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New Standard Methods and ASTM Methods for the Determination of Total Nitrogen in Aqueous Samples

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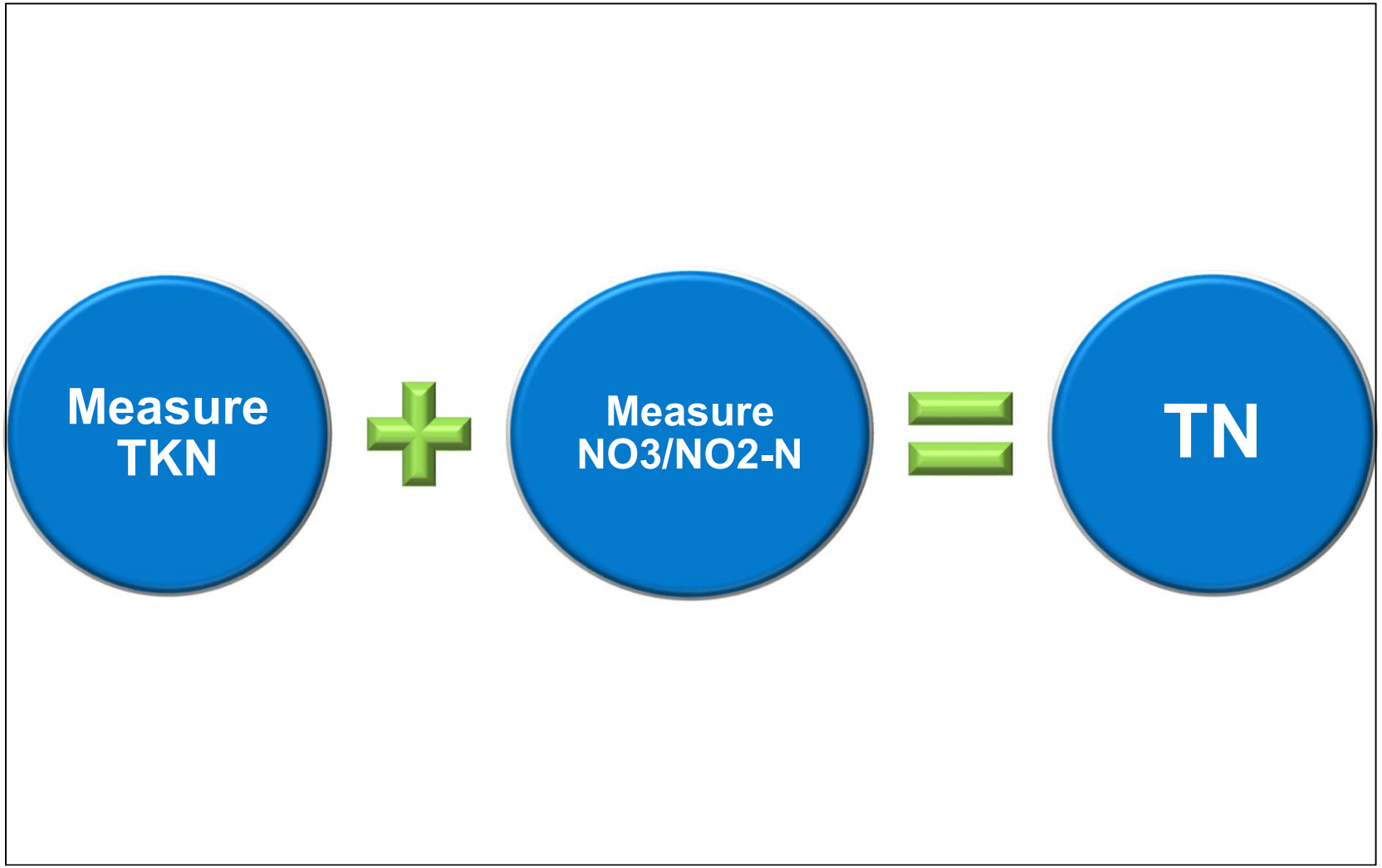
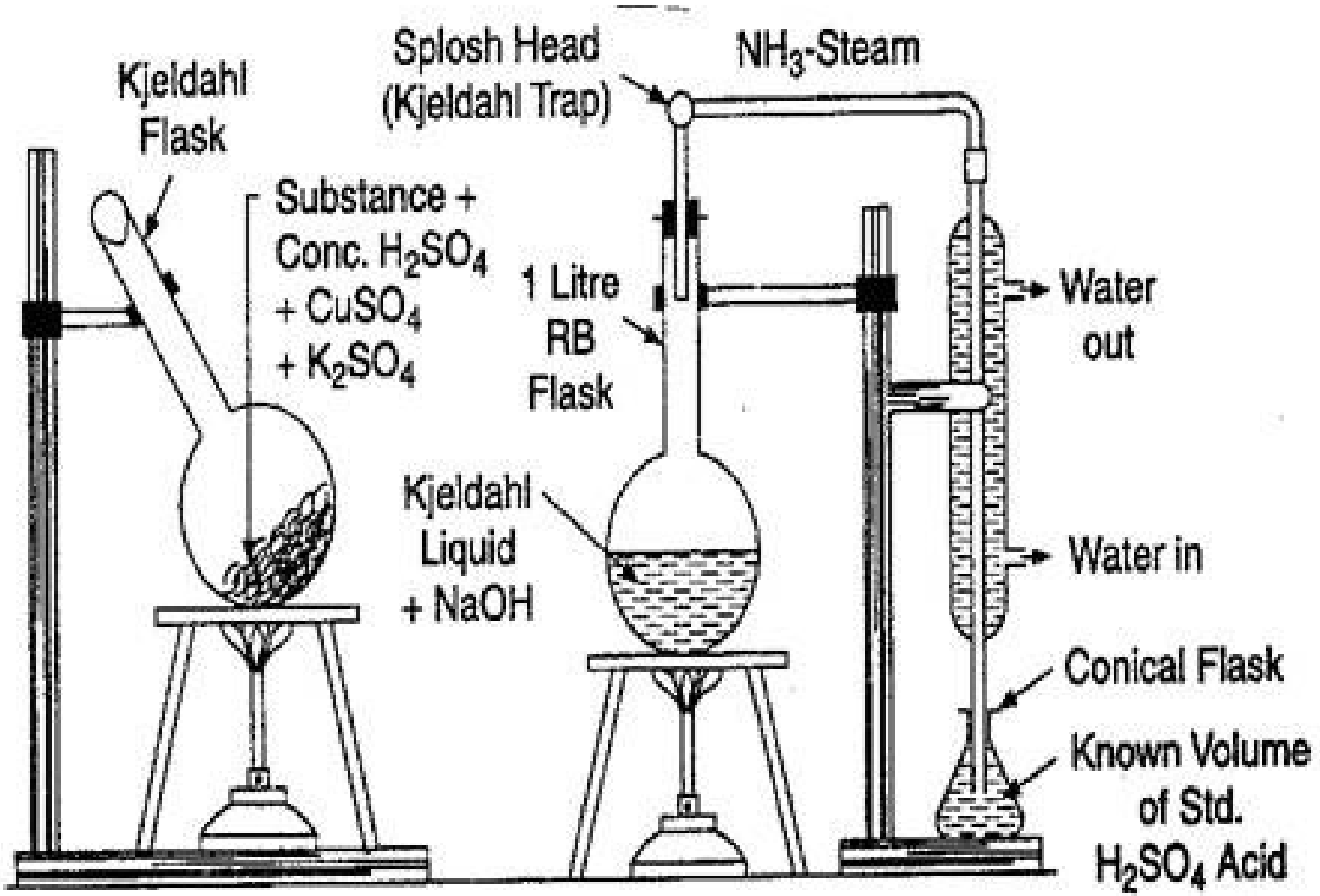
August 2016

The current EPA definition for Total Nitrogen requires two methods

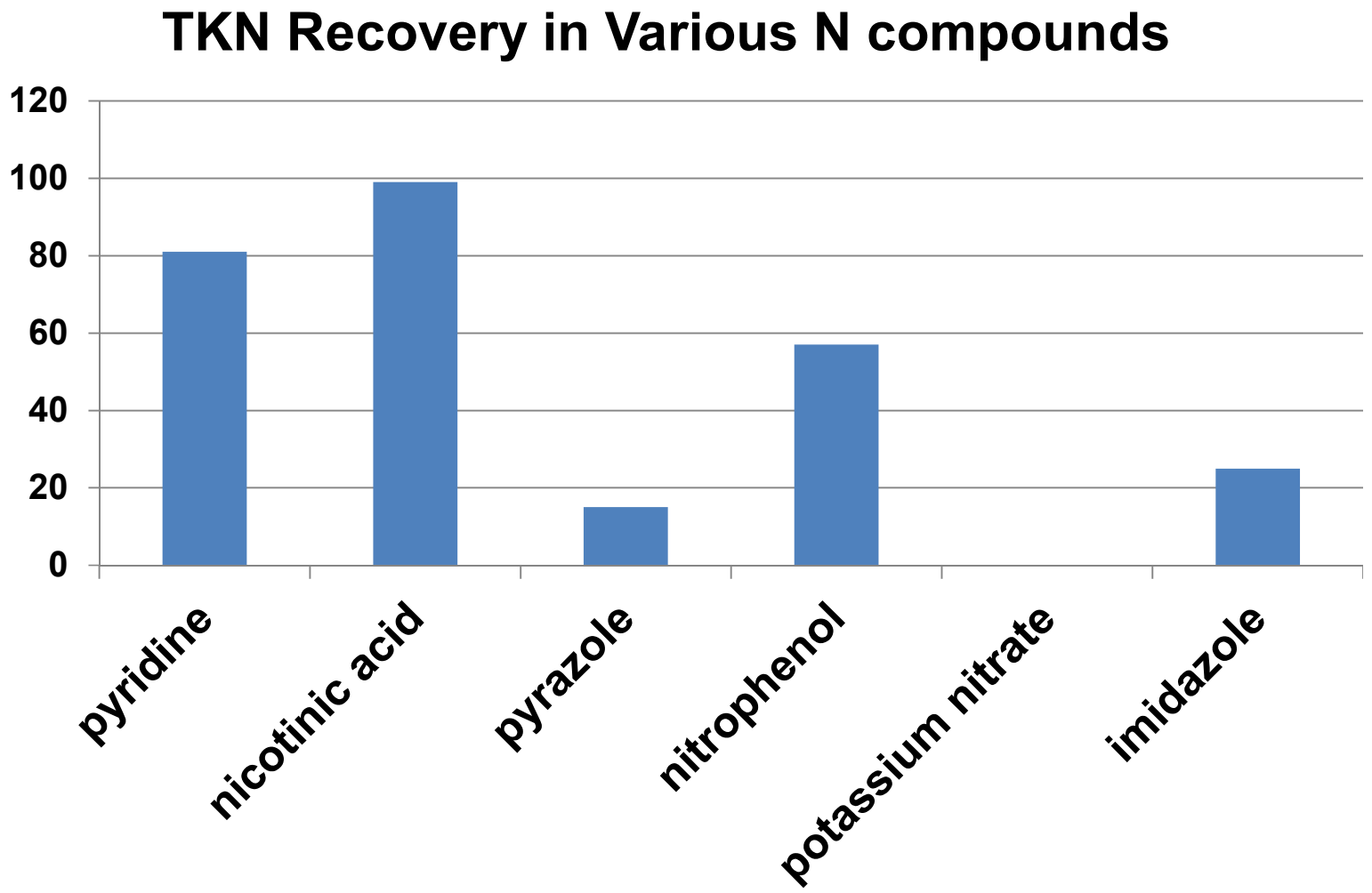



Kjeldahl Flask
Substance + Conc. H_2SO_4 + $CuSO_4$ + K_2SO_4
Splosh Head (Kjeldahl Trap)
NH_3-Steam
1 Litre RB Flask
Kjeldahl Liquid + NaOH
Water out
Water in
Conical Flask
Known Volume of Std. H_2SO_4 Acid

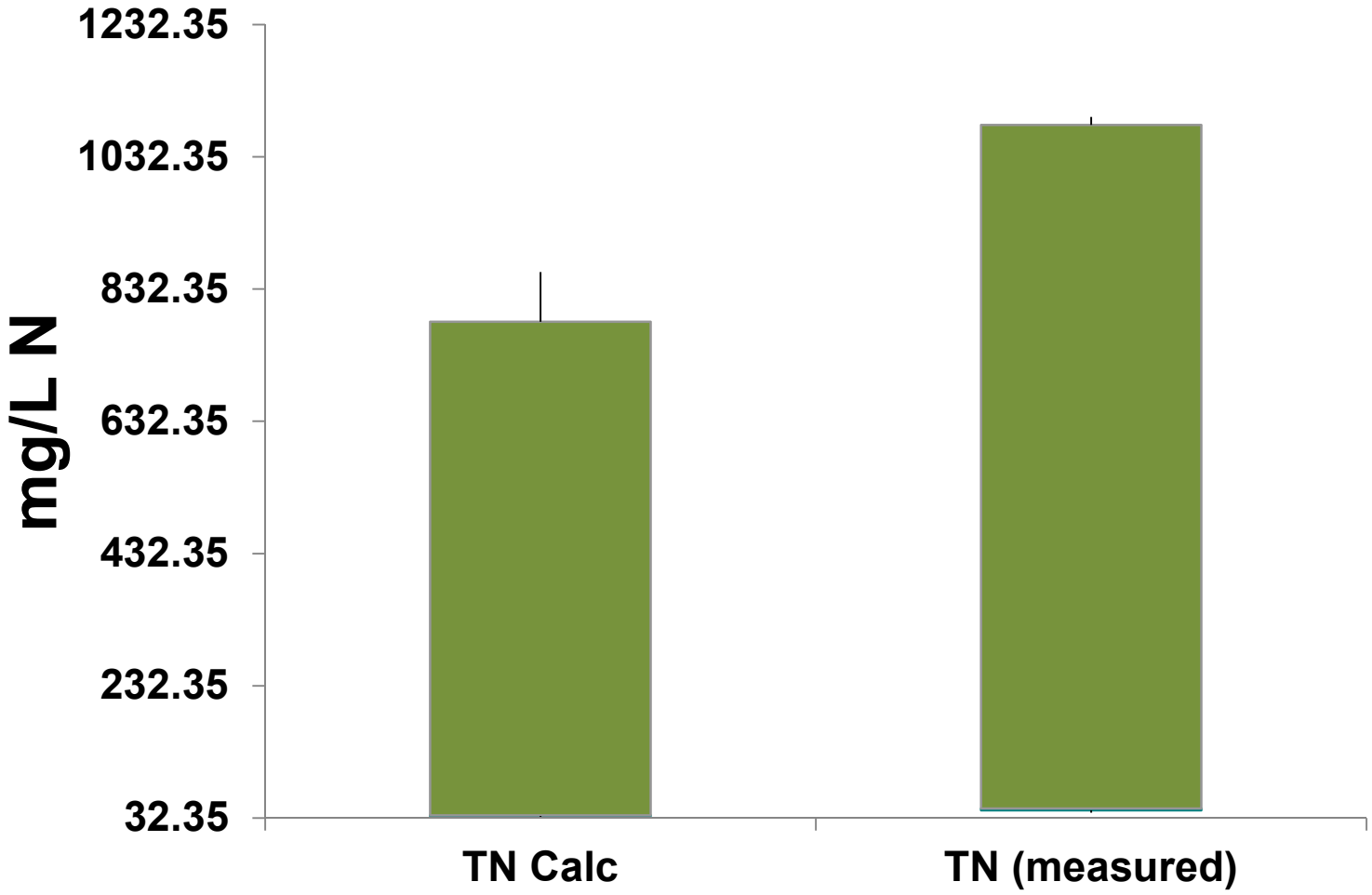
Some of the problems with the TKN method for TN

- Time consuming – 0.5 – 2 hour digestion
  - Separate distillation and/or analysis
- Uses hazardous reagents
  - Boiling sulfuric acid
  - Metal catalyst
- Must run NO_3 + NO_2 separately
- Not applicable to all N compounds

TKN suffers from low recovery of some organics

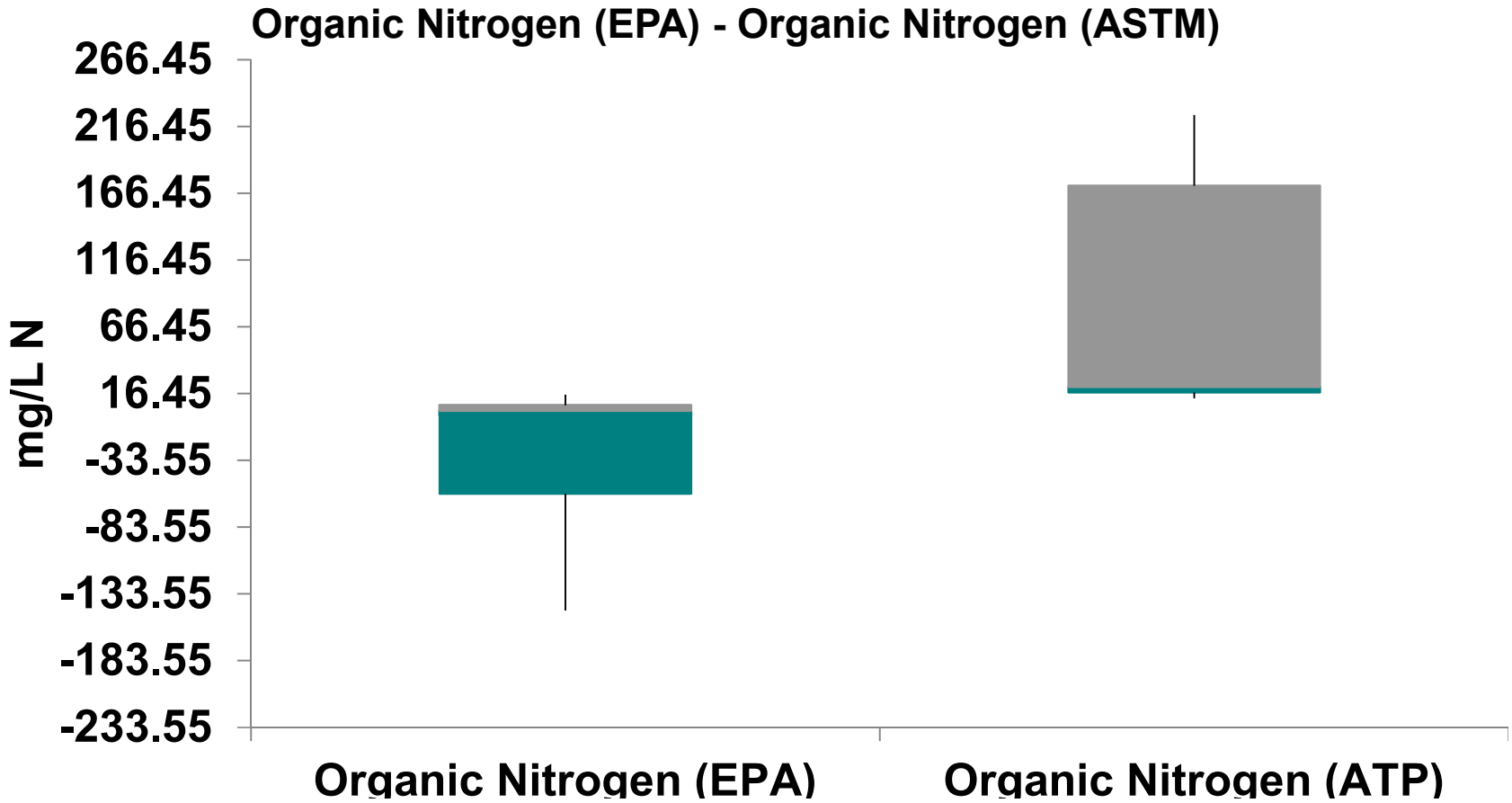


EPA Calculated TN can be lower than measured TN

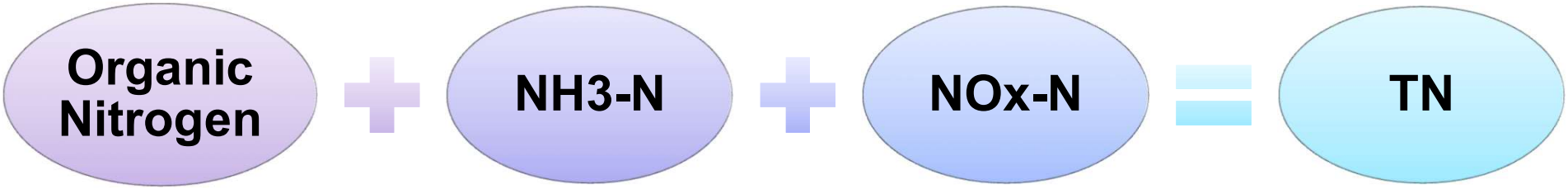


TKN	NOx-N	TN (EPA-calc)	NH_3-N	TN (ATP)
858	0.027	858	853	1078
790	0.077	790	910	1083
776	0.211	776	922	1093
35.4	0.565	36.0	19.8	40.5
34.8	0.482	35.2	31.2	44.0
33.4	0.625	34.0	22.9	44.3
35.6	0.701	36.3	32.5	46.5

A low TKN results in low bias for Organic Nitrogen calculations



New methods are needed that measure Total Nitrogen as a single result



Any new “method” for TN should:

- Obtain equivalent results (in absence of interference) to TKN and other TN methods
- Be “rugged”
- Use few reagents
- Have a large dynamic range
- Sample/”handle” a complex matrix

New ASTM method determines TN (and TP) by 120 °C alkaline persulfate digestion and ion chromatography

Digest on your COD Block

Only one hour digestion

Safer reagents – less hazardous

Calculate TKN by difference

The alkaline digestion oxidizes nitrogen to nitrate.

Nitrate is measured by Ion Chromatography

Potential interferences of the new ASTM ion chromatography TN method

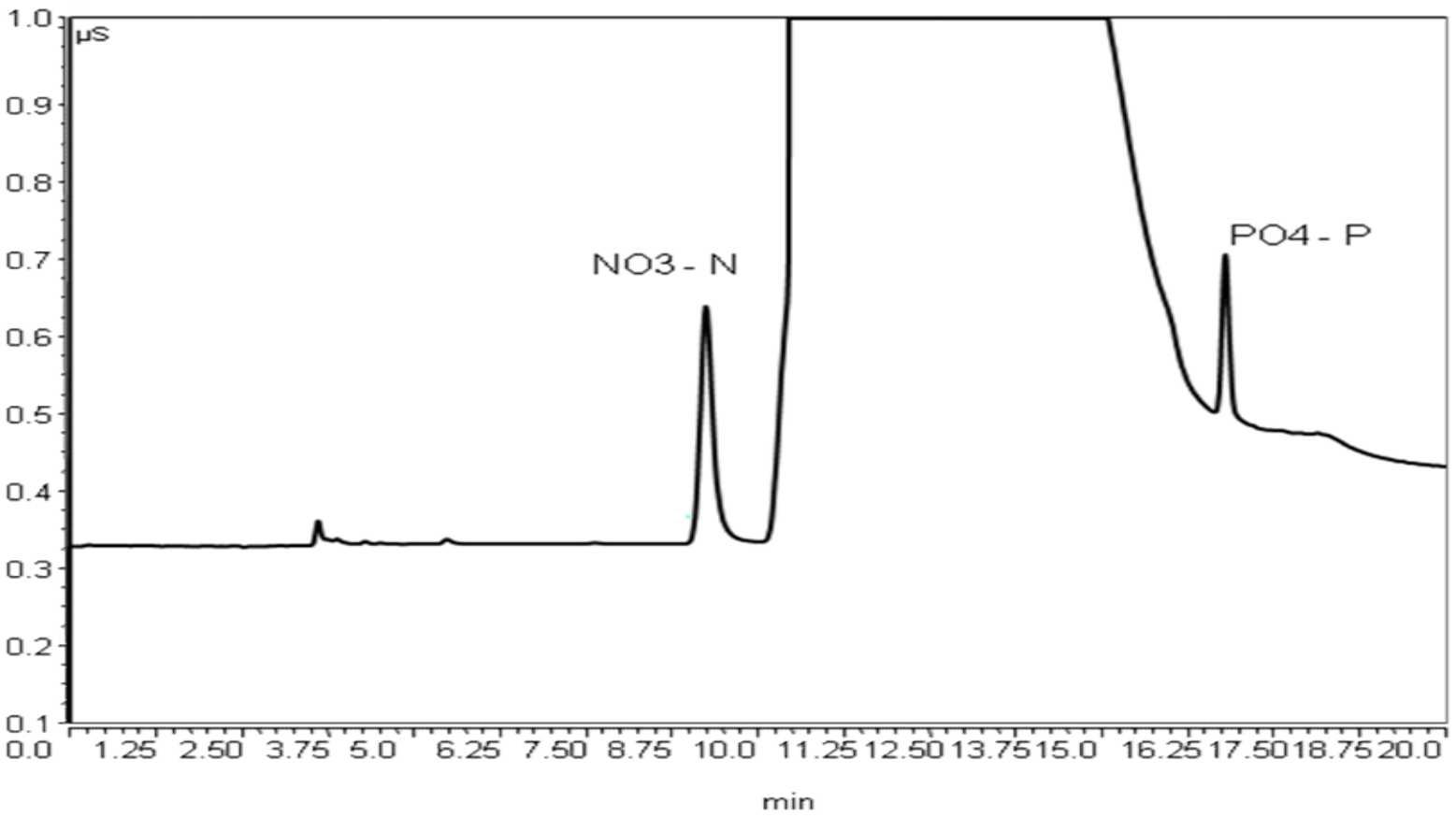
High sulfate – overload the column

High chloride – low recoveries

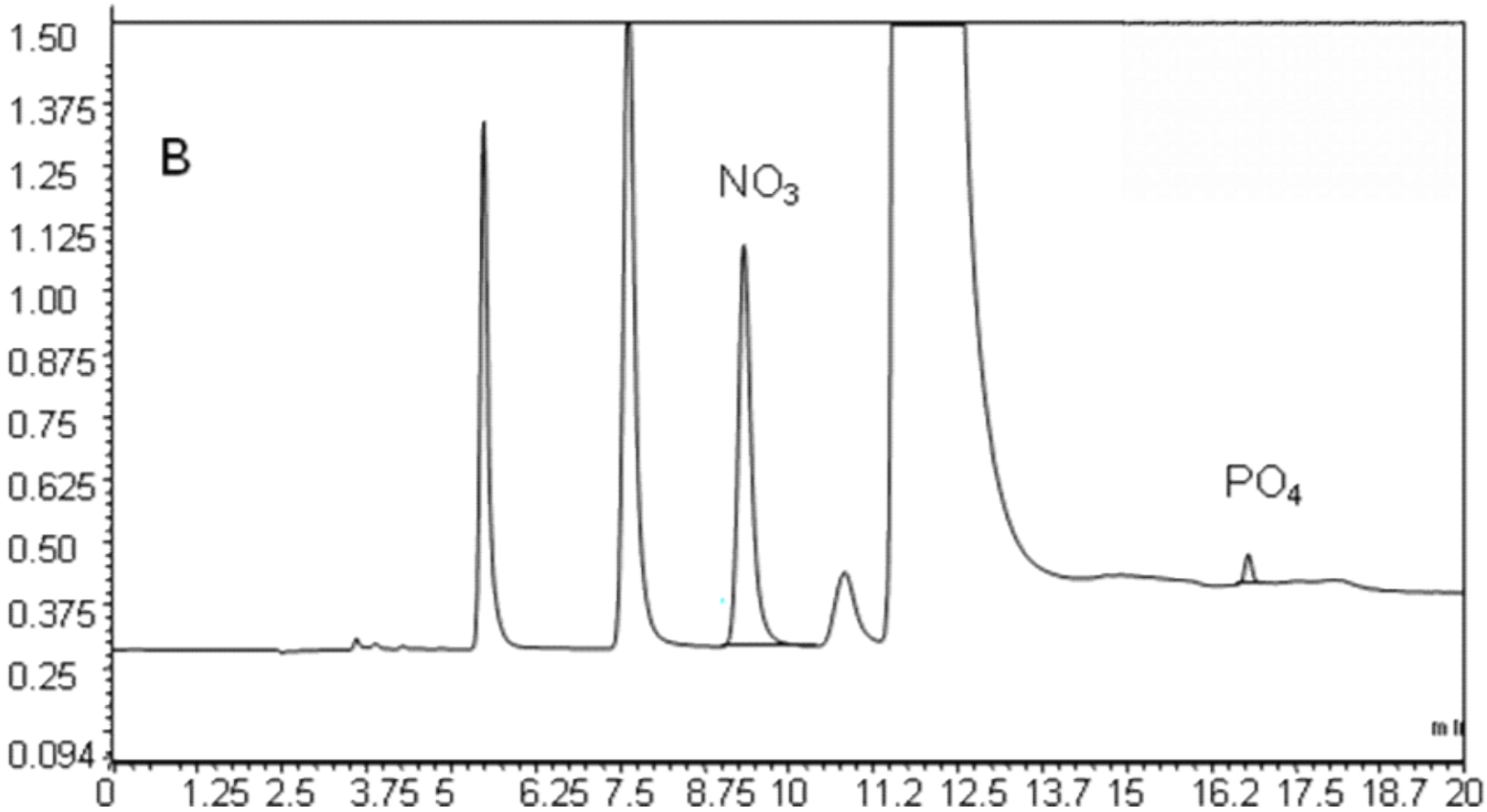
N in reagent – high blanks

High organic carbon – low recoveries

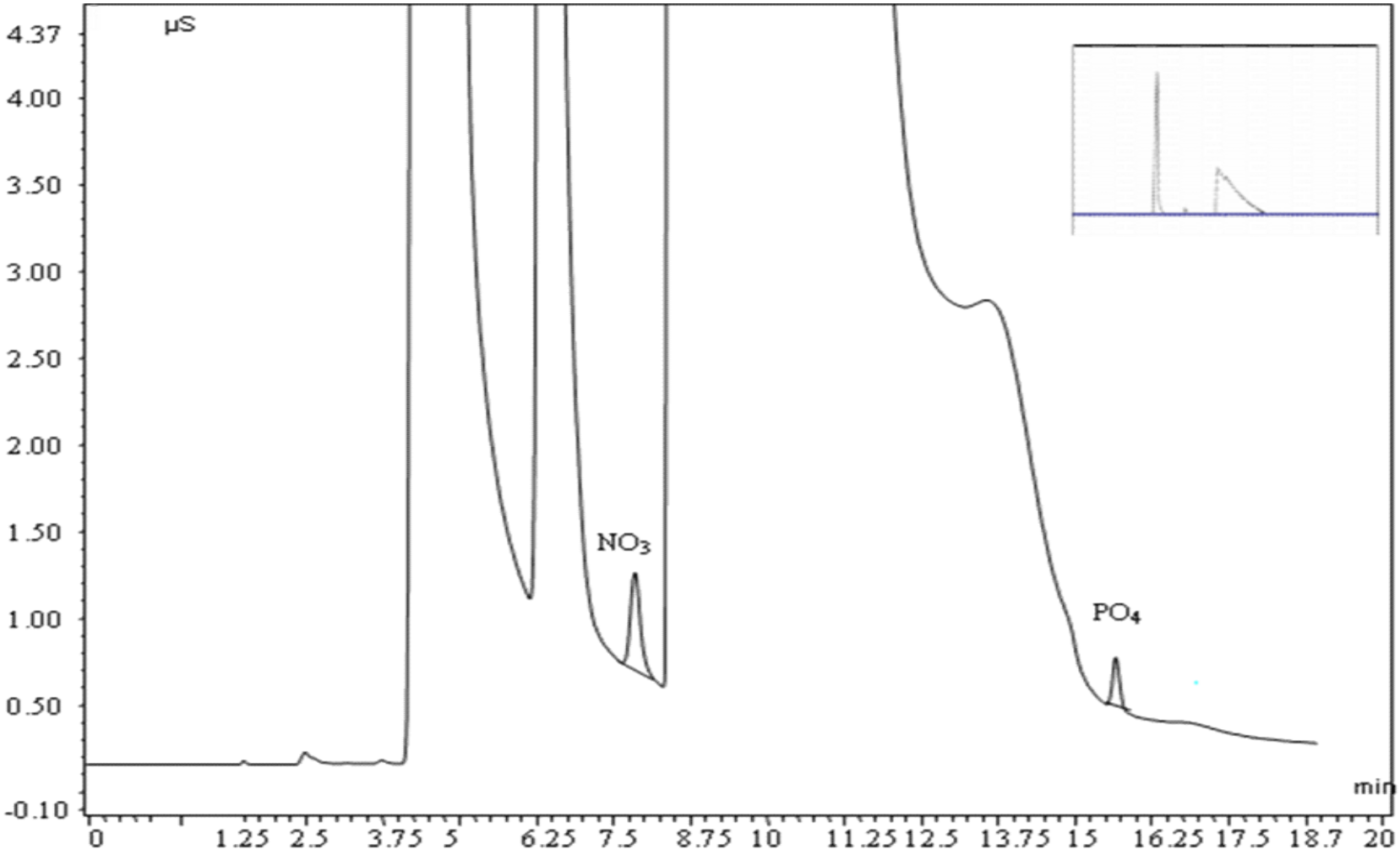
The method is capable of measuring analytes in the high sulfate matrix



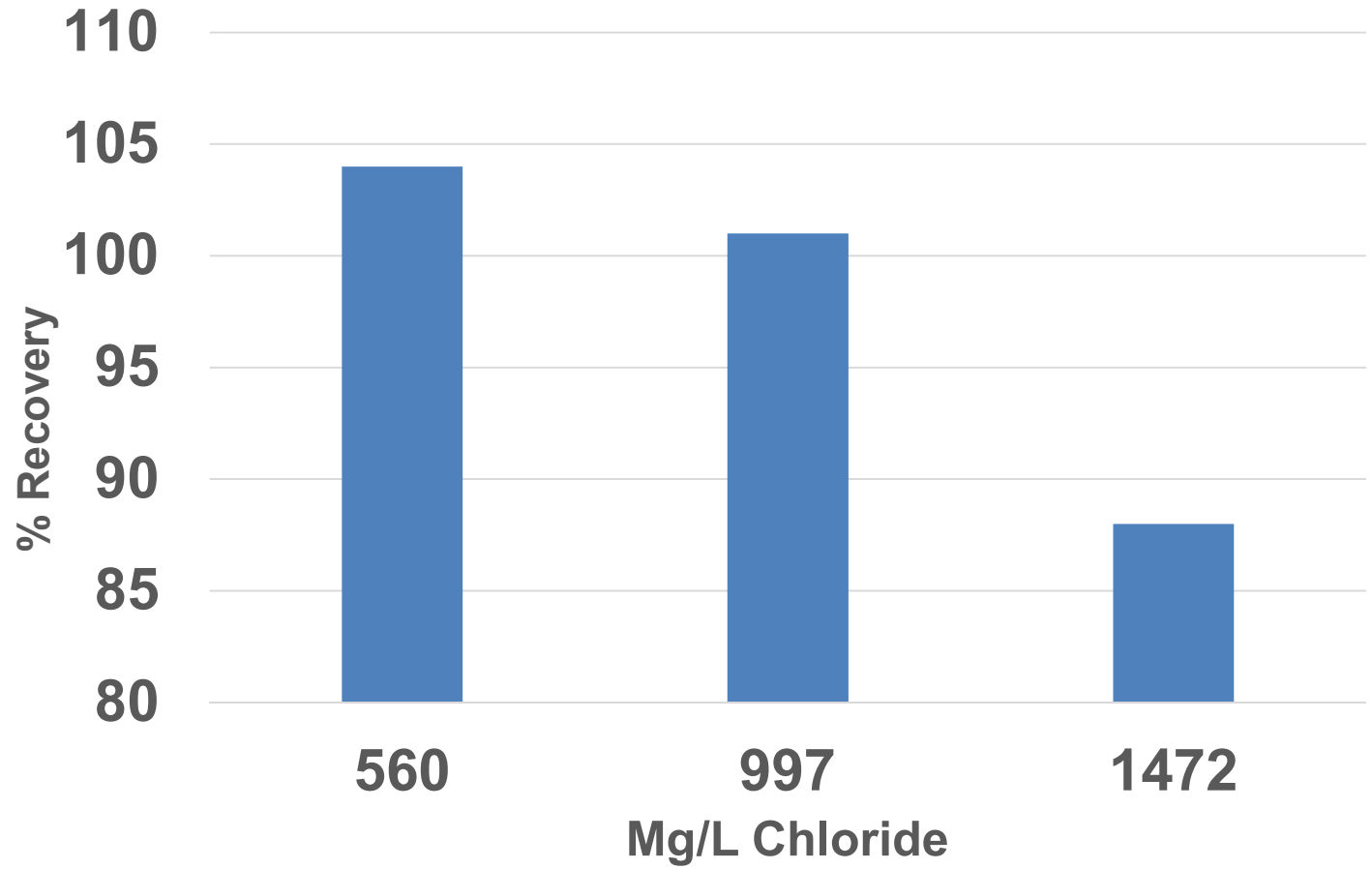
Chromatogram of persulfate digested wastewater



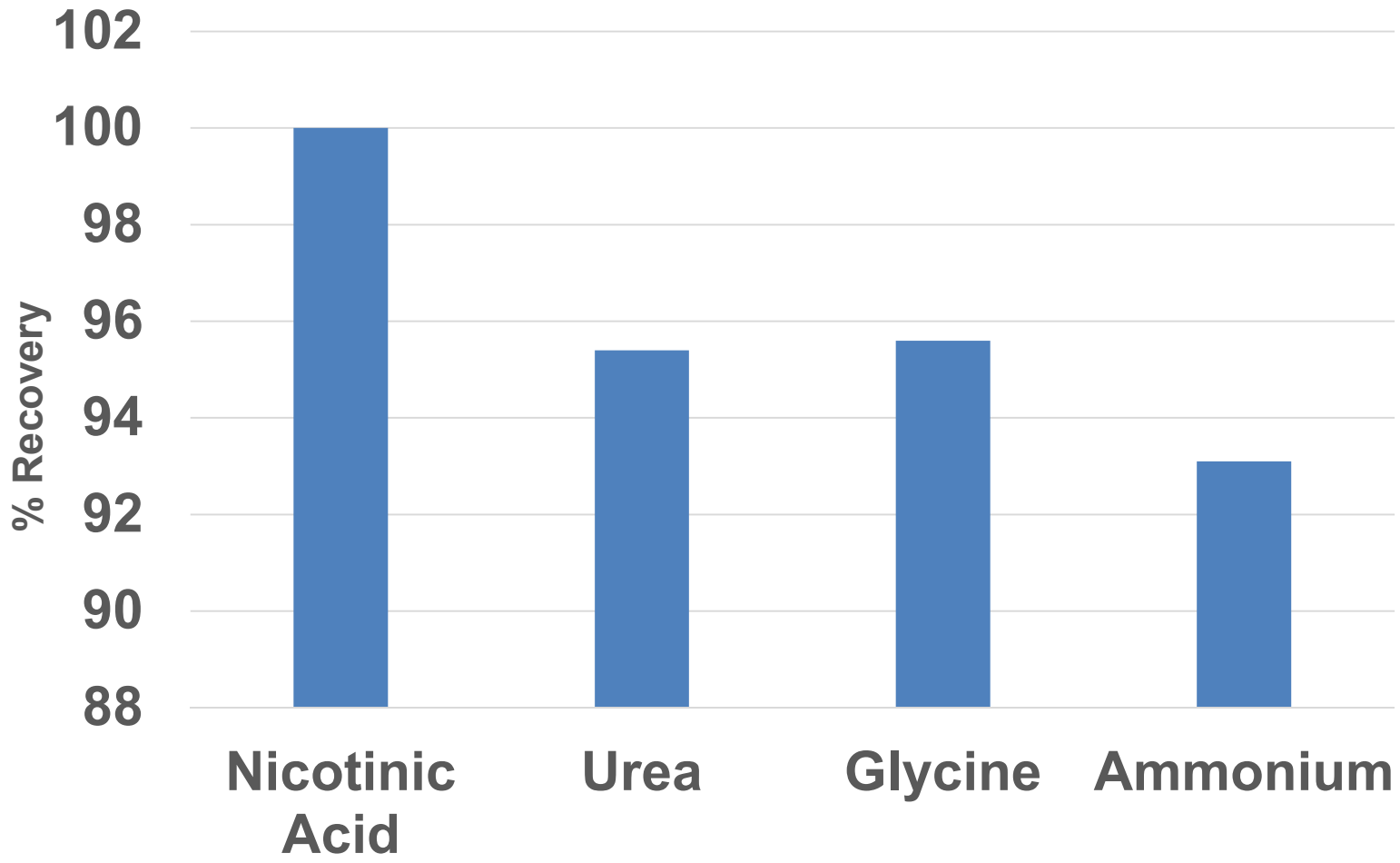
Chromatogram of persulfate digested in 1000 ppm Chloride



Recovery of TN (from glycine) in chloride containing samples



Recovery of TN in various nitrogen compounds



WK46665
Standard Test Method for Total Nitrogen in Water by High Temperature Catalytic Combustion and Chemiluminescence Detection

This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.
Current edition approved [date to come]. Published [date to come].
DOI:10.1520/Dxxx-xx.

Standard Methods for the Examination of Water and Wastewater

Total Nitrogen in Water by High Temperature Catalytic Oxidation and Chemiluminescence Detection

Total Nitrogen can be easily measured on a TOC analyzer

Catalytic Combustion (CC)

- $2(NH_2)_2CO + 5O_2 + \text{catalyst} \rightarrow 4NO + 4H_2O + CO_2$

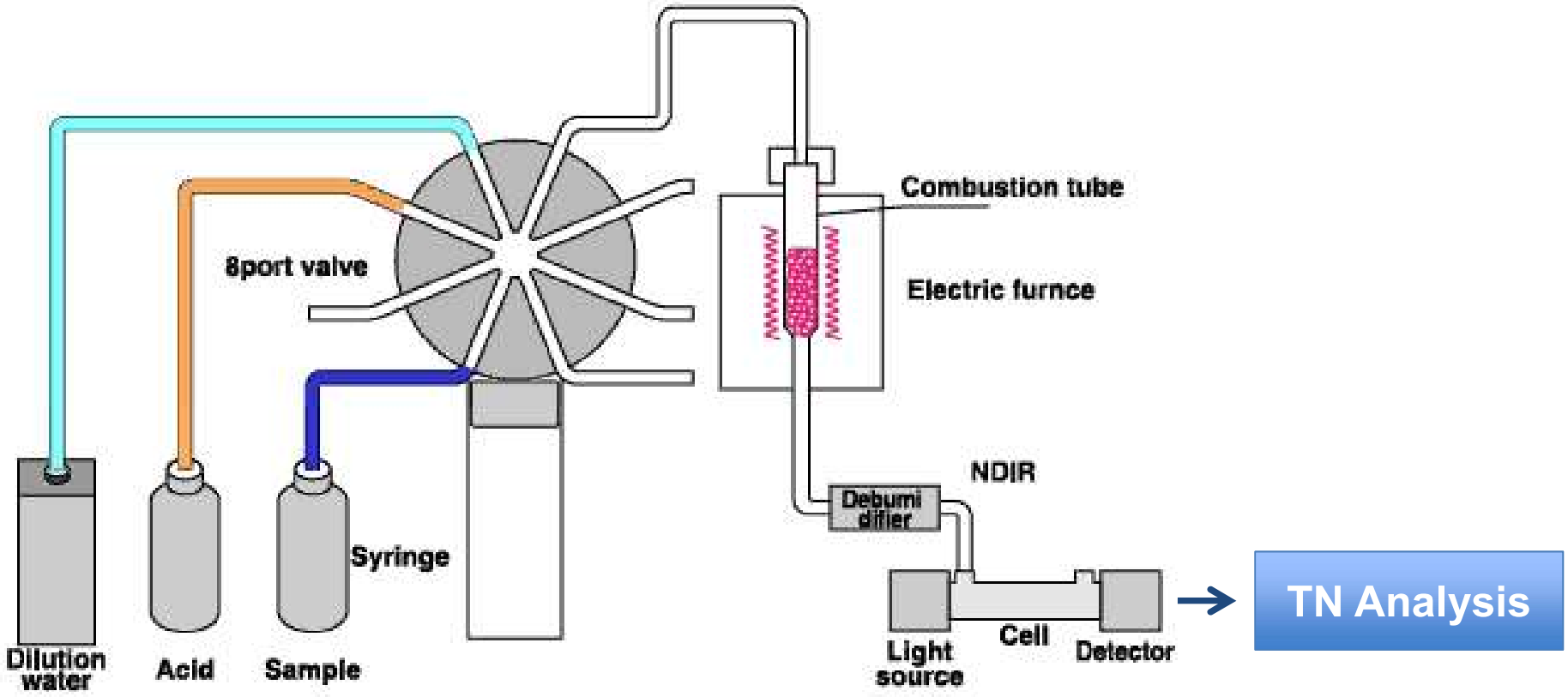
Ozonation

- $NO + O_3 \rightarrow NO_2 + O_2$
- $NO + O_3 \rightarrow NO_2^* + O_2$

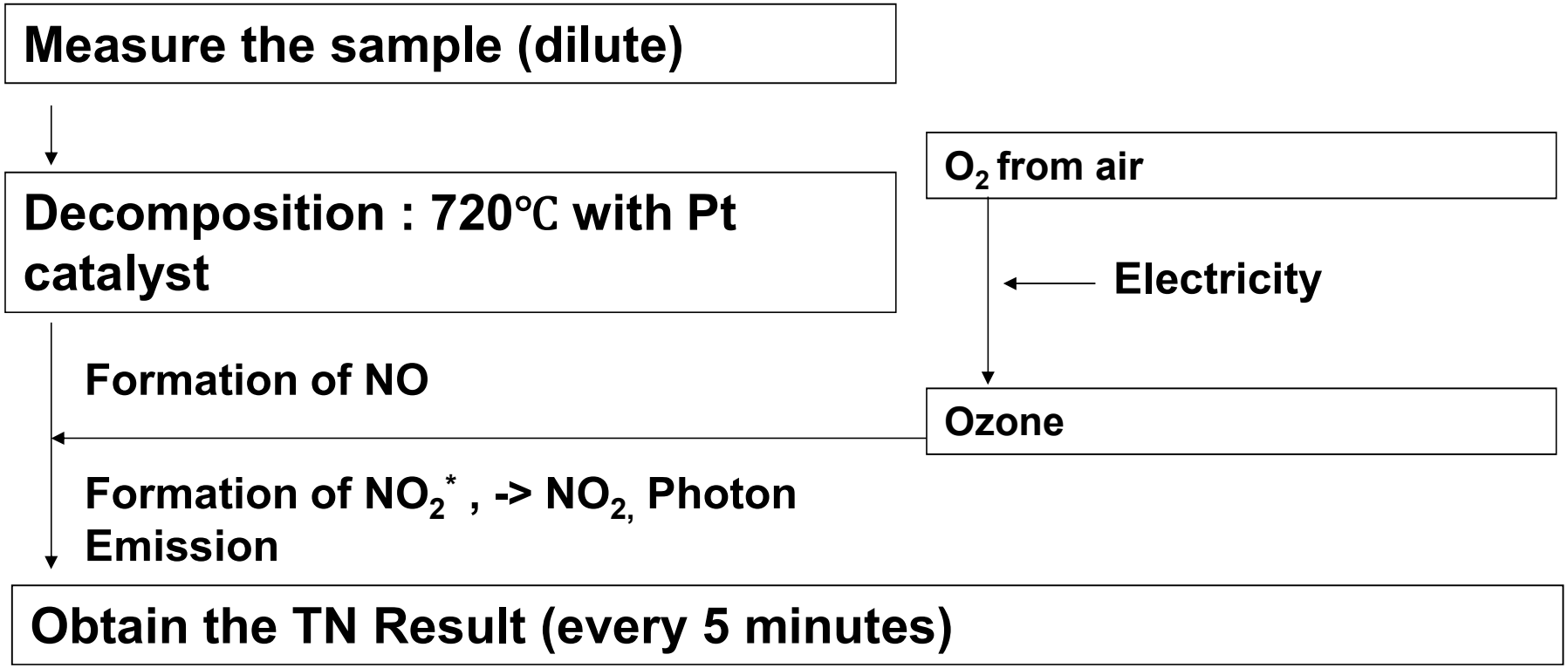
Detection

$NO_2^* \rightarrow NO_2 + \text{light}$

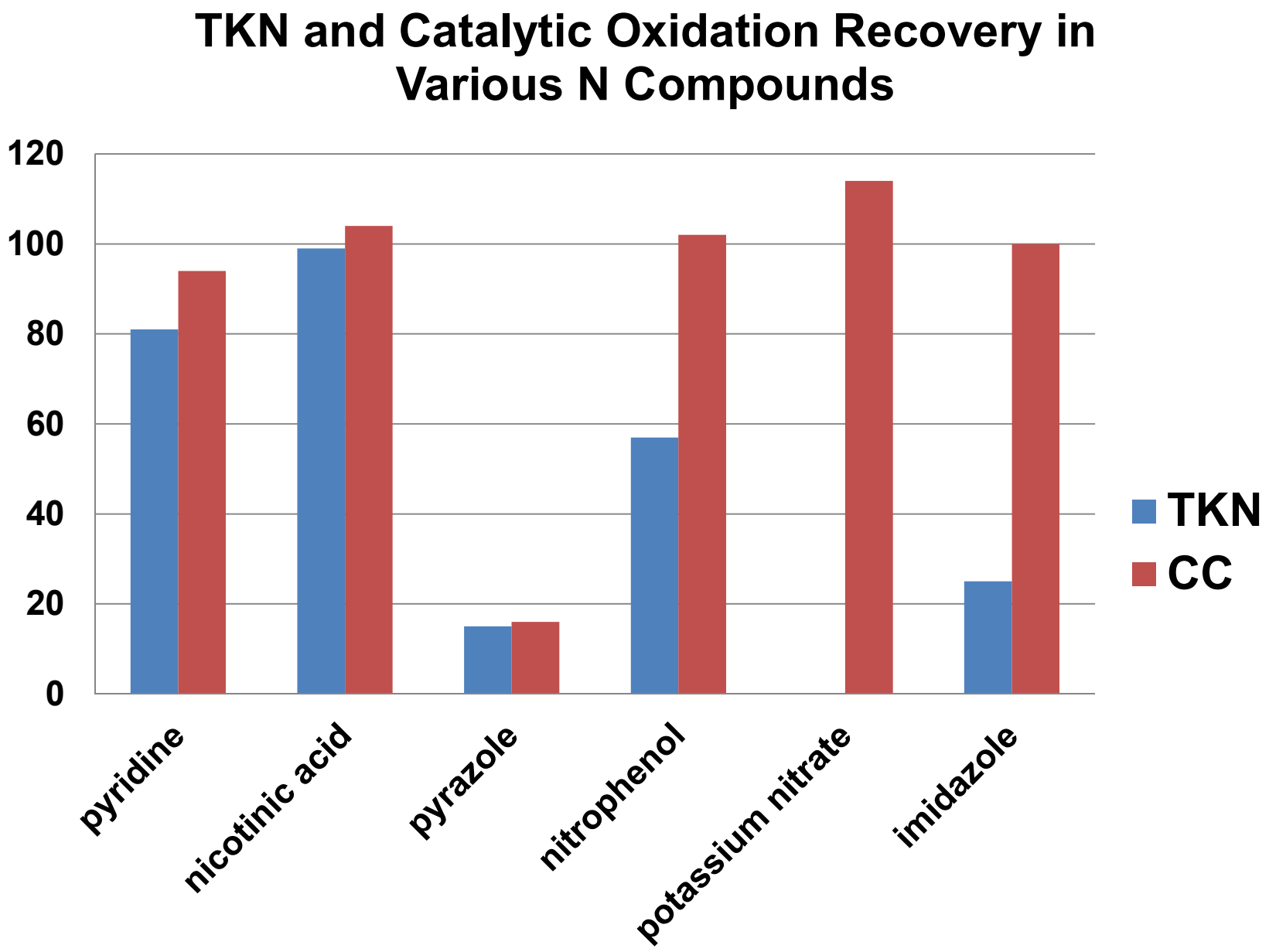
Schematic of the TOC + TN Analyzer



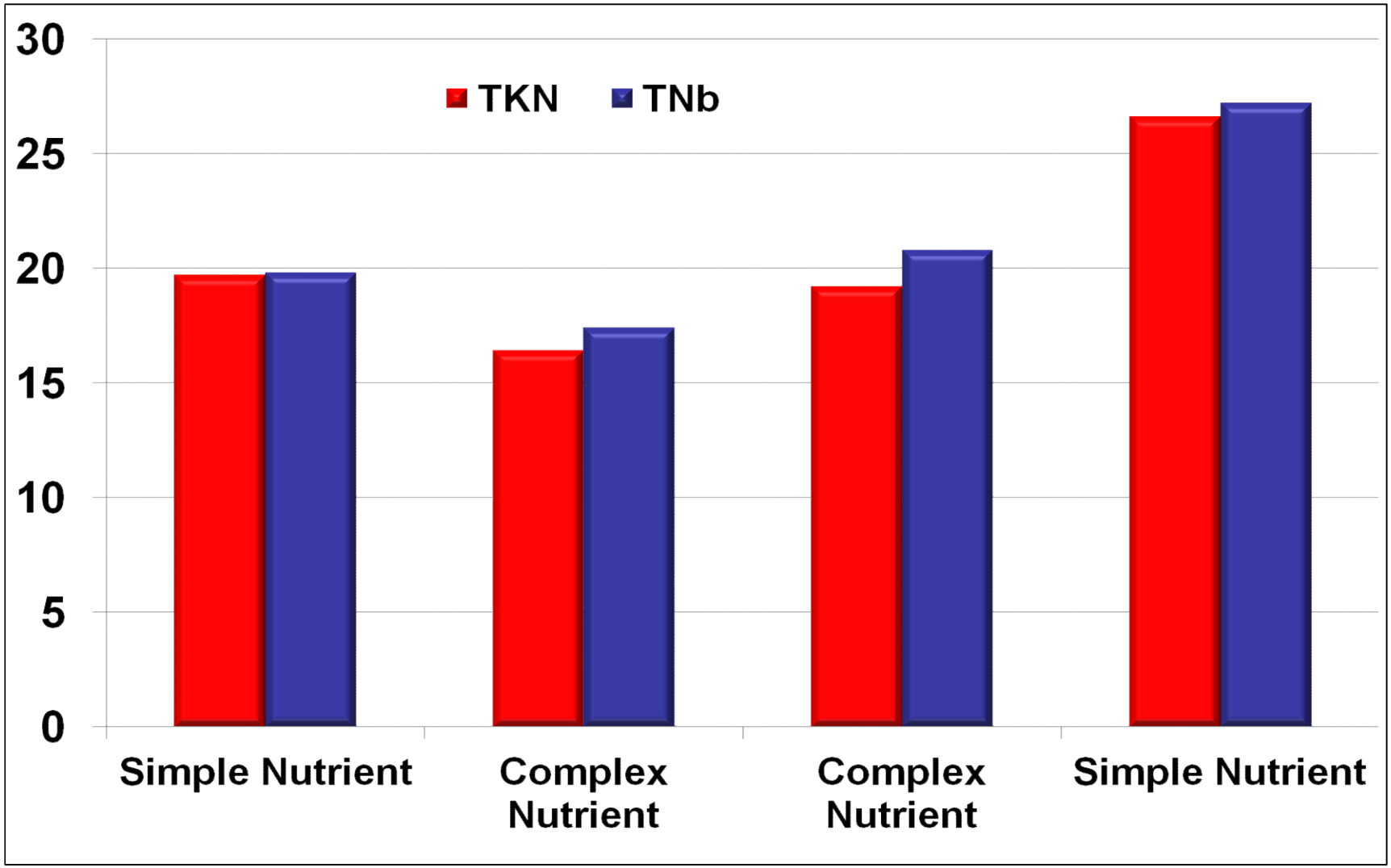
The Total Nitrogen Measurement is rugged and uses few reagents



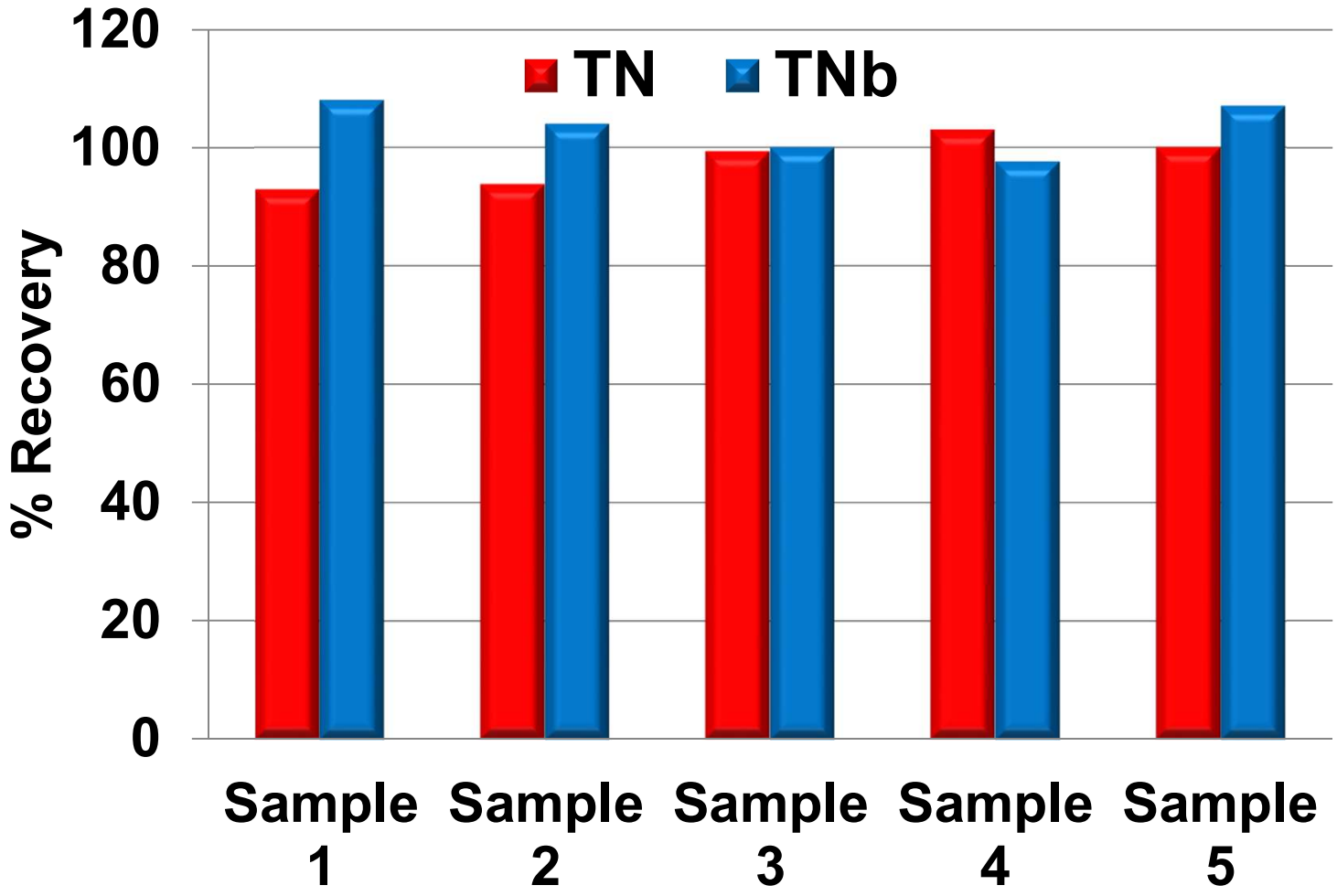
	TN	TKN
Measurement contains	- Ammonia - Nitrate - Nitrite - Organic nitrogen compounds	- Ammonia - Organic nitrogen compounds
Consumables	Catalyst hydrochloric acid	Mercury or selenium, sulphuric acid
Analysis time	3min -7 min (together with TOC measurement)	Minimum 60 min
On-line realisation	Easy	Not possible


TKN and Catalytic Oxidation Recovery in Various N Compounds
120
100
80
60
40
20
0
pyridine
nicotinic acid
pyrazole
nitrophenol
potassium nitrate
imidazole
TKN
CC

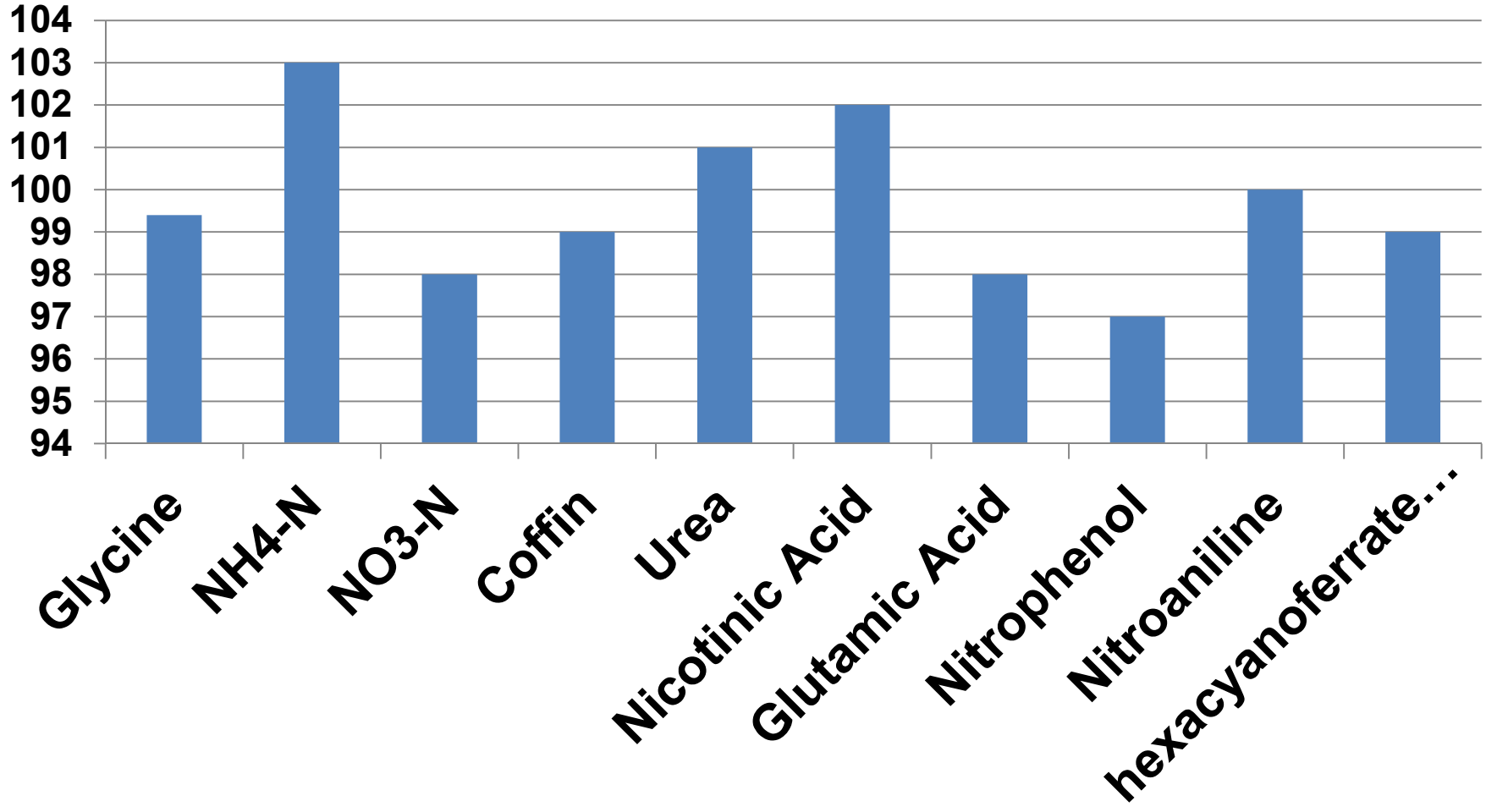
Comparison of TN to TKN (QC samples)



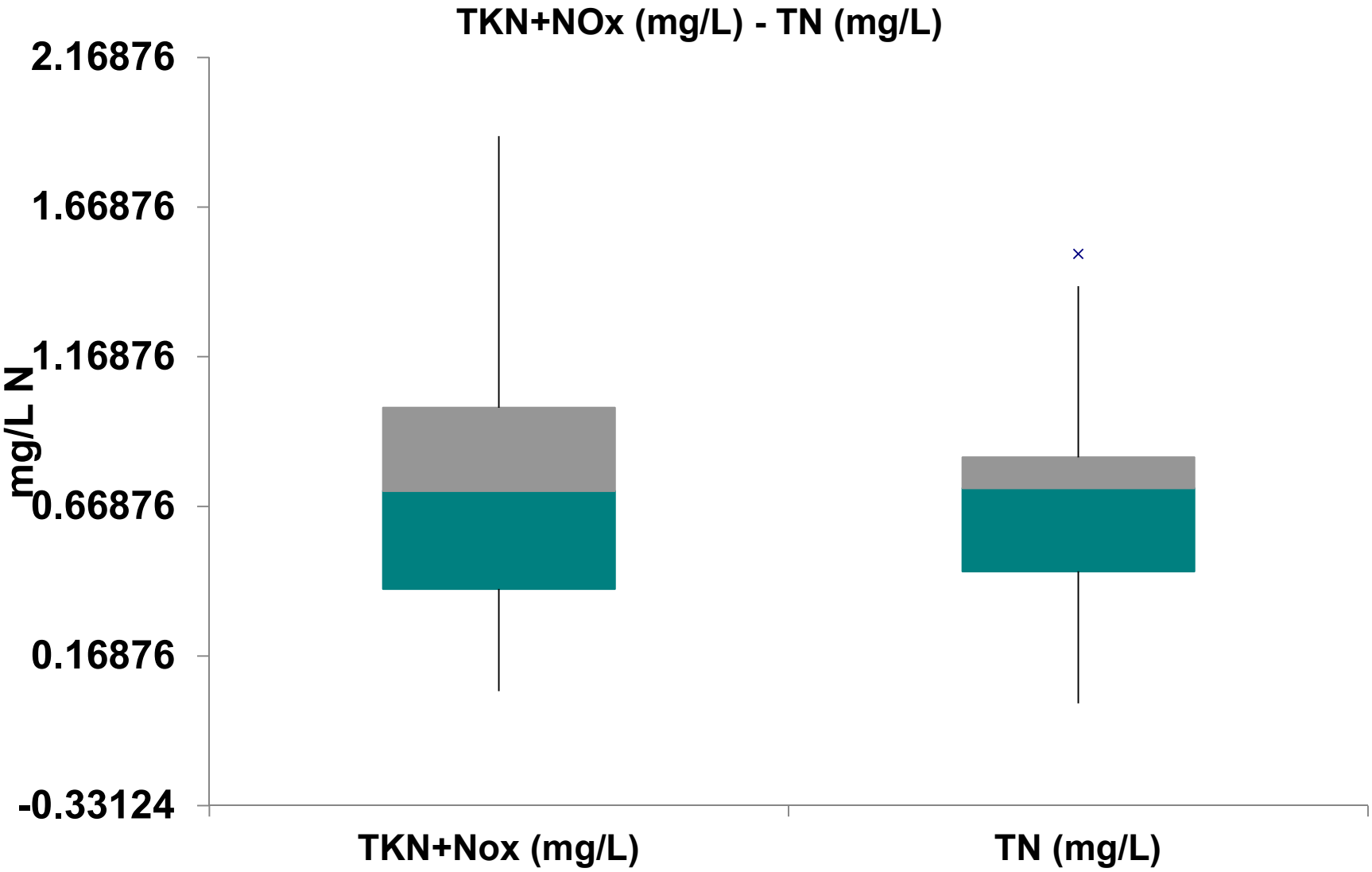
HTCO methods obtain near equal results with persulfate TN on unknown samples

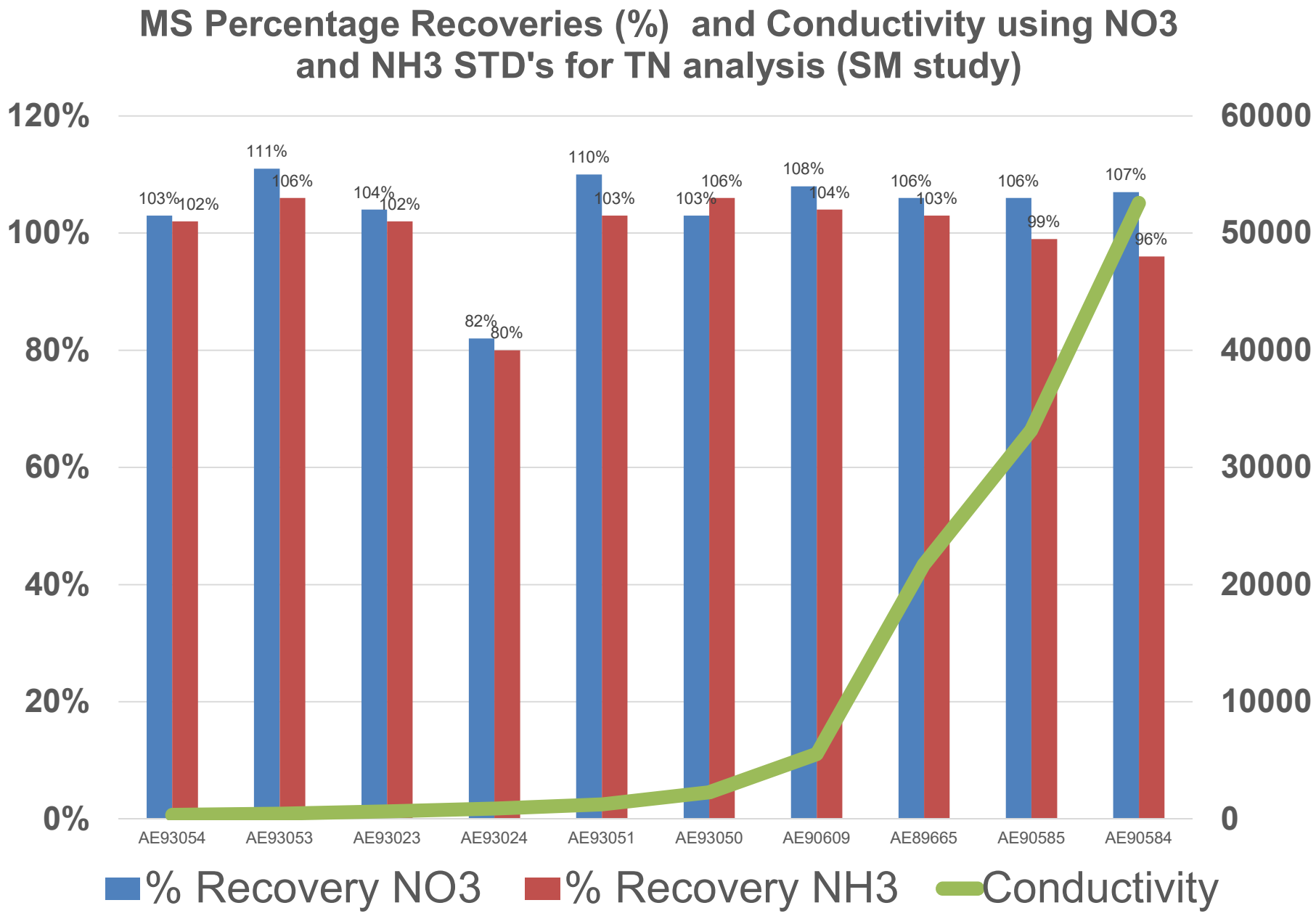


% Recovery of Various Nitrogen Compounds



Comparison of TKN + NOx and TN on 53 wastewater samples (Standard Methods study)



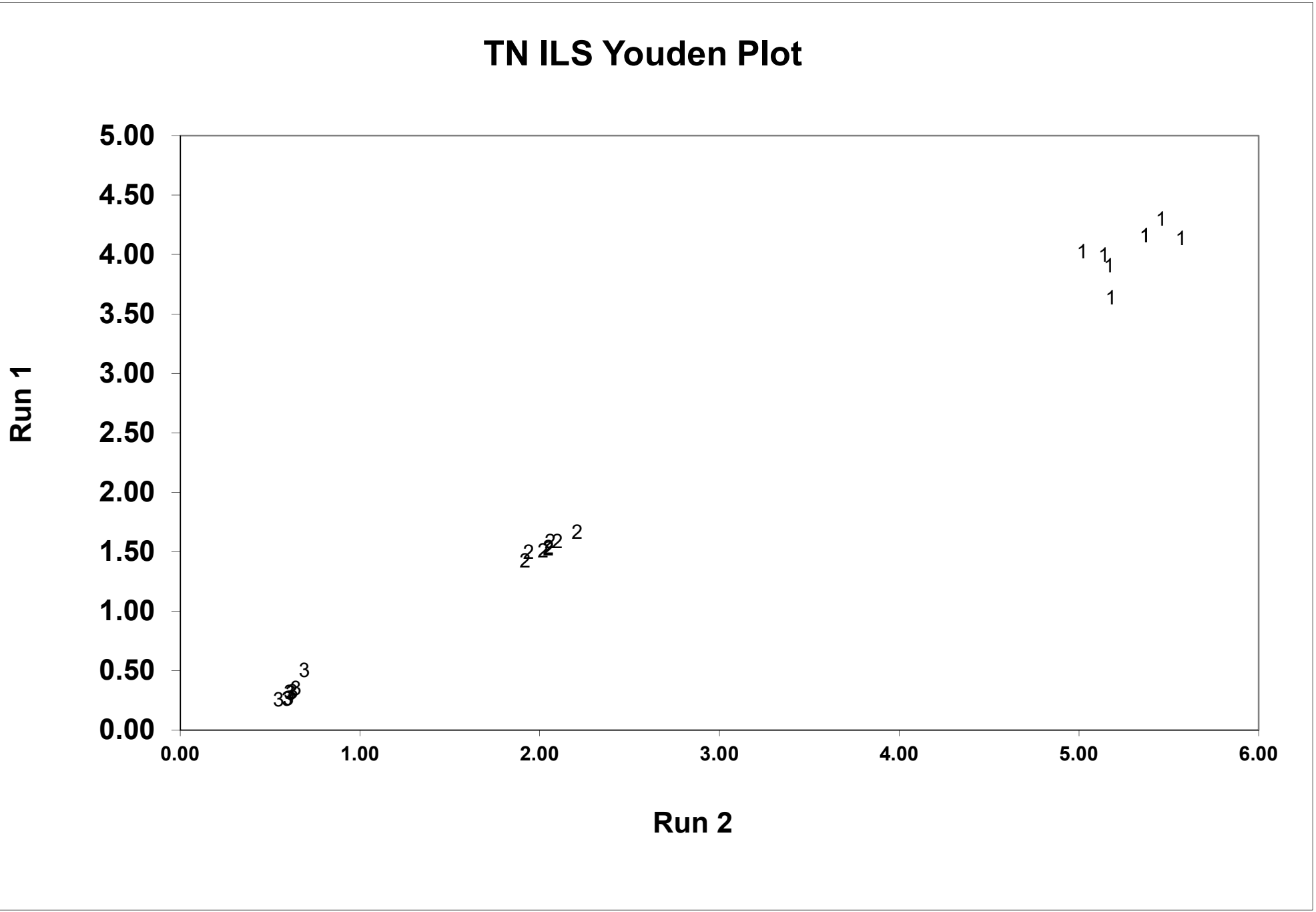

MS Percentage Recoveries (%) and Conductivity using NO3 and NH3 STD's for TN analysis (SM study)
120%
100%
80%
60%
40%
20%
0%
60000
50000
40000
30000
20000
10000
0
103%
102%
111%
106%
104%
102%
82%
80%
110%
103%
103%
106%
108%
104%
106%
103%
106%
99%
107%
96%
AE93054
AE93053
AE93023
AE93024
AE93051
AE93050
AE90609
AE89665
AE90585
AE90584
% Recovery NO3
% Recovery NH3
Conductivity

ASTM Inter-laboratory Study

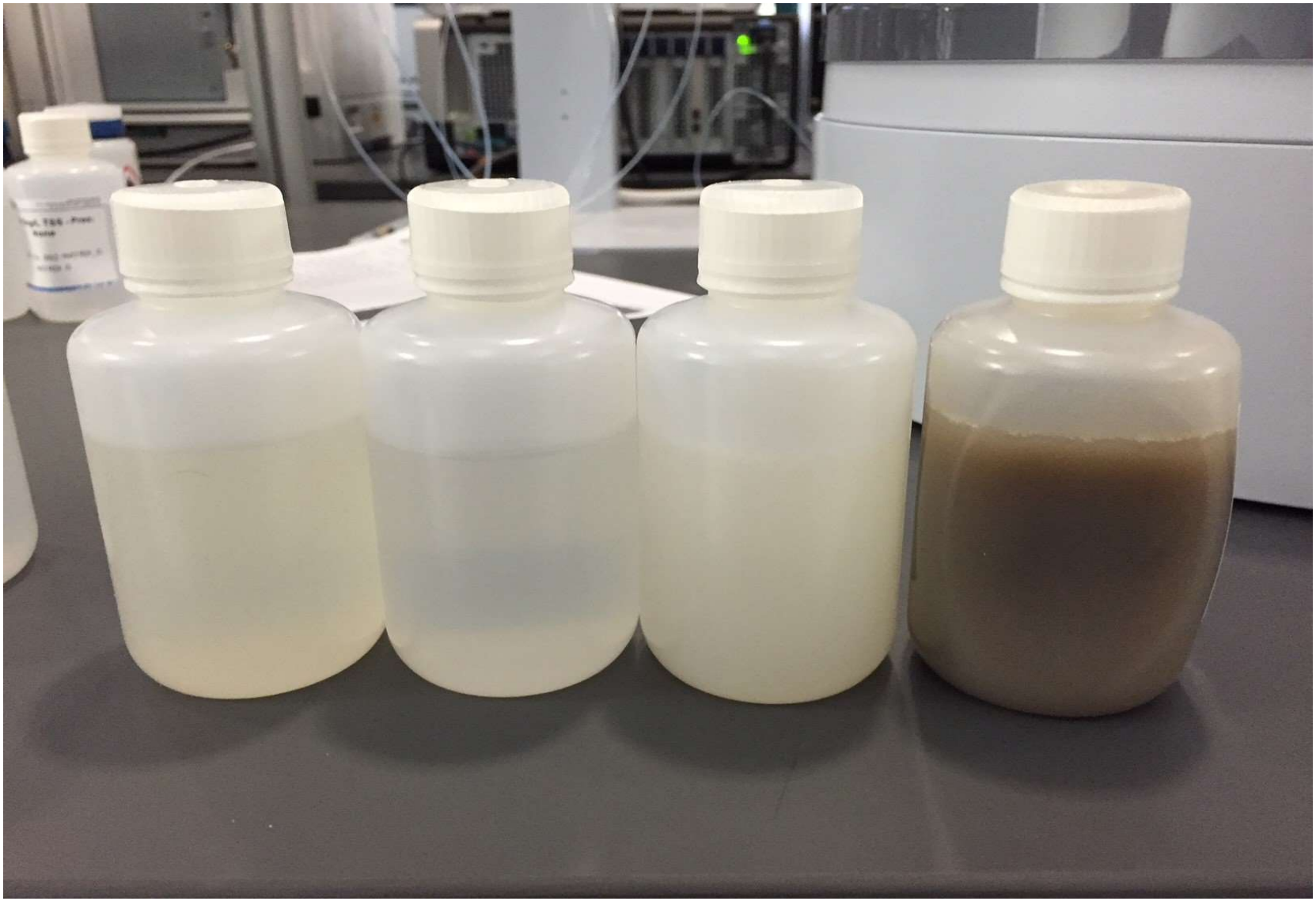
Lab ID	MDL (mg/L)
1	0.023
2	0.041
3	0.034
4	0.025
5	0.020
6	0.030
7	0.031
8	0.077

Sample #	Sample ID	Matrix Preparation	Source of N
1	Wastewater	3000 mg TDS/L	Glycine
2	Wastewater	3000 mg TDS/L	Glycine
3	Surface Water	500 mg TDS/L	Nicotinic Acid
4	Surface Water	500 mg TDS/L	Nicotinic Acid
5	Wastewater WP	ERA Ready to Use Waste-Water	glycine
6	Wastewater WP	ERA Ready to Use Waste-Water	glycine
7	Simple Nutrient (effluent)	ERA Ready to Use WasteWater	mix of NH3-N and NO3-N
8	Simple Nutrient (Influent)	ERA Solids WP	Ammonia - N
9	Wastewater effluent	WWTP influent	unknown
10	Wastewater	WWPP effluent	unknown
11	Wastewater	Pulp and Paper effluent	unknown
12	Wastewater	WWTP aeration basin	unknown
LCS	ERA QC Sample	ERA QC Sample	NH3-N+ NO3-N

Sample	Avg	certified value	% recovery	sx	%RSD
1	5.17	5.00	103%	0.183916	3.56%
2	4.04	4.00	101%	0.19761	4.89%
3	1.93	2.00	97%	0.091081	4.71%
4	1.54	1.61	96%	0.073403	4.75%
5	0.496	0.514	99%	0.041072	8.10%
6	0.302	0.313	97%	0.036859	12.2%
7	9.70	10.0	97%	0.770197	7.94%
8	28.5	30.0	95%	2.720779	9.5%
9	29.6			2.288575	7.74%
10	4.41			0.506283	11.5%
11	9.30			2.885724	31.0%
12	339			128.3746	37.9%
LCS	3.90	3.92	99.6%	0.215698	5.5%


TN ILS Youden Plot
Run 1
Run 2
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00

Samples 9 – 12 ASTM TN ILS



TKN

Thank You!

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For more information contact