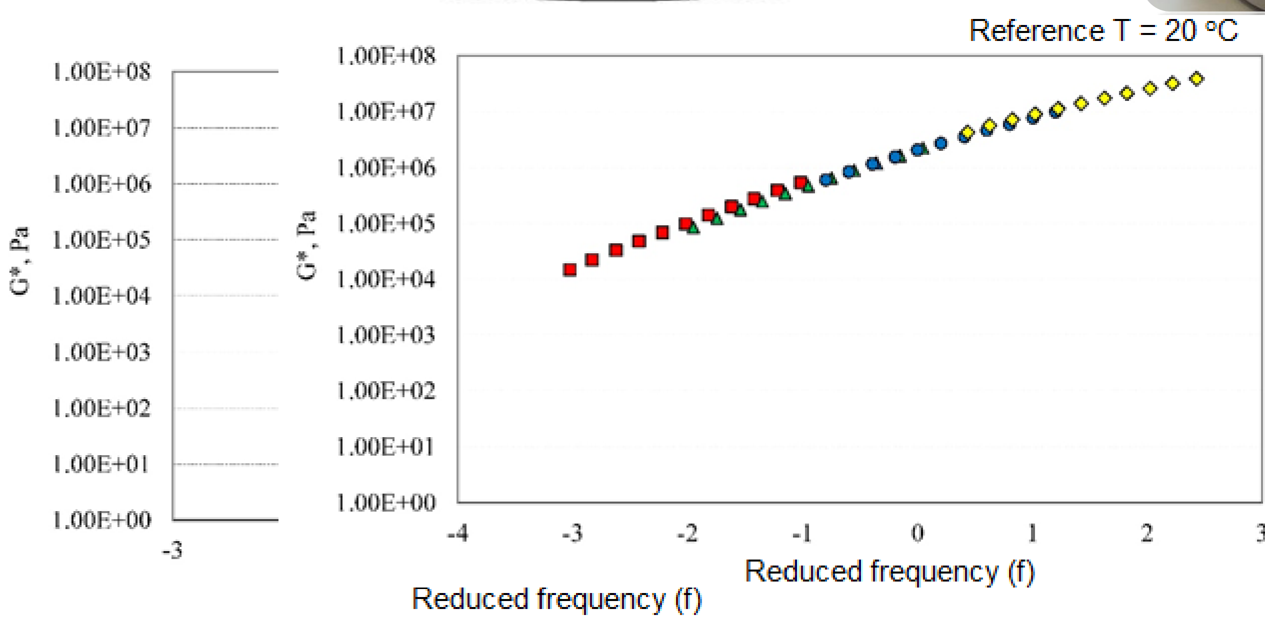
BITUMEN RHEOLOGICAL PROPERTIES



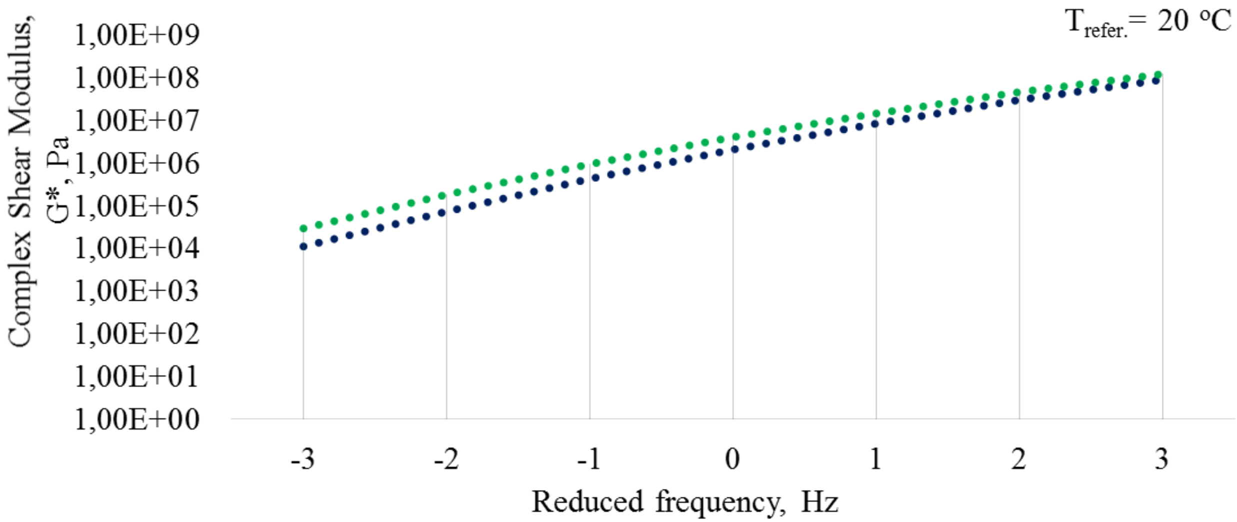




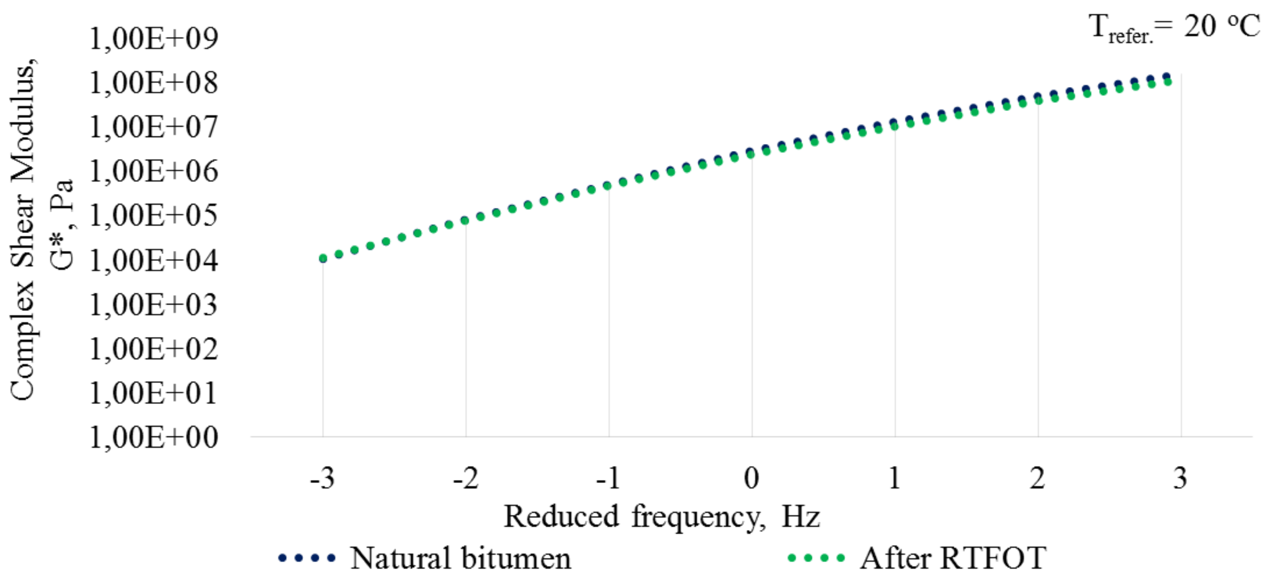




RESULTS OF BITUMEN RHEOLOGICAL PROPERTIES



Producer A (Russian)



Producer C (Venezuelan)

Producer	Aging	Critical temperature, °C: G*/sinδ = 1	Critical temperature, °C: G*/sinδ = 2,2	The highest temperature according to Performance Grade (PG)						
A	before RTFOT	64,87		64	–10	–16	–22	–28	–34	–40
	after RTFOT		60,91	58	–16	–22	–28	–34	–40	
B	before RTFOT	64,97		64	–10	–16	–22	–28	–34	–40
	after RTFOT		63,78	58	–16	–22	–28	–34	–40	
C	before RTFOT	63,52		58	–16	–22	–28	–34	–40	
	after RTFOT		60,32	58	–16	–22	–28	–34	–40	

Producer	Aging	Critical temperature, °C		The highest temperature according to Performance Grade (PG)					
		G*/sinδ = 1	G*/sinδ = 2,2						
D	before RTFOT	67,03		64					
				–10	–16	–22	–28	–34	–40
	after RTFOT		69,04	64					
				–10	–16	–22	–28	–34	–40
E	before RTFOT	66,01		64					
				–10	–16	–22	–28	–34	–40
	after RTFOT		68,51	64					
				–10	–16	–22	–28	–34	–40

BITUMEN ADHESION RESEARCH

BITUMEN ADHESION

- Quality of asphalt mixes
- Asphalt pavement performance
- Resistance to rutting

Reduction of bitumen adhesion properties leads to asphalt pavement fragmentation

THE AIM OF EXPERIMENTAL RESEARCH

To determine an effective test method for bitumen and aggregates adhesion properties

PROBLEMATIKA

Determination of bitumen and aggregates adhesion properties (according to LST 1362.23)

Bitumen adhesion with aggregates

Determination of bitumen and aggregates adhesion properties (according to LST EN 12697-11)

Rolling bottle method

Static method

Boiling water stripping method

THERE IS NO COMMON PRACTICE FOR:

- **bitumen adhesion test method**
- **limit values**

TEST OBJECT AND METHODS

Test object:

- Aggregates – granite, dolomite, crushed gravel, kvarcdeorit
- Bituminous binders – 50/70, 70/100, PMB 45/80-55
- Additives – Iterlen 400/IL, Adhezin

Test methods:

- LST 1362.23 – Bitumen adhesion with aggregates
- LST EN 12697-11 5 p. – Rolling bottle method
- LST EN 12697-11 6 p. – Static method

SUMMARY OF ADHESION RESEARCH

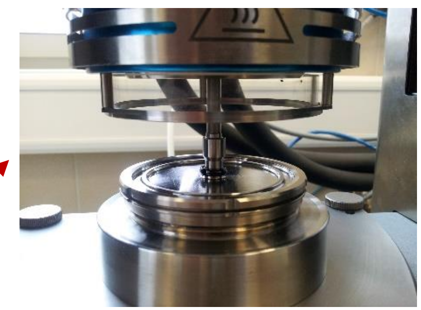
- Bitumen adhesion depends on chemical reaction, surface energy, molecular orientation and mechanical adhesion
- In the European standard: Rolling-Bottle test, static water storage, detachment in boiling water.
- Methods differ in their methodology, preparation of the samples and results of the measurement unit
- Future work…

CHANGES OF BITUMEN FRACTIONAL COMPOSITION AND MECHANICAL PROPERTIES DURING AGING PROCESS

Purpose: To determine bitumen fractional composition and mechanical properties after PAV, 2PAV and find a relationship with recovered bitumen.

Objective: 50/70, PMB 45/80-55 and recovered bitumen after 7 years of road exploitation

1 PAV and 2 PAV



SUMMARY AND CONCLUSIONS

1. Crude oil type and processing cause changes in bitumen fractional composition
2. Chemical composition, microstructure of bitumen and their variation of environmental factors influence bitumen performance in asphalt pavement structure
3. Critical temperature for bitumen resistance to rutting +64 ^{o}C (Russian crude oil) and +58 ^{o}C (Venezuelan crude oil)
4. Instability of bitumen physical properties was identified depending on crude oil
5. All of the investigated bitumens show a satisfactory stability
6. Recommended range of bitumen fractional composition

RECOMMENDATIONS

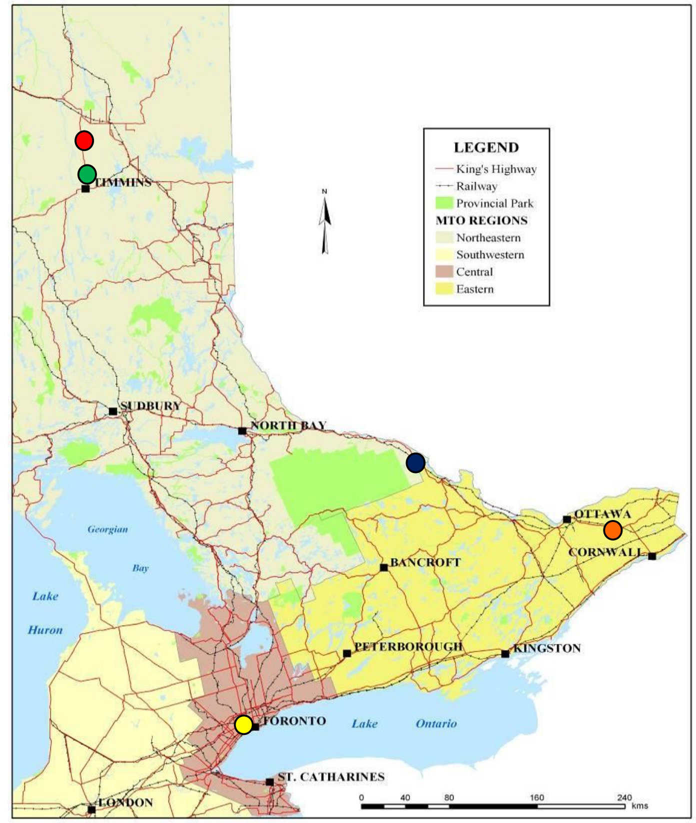
1. Comprehensive analysis of bitumen constitution is necessary, in order to achieve proper bitumen properties
2. Fractional composition of bitumen should be determined each time when buying bitumen from certain producer
3. It is recommended to determine bitumen elemental composition, structural elements, functional groups and fractional composition of bitumen seeking to predict the changes in bitumen properties under the effect of bitumen aging:
   - Content of sulphur and oxygen indicates bitumen resistance to oxidation
   - Based on the branches of molecular structure the best bitumen can be chosen for modification purposes
   - Bitumen sensitivity to oxidation can be assessed according to the functional groups
   - Fractional composition evaluates its colloidal stability

ON-GOING STUDY IN ONTARIO

Field Validation

Ontario's 33 active pavement test sections:

- Low temperature, fatigue, and aging studies
- Each 500 m in length
- Ten different suppliers
- Various technologies
  - SB, RET, Fibers
  - Air Blown, Acid (PPA), Base
  - Waste Engine Oil, etc



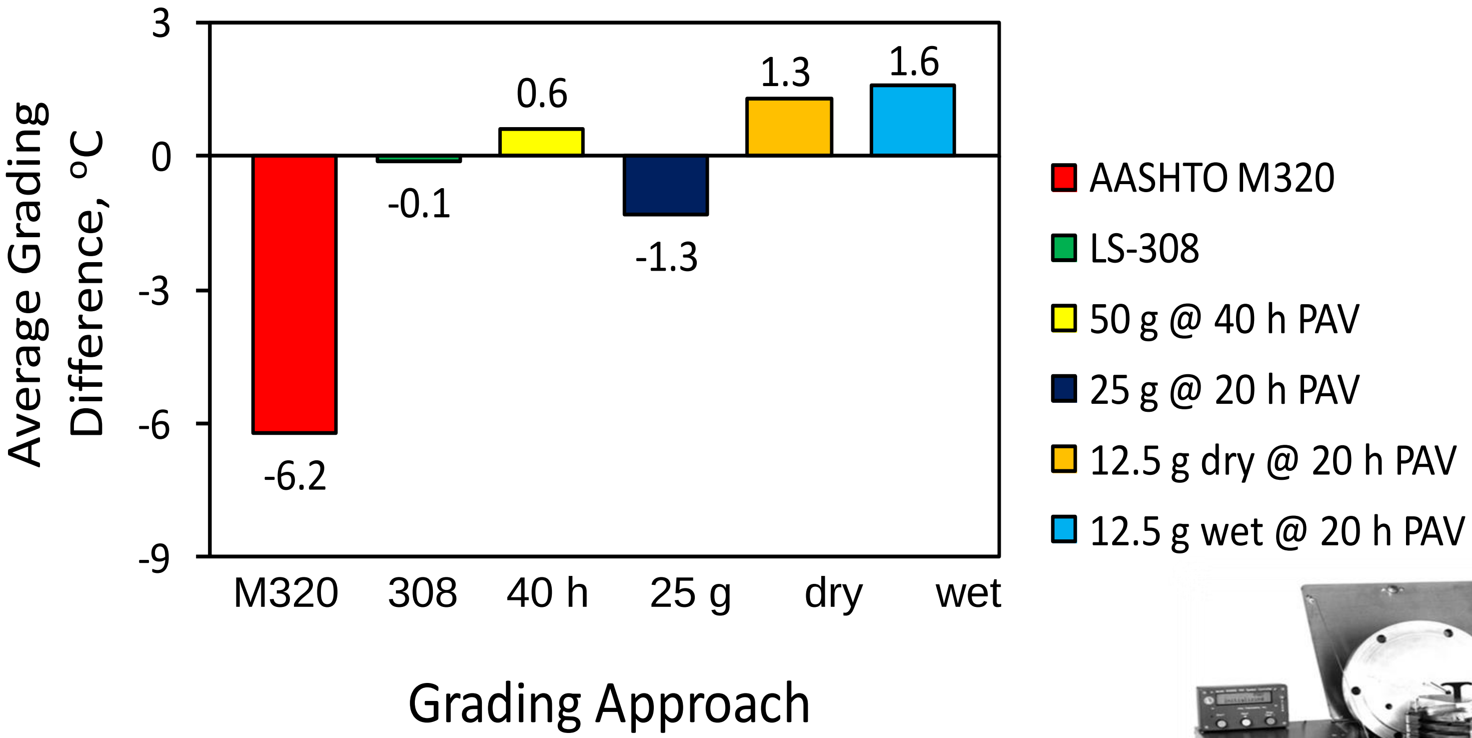
- 1996
- 2003
- 2006
- 2007
- 2008

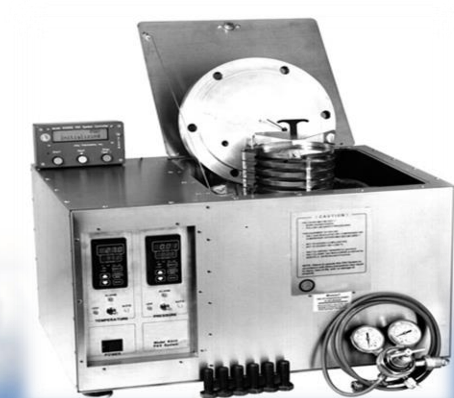
Highway 138

ONTARIO'S IMPROVED AGING PROTOCOLS AND PHYSICAL PROPERTY TESTS FOR ASPHALT CEMENT

1. LS-228 Modified PAV (Grade + Loss) provides improved oxidative aging
2. LS-308 Extended BBR (Grade + Loss) gives an improved low temperature grade
3. LS-299 DENT (CTOD) gives an improved measure of ductility

LS-228 Modified PAV





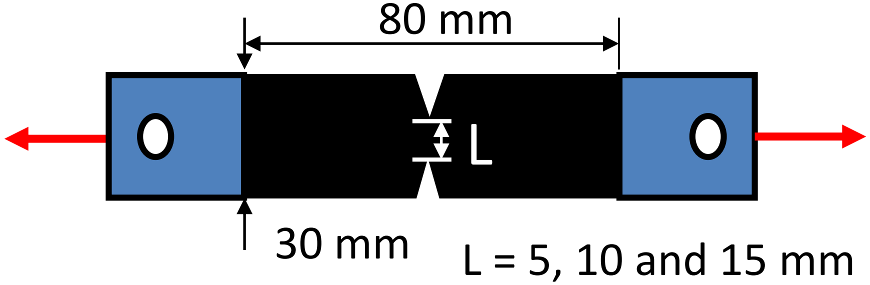
Erskine *et al.*, Eurobitume 2012

LS-308 Extended BBR

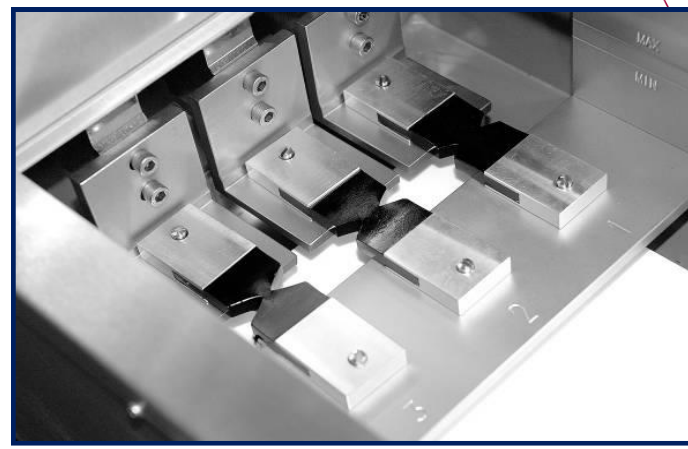
1. Conditions at T + 10 and T + 20 and measures grades after 1, 24 and 72 hours of cold conditioning.
2. Measures grade loss from 1 hour.

LS-299 Double-Edge-Notched Tension

Improved Ductility Test



T = 15^{o}C and Rate = 50 mm/min

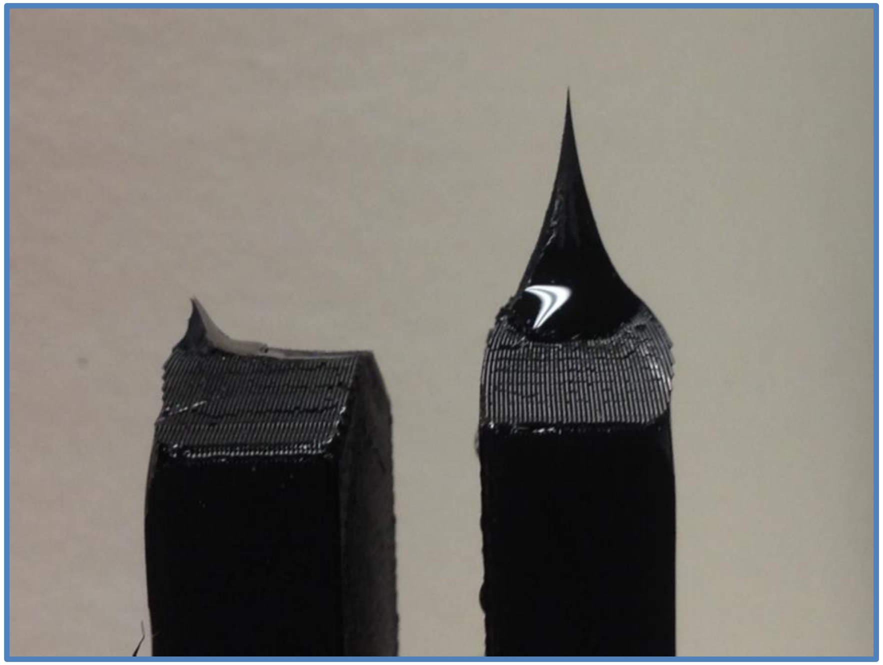


$$W_{total} = W_{essential} + W_{plastic} = w_{essential}BL + w_{plastic}bBL^2$$

$$w_{total} = W_{total}/BL = w_{essential} + bw_{plastic}L$$

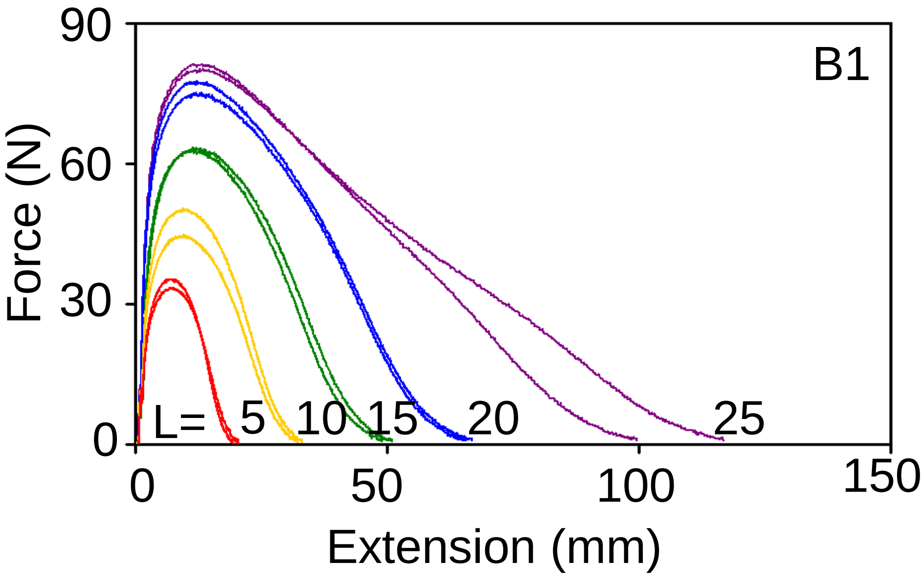
$$\mathbf{CTOD \sim w_{essential}/s_{net\ section\ stress\ at\ 5\ mm}}$$

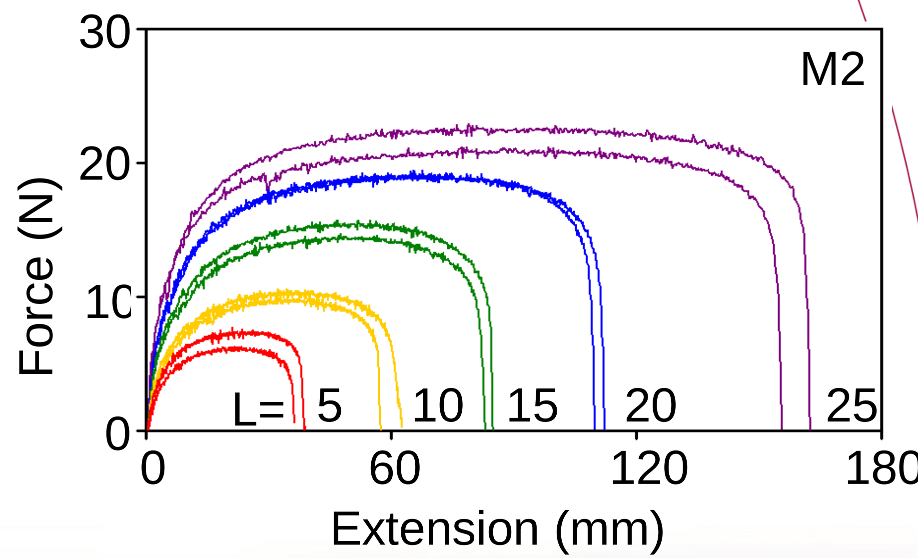
Brittle-to-Ductile Transition



- ✓ **Cracking is inversely proportional to CTOD!**

LS-299 Double-Edge-Notched Tension

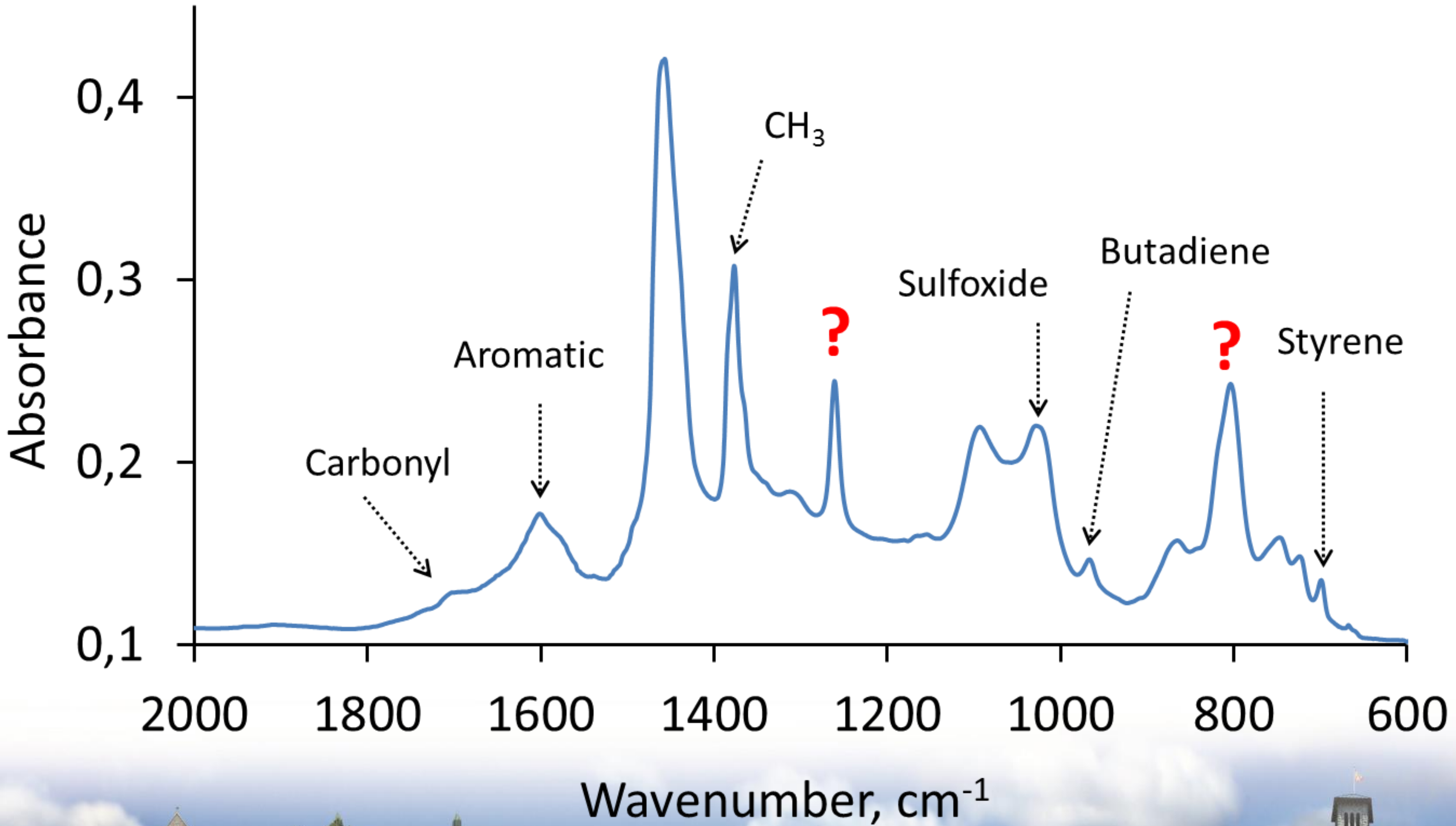




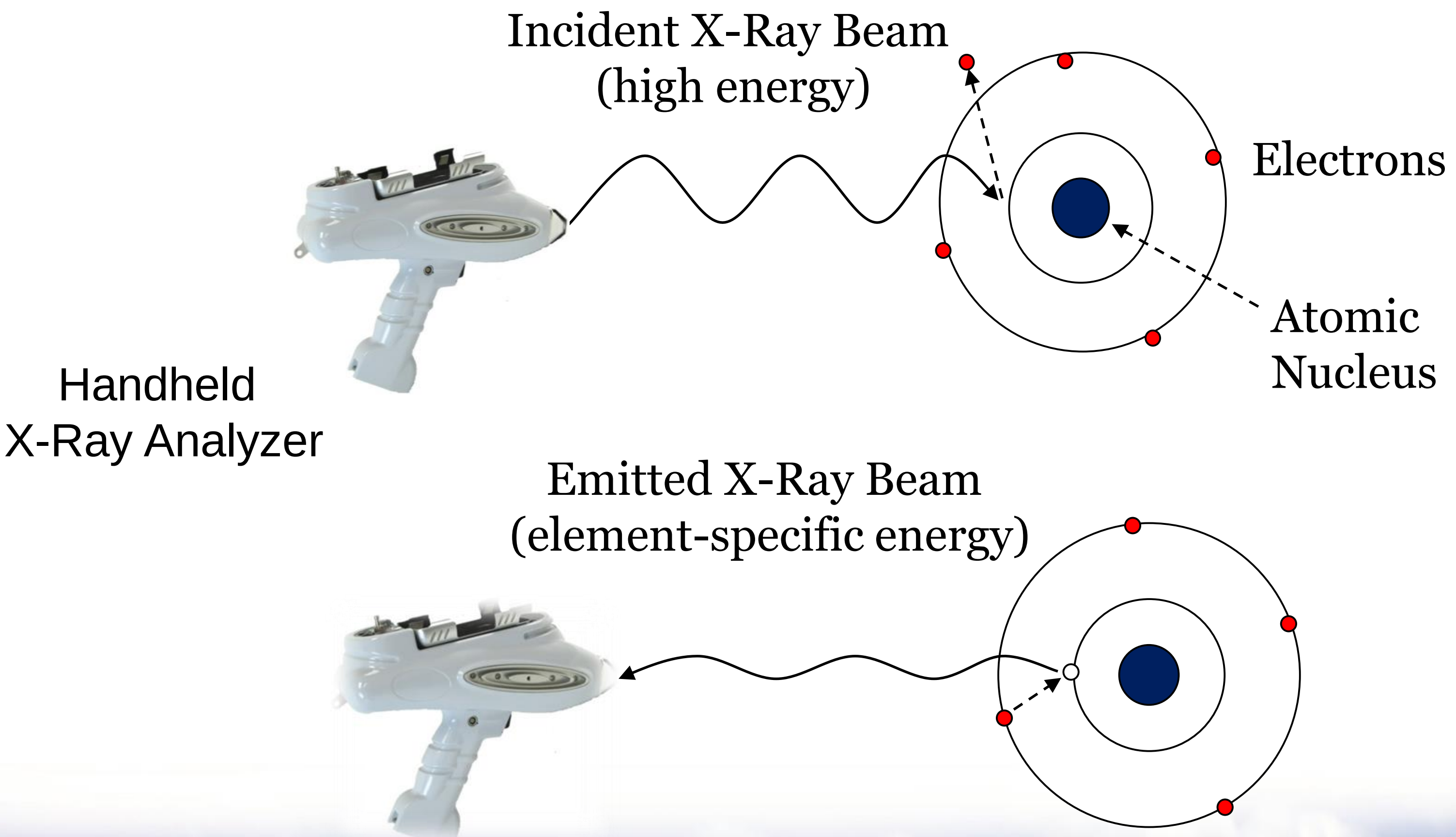
SPECTROSCOPY ON ASPHALT CEMENT

- Infrared Spectroscopy (IR)
- X-Ray Fluorescence Spectroscopy (XRF)
- Nuclear Magnetic Resonance (NMR) Spectroscopy
- Mass spectroscopy

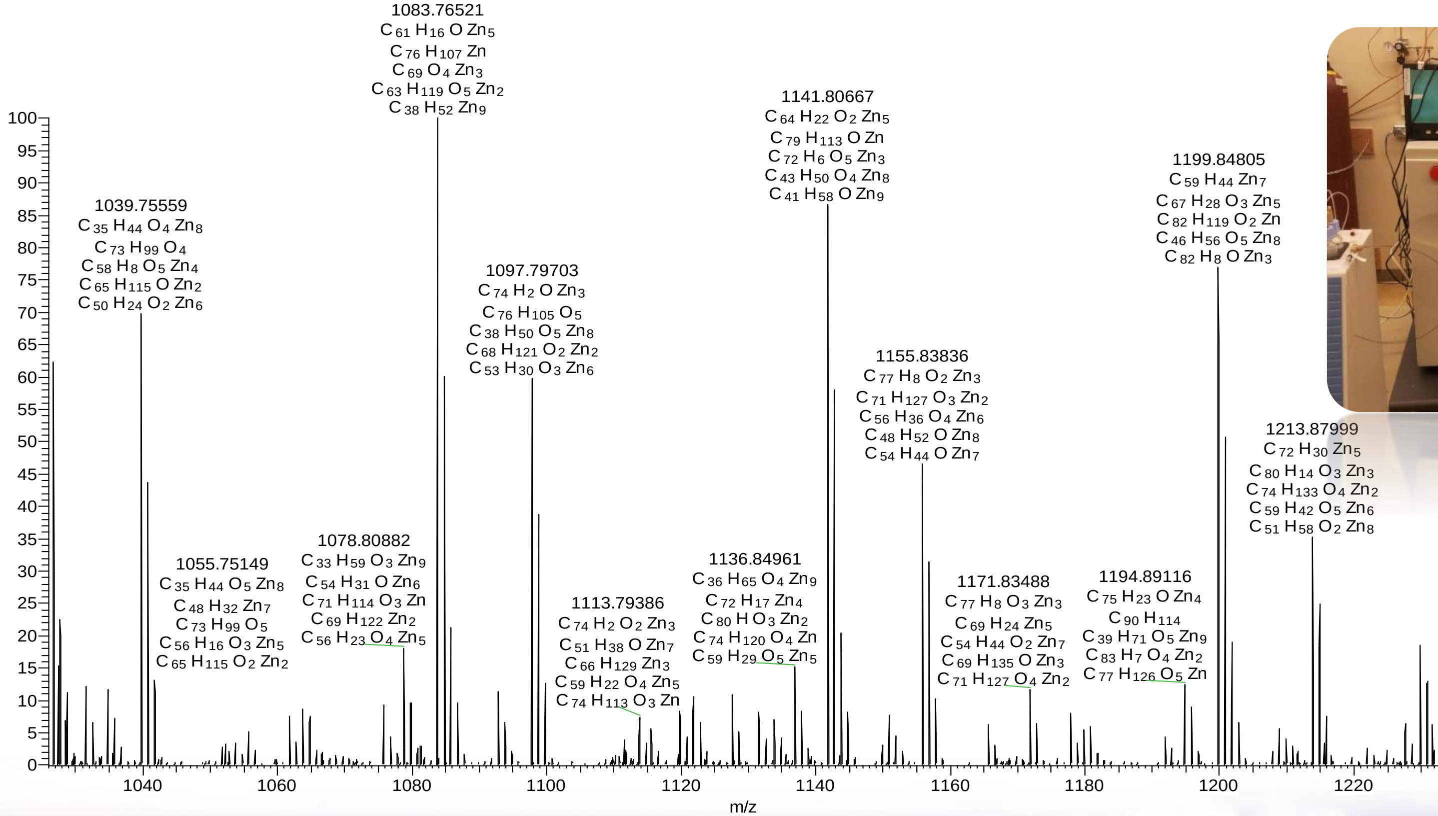
INFRARED SPECTROSCOPY

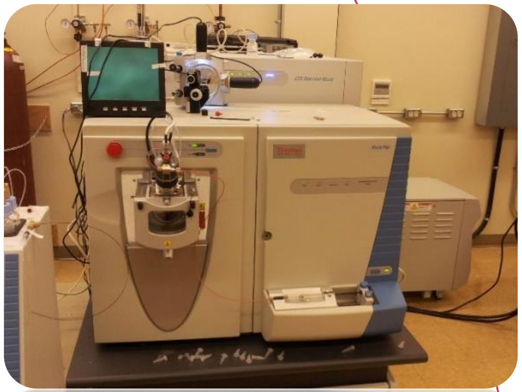


X-RAY FLUORESCENCE

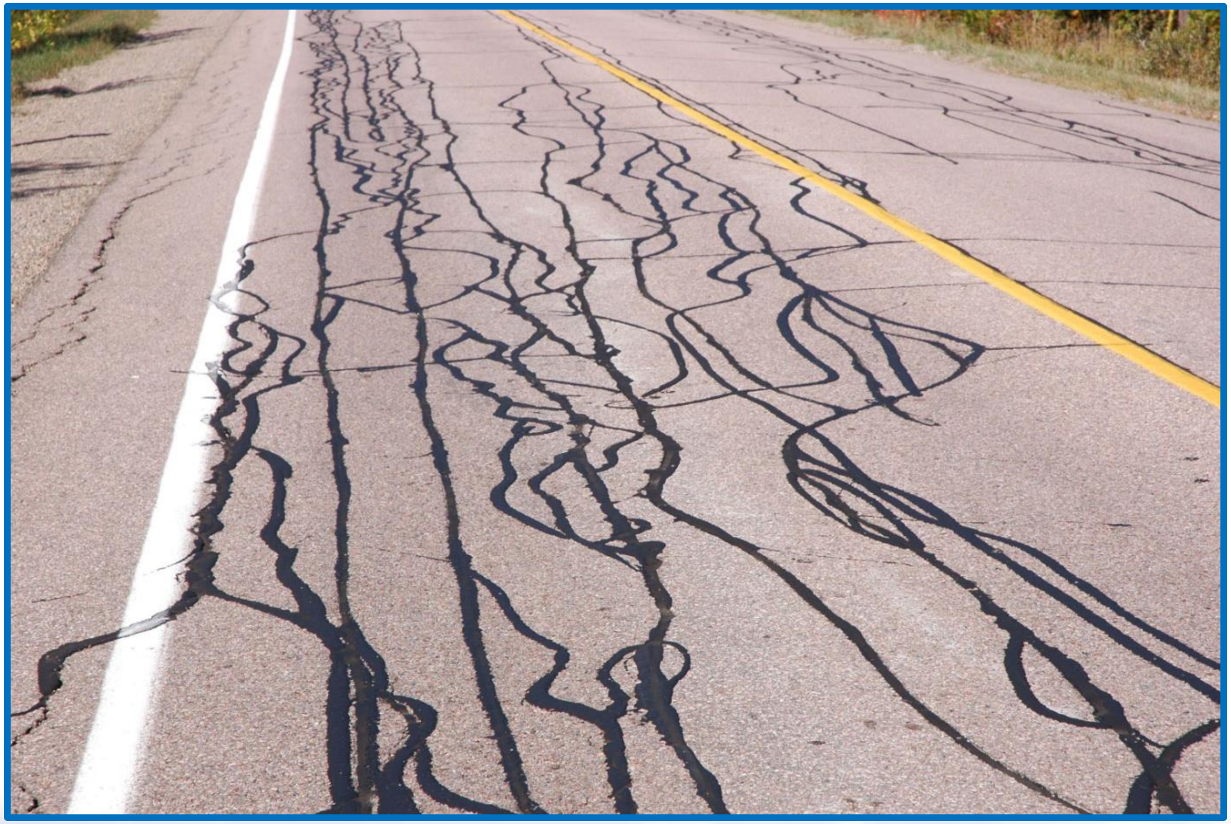


MASS SPECTROSCOPY





Questions?



Contact Information

Miglė Paliukaitė
Department of Chemistry
Queen’s University
Tel. 613-217-9727 (Cell)
E-mail: migle.paliukaite@chem.queensu.ca