

Detection of Foam-Negative Lubricants on Can Lids by Gas Chromatography / Mass Spectrometry

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Our Woesome Story..

Summer of 2014

Cans of low hop beer sporadically presented poor head retention

Same batch: bottles OK, cans bad (... sometimes)

Heat forced samples which were subsequently refrigerated, were usually OK – but not always

Occasionally, only the first pour from a can was problematic

Sometimes
foamy...



Sometimes Flat ...



Dirty tasting glasses might
be the problem...

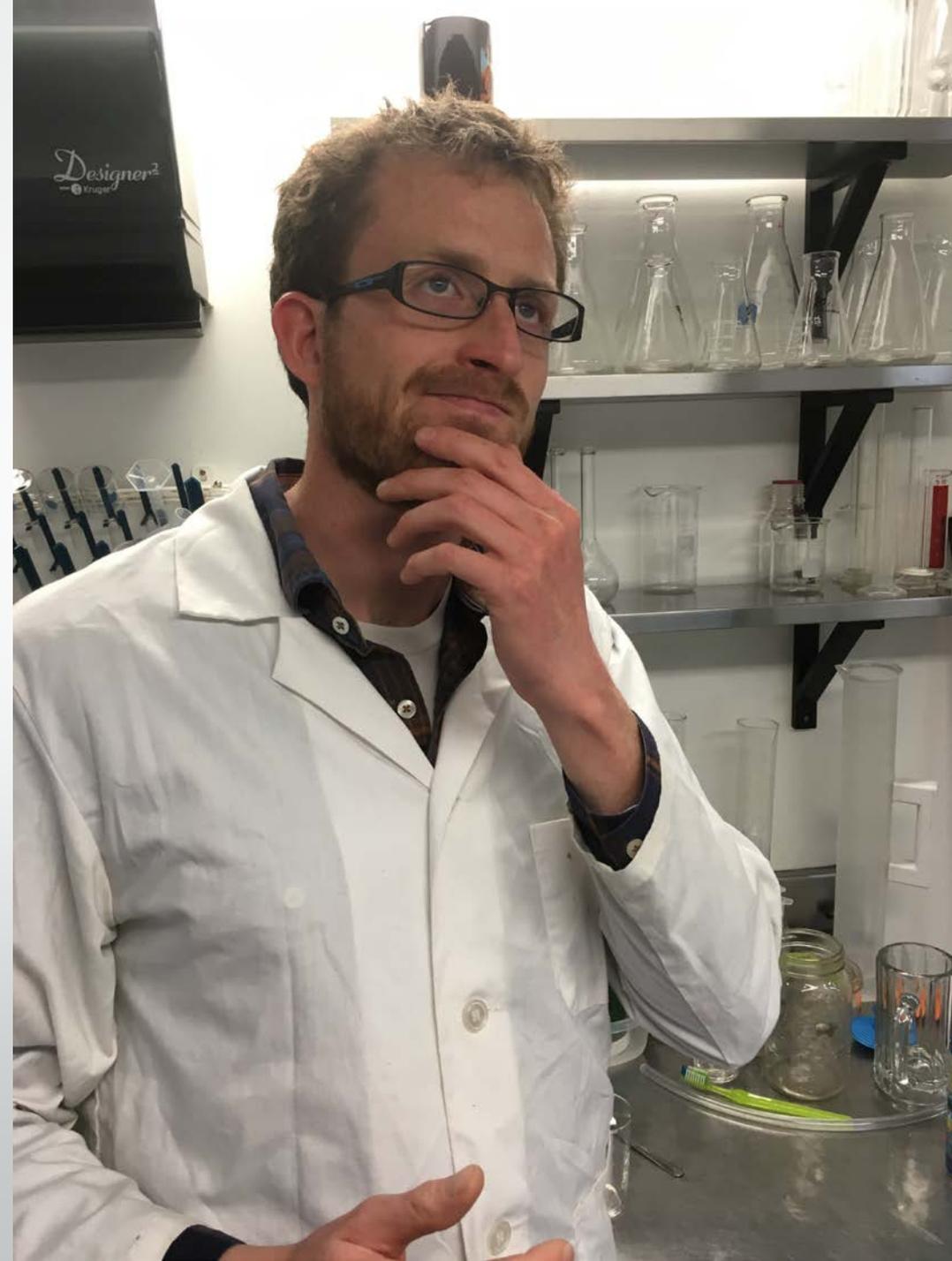
Clean with organic acid!



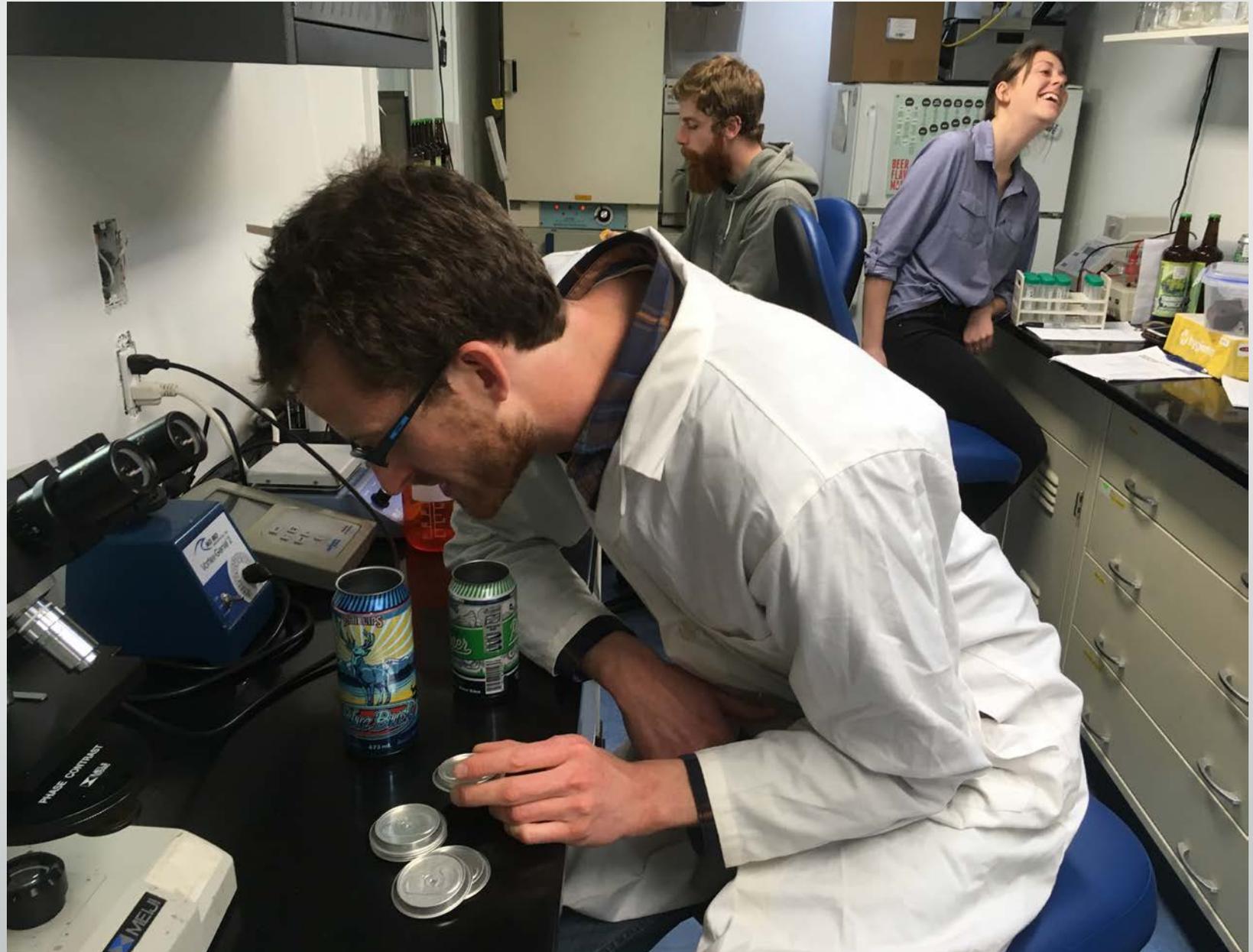
But our troubles persisted...



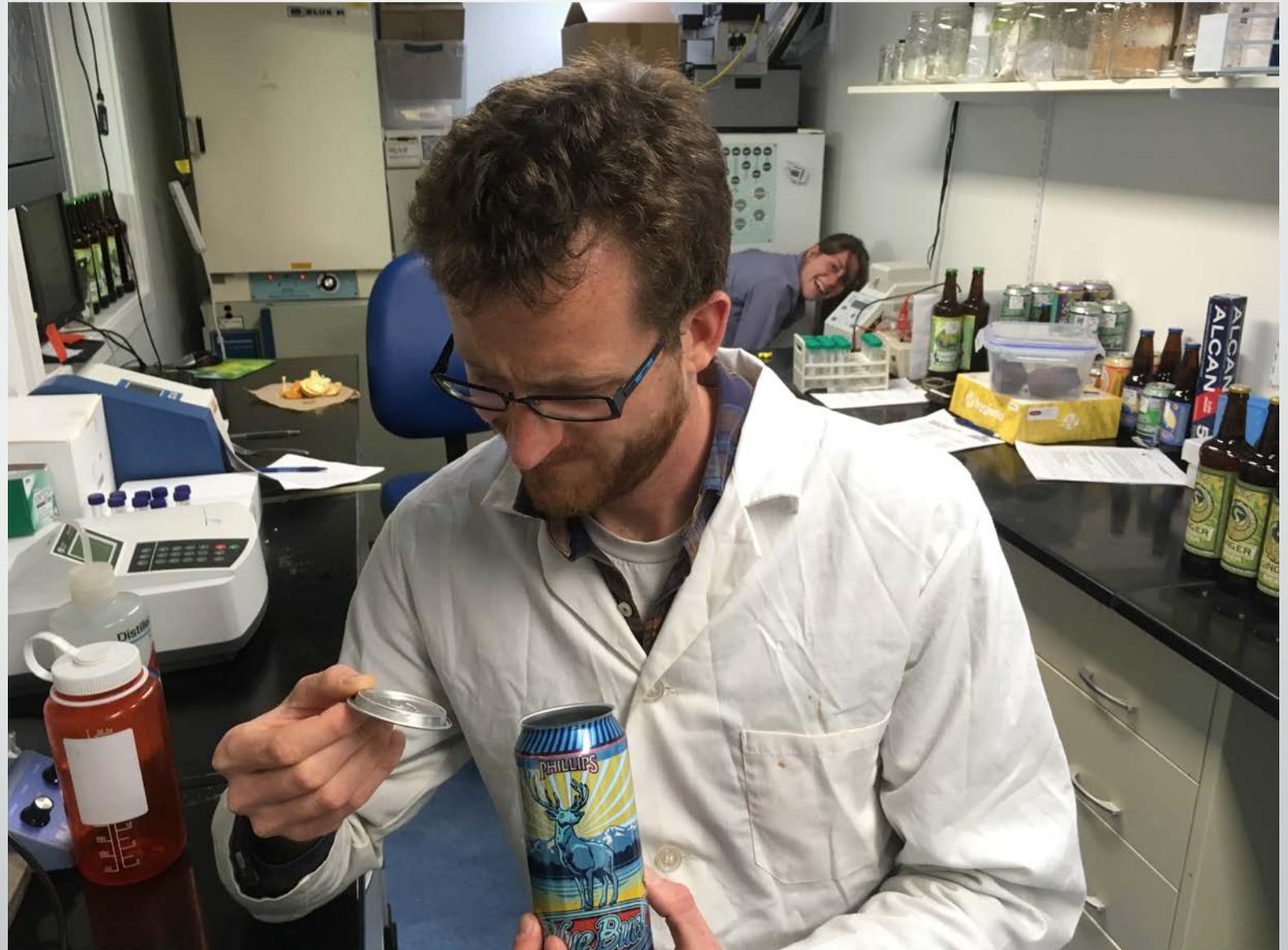
Hmmmm ...



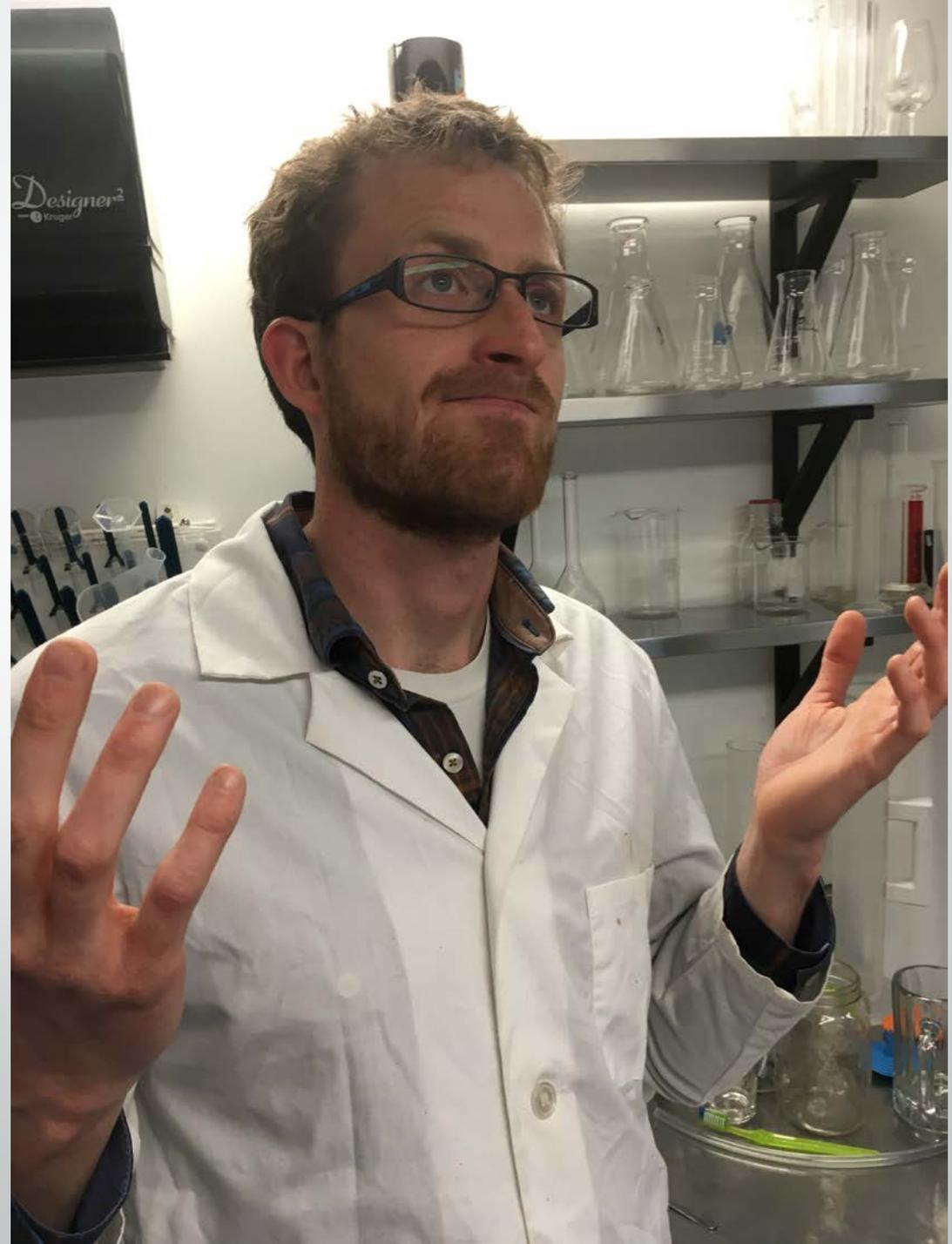
We looked at
our cans...



We looked at
our lids...



But didn't find anything
suspicious



Surely the seamer is at fault!



Seamer grease inclusion during canning runs?



Blair SurrIDGE & College Students on the Case

Experiment Outline:

- 1) Spike a sample of water with seamer grease
- 2) Identify seamer grease in spiked sample via solid-phase microextraction gas chromatography/mass spectrometry (SPME-GC/MS)
- 3) Test canned & bottled beer samples, from same batch, for seamer grease



SPME-GC/MS analysis:

Two organic amines commonly used in lubricants were detected
In deionized water + seamer grease at approximately 100:1

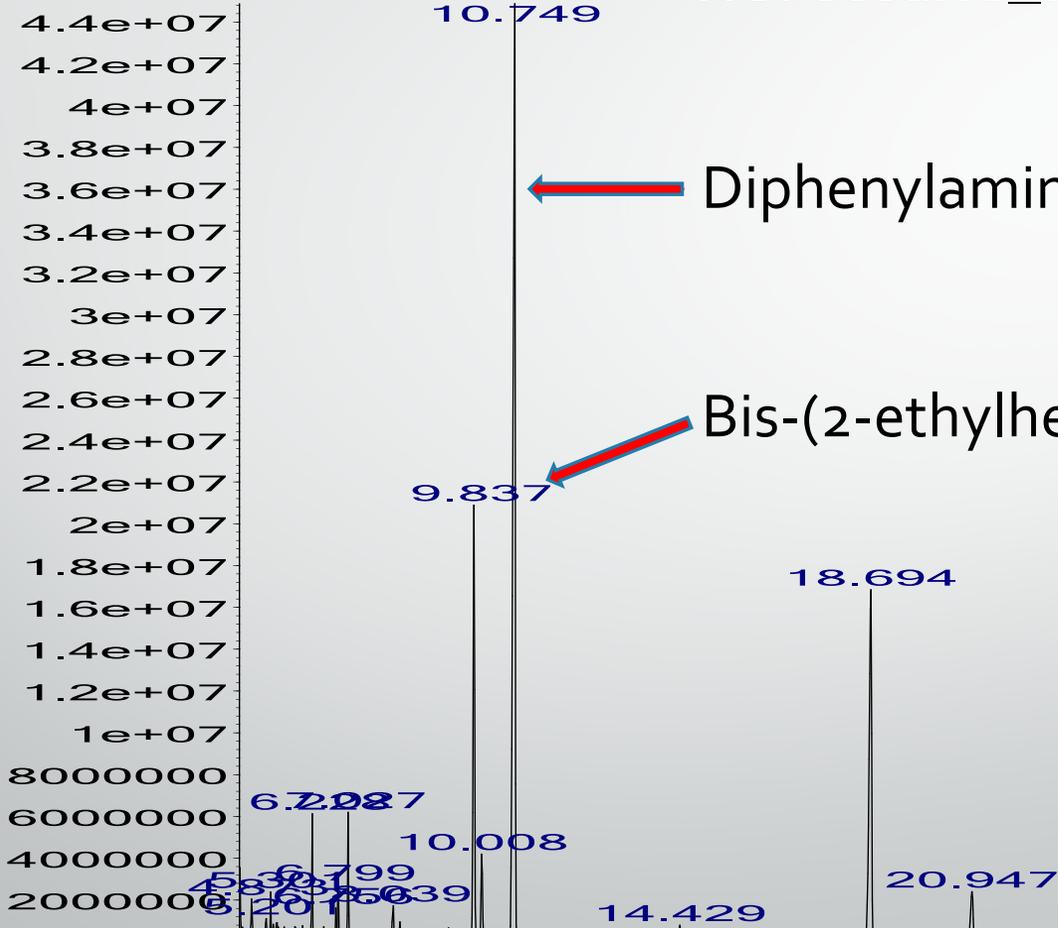
bis-(2-ethylhexyl)-amine
Diphenylamine

Water Spiked With Can Seamer Grease

SPME-GC/MS

Abundance

TIC: 06Jul15_034.D\DATA.MS



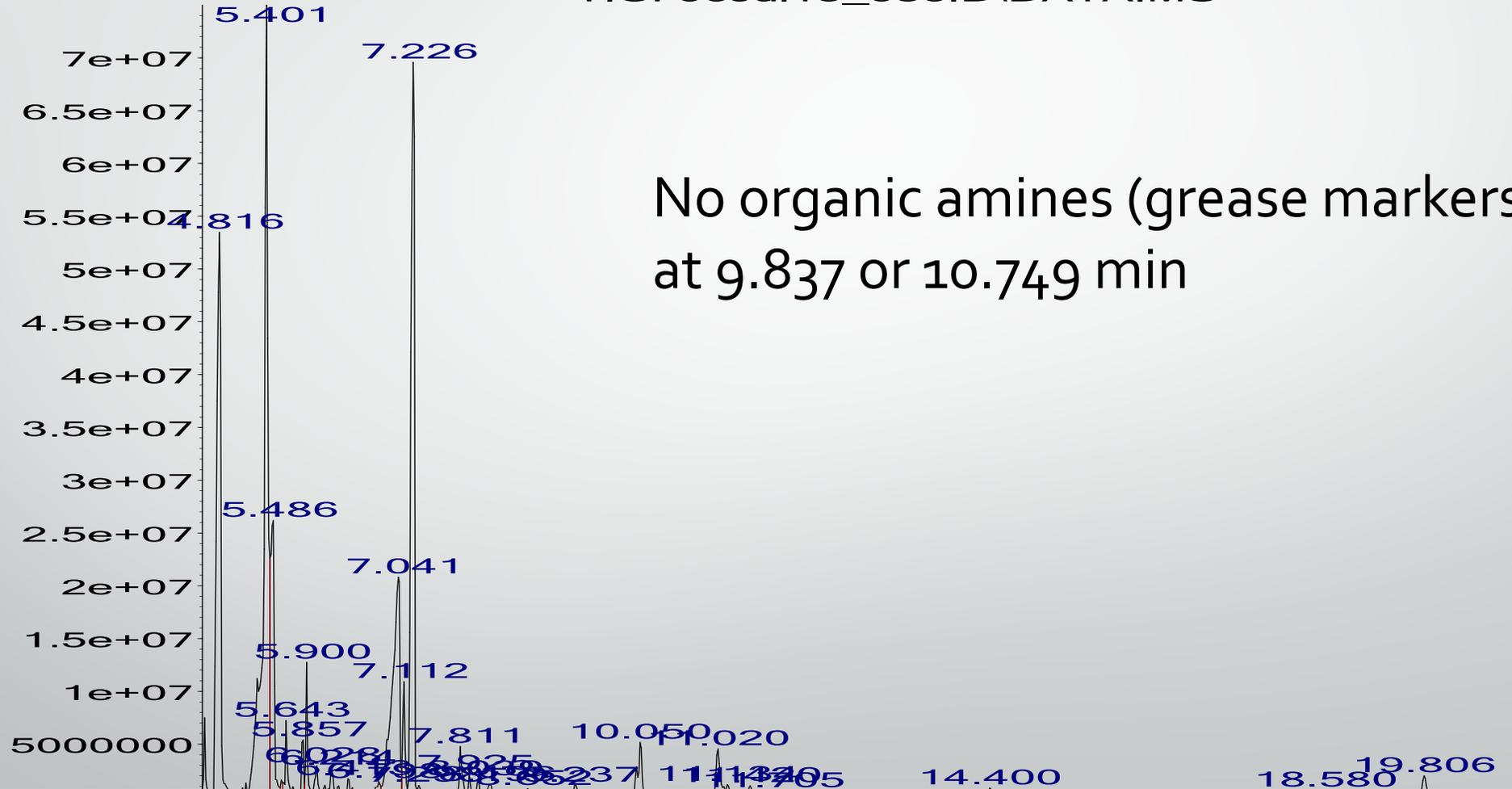
← Diphenylamine (retention time 10.749 min)

↙ Bis-(2-ethylhexyl)-amine (retention time 9.837 min)

Canned Blue Buck SPME-GC/MS

Abundance

TIC: 06Jul15_036.D\DATA.MS



Maybe our cans or
lids have residues
that we can't see...



Can and can lid washing trial

Experiment:

Wash lids but not cans (water, soap soln, IPA)

Wash cans but not lids (water, soap soln, IPA)

Wash lids and cans (water, soap soln, IPA)

Wash neither lids or cans

Heat force half / Keep other half at room temp

Triplicate

114 cans

evaluate foam after 2 weeks storage at 30 C and room temp

Can and can lid washing trial

Results:

Heat treatment	Wash Treatment	Replicate	Head immediately after pour (cm)	Head after 1 min (cm)	Head after 2 min (cm)	Head after 3 min (cm)	Head after 4 min (cm)
No heat force	Unwashed can and lid	1					
		2					
		3	6	~1 cm, very airy, big bubbles dying fast	20% bare	60% bare	70% bare
		4		spritzed to just a weak 1/2 cm ring @ perim	same	perim foam shrinking	2mm perim
		AVG					
		SD					
Heat force	Unwashed can and lid	1					
		2					
		3	5	2.5, denser head than No HF	~0.25 cm	very thin but even layer	very sparse but even, no bare spots
		4		spritzed to 2mm ring @ perim	same	same	same
		AVG					
		SD					

Can and can lid washing trial

Results Continued:

No heat force	Unwashed can, washed lid (isopropyl)	1						
		2						
		3	7	3cm decent performance		0.5 cm. airy foam	5% bare, 95% > 1 layer of bubbles	15% bare, decent foam @ perimeter
		4		jagged 5 - 9 mm ring		3-4 mm ring	2mm ring	1-2 mm ring
		5		5 mm ring + 30% sparse coverage		4mm ring, no streaming bubbles	3 - 4 mm ring, sparse foam	2 - 5 mm ring extremely sparse foam inside, no streaming bubbles
		6						
		AVG						
		SD						
		Heat force	Unwashed can, washed lid (isopropyl)	1				
2								
3	5.5			2 cm		0.5 cm	5% almost bare, 50% > 1 layer of bubbles	40% sparse, no bare spots
4				5mm ring + sparse foam inside perim		no streamin bubbles!?!	5mm ring	5 mm ring, some sparse foam inside perim, no streaming bubbles
5				3mm ring		same	2mm ring	2 mm ring
6								
AVG								
SD								

Data, Data, Numbers



Can and can lid washing trial:

BUST!

No significant difference in head retention for any samples, heat forced or not

Beer chosen for the trial probably did not contact our mystery head killer

Well, shucks.



We took an
EVEN CLOSER
look at our can
lids ...



Eureka!



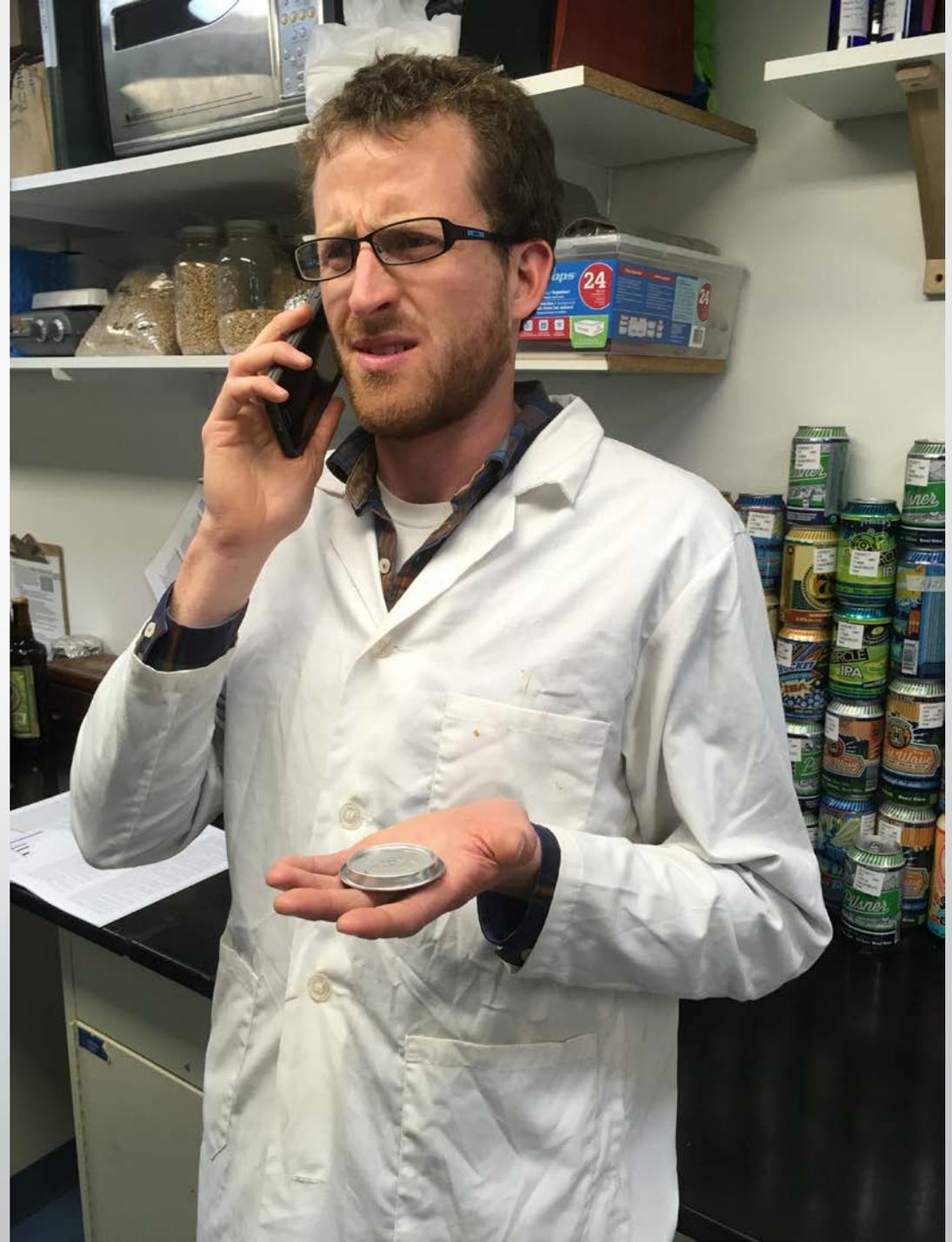
Aha!



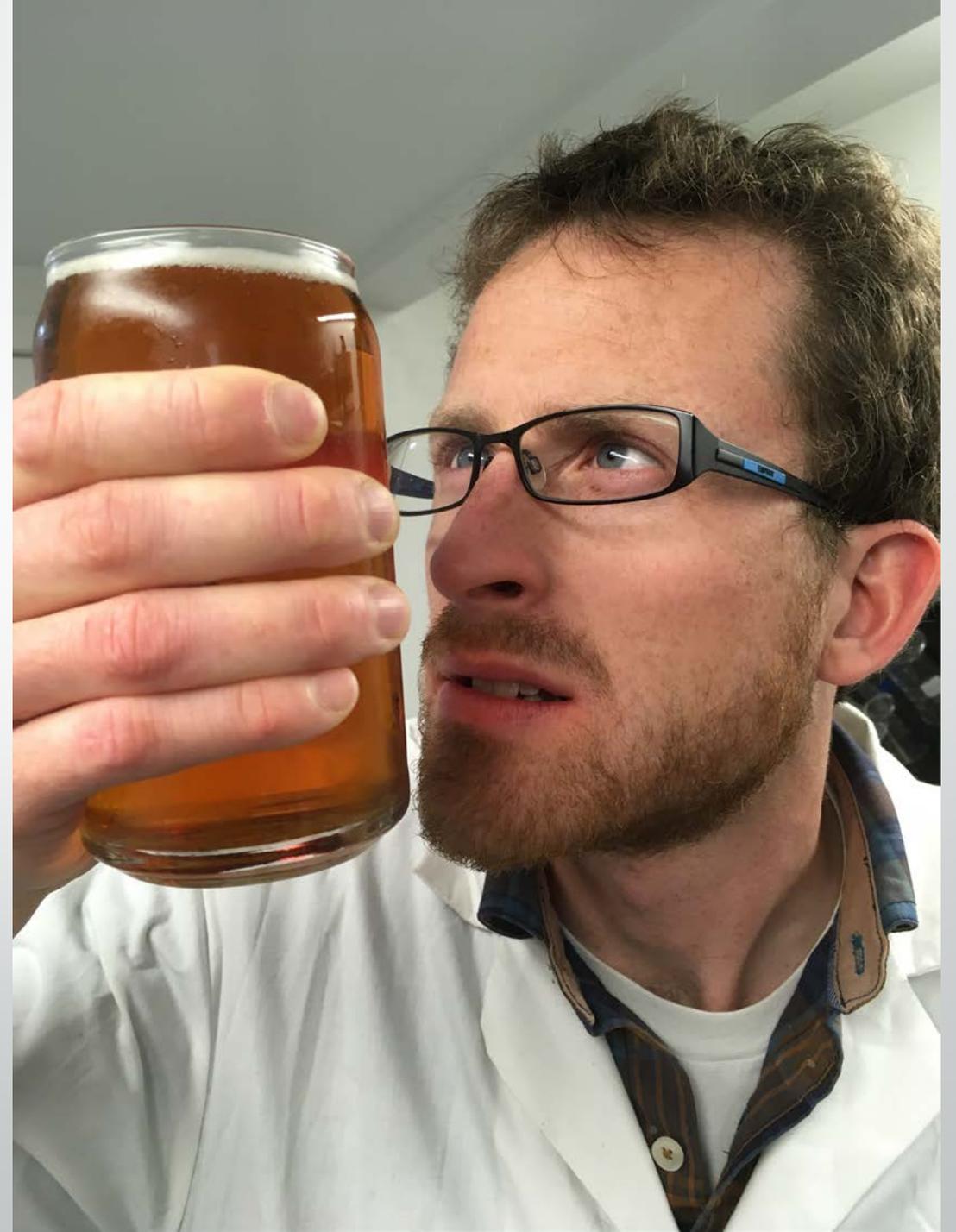
We immediately called
our supplier with this
very important news!



Can lid supplier:
“That’s just our tab lube”



What the heck is in
our beer!?!



Camosun College Chem. Department, Victoria BC

Blair Surridge



Corrine



Laura



Karl



Jennifer



GC/MS Experiment Outline

Flush tab lube from can lids using methanol followed by toluene

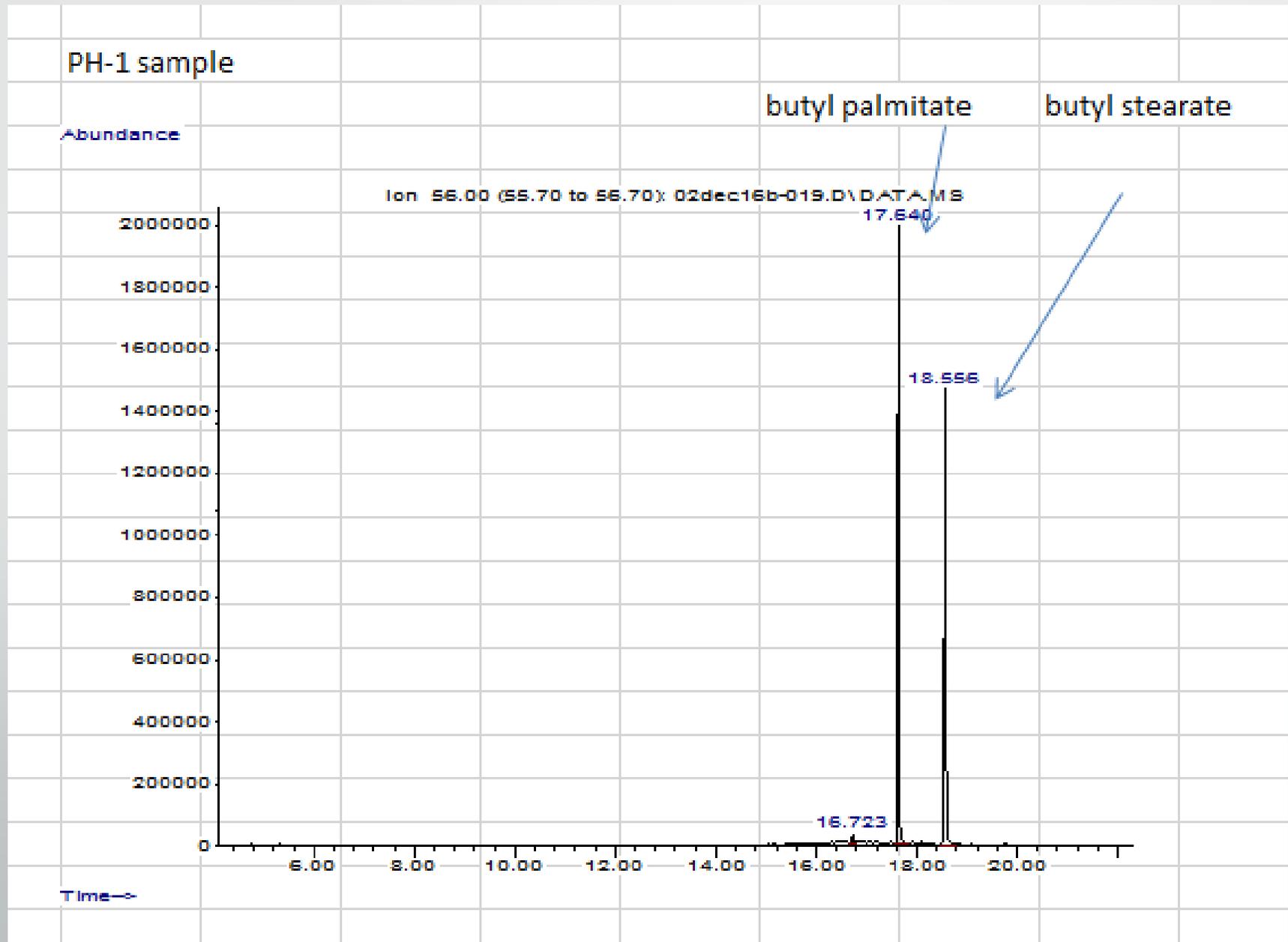
Employ an internal standard of carvone

Blanks: methanol and toluene

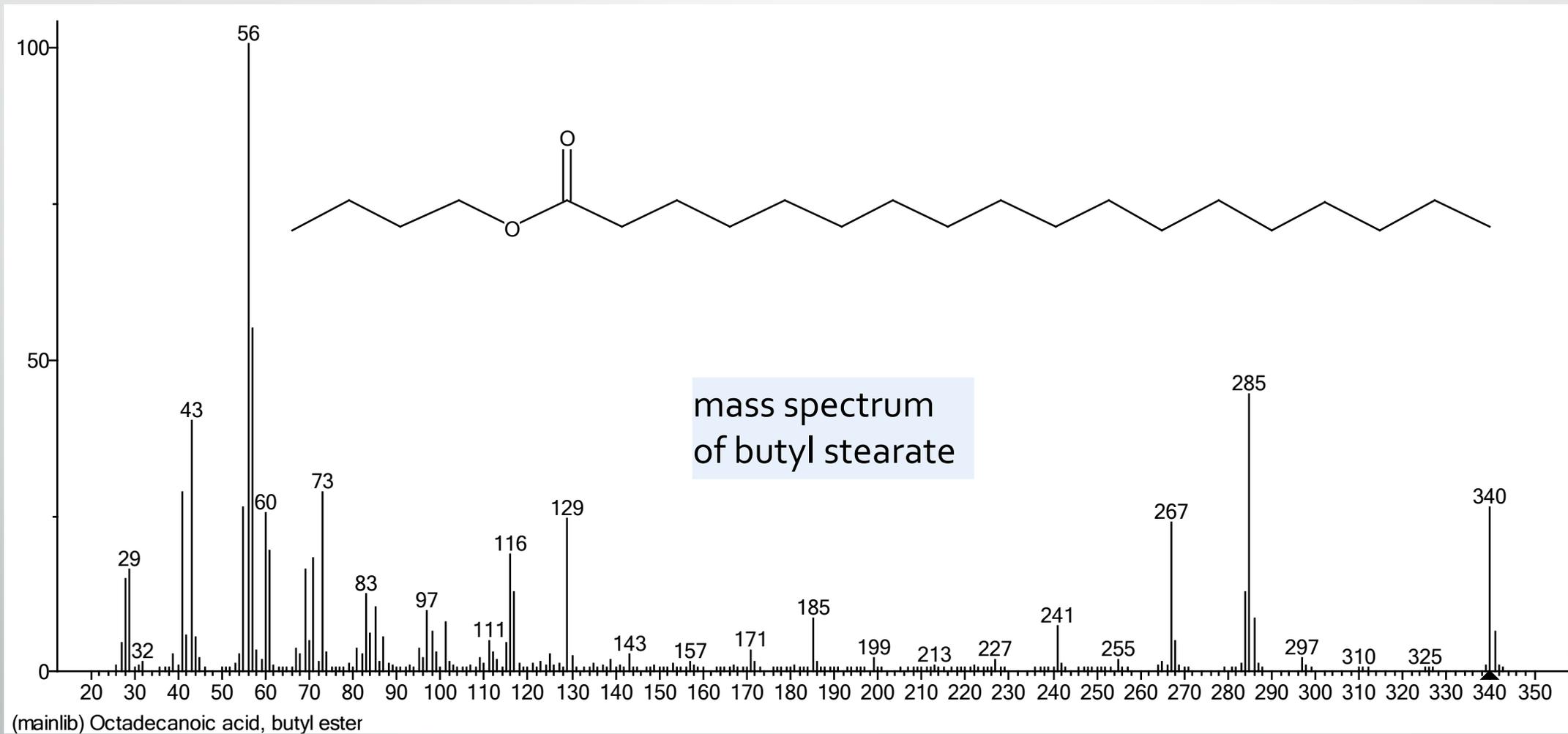
Identify and quantify presence of tab lube in methanol/toluene solutions used to flush lube from lids

Test can lids from our supplier plus another supplier

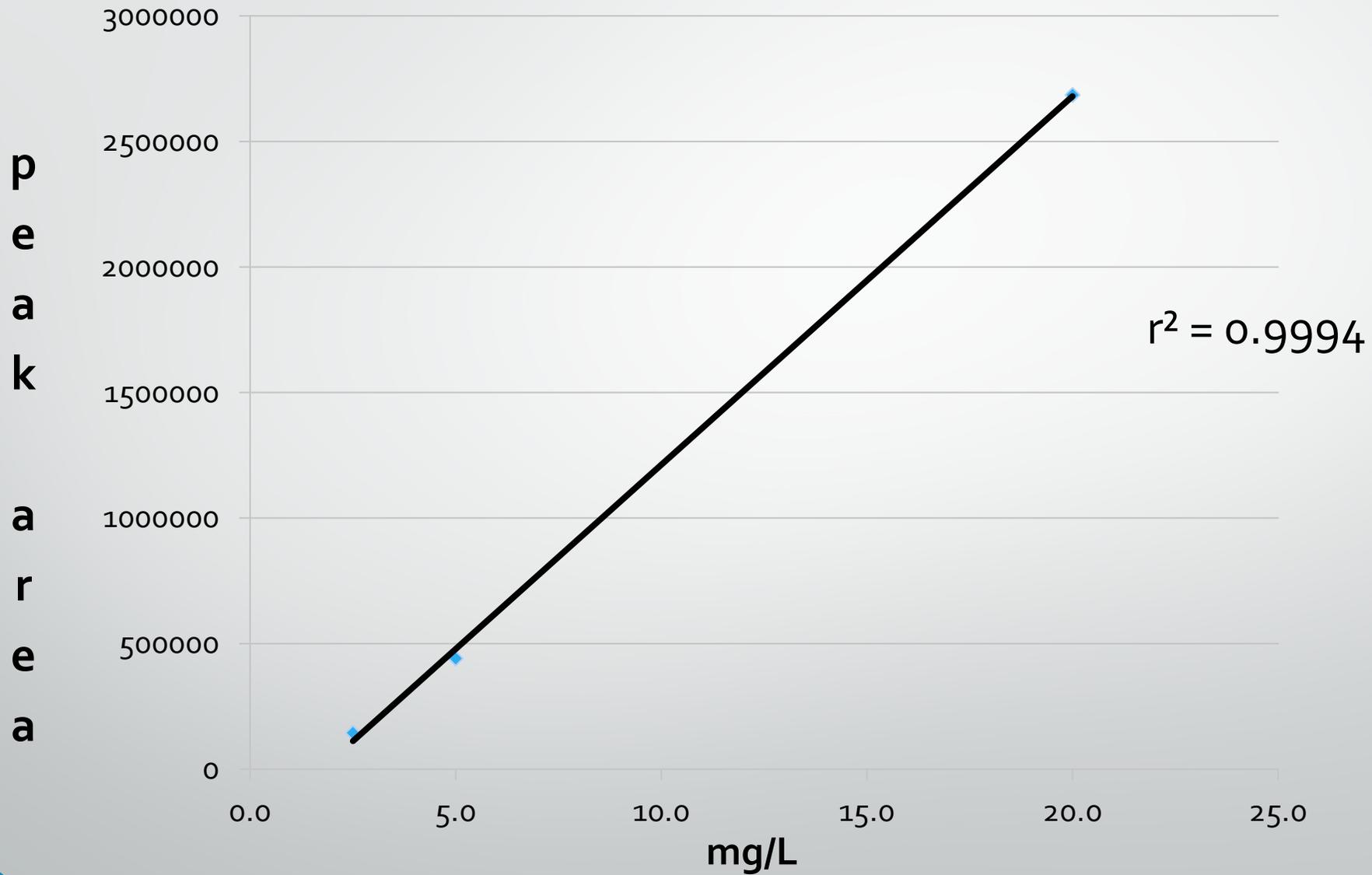
GC-MS Analysis of PH-1 Can Lid



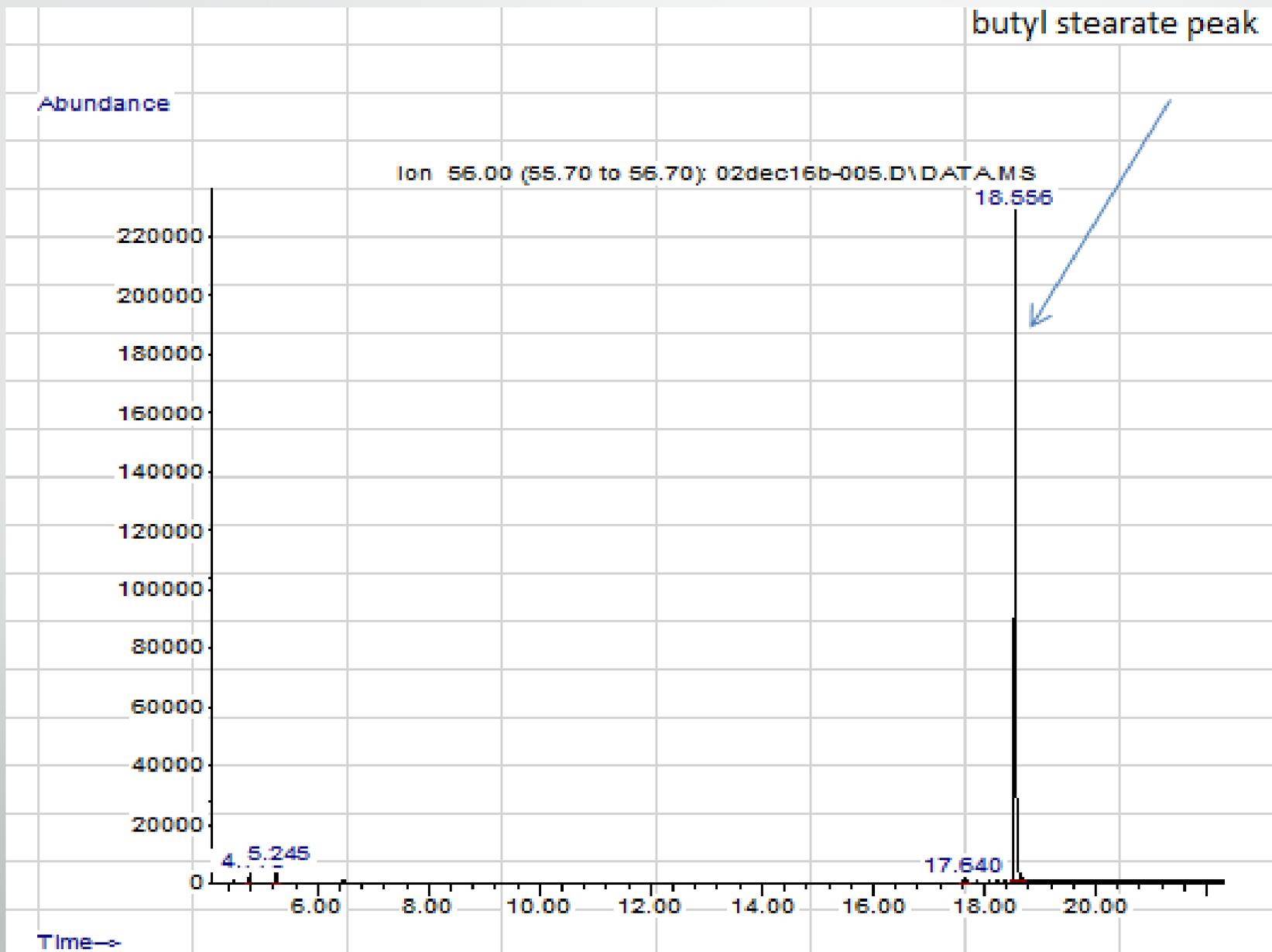
Mass Spectrum of Butyl Stearate



Butyl Stearate Calibration Curve

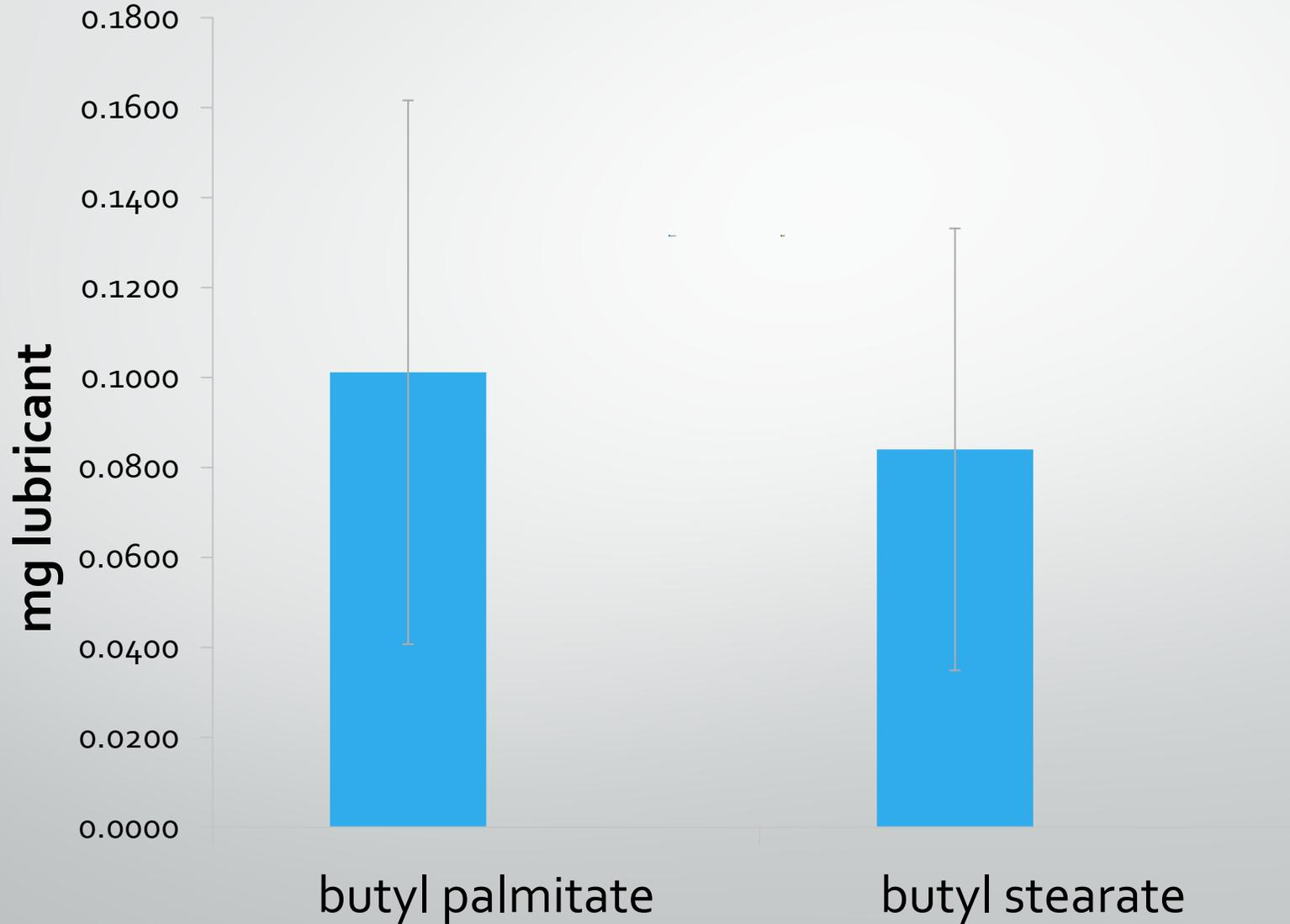


Butyl Stearate Standard Solution GC/MS



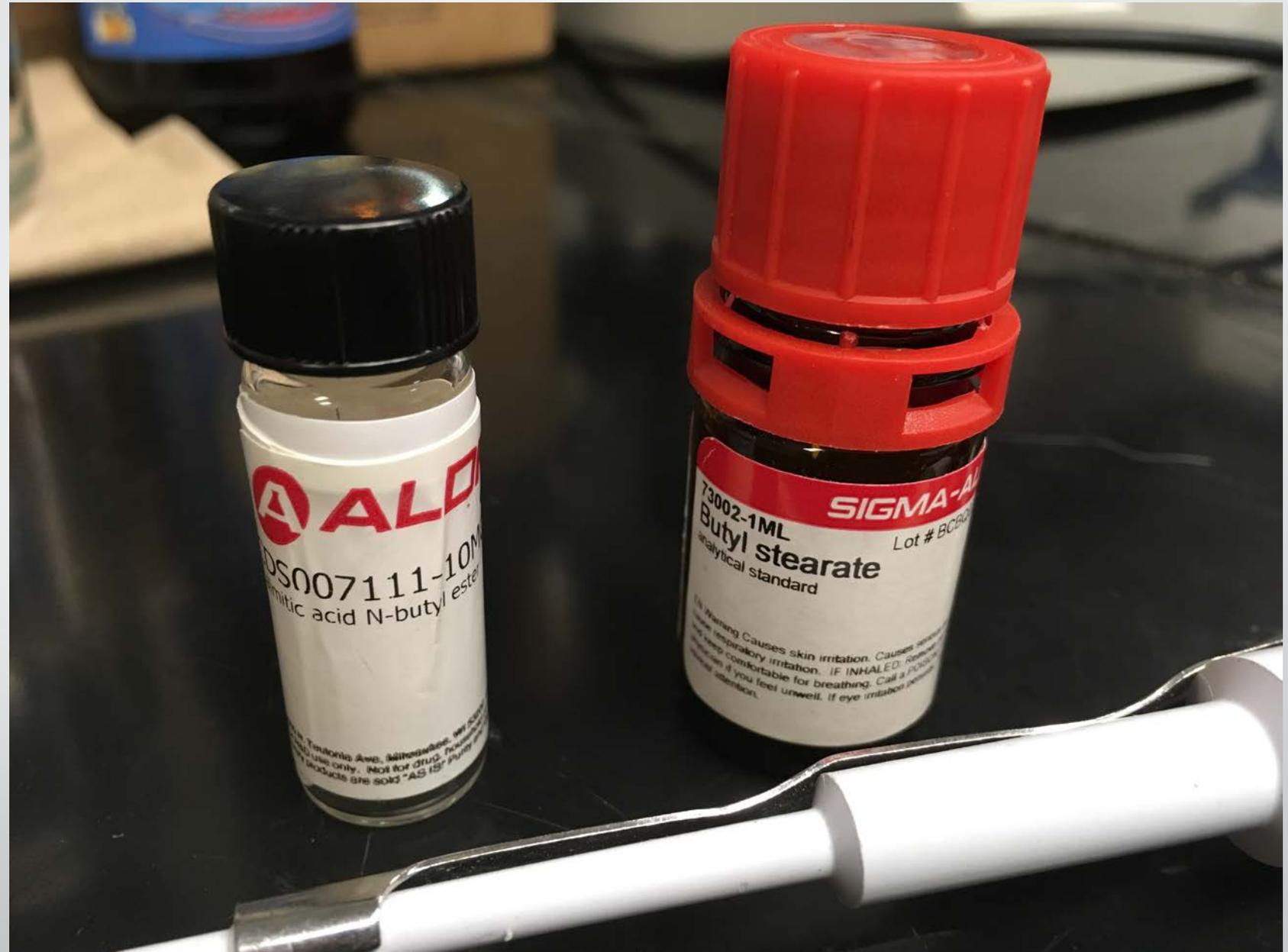
	butyl palmitate	butyl stearate	butyl palmitate	butyl stearate
	area	area	mg per can	mg per can
	17.64 min	18.556 min		
sp-1	nd	nd	nd	nd
sp-2	nd	nd	nd	nd
sp-3	nd	nd	nd	nd
sp-4	nd	nd	nd	nd
Ph-1	3949601	3326072	0.1433	0.1220
Ph-2	81981	91788	0.0115	0.0118
Ph-3	3480354	2694180	0.1273	0.1005
Ph-4	3343719	2730012	0.1226	0.1017
		avg:	0.1012	0.0840
		st deviation:	0.0604	0.0491

Average mg Lubricant for Can Lids Tested



Butyl
Palmitate

Butyl
Stearate



Butyl Stearate

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid. (A liquid at temperatures above 20 C)

Odor: Odorless. Faintly Fatty

Taste: Fatty Fruity, acid.

Molecular Weight: 340.57 g/mole

Color: Colorless to light yellow

pH (1% soln/water): Not applicable.

Boiling Point: 343°C (649.4°F)

Melting Point: 27°C (80.6°F)

Critical Temperature: Not available.

Specific Gravity: 0.854 - 0.875 (Water = 1)

Vapor Pressure: 0 kPa (@ 20°C)

Vapor Density: 11.4 (Air = 1)

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water, acetone.

Solubility:

Easily soluble in acetone. Insoluble in cold water, hot water. Soluble in ethanol, mineral oils, vegetable oils. Solubility in Water: 0.29% @ 25 deg. C

Butyl Palmitate aka Palmitic Acid N-butyl Ester

Physical & Chemical Properties

Physical state	Liquid.
Appearance	Clear, colorless liquid.
Form	Liquid.
Odor	Not available.
Odor threshold	Not available.
pH	Not available.
Vapor pressure	0.0000099 kPa at 25°C
Vapor density	Not available.
Boiling point	338 °F (170 °C) at 10 mm Hg
Melting point/Freezing point	57.2 - 62.6 °F (<u>14 - 17 °C</u>)
Solubility (water)	Practically insoluble

Effects of Butyl Stearate and Butyl Palmitate on Beer Foam Trials

Trial	Description	uL
0	Unopened ctrl	0
1, 2, 3	Resealed ctrl	0
4, 5, 6	palmitate	0.14
	stearate	0.18
7, 8, 9	palmitate	0.28
	stearate	0.36
10, 11, 12	palmitate	0.42
	stearate	0.54

Effects of Butyl Stearate and Butyl Palmitate on Beer Foam

Results:

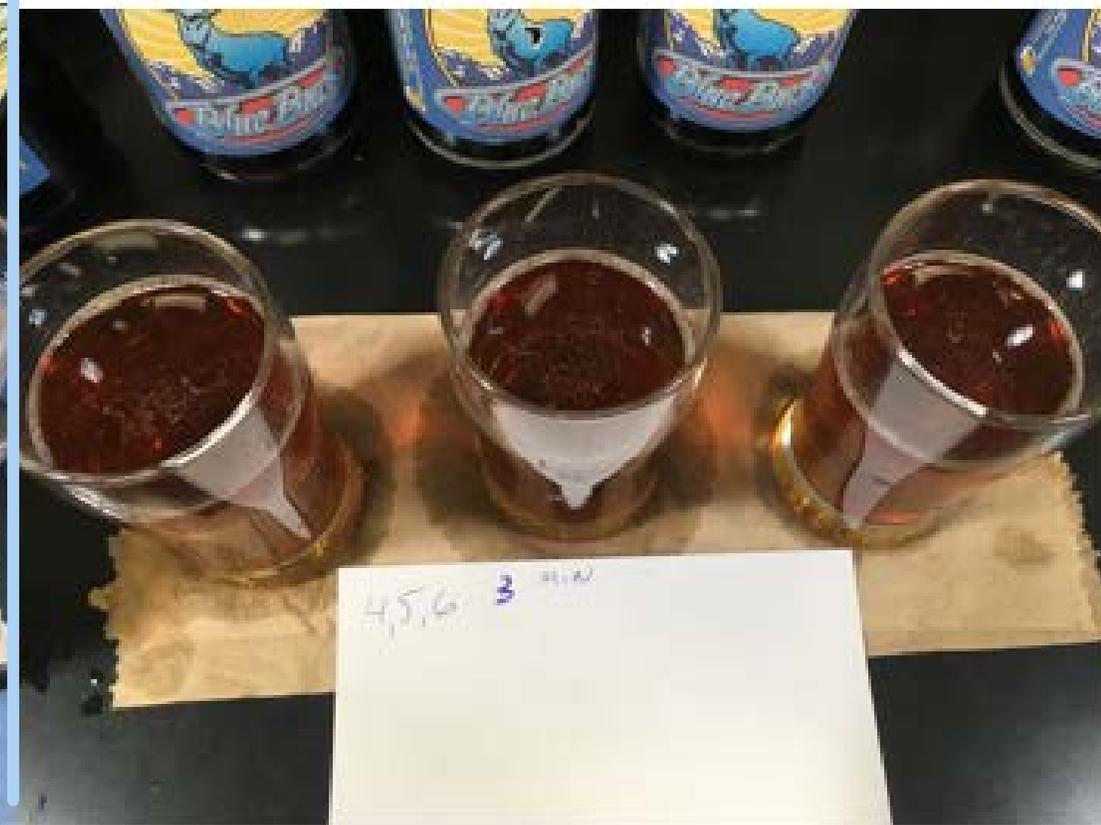
~100 mL of beer poured with ~ 1 inch heads, after 4 minutes:

	mm ring of foam
Unopened ctrl	< 4
Resealed ctrls	<3, <4, <3
Dosage rate 1	<1, <1, <1
Dosage rate 2	<1, <1, <1
Dosage rate 3	<1, <1, <2

Samples at 3 minutes after pouring ~100 mL samples with ~1 inch heads @ 28 to 30 C

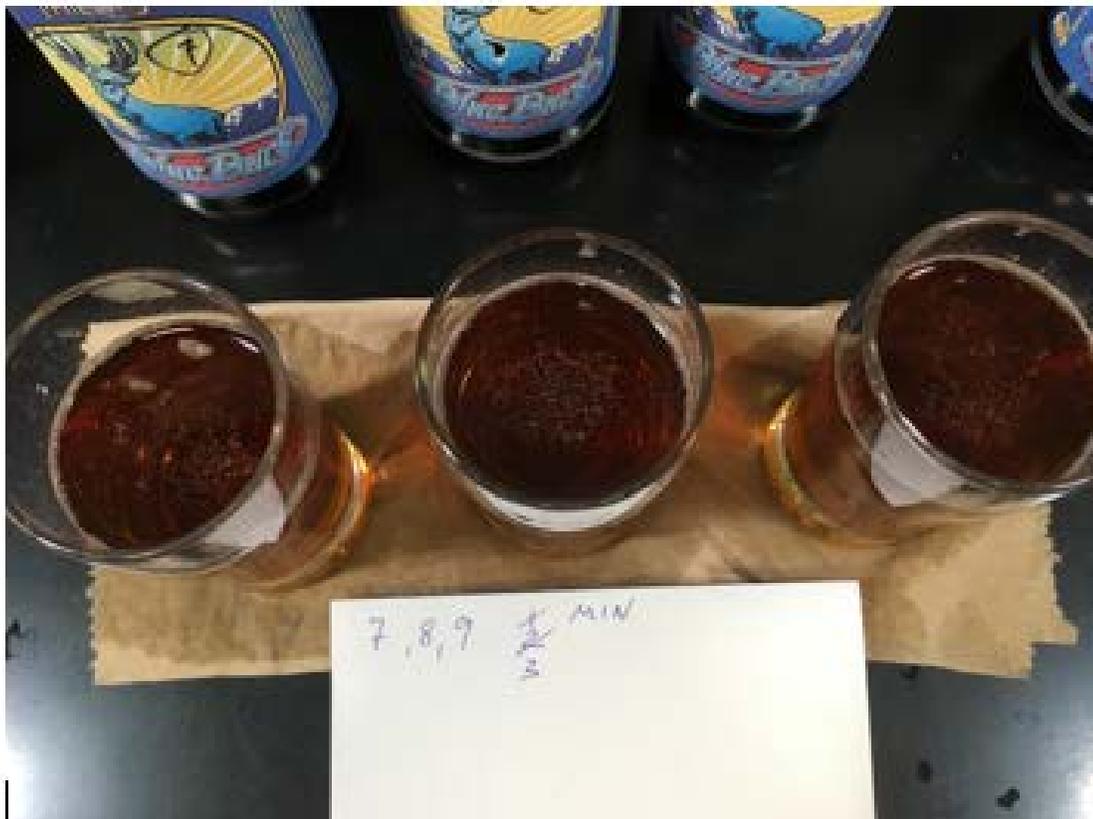


1, 2, 3 opened & resealed controls



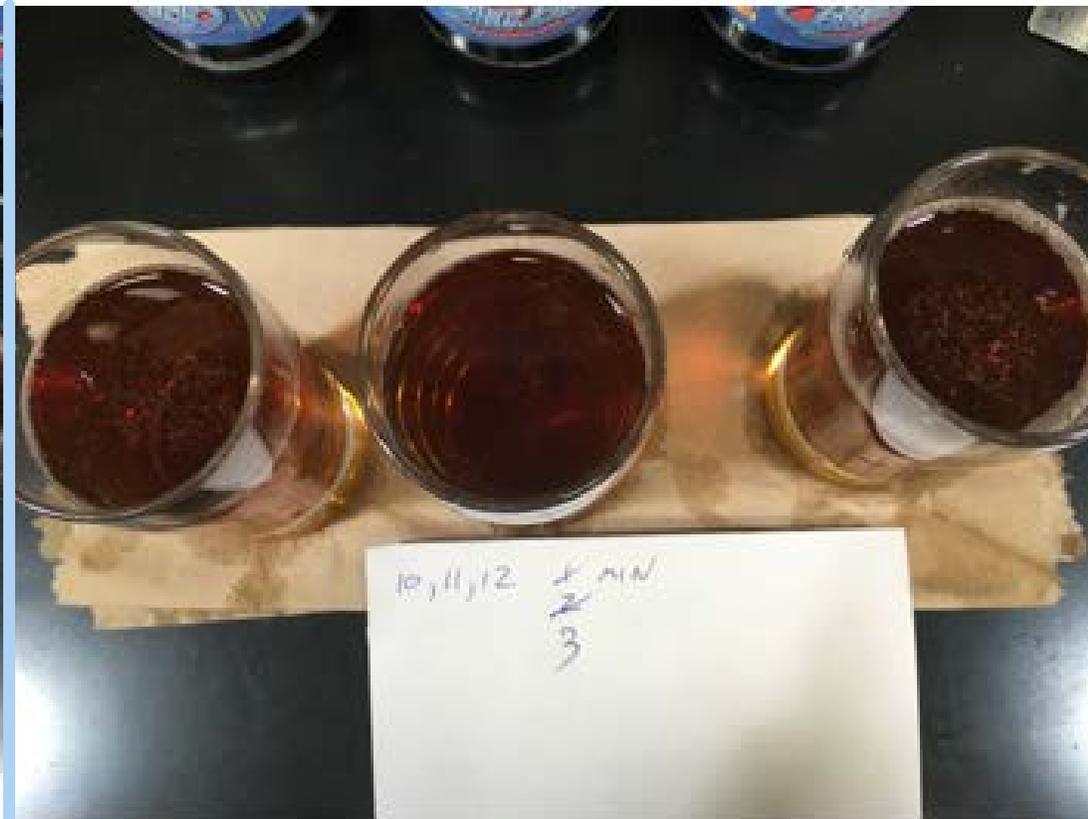
4, 5, 6 0.14 uL BP 0.18 uL BS

Samples at 3 minutes after pouring ~100 mL samples with ~1 inch heads @ 28 to 30 C



7, 8, 9 0.28 uL BP

0.36 uL BS



10, 11, 12 0.42 uL BP

0.54 uL BS

Conclusions:

Heat forced beer spiked with butyl stearate & palmitate exhibited impaired head retention between 28 & 30C compared to controls

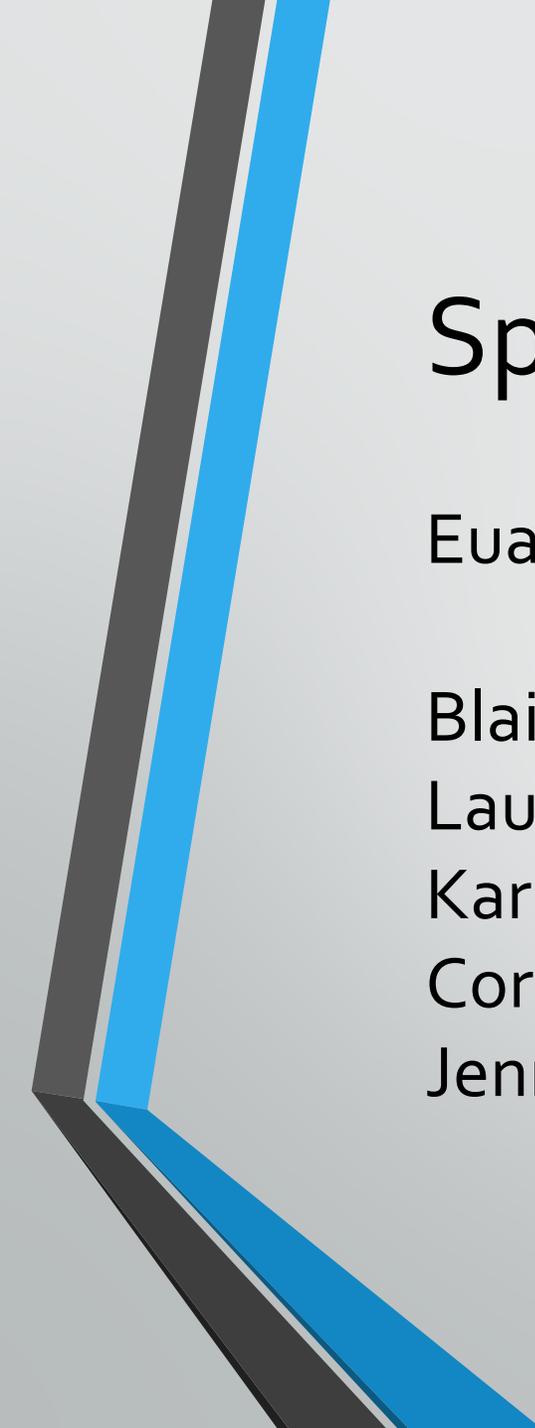
Visual can lid inspections are sufficient to determine lube presence

Not all can lids are made equal

- Presence of tab lube is variable, within lots, even within sleeves
- Presence of tab lube is variable from one supplier to another

Libel suits against me are not encouraged

Ties with your local schools are highly valuable!



Special Thanks To:

Euan Thomson, model, gentleman, Esquire

Blair Surridge, Camosun College, Victoria BC

Laura McPherson

Karl Carriere

Corrine Guan

Jennifer Dolberg

Thank You!

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What makes a long-lasting beer head

