Update on Proposed ASTM D4929 Procedure C - XRF

Presented at the Crude Oil Quality Association meeting, St. Louis, MO June 8, 2017

By Leslie Johnson, XOS Applications Engineer/ASTM WK57076 Technical Contact

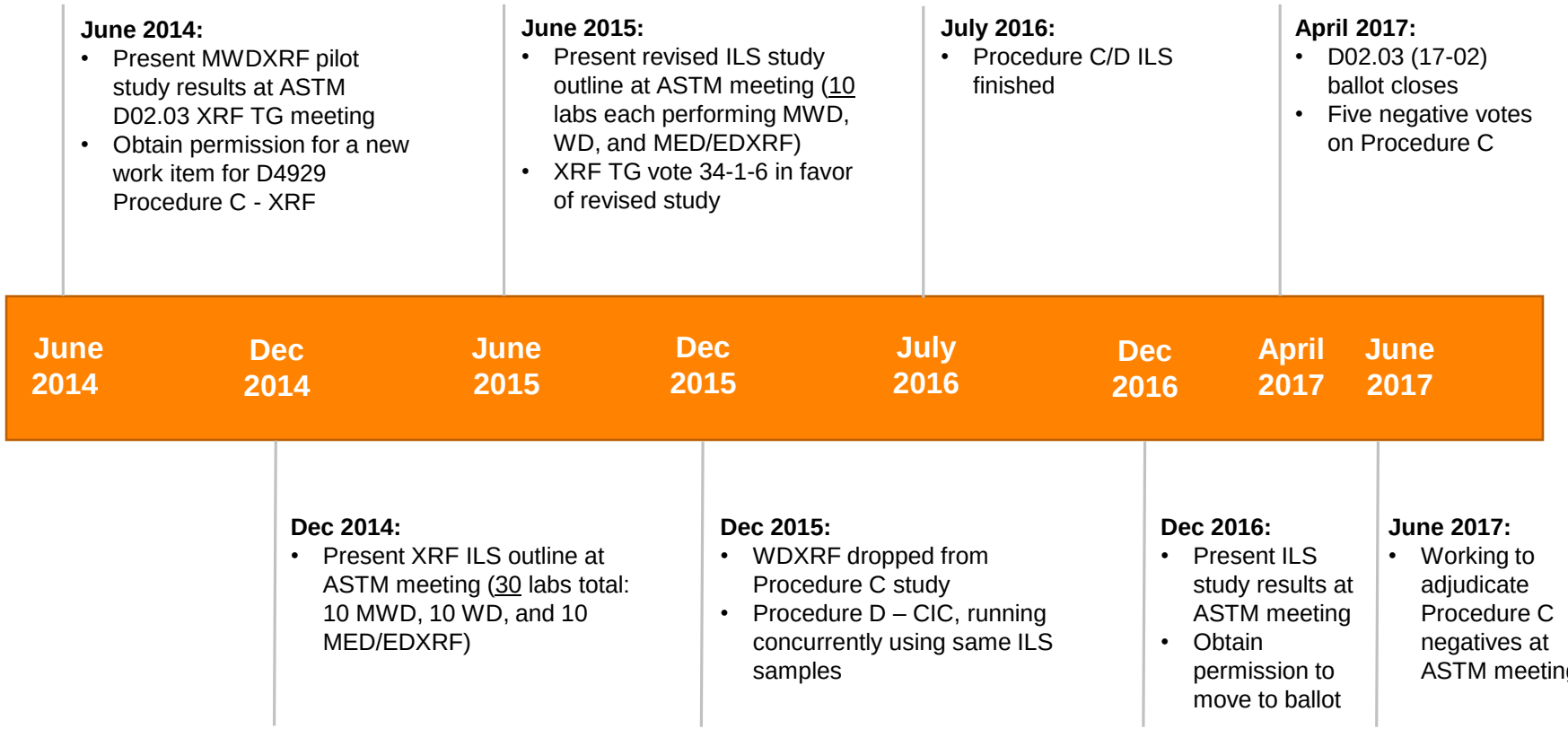
ASTM D4929 Organic Chlorides in Crude

Methodology:

- A crude oil sample is distilled to 400°F to collect the naphtha fraction.
- Inorganic chlorides are removed by water wash
- Chloride content of the naphtha fraction is determined by one of two methods:
  - Procedure A, sodium biphenyl reduction and potentiometry
  - Procedure B, combustion and microcoulometry
- Chloride content of the crude is determined by multiplying the naphtha chloride concentration by the naphtha fraction

→ What if there was a Procedure C, using XRF?

ASTM D4929 Procedure C – XRF Timeline



D4929 Procedure C ILS Design

- ILS design was presented to the ASTM D02.03 XRF task group for approval (ASTM WK57076, ILS 1122):
- Distillation and wash procedure retained as written in the method
- No revisions to Procedures A or B
- Procedure C includes multiple XRF technologies: MWDXRF, MEDXRF, EDXRF
  - Original design included WDXRF as well, but it was dropped in Dec 2015
- ILS designed to replicate existing 1987 Procedure A/B ILS as much as possible
  - 10 crude oil samples in blind duplicate per original D4929 design
    - Thank you Dennis Sutton for identifying crude oil equivalents
    - Thank you Marathon for supplying WTI, LLS, Mars bulk crude samples
  - 0-12 mg/kg doped organic chloride per original design

D4929 Procedure C ILS Design (cont.)

- Up to 10 end user participants
  - June 2015: reduced from the originally proposed 30 participant design (10 MWD, 10 WD, 10 MED/EDXRF labs) due to lack of participants and funding for the ILS study
- Each lab ran one distillation per sample aliquot (10 samples in blind duplicate = 20 distillations)
- XRF analysis to be performed on each naphtha fraction using MWDXRF, WDXRF, MED/EDXRF analysis
  - WDXRF dropped in Dec 2015 due to lack of available participants or demo analyzers

Note: participants did not run Procedures A and B for bias.

Why? Financial and participant constraints.

This information was discussed with and approved by the ASTM D02.03 XRF task group prior to the start of the ILS.

D4929 Procedure C ILS Design (cont.)

- The ASTM Statistician will determine whether Procedure C precision should be pooled or separated for each technology based on the ILS data.
- Results will be balloted as D4929 Procedure C unless otherwise advised by ASTM Statistician to ballot as a stand alone method.

This ILS design was presented to the D02.03 XRF task group at the June 2015 Fort Lauderdale meeting, and it was approved by a vote.

- ILS design changes/additions after XRF task group vote:
  - Dec 2015: WDXRF dropped in due to lack of available participants and demo analyzers
  - Dec 2015: Procedure D - CIC analysis added as a concurrent ILS (WK53424, ILS 1329). Naphtha samples were analyzed by XRF and CIC when possible.

D4929 Procedure C XRF Participants

I would like to thank the following D4929 XRF Method C participants:

- Amspec Corpus Christi
- Inspectorate New Orleans
- Intertek Chicago
- Intertek Los Angeles
- Intertek New Orleans
- Intertek San Francisco
- Marathon Catlettsburg
- SGS Deer Park
- Shell Global Solutions Houston

D4929 XRF Participant Breakdown

Lab Code (randomized)	MWDXRF	MEDXRF	EDXRF
1	X	X	X
2	X	X	X
3	X	X	X
4	X	X*	X
5	X	X	X
6	X	X	X
7	X	X	
8	X	X	
9	X	X	
10			
Total participants	9	9 (10)	6

*Submitted results from two different MEDXRF systems

D4929 ILS Sample Set Comparison

D4929 Procedures A/B 1987 ILS:

ID	Crude	Dopant	Doped Cl (mg/kg)
A	Liberty	1,1,1-trichloroethane	1
B	Butte	1,2-dichloropropane	12
C	Butte/ Liberty	1,1,1-trichloroethane	10
D	Butte	1,2-dichloropropane	3
E	WTI	blank	0
F	Liberty	1,2-dichloropropane	1
G	Butte	o-dichlorobenzene	5
H	Liberty	blank	0
I	WTI/Butte	methylene chloride	6
J	WTI	1,1,1,-trichlorethane	5

D4929 Procedure 2016 ILS:

ID	Crude	Dopant	Doped Cl (mg/kg)
A	LLS	1,1,2-trichloroethane	1
B	Mars	1,2-dichloropropane	12
C	Mars/LLS	1,1,2-trichloroethane	10
D	Mars	1,2-dichloropropane	3
E	WTI	blank	0
F	LLS	1,2-dichloropropane	1
G	Mars	o-dichlorobenzene	5
H	LLS	blank	0
I	WTI/Mars	methylene chloride	6
J	WTI	1,1,2,-trichlorethane	5

D4929 Procedure C ILS Statistics

- Statistical analysis was performed by ASTM Statistician Alex Lau, D02 CS94 chair:
  - Extreme results were identified and excluded using the GESD Many-Outlier Detection technique as per ASTM D7915.
  - The pre-screened data was then analyzed in accordance with ASTM D6300 to obtain the precision.
  - A D6708 assessment was performed to determine relative bias between XRF techniques.

- Recommendations:
  - Precision for EDXRF needs to be listed separately.
  - Notwithstanding the similarity between MWDXRF and MEDXRF precision, these also should be listed separately due to the observed bias.
  - The observed relative bias between technologies should also be listed.

Statistical Findings

Precision Equations, Method C XRF

	Repeatability r, mg/kg[A]	Reproducibility R, mg/kg[A]
MWDXRF	$r = 0.643 * X^{0.44}$	$R = 1.235 * X^{0.44}$
MEDXRF	$r = 0.591 * X^{0.44}$	$R = 1.500 * X^{0.44}$
EDXRF	$r = 0.934 (X + 0.4)^{0.48}$	$R^{B} = 2.000 (X + 0.4)^{0.48}$

[A]Where X = mg/kg chloride

[B]The degrees of freedom associated with the reproducibility estimate from this round robin study are 29. Since the minimum requirement of 30 (in accordance with Practice D6300) is not met, users are cautioned that the actual reproducibility may be significantly different than these estimates.

Between-Method Bias Outcome

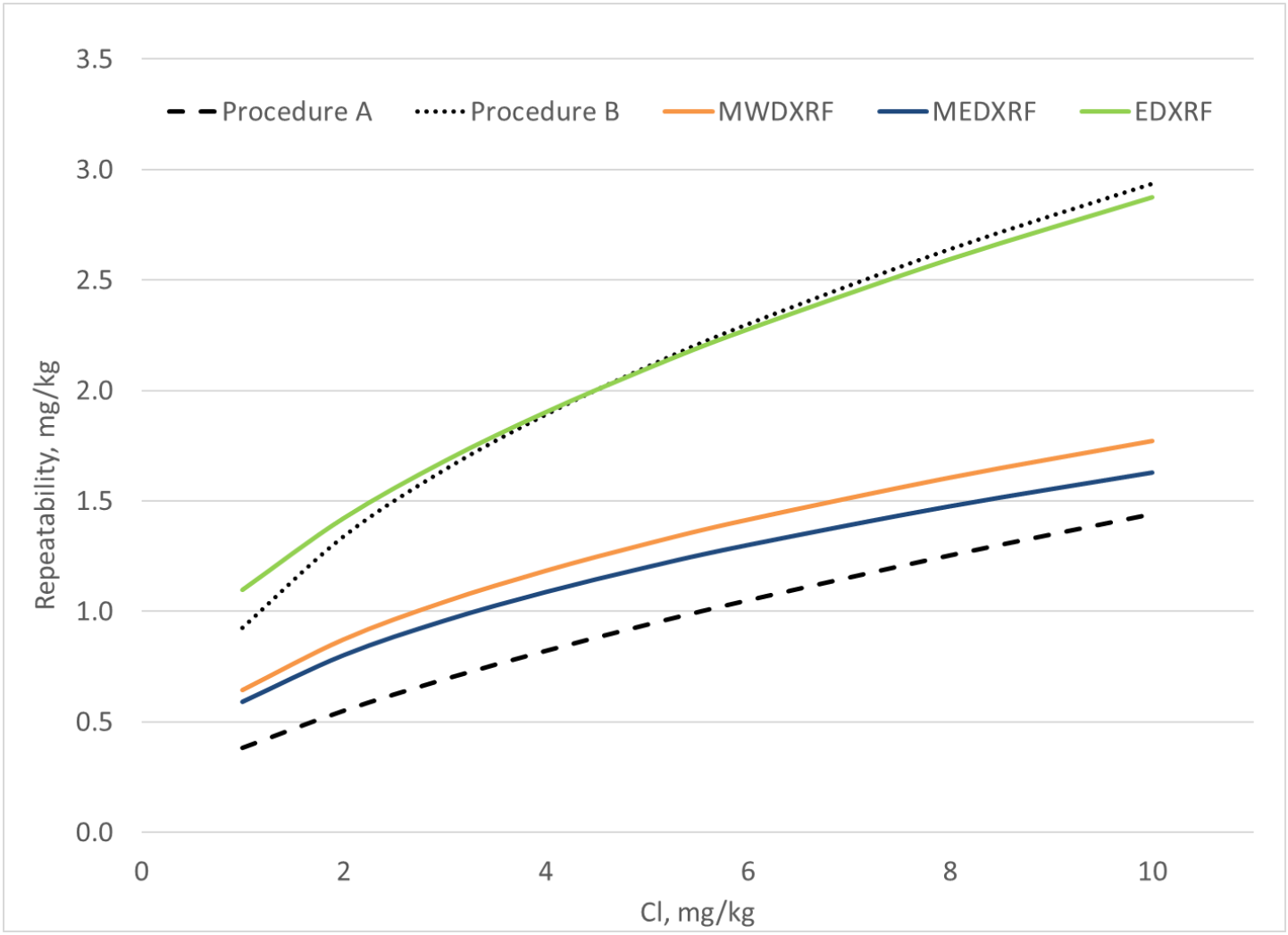
Method X	Method Y	Suggested Bias Correction[A]
MEDXRF	MWDXRF	$\hat{Y} = X - 0.658$
EDXRF	MEDXRF	$\hat{Y} = X + 0.519$
EDXRF	MWDXRF	No bias correction

[A]Where:

$\hat{Y}$ = predicted Y-method value

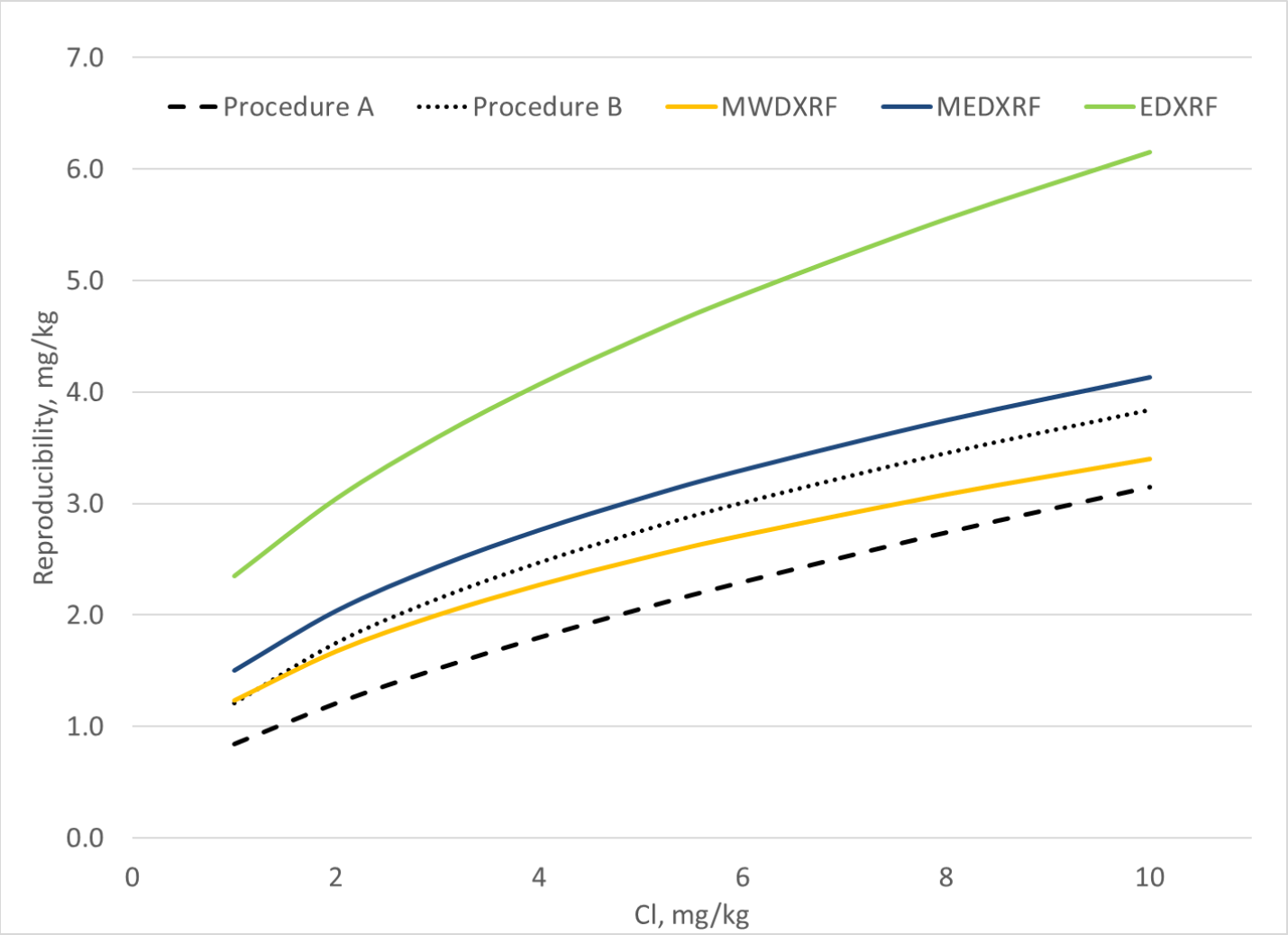
X = single X-method measured results

Repeatability Comparison: A, B, C



Note: data is from two different studies, 1987 Procedure A and B study and 2016 Procedure C study.

Reproducibility Comparison: A, B, C



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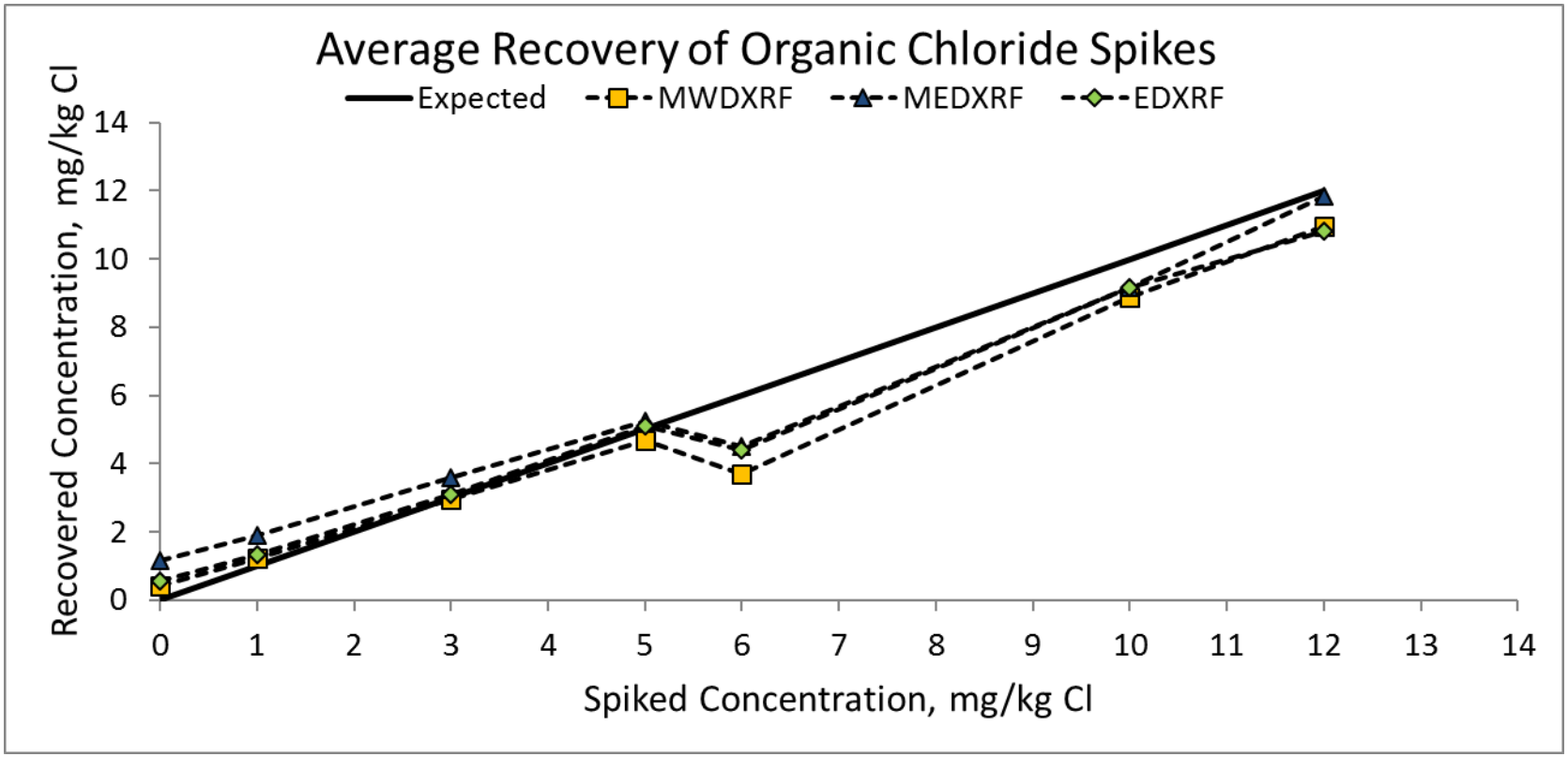

- Low concentration samples appear to be dominated by naturally occurring chlorides (100+% recovery)
- High concentration samples show that not all of the volatile compounds will distill from a complex crude oil under the conditions of this test method

D02.03 (17-02) Subcommittee Ballot

- D4929 Procedure C results were authorized at the December 2016 meeting to go to subcommittee ballot.

- D02.03 (17-02) Item 1: D4929 Procedure C – XRF subcommittee ballot results:
  - 45 affirmative
  - 5 negatives + 1 non-subcommittee member negative
  - 110 abstain
  - 3 comments

Item	Sub	Action		Committee	AFF	NEG	ABST	PCNT
001	03	REVISION D4929-2016 Test Method For Determination of Organic Chloride Content in Crude Oil		D02.03	45.00	5.00	110.00	90.00
		TECHNICAL CONTACT: Leslie Johnson						
		WORK ITEM: WK57076						
		add Procedure C for XRF						

Summary of Negative Voter Rationale

1. Relative bias between procedure C vs. procedures A and B was not determined.
2. This should be balloted as a separate stand alone test method rather than as a part of D4929.
3. Procedure C has poor precision and should not be added to D4929, particularly EDXRF.

- Other negative voter concerns:
  - Scope of the proposed procedures is well above what is normally encountered.
  - The distillation step was not performed in duplicate.
  - The recommended calibration range is too high (0-100 mg/kg).
  - Each XRF method should have its own procedure (e.g. C, D, E).
  - All XRF equipment manufacturers should be named in the method (instead of naming one sole source manufacturer).
  - No XRF equipment manufacturers should be named in the method.
  - A reference to the concurrent CIC ILS should have been included in the ballot rationale.

Next Steps

- Working to adjudicate negative votes
- Next ASTM D02 meeting is June 26-29th in Boston, MA
- A ballot item must pass subcommittee and main committee ballots before approval

Questions?

Thank you for your time.

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