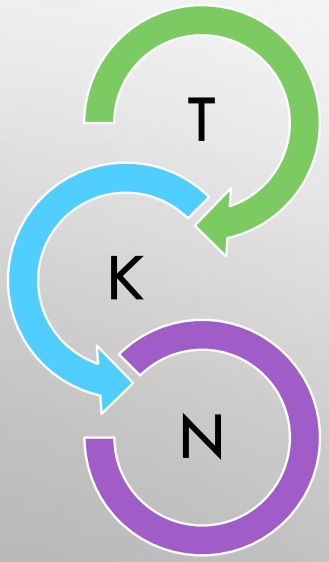
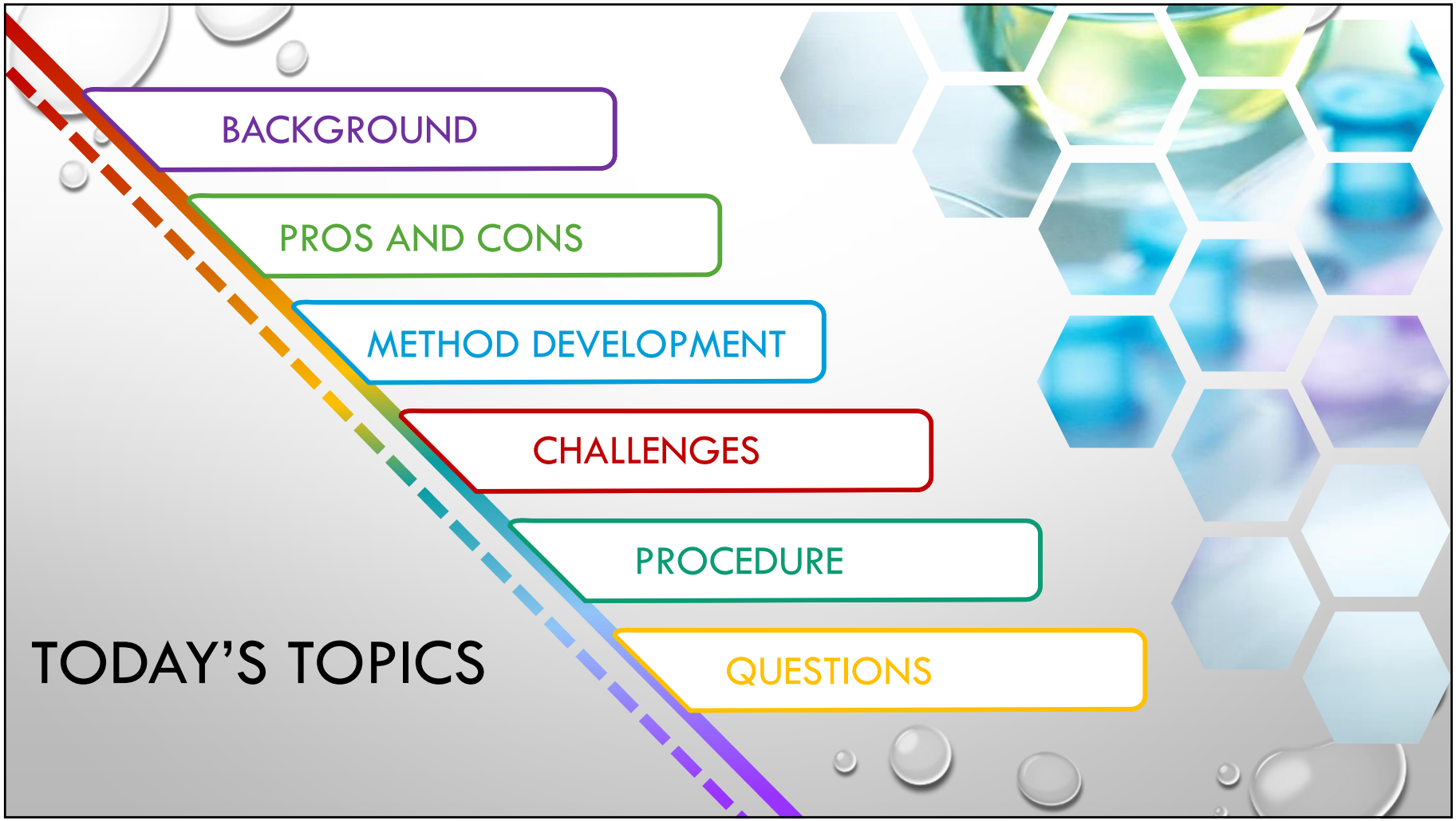
Total Kjeldahl Nitrogen



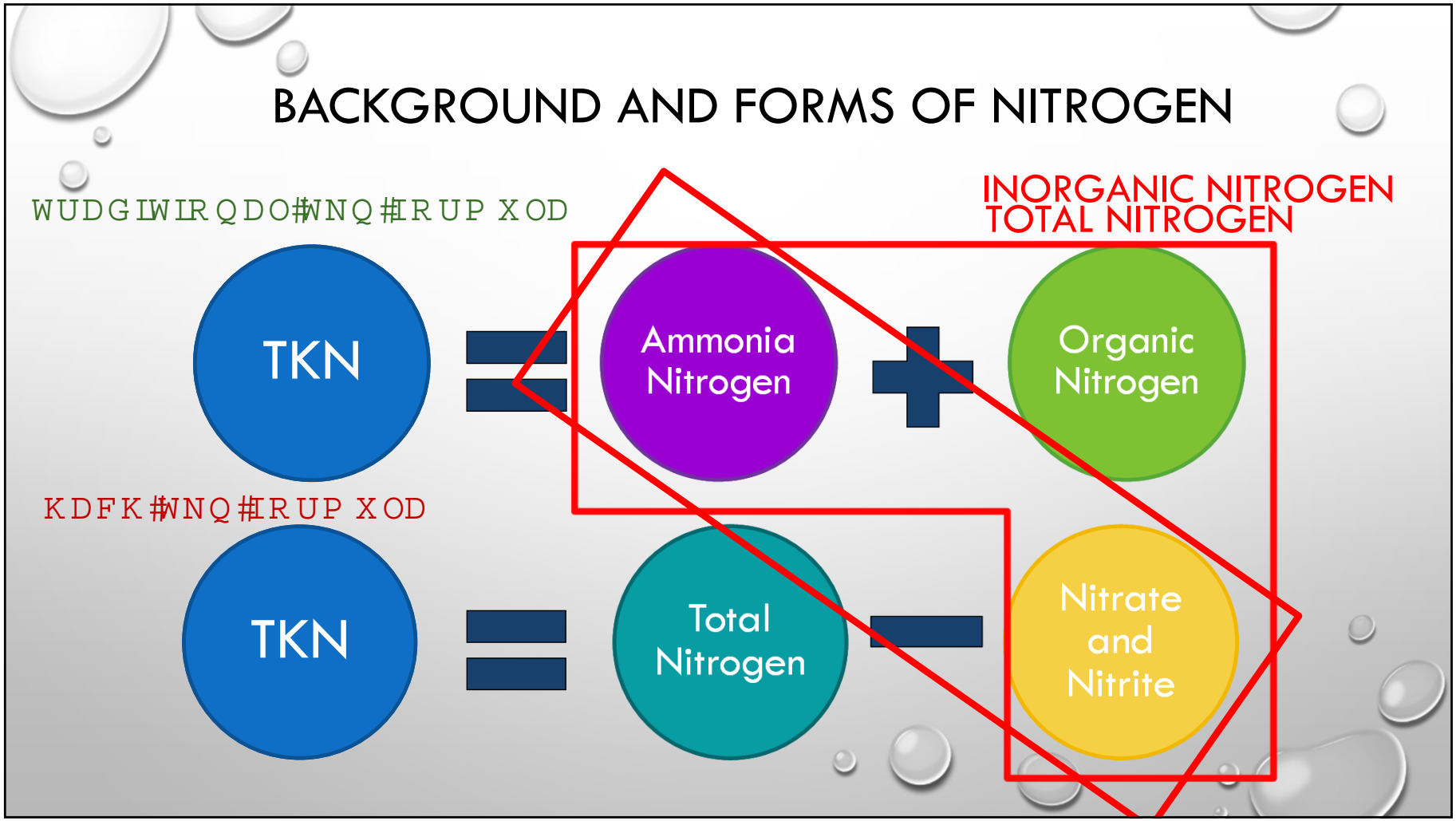
Presented by:
Joga Chizer and Nicole Van Aken

Method:
Hach Company Method 10242,
Simplified Spectrophotometric Measurement of Total Kjeldahl Nitrogen in Water and Wastewater


BACKGROUND
PROS AND CONS
METHOD DEVELOPMENT
CHALLENGES
PROCEDURE
QUESTIONS
TODAY'S TOPICS

2

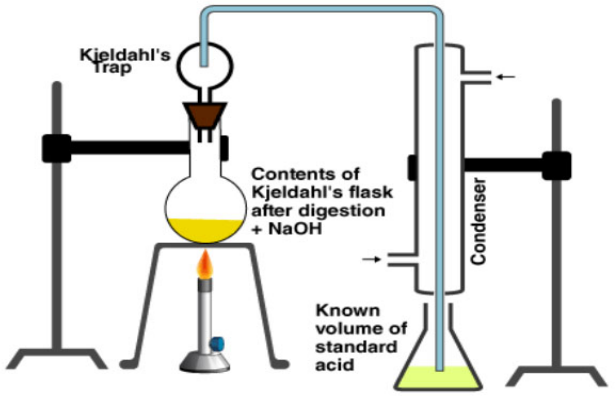
BACKGROUND AND FORMS OF NITROGEN



DIFFERENT TKN METHODS

Hach Method

Distillation Method



4

WHY SHOULD I CHOOSE THIS METHOD?

PROS

1. Fast
2. Uses Equipment Already in the Lab
3. Contained (Reagents in Kit, No Outside Chemicals Needed)
4. Minimal Training Required

CONS

1. Cost
2. Dependency on Hach Reagents
3. Limited Customization
4. Method Deviations Needed for Compliance

METHOD DEVELOPMENT

IS IT ACCURATE?

- Side-by-Side Analysis
- Practice QC Elements

DOCUMENTATION

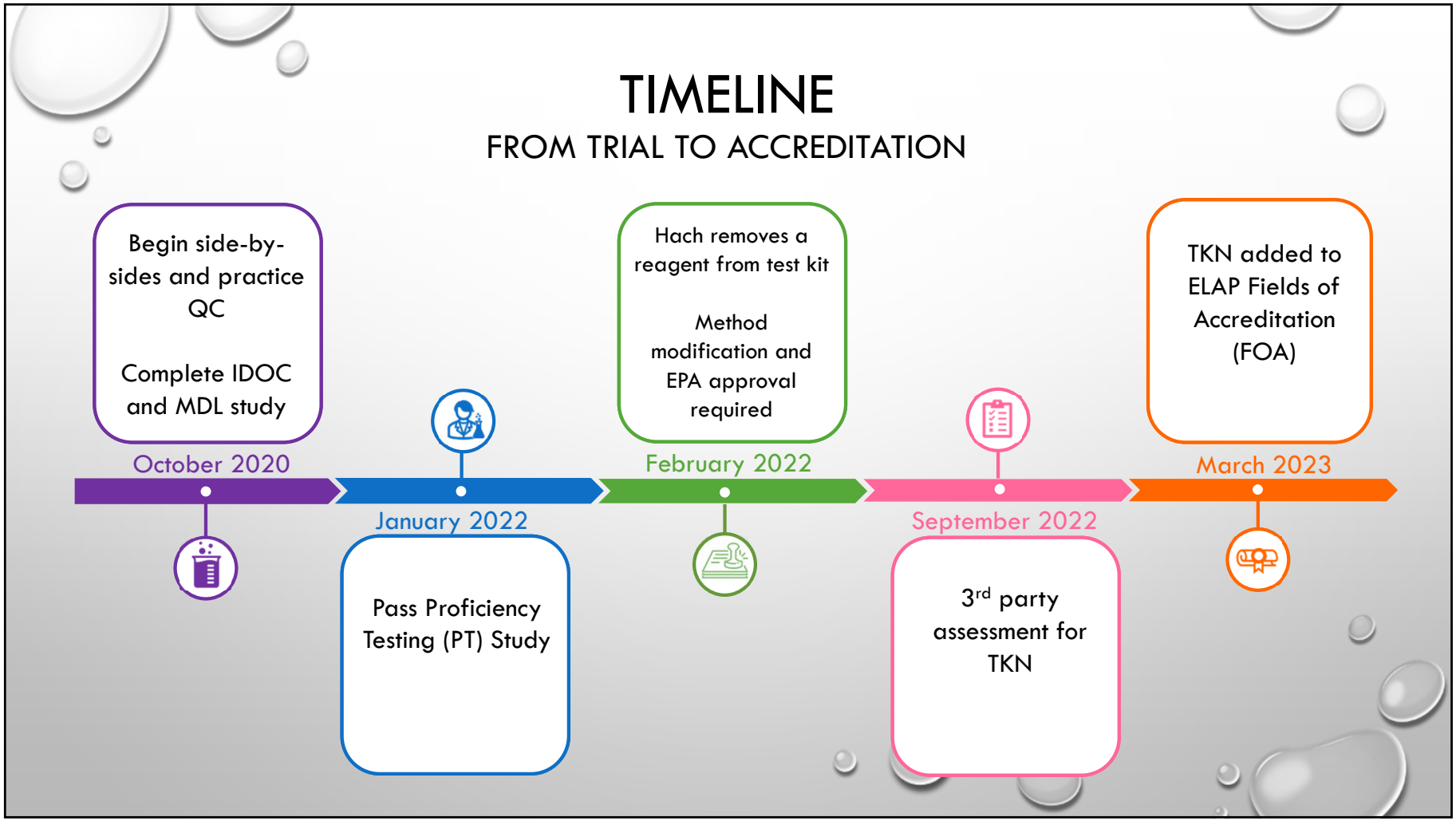
- Create an SOP
- Contact Customers and EPA about Method Deviations

REQUIREMENTS FOR ACCREDITATION

- IDOC
- MDL Study
- PT Standard
- Assessment

TIMELINE

FROM TRIAL TO ACCREDITATION




TKN Side-by-Side
75
70
65
60
55
50
45
40
10/8/2020
11/8/2020
12/8/2020
1/8/2021
2/8/2021
3/8/2021
4/8/2021
5/8/2021
6/8/2021
7/8/2021
8/8/2021
9/8/2021
10/8/2021
FSSD SPEC 1 Result (mg/L)
FSSD SPEC 2 result (mg/L)
Caltest result (mg/L)

8

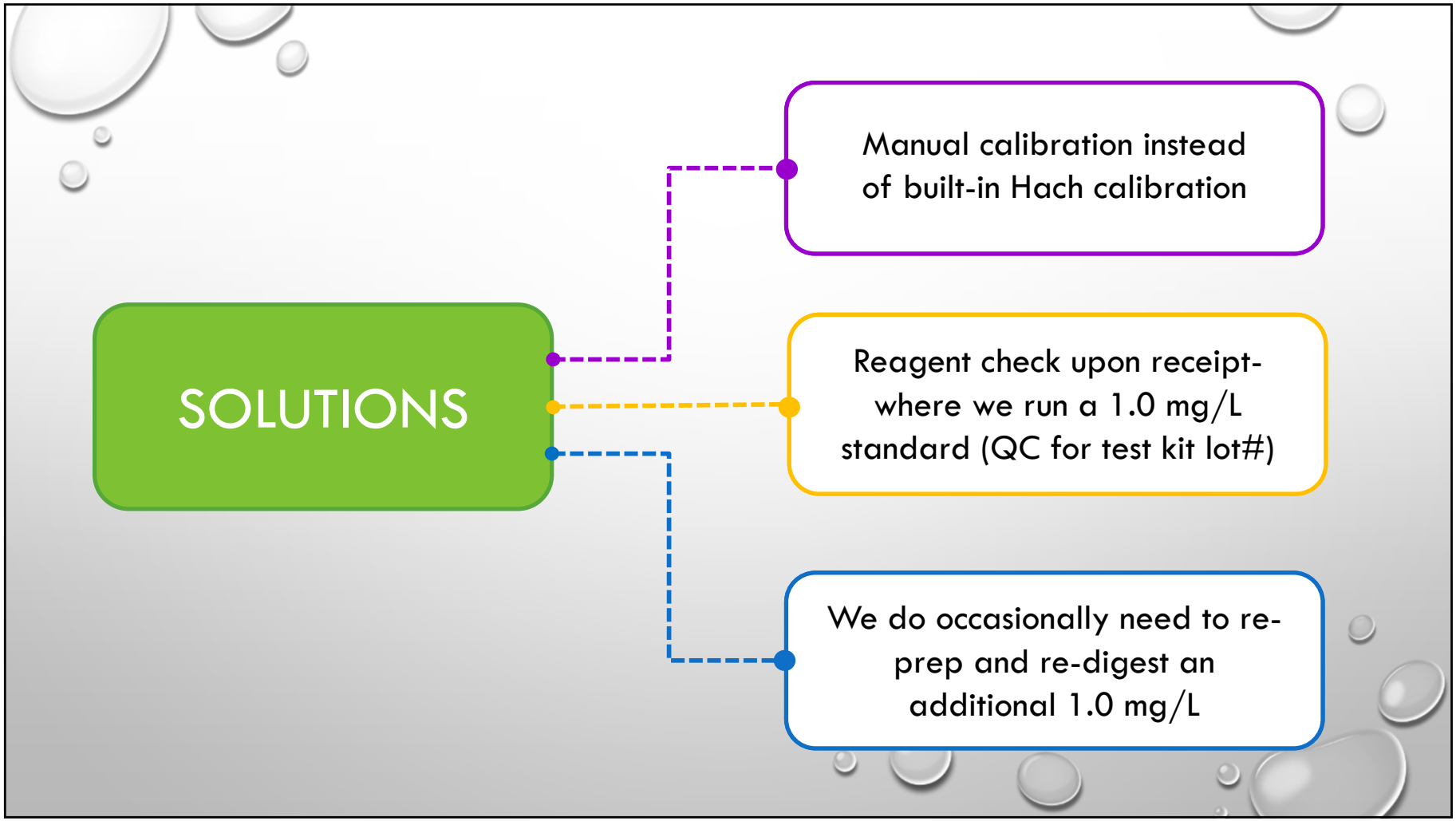
Sample Number	QC template Name	Parameter Name	Corrected Result
Bat-240924-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.959
Bat-240911-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.979
Bat-240815-003-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.04
Bat-240813-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.838
Bat-240813-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.716
Bat-240716-002-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.98
Bat-240704-005-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.919
Bat-240619-012-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.08
Bat-240619-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.08
Bat-240515-004-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.919
Bat-240507-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.08
Bat-240419-006-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.08
Bat-240410-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.02
Bat-240317-002-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.18
Bat-240214-010-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.08
Bat-240214-004-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.06
Bat-240119-005-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.06
Bat-231220-004-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.02
Bat-231212-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.22
Bat-231107-001-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.06
Bat-231019-003-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.08
Bat-230921-003-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.959
Bat-230916-002-ICV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.939
Bat-230824-001-CCV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	0.959
Bat-230605-008-CCV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.33
Bat-230605-007-CCV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.12
Bat-230519-006-CCV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.21
Bat-230506-002-CCV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.2
Bat-230421-007-CCV-01	TKN ICV (1.0 mg/L)	Total Kjeldahl Nitrogen	1.15

CHALLENGES

#1: THE LOW-LEVEL CALIBRATION VERIFICATION (ICV) WAS NOT PASSING CONSISTENTLY

10.2 Calibration Verification

10.2.1 To verify that the instrument is measuring TKN properly, analyze a 1.0 mg/L and 10.0 mg/L NH3-N standard. Results shall be within 10 percent of the actual value. Perform this calibration verification daily while instrument is in use.


SOLUTIONS
Manual calibration instead of built-in Hach calibration
Reagent check upon receipt- where we run a 1.0 mg/L standard (QC for test kit lot#)
We do occasionally need to re-prep and re-digest an additional 1.0 mg/L

MANUAL CALIBRATION

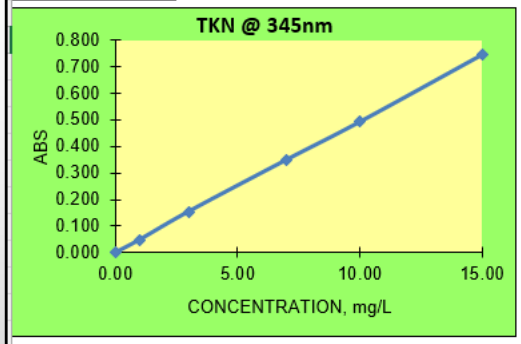
Read standards at 345nm and plot in excel

Uses y=mx+B

Plugs sample absorbance into the excel calibration curve

TKN CALIB. CURVE Calibration Date 8/14/2024

STD mg/L	ABS
0.000	0.000
1.00	0.049
3.00	0.155
7.00	0.350
10.00	0.493
15.00	0.746



COEFFICIENT OF DETERMINATION = 1.000

Sample	FOUND, ABS	Dilution	CONC, mg/L	%RE
QC- TKN ICV (1.0 mg/L)	0.048	1	0.939	
QC- TKN ICV (10 mg/L)	0.498	1	10.019	
QC- TKN MB	0.004	1	0.051	
Influent, INF-001	0.125	10	24.924	
Influent, INF-001MS	0.367	1	7.375	
Influent, INF-001MSD	0.386	1	7.759	
QC- TKN LCS/OPR	0.252	1	5.055	
QC- TKN LCS/OPR	0.248	1	4.974	
		1		
		1		
		1		
		1		
		1		
		0		
		0		
		0		
0.000 (STD)	0.000			
1.00 (STD)	0.049		0.96	4.1
3.00 (STD)	0.155		3.10	3.3
7.00 (STD)	0.350		7.03	0.5
10.0 (STD)	0.493		9.92	0.8
15.00 (STD)	0.746		15.02	0.2

CHALLENGES

#2: METHOD MODIFICATION NEEDED

A. Hach removed Microcap C from the TKN test kit

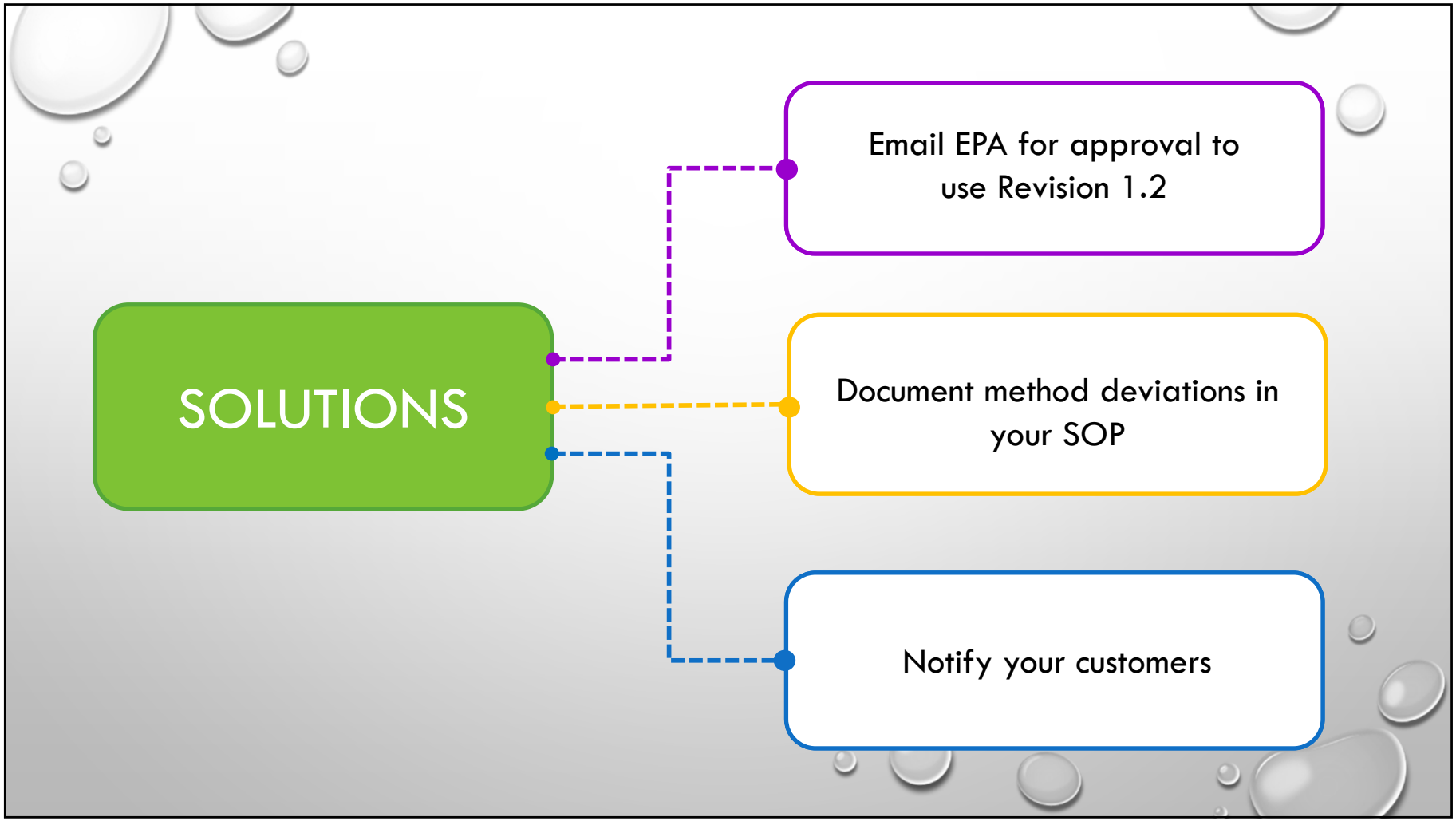
B. 40 CFR part 136 approved method cannot be used

C. Alternate Test Procedure (ATP) is not required, but EPA approval is needed

Method listed in 40 CFR

Current Hach Method

Method 10242 rev 1.1	Modifications: Method 10242 rev 1.2
No pH adjustment prior to analysis	Adjust preserved samples to pH 7 with 5 N NAOH
Digestion at 100°C	Digestion at 120°C
Digest for 1 hour	Digest for 30 minutes
Add Micro Cap C after digestion	No Micro Cap C
MDL limit is 0.43 mg/L	MDL limit is 0.11 mg/L


SOLUTIONS
Email EPA for approval to use Revision 1.2
Document method deviations in your SOP
Notify your customers

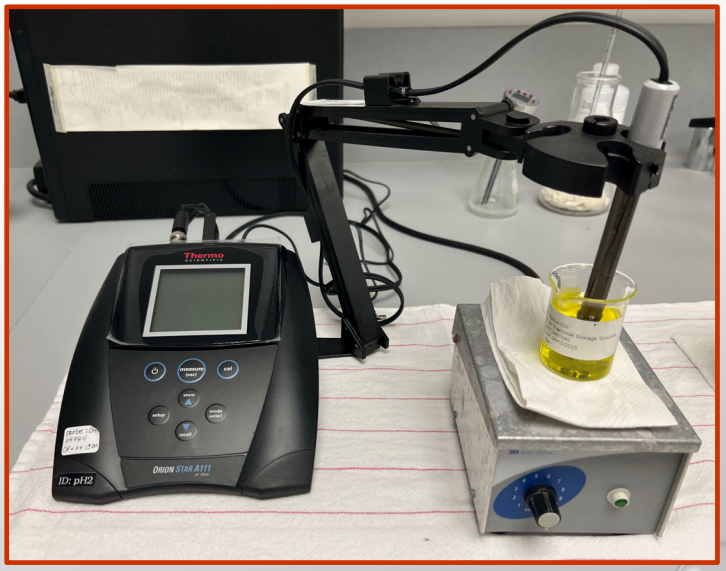
13

14

PROCEDURE

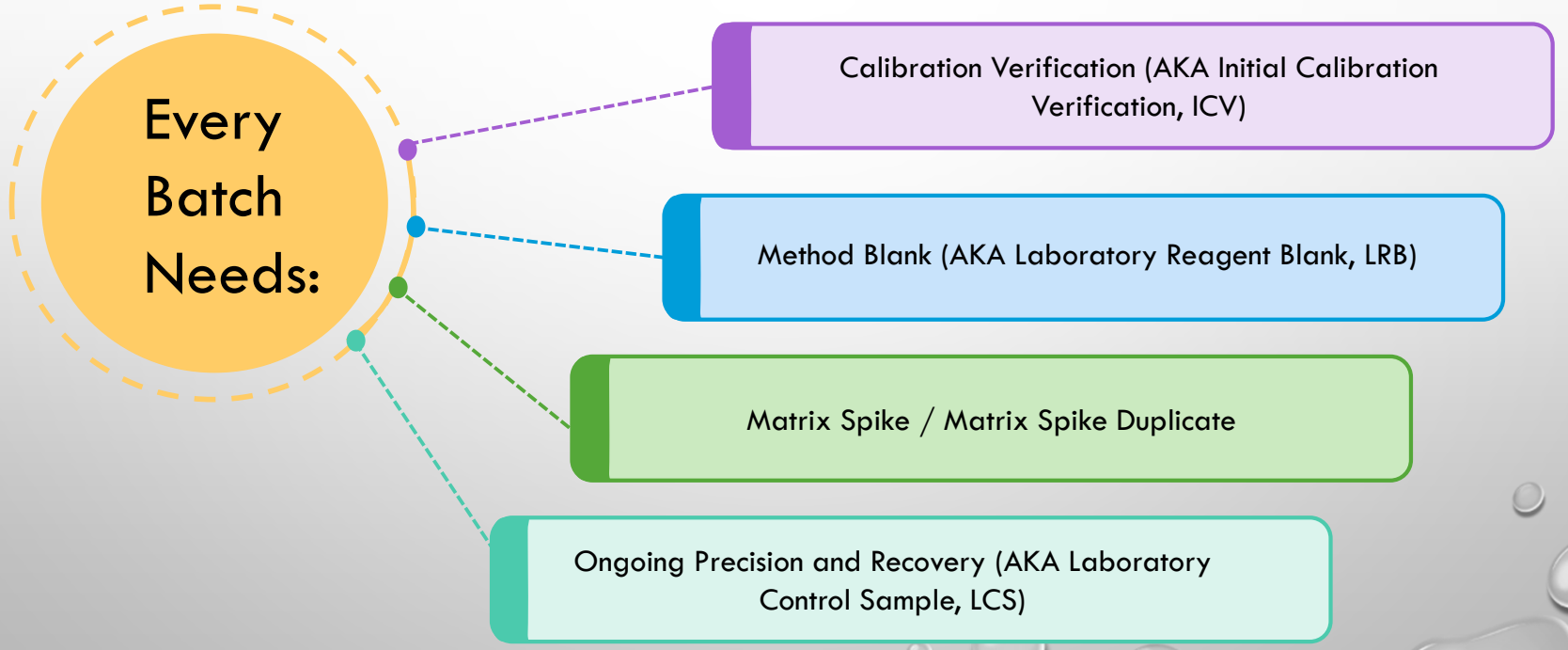
STEP 1: PH ADJUST YOUR SAMPLES

- Samples are preserved during collection
- Hach method states “Adjust to pH 7”
- Tip: Use your sample as the acid if needed



15

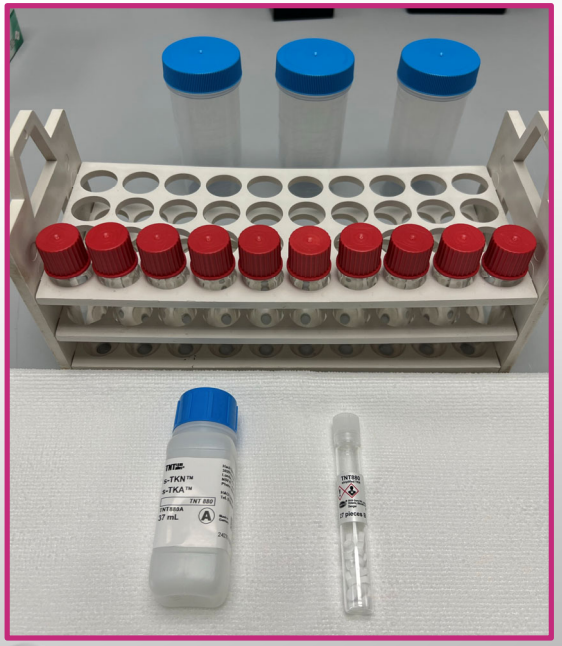
WHAT QUALITY CONTROL (QC) IS NEEDED?



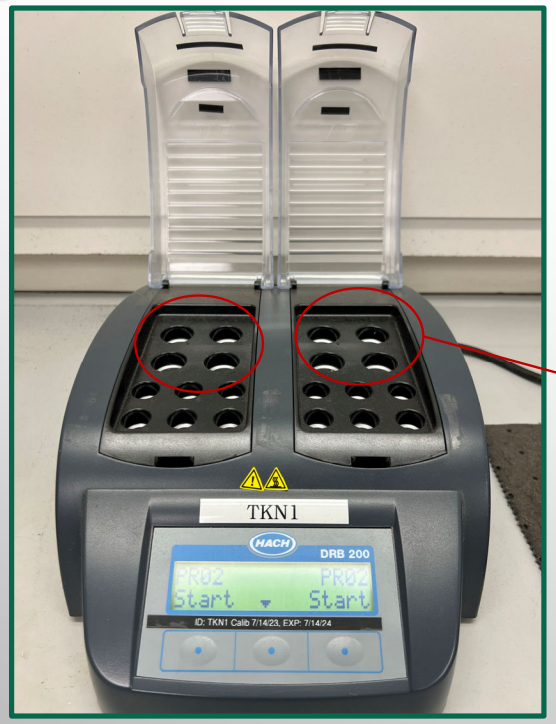
PROCEDURE

STEP 2: QC and SAMPLE PREPARATION

- Make dilutions before digesting
- Add Solution A and Tablet B
- Do NOT invert or mix before digestion



PROCEDURE



STEP 3: DIGEST SAMPLES

20mm cell size needed

Hach only sells heat block with eight (8) vial wells

QC take 6 spots (at least), so multiple digestions need to be done

DIGESTION

Digestion converts all forms of nitrogen to nitrate

The digested sample represents the total nitrogen content

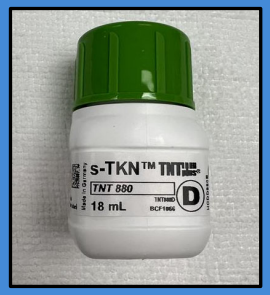
PROCEDURE

STEP 4: ALIQUOT INTO VIALS

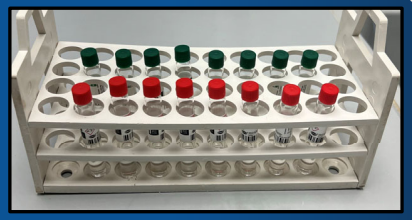
Small volumes used, so precise pipetting is needed

Red Vials	Add **digested sample** → determines total nitrogen (TN)
Green Vials	Add **undigested sample** → determines oxidized forms of nitrogen (NO_3+NO_2)

TKN Kit – TNT880



Solution D



Test Vials

20

PROCEDURE

STEP 5: ANALYZE SAMPLES

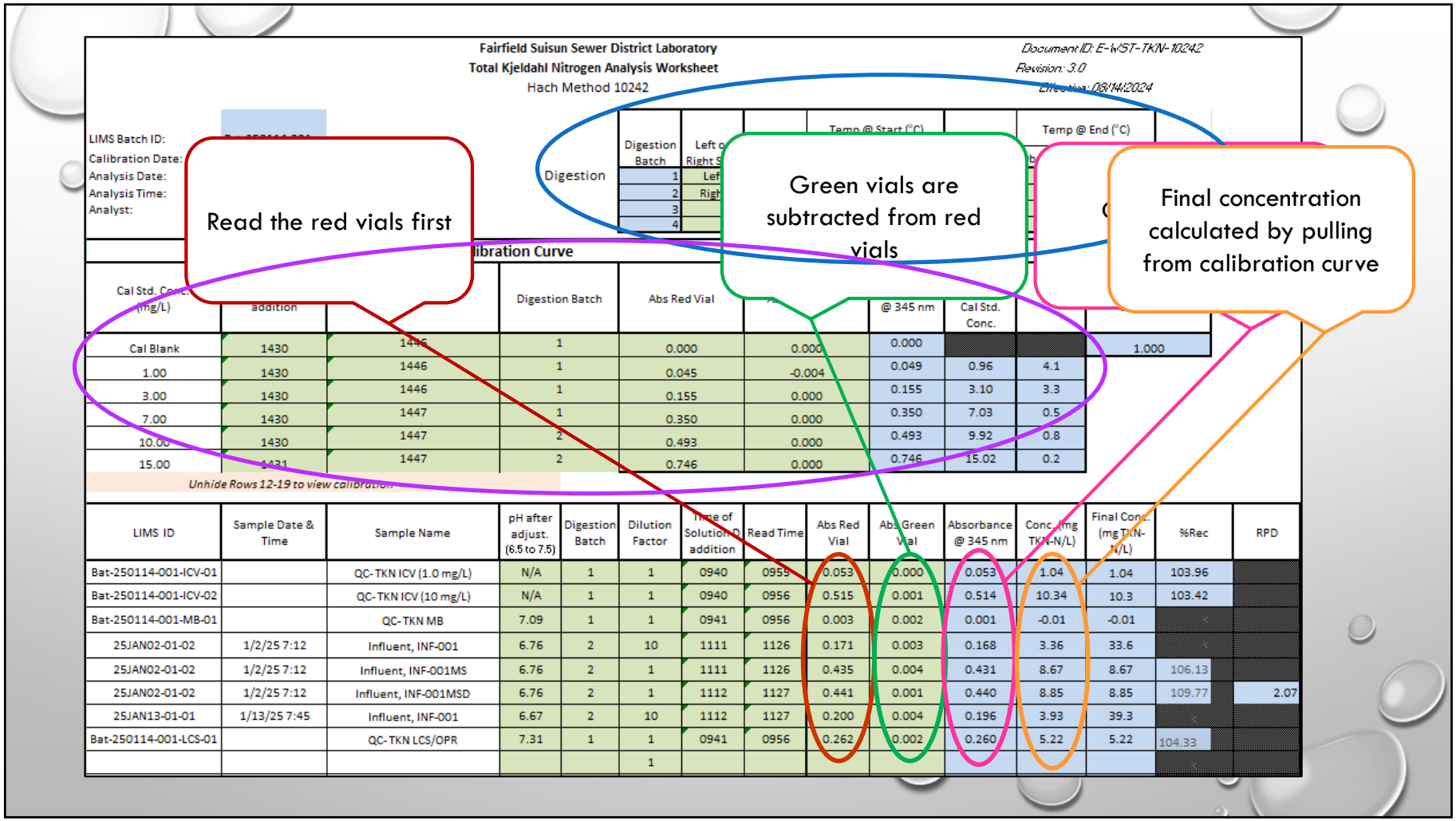
We don't use the TNT auto-read, we read absorbance manually @345nm

Because of that, we prepare a zero standard to zero the machine

(Total Nitrogen) – (Nitrate plus Nitrite)

Red Vial — Green Vial = TKN

21


Fairfield Suisun Sewer District Laboratory
Total Kjeldahl Nitrogen Analysis Worksheet
Hach Method 10242
Document ID: E-WST-TKN-10242
Revision: 3.0
LIMS Batch ID:
Calibration Date:
Analysis Date:
Analysis Time:
Analyst:
Digestion
Digestion Batch
Temp @ Start (°C)
Temp @ End (°C)
Read the red vials first
Green vials are subtracted from red vials
Final concentration calculated by pulling from calibration curve
Cal Std. Conc. (mg/L)
Digestion Batch
Abs Red Vial
@ 345 nm
Cal Std. Conc.
Cal Blank 1430 1446 1 0.000 0.000 0.000 1.000
1.00 1430 1446 1 0.045 -0.004 0.049 0.96 4.1
3.00 1430 1446 1 0.155 0.000 0.155 3.10 3.3
7.00 1430 1447 1 0.350 0.000 0.350 7.03 0.5
10.00 1430 1447 2 0.493 0.000 0.493 9.92 0.8
15.00 1431 1447 2 0.746 0.000 0.746 15.02 0.2
Unhide Rows 12-19 to view calibration
LIMS ID
Sample Date & Time
Sample Name
pH after adjust. (6.5 to 7.5)
Digestion Batch
Dilution Factor
Time of Solution D addition
Read Time
Abs Red Vial
Abs Green Vial
Absorbance @ 345 nm
Conc. (mg TKN-N/L)
Final Conc. (mg TKN-N/L)
%Rec
RPD
Bat-250114-001-ICV-01 QC-TKN ICV (1.0 mg/L) N/A 1 1 0940 0955 0.053 0.000 0.053 1.04 1.04 103.96
Bat-250114-001-ICV-02 QC-TKN ICV (10 mg/L) N/A 1 1 0940 0956 0.515 0.001 0.514 10.34 10.3 103.42
Bat-250114-001-MB-01 QC-TKN MB 7.09 1 1 0941 0956 0.003 0.002 0.001 -0.01 -0.01
25JAN02-01-02 1/2/25 7:12 Influent, INF-001 6.76 2 10 1111 1126 0.171 0.003 0.168 3.36 33.6
25JAN02-01-02 1/2/25 7:12 Influent, INF-001MS 6.76 2 1 1111 1126 0.435 0.004 0.431 8.67 8.67 106.13
25JAN02-01-02 1/2/25 7:12 Influent, INF-001MSD 6.76 2 1 1112 1127 0.441 0.001 0.440 8.85 8.85 109.77 2.07
25JAN13-01-01 1/13/25 7:45 Influent, INF-001 6.67 2 10 1112 1127 0.200 0.004 0.196 3.93 39.3
Bat-250114-001-LCS-01 QC-TKN LCS/OPR 7.31 1 1 0941 0956 0.262 0.002 0.260 5.22 5.22 104.33

22

Thank you

Questions ~ Comments ~ Thoughts…

For more information:
JChizer@FairfieldSuisunSewer.ca.gov
NVanAken@FairfieldSuisunSewer.ca.gov

A Special *Thank You* To:
Jennifer Vo & Raymona Shirmard

23