



# Assessment of the Stability of the Methylene Blue Solution and the Properties of Various Filter Media for Methylene Blue Titration

Yunhui Li, Heather Kaminsky, Andrea  
Sedgwick, Taimur Qureshi, and Yuki Gong

# Clays are Influential in Oil Sands Operations

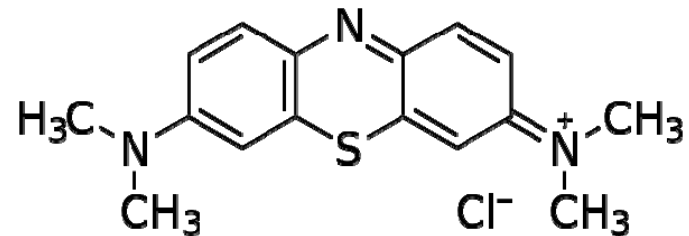


- Clay content affects bitumen extraction efficiency – for example, one lab study found;<sup>1</sup>
  - Clay content < 6 wt% → bitumen loss < 18%
  - Clay content > 18 wt% → bitumen loss > 60%
- Clay content and activity affects tailings management.
  - Clay content affects consolidation strategies.

1. Xu, Z., L. Yan, L. Alagha and J. Masliyah, 2013. CONRAD Oilsands Clay Conference, February, 2013, Edmonton, Alberta.

# Methylene Blue Test Method

Methylene blue (MB) is used as an indicator of clay activity and clay content.<sup>2</sup>

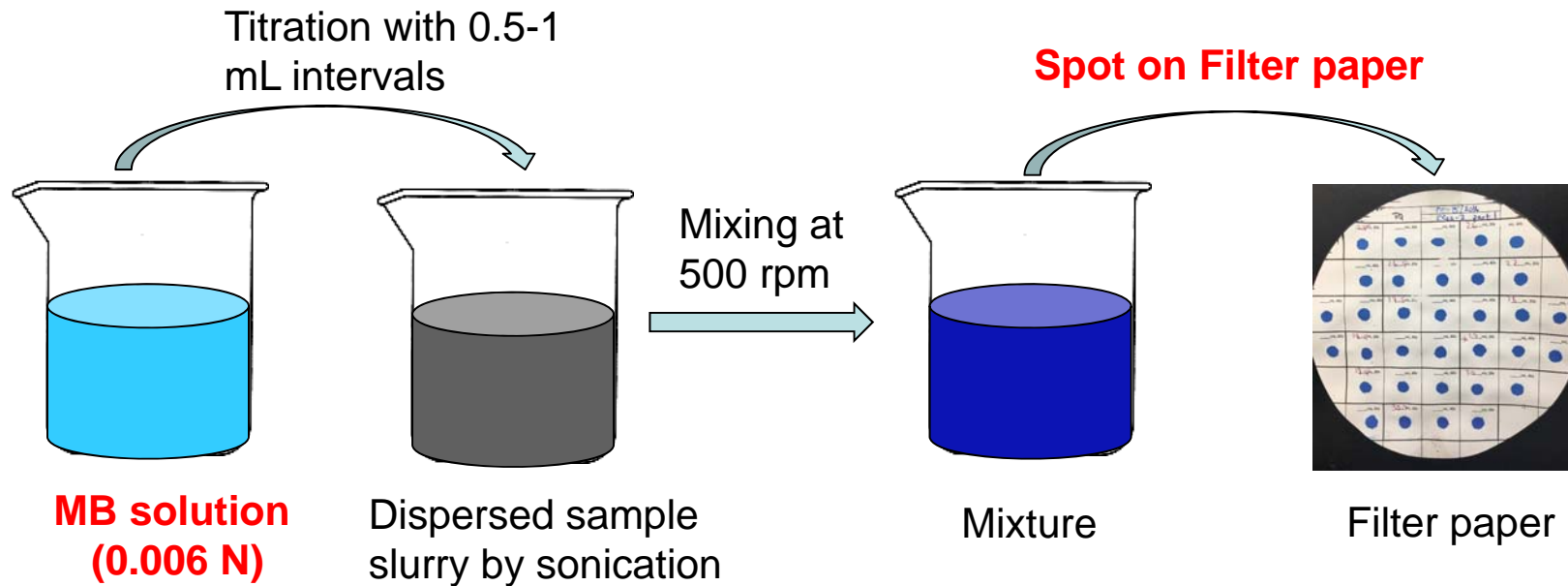


Advantages of MB test method:

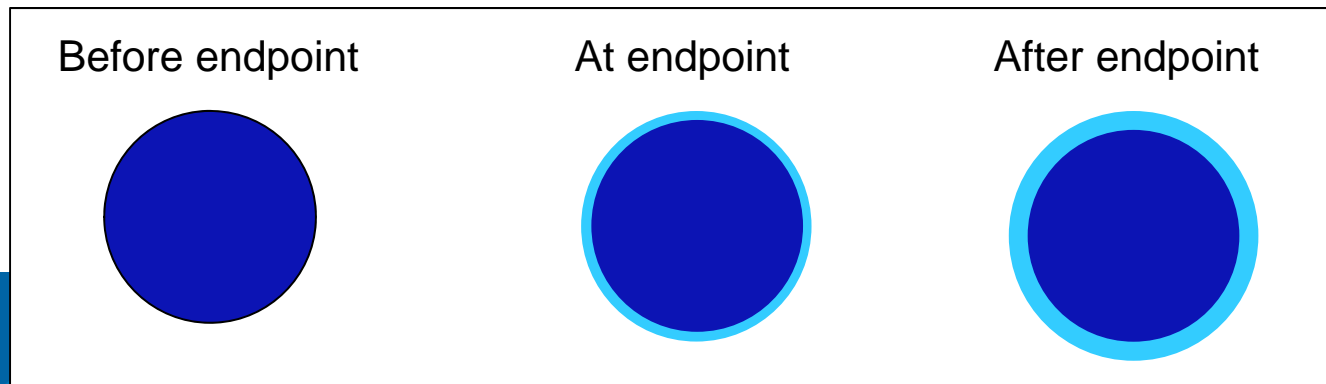
- Easily applicable;
- Need no special equipment;
- Yield useful results which reflect clay content and activity.



# Spot Test Method



Spot at different stages of titration:



# MBI Test Method used by Oil Sands Operators

- Clay content (or clay activity) as determined by methylene blue index (MBI)

$$\text{MBI} \left( \frac{\text{meq}}{100 \text{ g}} \right) = \frac{\text{mls MB} \times \text{Normality of MB}}{\text{mass of dried sample (g)}} \times 100$$

- The Methylene blue index (MBI) has been correlated to a typical wt% of oil sands clay using the following empirical equation:<sup>3</sup>

$$\text{Wt\% Clay} = \frac{\text{MBI} \left( \frac{\text{meq}}{100 \text{ g}} \right) + 0.04}{0.14}$$

3. Yong, R.N. and A. Sethi, 1981. Patent# 44529000.

## Two Key Aspects of the MBI Test

1. Assess the stability of the methylene blue (MB) solution
2. Assess the properties of various filter media for MB titration

# Stability of the Methylene Blue Solution

- MB solution is believed to degrade with time due to the decrease in the visible adsorption of aqueous monomer and dimer MB species. So most labs make a fresh MB solution each day;
- Preparing the MB solution is a time consuming process due to the slow dissolution rate;
- Ability to store MB solution could increase the number of tests;
- It is desirable for on-line MBI applications.



# Stability Testing Factors of the MB Solution

- Effect of light – different storage bottles:
  - Glass bottle covered with aluminum foil – dark condition;
  - Clear glass bottle under light – light condition;
  - Amber glass bottle under light – a condition between light and dark.
- Effect of temperature – room temperature (RT, 22°C) and 4°C.
- Effect of days: 0–23 days.

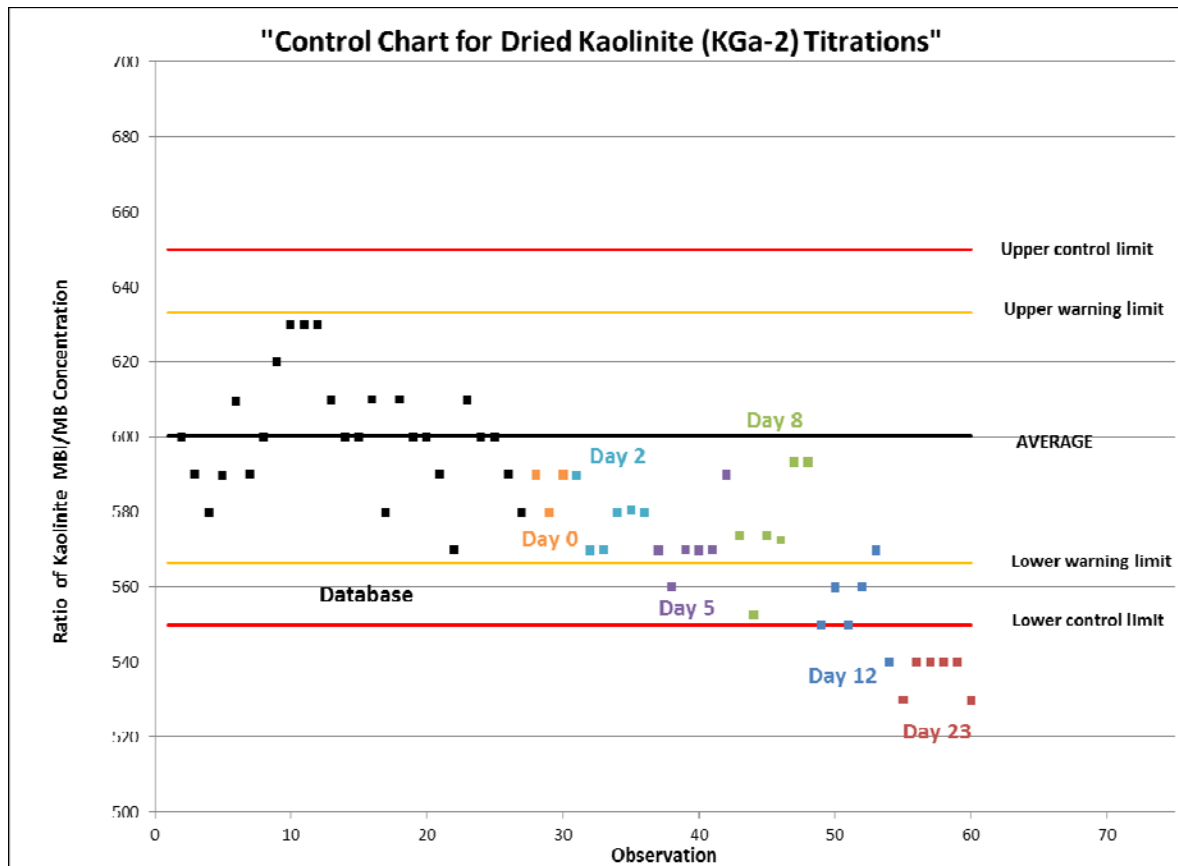
Standard check sample: Kaolinite from the Clay Minerals Society source clay repository.



# Stability Testing of the MB Solution

Degradation of the solution is noticed with time.

The change does not hit the control limit until Day 12.



$$\text{Upper Control Limit} = \text{Average} + 3 \times \text{STDEV}$$

$$\text{Upper Warning Limit} = \text{Average} + 2 \times \text{STDEV}$$

$$\text{Lower Warning Limit} = \text{Average} - 2 \times \text{STDEV}$$

$$\text{Lower Control Limit} = \text{Average} - 3 \times \text{STDEV}$$

The ratios of kaolinite MBI and MB concentrations instead of MBI values are used to generate the control chart in order to eliminate the variation of prepared MB solution concentrations.

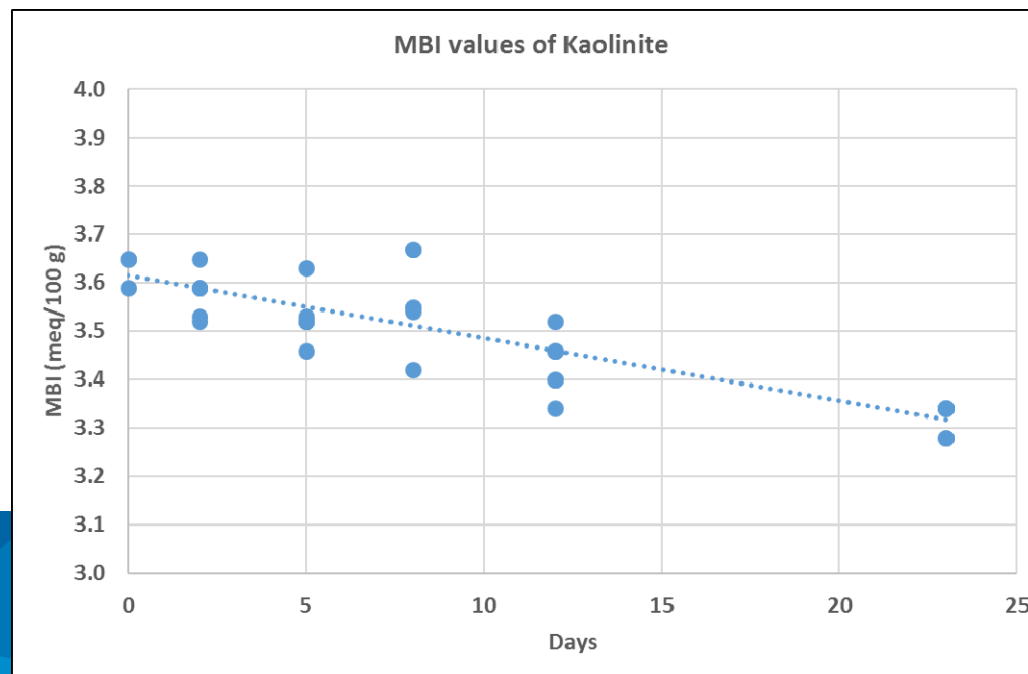
# Stability Testing of the MB Solution

ANOVA statistical analysis

$p$ -value < 0.05: significant difference

Factors	$p$ -Value			
	5 days	8 days	12 days	23 days
Days	0.005	0.026	1.88e-5	1.59e-09

Degradation of the solution is noticed with time.



# Stability Testing of the MB Solution

ANOVA statistical analysis

$p$ -value < 0.05: significant difference

Factors	$p$ -Value			
	5 days	8 days	12 days	23 days
Temperature	0.463	0.059	0.163	0.169
Light condition	0.335	0.289	0.844	0.938
Days & Temperature	0.196	0.02	0.363	0.974
Days & light condition	0.898	0.795	0.503	0.501
Temperature & light condition	0.315	0.086	0.371	0.594
Days & Temperature & light condition	0.274	0.115	0.868	0.527

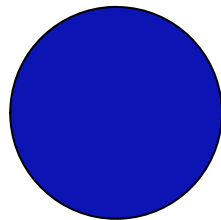
Temperature and Light condition generally do not have a statistically significant effect on the stability during the 23-day test.

Temperature and the combinations of temperature and days during the 8-day test show a statistically significant effect on the stability.

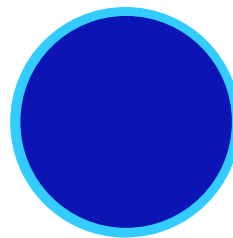
# Assess the Properties of Various Filter Media

- The determination of MBI – visually observe the light blue halo;
- Desirable filter paper – halo can be well observed.
- Grade 42 Filter Paper is typically used in published studies<sup>4</sup> – halo is difficult to be visually observed

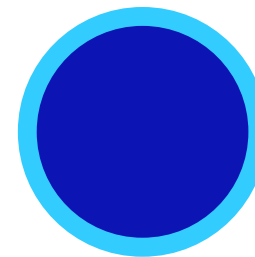
Before endpoint



At endpoint



After endpoint



4. Omotoso, O. and Morin, M. 2008. Methylene Blue Procedure. CanmetENERGY: Devon.

# Variation of Endpoint Determination on Grade 42 Filter Paper

Sample	Person -1	Person -2	Person -3	Person -4	Person -5	Person -6	Person -7	Person -8	Person -9	Person -10	Average	range
#1	30.5	28.5	28.5	30	29.5	29.5	29.5		28.5	29	29.31	2
#2	25.5	25.5	25.5	25.5	25.5	26.5	25.5	25.5	25.5	25.5	25.61	1
#3	28.5	29		28		26		25		29	27.30	4
#4	28	27.5	29	28			28.5		27.5	28	28.08	1.5
#5	30.5								29.5	28.5	30.00	
#6		27.5	28.5	29	28.5	29.5	29		29	29	28.71	2
#7	27	26	26	27	26.5	26	26		26	25.5	26.31	1
#8	29.5	29	29.5	30	29.5	33			29		29.93	4
#9	25.5	24.5	25	26	26.5	25.5	24	26	25.5		25.44	2.5
#10		24	25	26	25	26.5					25.30	2.5

Up to 4 ml of variation in where people call the endpoint  
 → ~13% difference in clay wt%

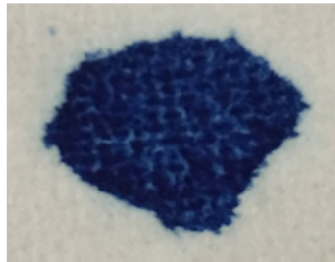
# Various Filter Media

Various filter media chosen covers a range of properties, especially the composition.

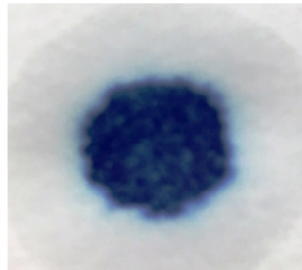
Filter Paper	Brand	Type of material	Pore size (µm)	Diameter (mm)
Grade 42	Company-A	Cellulose	2.5	150
Grade 1	Company-A	Cellulose	11	150
Anopore inorganic membrane	Company-A	Aluminum oxide with a high pore density	0.2	47
Cellulose nitrate membrane #1	Company-A	Cellulose nitrate	3	47
Cellulose nitrate membrane #2	Company-A	Cellulose nitrate membrane	8	47
Nylon-1 membrane	Company-A	Hydrophilic nylon	1	47
RC55	Company-A	Regenerated cellulose membrane	0.45	47
Nylon-2 (HNWP)	Company-B	Hydrophilic nylon	0.45	47
Nylon-3 (GNWP)	Company-B	Hydrophilic nylon	0.2	47
PTFE-1 (JVWP)	Company-B	Hydrophilic PTFE	0.1	47

# Endpoints on Various Filter Media

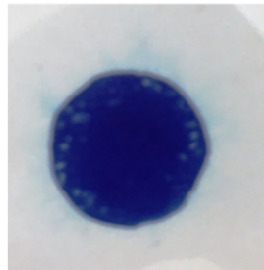
Grade 42



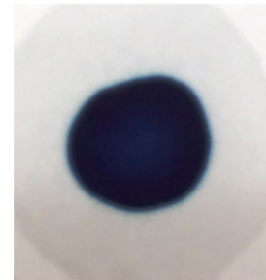
Grade 1



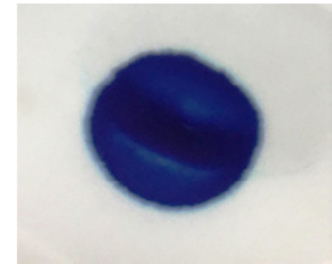
Anopore Inorganic membrane



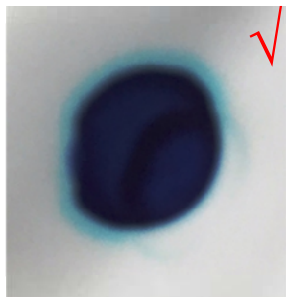
Cellulose nitrate Membrane #1



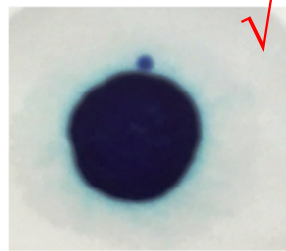
Cellulose nitrate Membrane #2



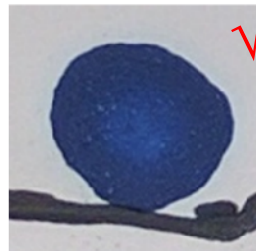
RC55



Nylon membrane-1



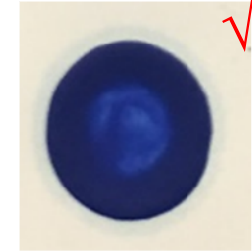
Nylon membrane-2



Nylon membrane-3



PTFE-1 membrane



RC55 good for visual detection, but the filter paper shrank when it was wet



# Various Filter Media

Filter Pape	Type	Pore Size	Diameter	Price	
Grade 42	Company-A Cellulose filter paper	2.5 $\mu\text{m}$	150 mm	\$85/100	<b>Standard</b>
Grade 1	Company-A Cellulose filter paper	11 $\mu\text{m}$	150 mm	\$31/100	
Anopore inorganic membrane	Company-A Composed of aluminum oxide with a high pore density	0.2 $\mu\text{m}$	47 mm	\$583/100	
Cellulose nitrate membrane #1	Company-A Cellulose nitrate membrane	3 $\mu\text{m}$	47 mm	\$230/100	
Cellulose nitrate membrane #2	Company-A Cellulose nitrate membrane	8 $\mu\text{m}$	47 mm	\$230/100	
RC55	Company-A Regenerated cellulose membrane	0.45 $\mu\text{m}$	47 mm	\$311/100	✓
Nylon membrane-1	Company-A Hydrophilic nylon membrane	1 $\mu\text{m}$	47 mm	\$192/100	
Nylon membrane-2	Company-B	0.45 $\mu\text{m}$	47 mm	\$174/100	✓
<b>Nylon membrane-3 (GNWP)</b>	<b>Company-B</b>	<b>0.2 <math>\mu\text{m}</math></b>	<b>47 mm</b>	<b>\$162/100</b>	✓ <b>Recommend</b>
PTFE-1 membrane	Company-B	0.1 $\mu\text{m}$	47 mm	\$377/100	✓

- Consumable cost per sample at COSS:

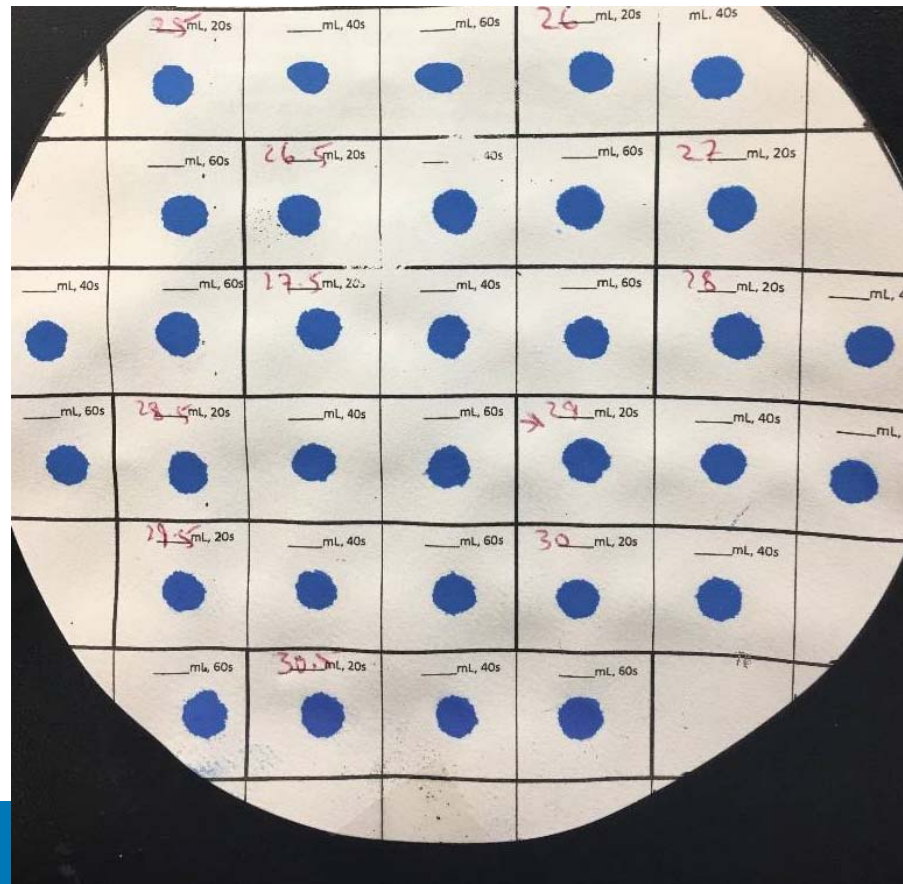
Using Grade 42: \$11.3; Using Nylon-3 membrane (GNWP): \$11.4

- Nylon membrane-3 is recommended: easy and repeatable endpoint detection, not shrink, and reasonable cost.



# Spot Size on Filter Paper

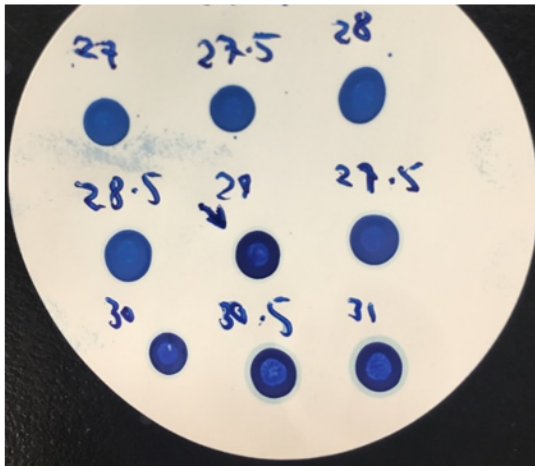
Recommendation: 15  $\mu$ L of droplet on large size of filter paper (> 110 mm of diameter)



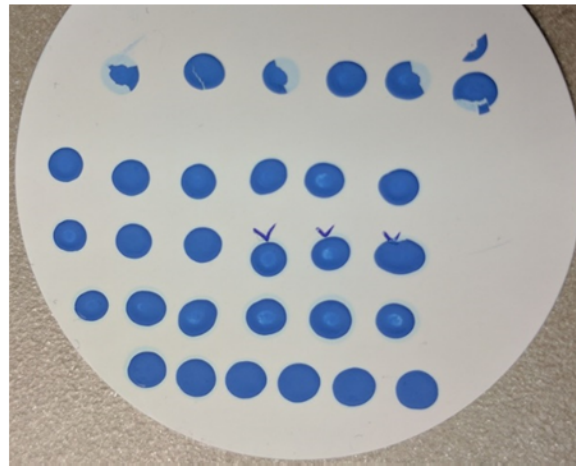
# Spot Size on Filter Paper

Recommendation: 5  $\mu$ L of droplet on small size of filter paper (typically 47 mm of diameter)

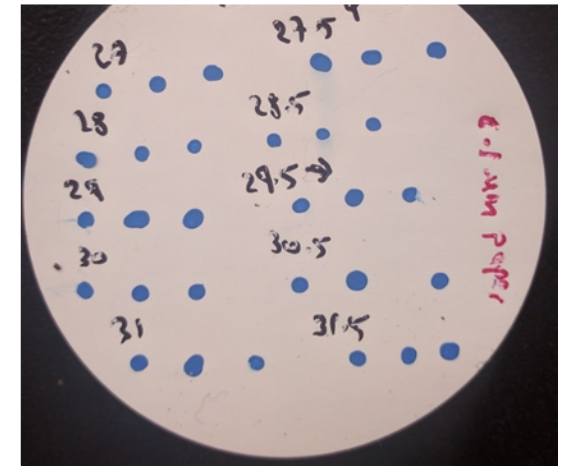
15  $\mu$ L of droplet using micropipette



5  $\mu$ L of droplet using micropipette



Glass Pasteur pipette



# Conclusion and Recommendation

- MB solution (0.006 N) is reasonably stable up to 5 days according to kaolinite titration test.
- Although different storage conditions in this study did not show significant effect on MB solution during the 23-day test, MB solution is recommended to be stored at dark condition and 4°C during the week in order to ensure the stability throughout the week.
- Nylon filter membrane with 0.2  $\mu\text{m}$  pore size from Company-B is highly recommended for the MB titration test.
- 15  $\mu\text{L}$  of droplet is recommended for the large size filter paper.
- 5  $\mu\text{L}$  of droplet is recommended for the small size filter papers.

# Acknowledgement

Thank you to COSIA Tailing Group for supporting the study on the characterization of clays in oil sands using methylene blue.

Questions?