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Total Nitrogen – A new parameter at Part 136?

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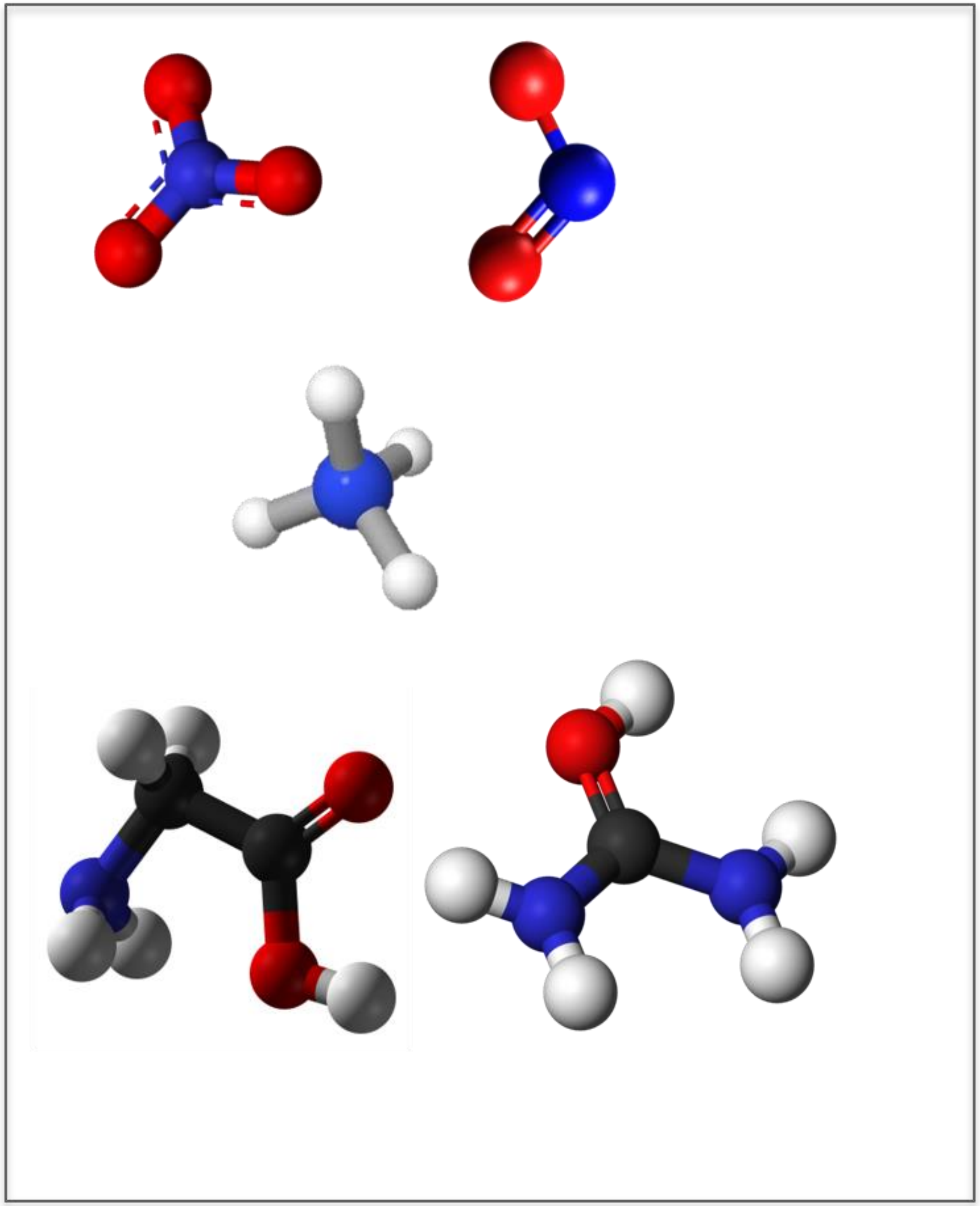
Nitrogen compounds that are found in water

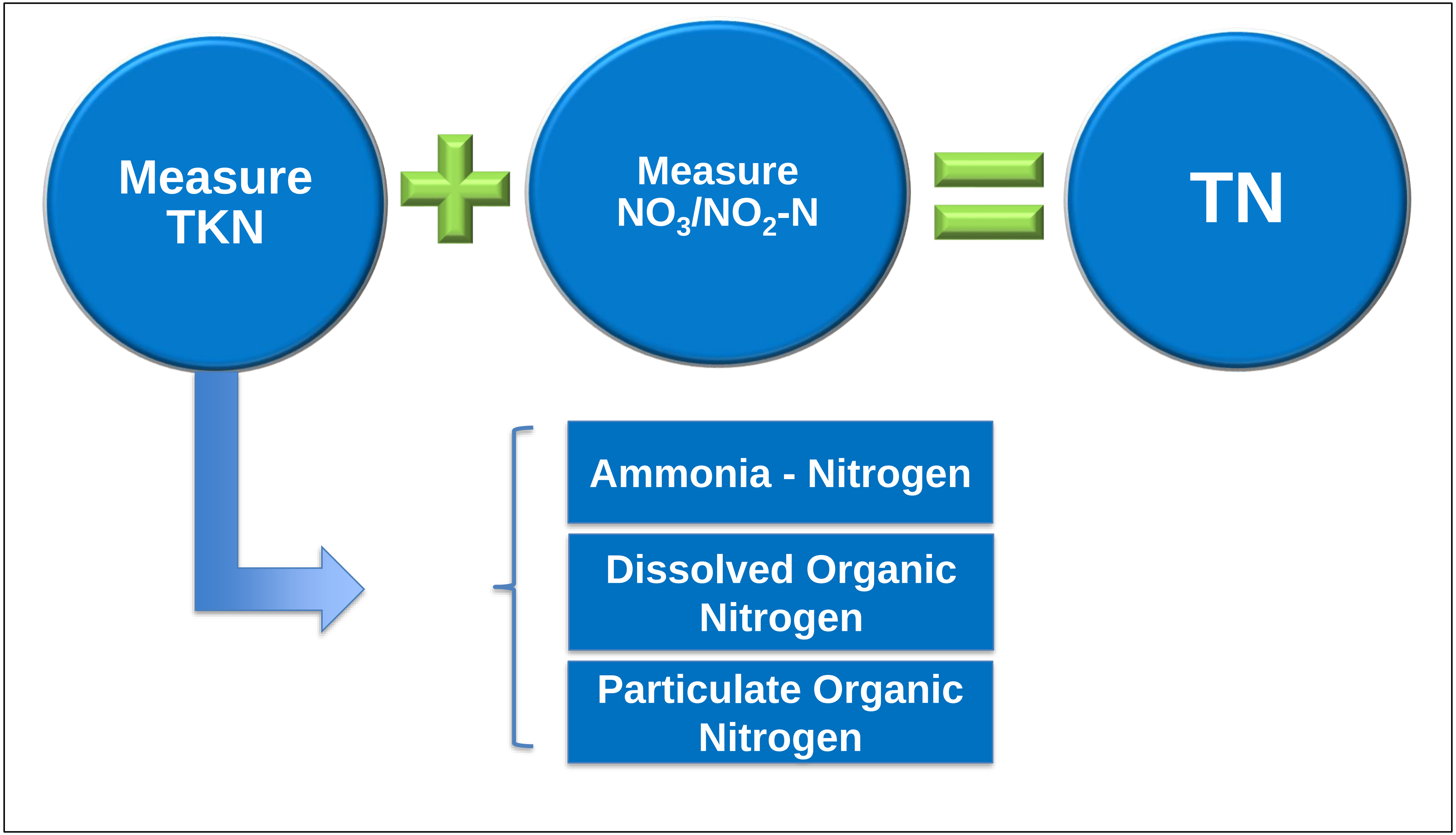


Nitrate and Nitrite ions

Ammonium ion

Organic Nitrogen Compounds

The current "EPA" definition for Total Nitrogen is TKN plus nitrate/nitrite



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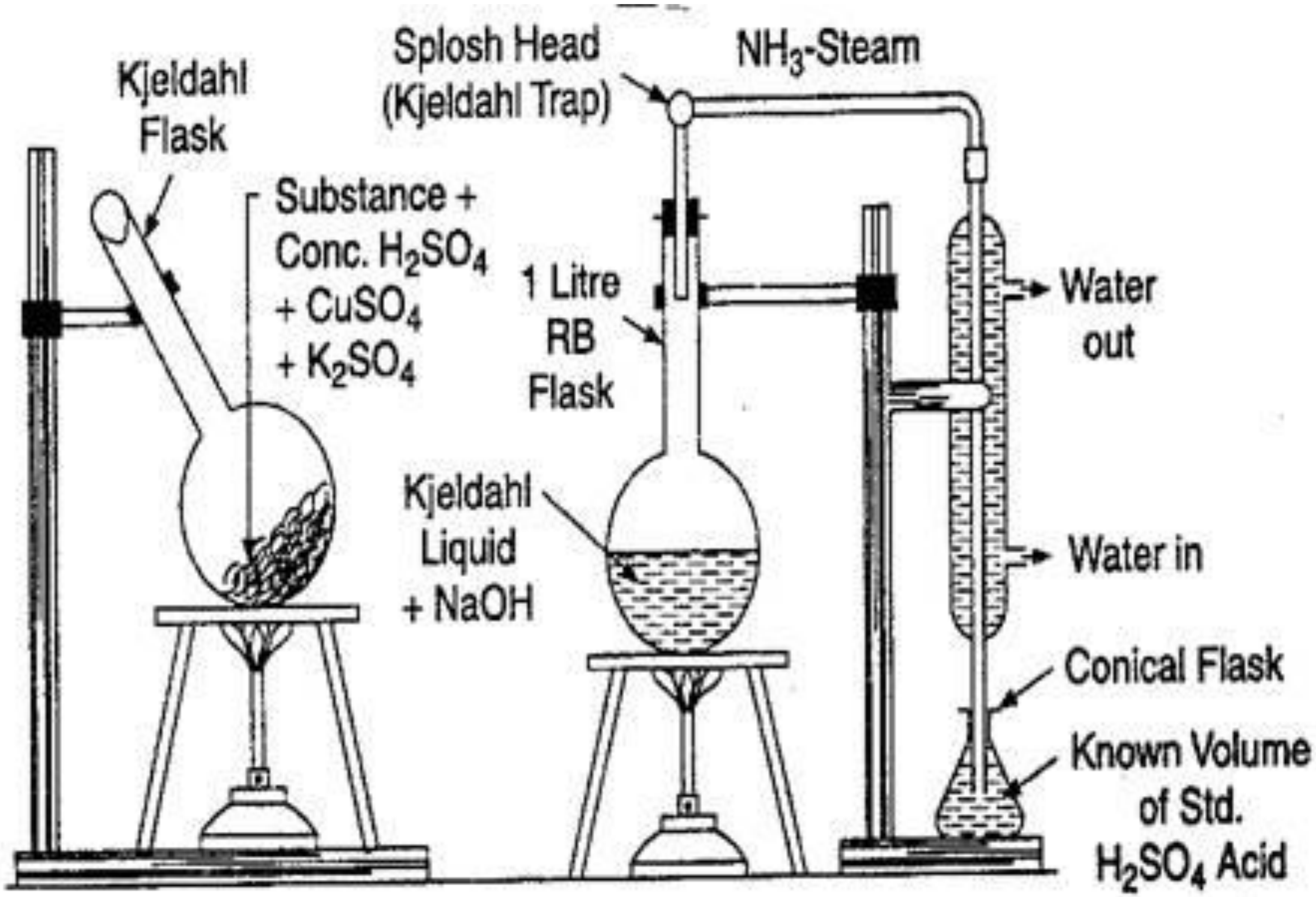
"Newer" methods measure Total Nitrogen as a single result

TN = NO_x-N + NH_3-N + Organic Nitrogen

(NH_3-N + Organic Nitrogen): Dissolved and Particulated

- Alkaline Persulfate Digestion
- High Temperature Combustion (or catalytic)

Challenges for TKN = modification of 1883 digestion/distillation



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Which TKN procedure (Part 136 methods)?

Manual Digestion + Distillation	Digestion + Direct Analysis	By Difference
SM 4500-N_{org} B or C **4500-NH_3 C, D, G, F**	**EPA 351.1 (on-line distillation/digestion)**	**S-TKN™**
ASTM D3590 A	**EPA 351.2 (block)**	
EPA 350.1	**SM 4500-N_{org} D**	
ASTM D1426	**ASTM D3590 B**	
	USGS I-4515	

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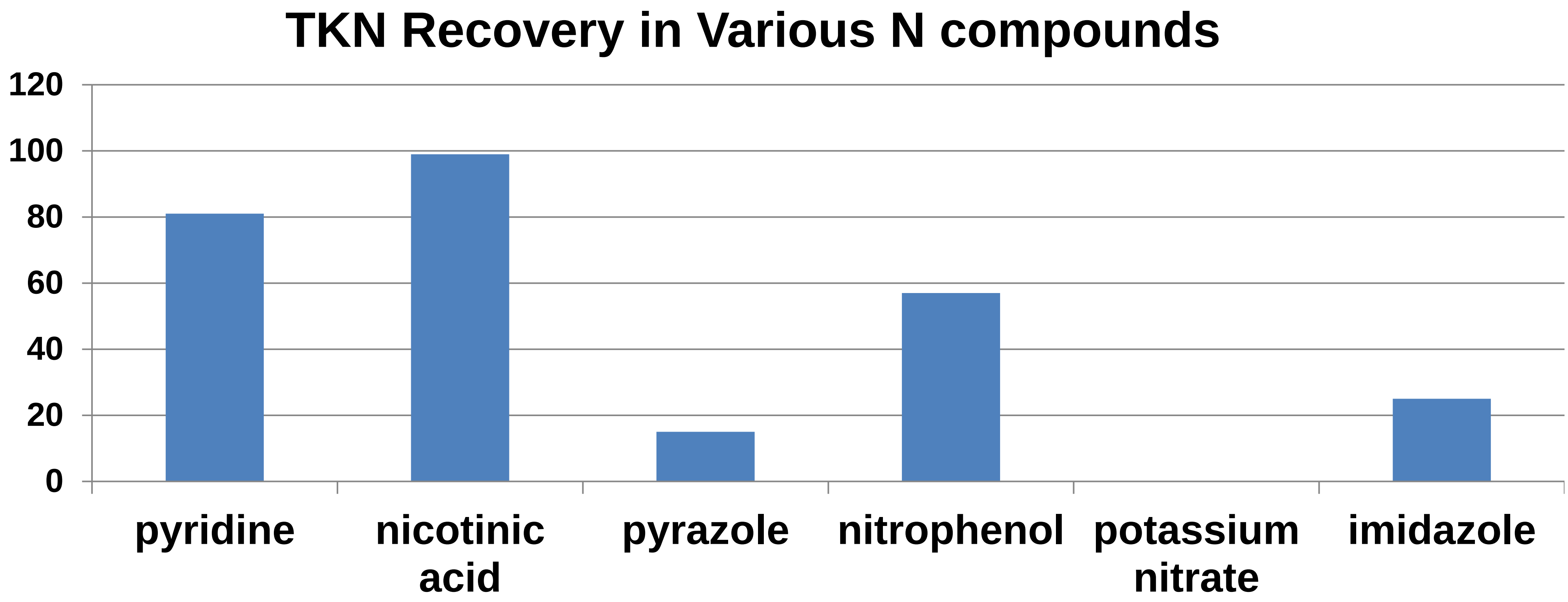
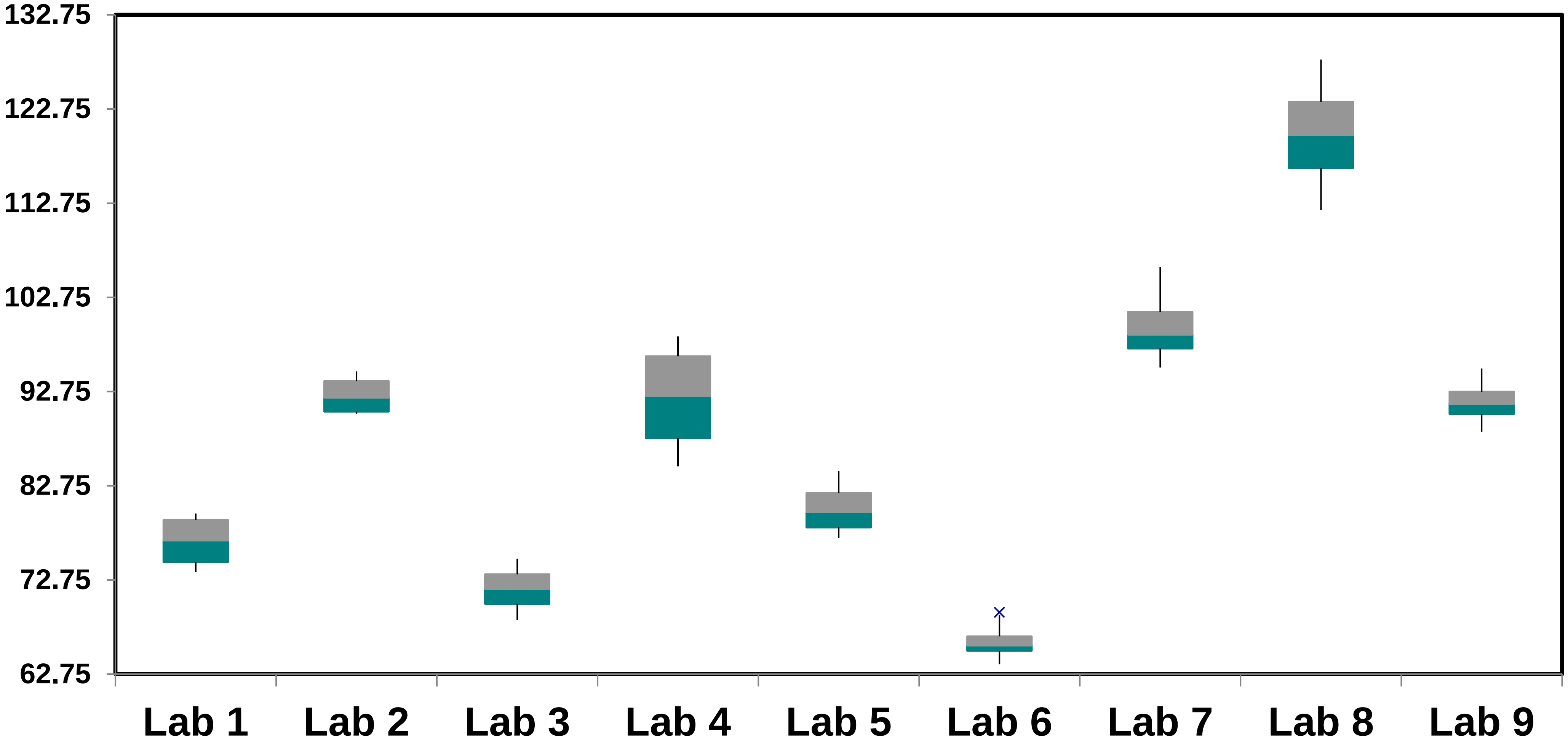
Which TKN digestion procedure (Part 136 methods)?

Sample Volume	Water Removal	Digestion
25 ml	160 °C for 1 hour	380 °C for 1.5 hour
10 ml	220 °C for 30 minutes	370 °C for 15 minutes
Up to 500 ml	Boil down to 25 – 30 ml	Heat to fumes at 375 – 380 °C then 30 minutes
5 – 50 ml	Boil 30 minutes	Heat to fumes at 375 – 380 °C then 30 minutes
25 ml	220 °C for 1 hour	380 °C for 1 hour

TKN suffers from low recovery of some organics



Results of a TKN Inter-laboratory Study (LCS data)



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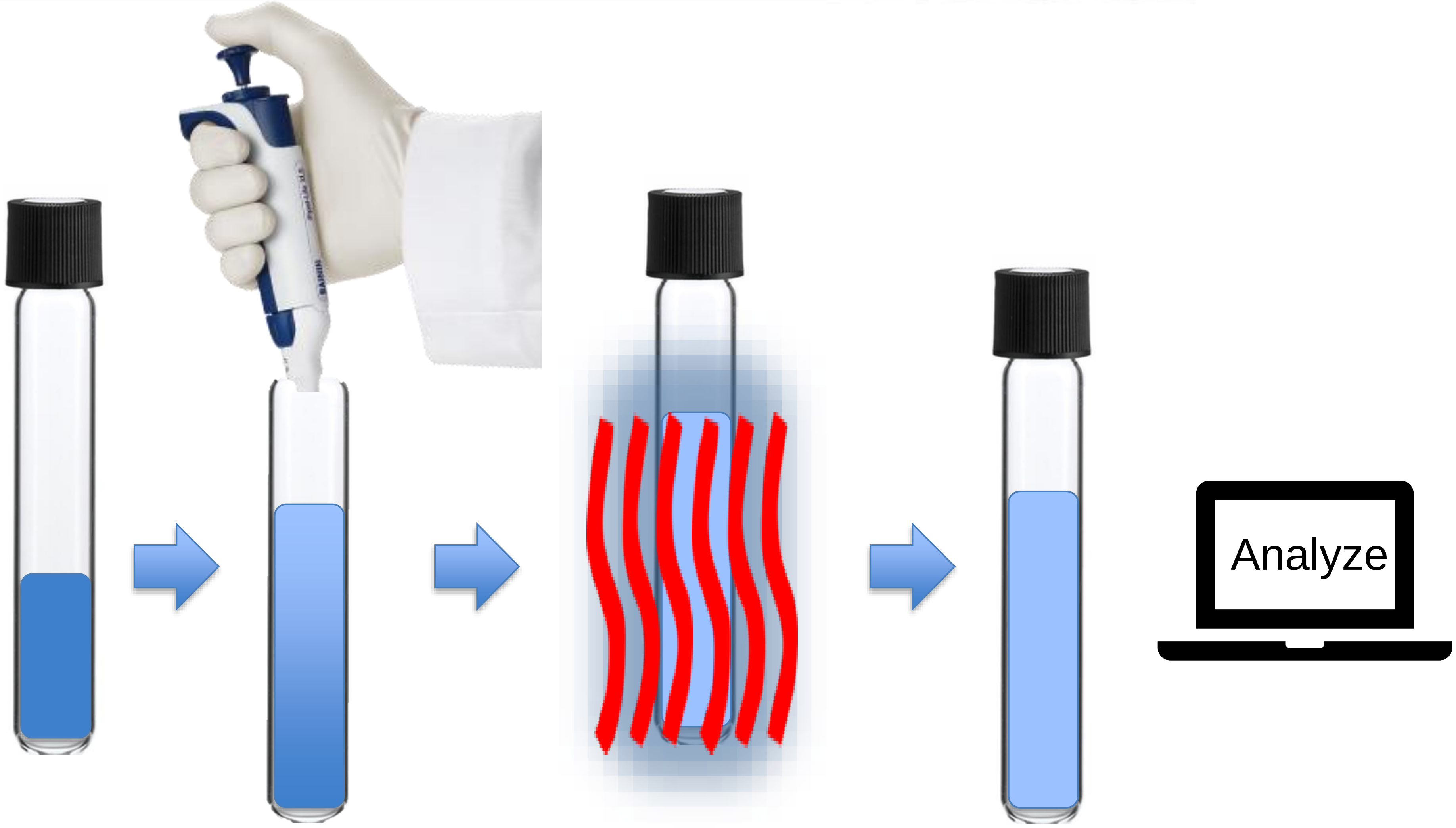
Alkaline Persulfate Digestion TN Methods



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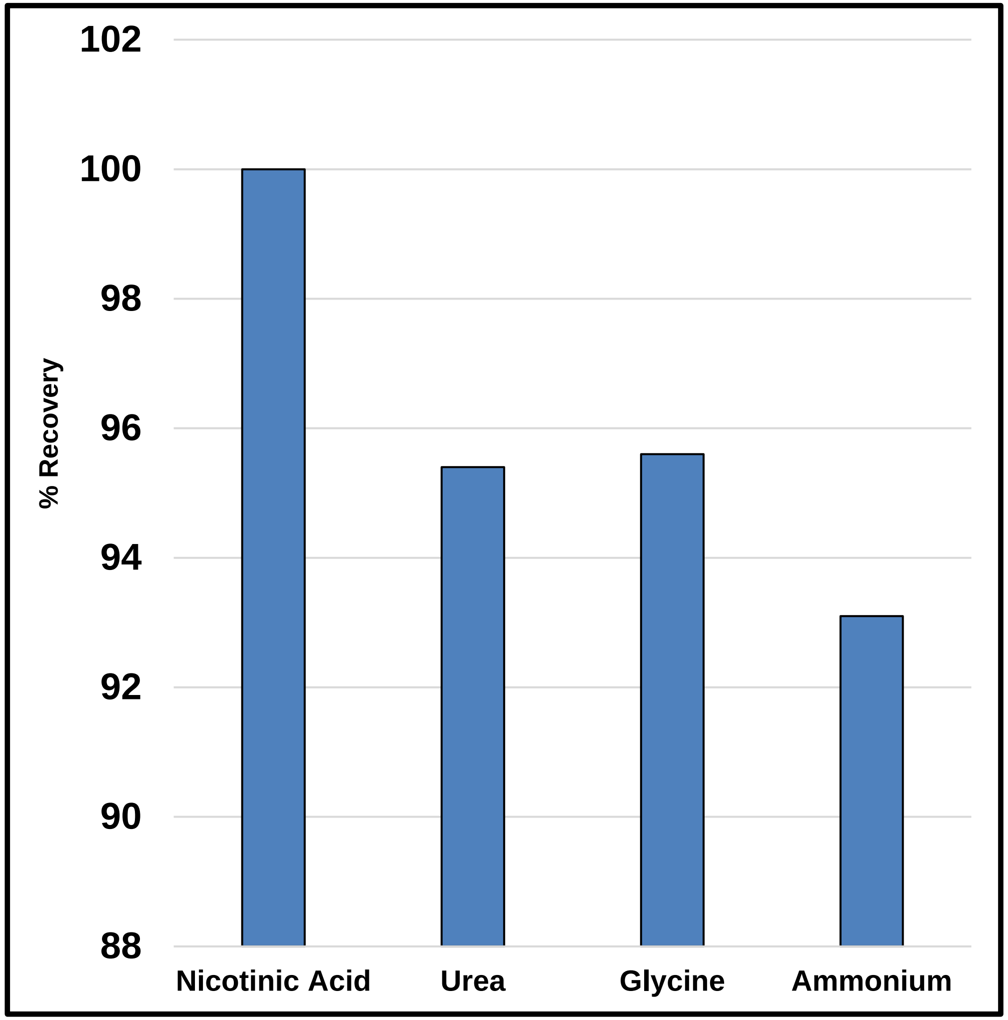
ASTM D8003 = TN (and TP) by 120 °C alkaline persulfate digestion and ion chromatography

- Digest on your COD Block to Nitrate
- Only one hour digestion
- Safer reagents – less hazardous
- Nitrate (TN and NO_3-N) is measured by Ion Chromatography
- Calculate TKN by difference (TN-NO_3-N)



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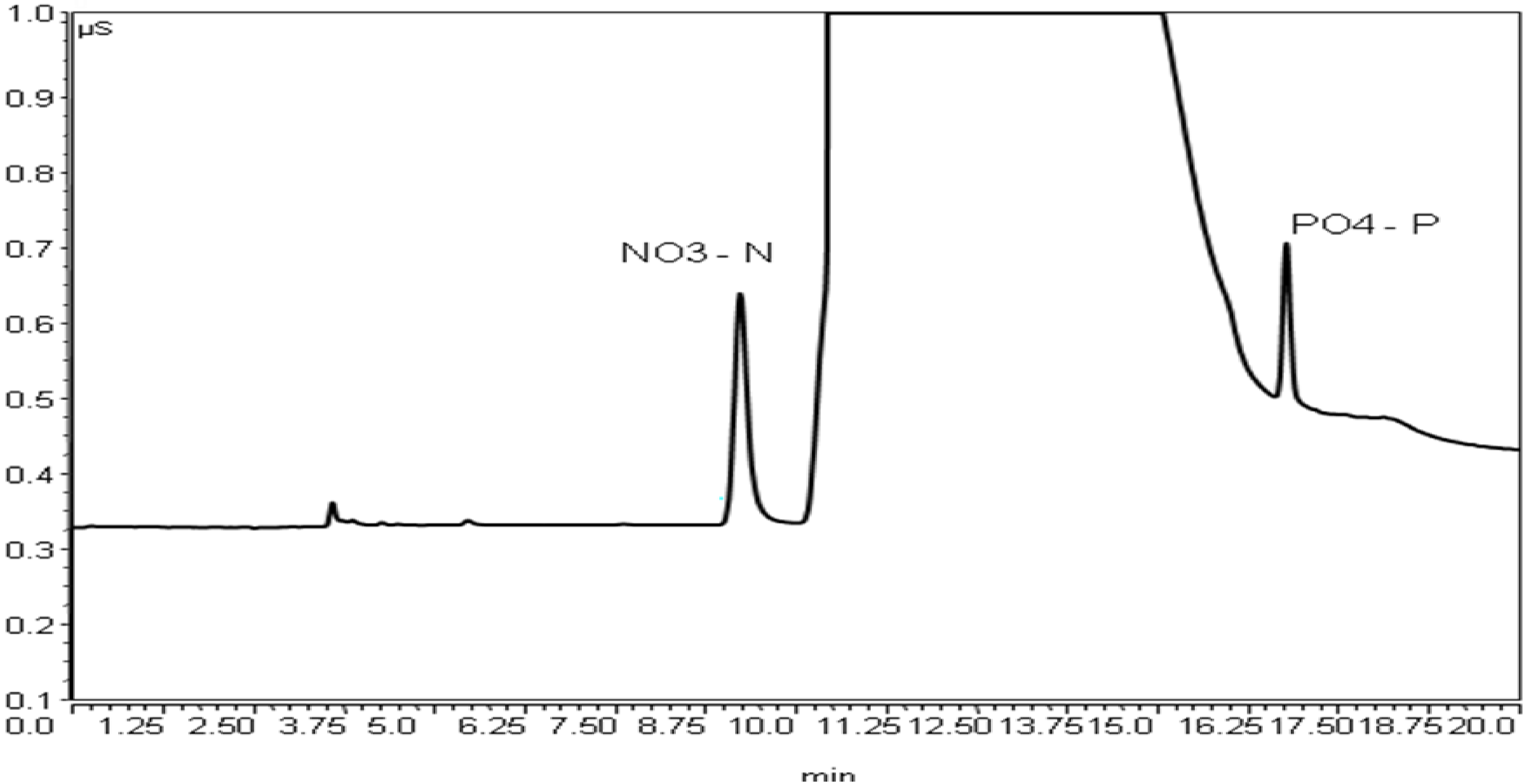
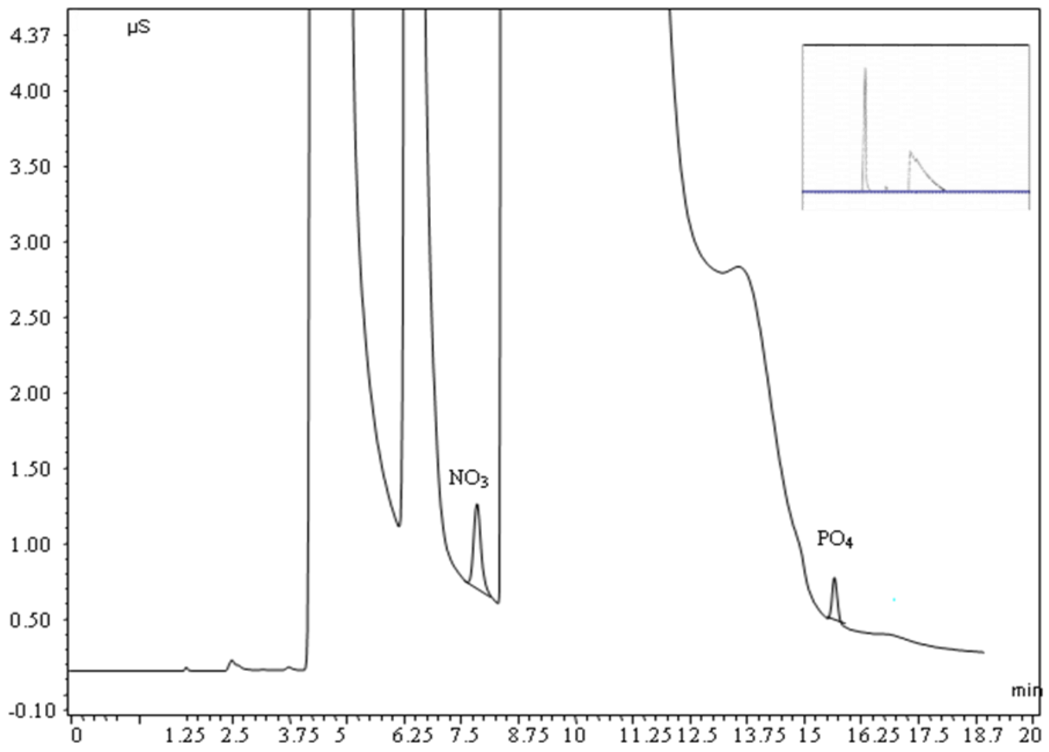
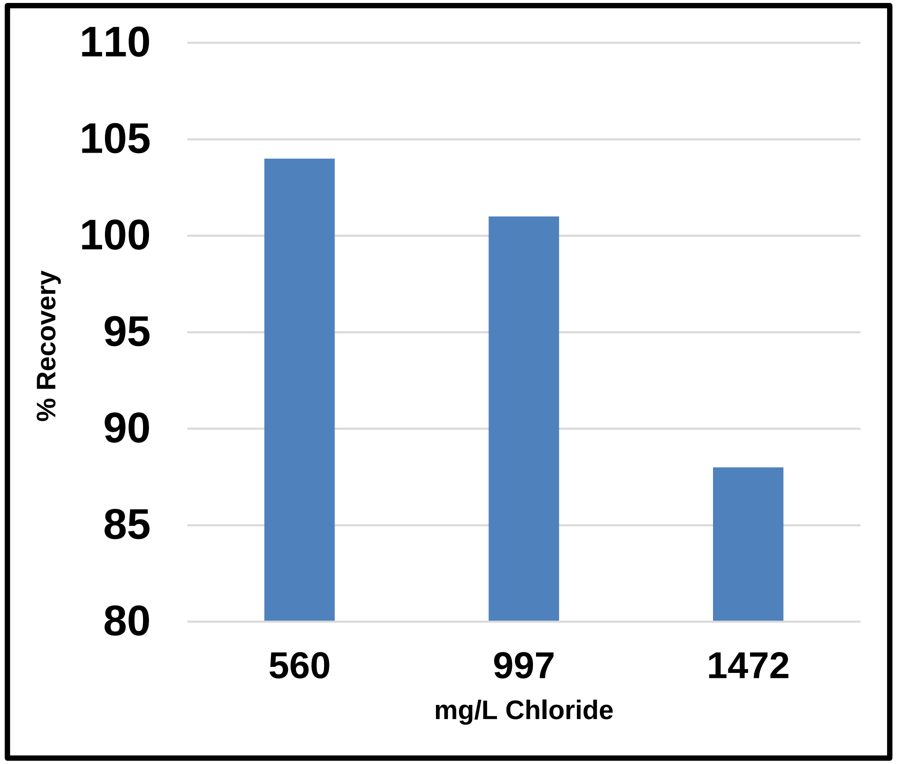
The method is capable of measuring analytes in the high sulfate matrix



Chromatogram and recovery with chloride present





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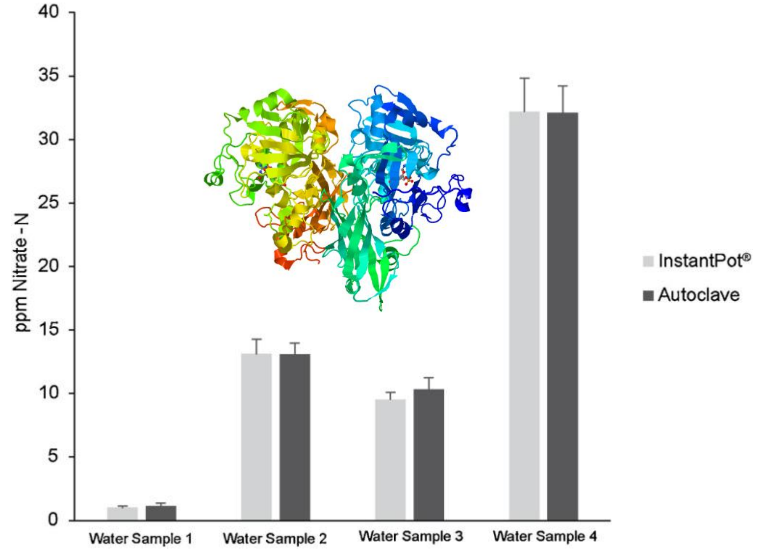
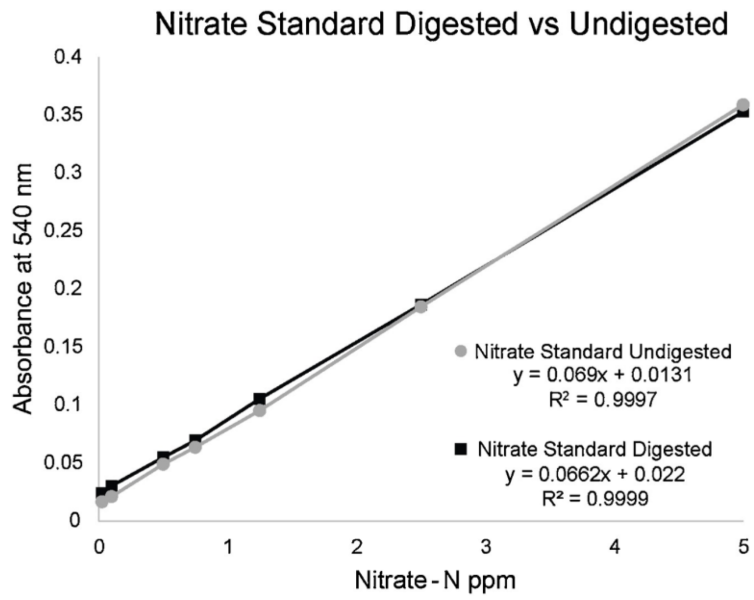
SM 4500-N C → TN (and TP) by 105°C alkaline persulfate digestion and colorimetry

- Digest on your COD Block, pressure cooker or autoclave (121 °C) to Nitrate
- One hour digestion
- Safe reagents
- Nitrate (TN) is measured by reductase (*pictured*) or Cd Reduction

- MDL ~ 0.02 mg/L

www.nitrate.com

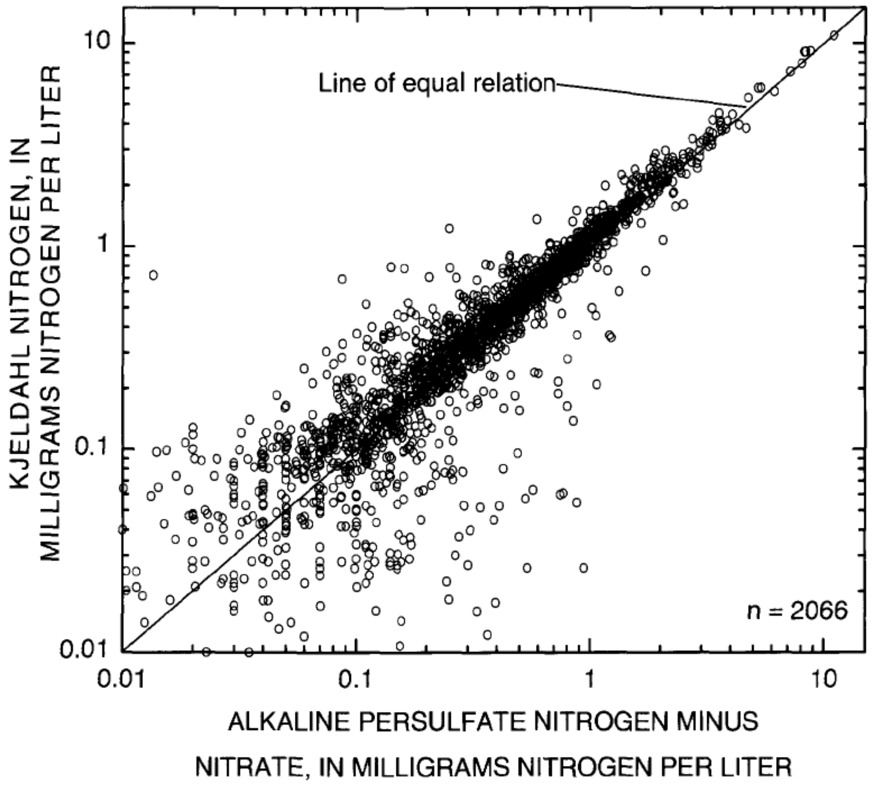




USGS I 4650-03 TN (and TP) by 121°C alkaline persulfate digestion and semi-automated colorimetry

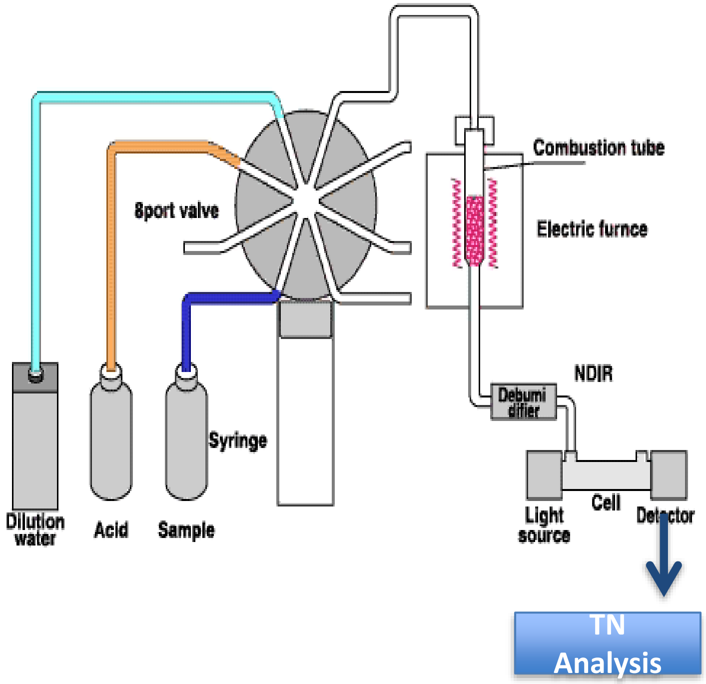
- Digest in autoclave (121 °C) · Nitrate
- One hour digestion
- Safe reagents
- Nitrate (TN) is measured by Cd Reduction

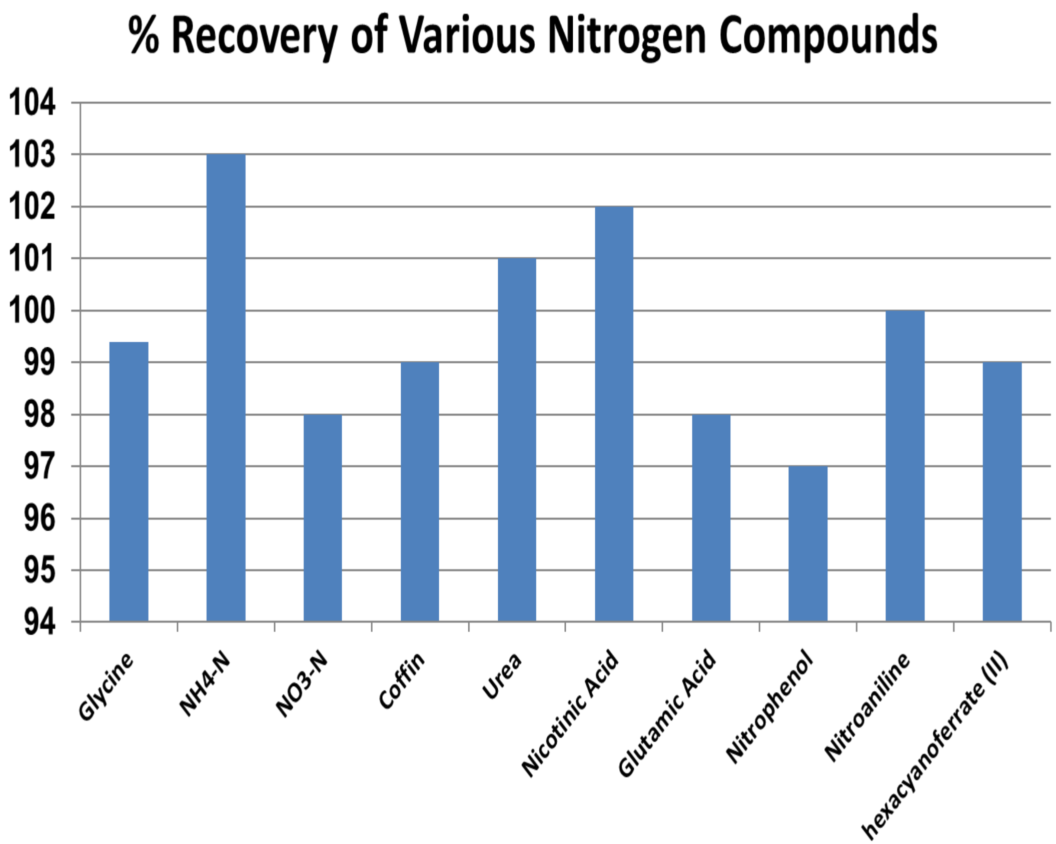
- MDL ~ 0.05 mg/L



USGS Water-Resources Investigations Report 03-4174

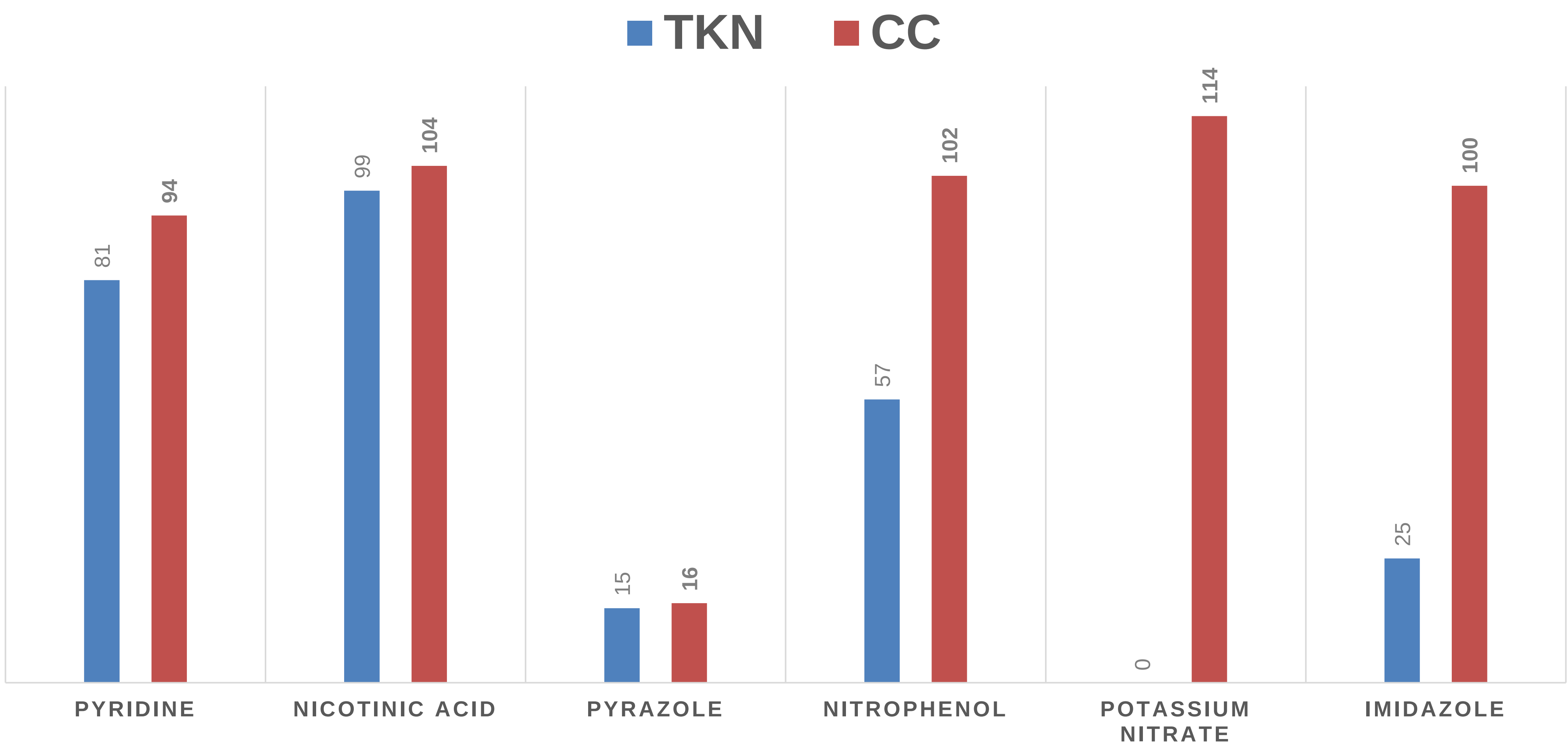
D8083 and new SM TN methods Schematic of a TOC + TN Analyzer



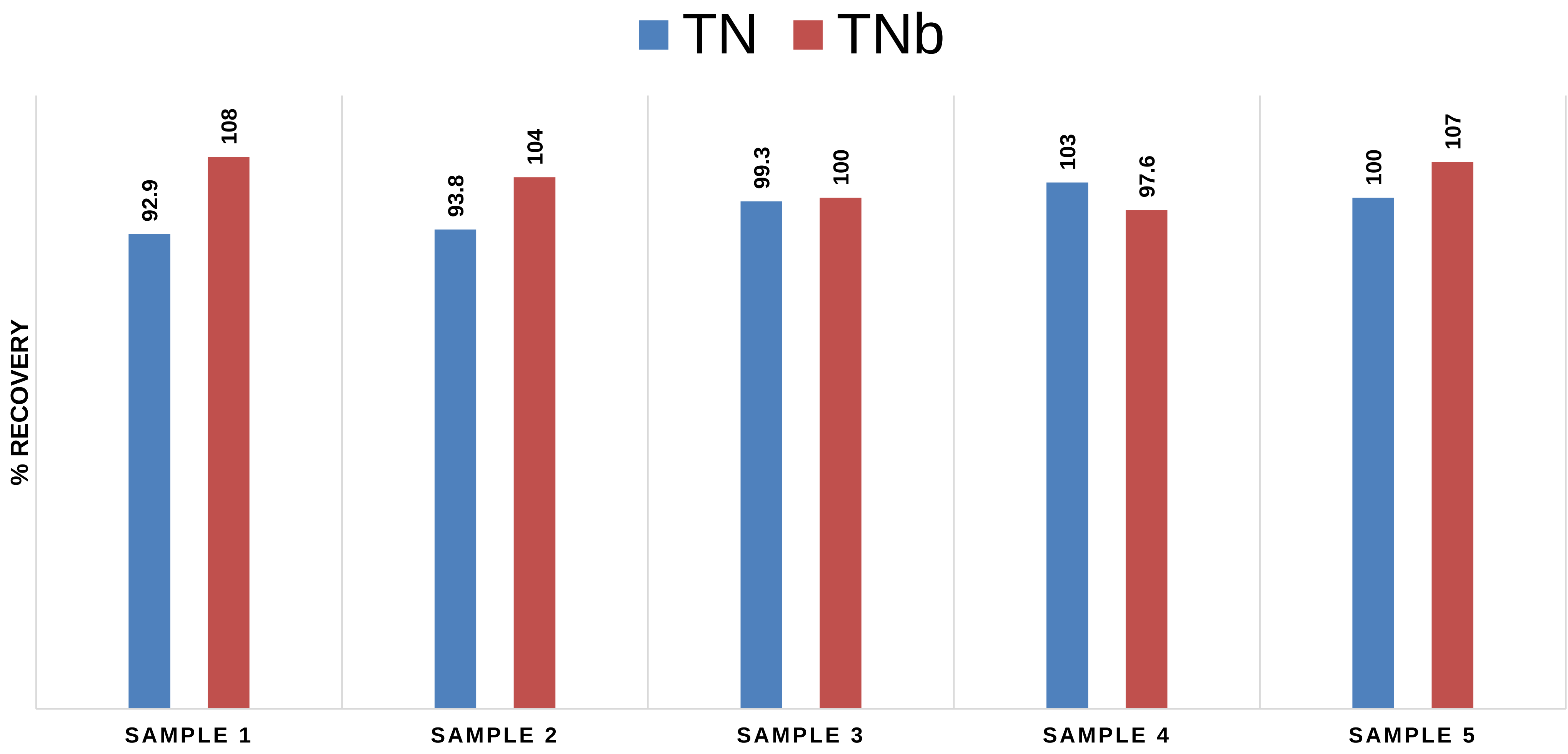


Decomposition : 720℃ with Pt catalyst

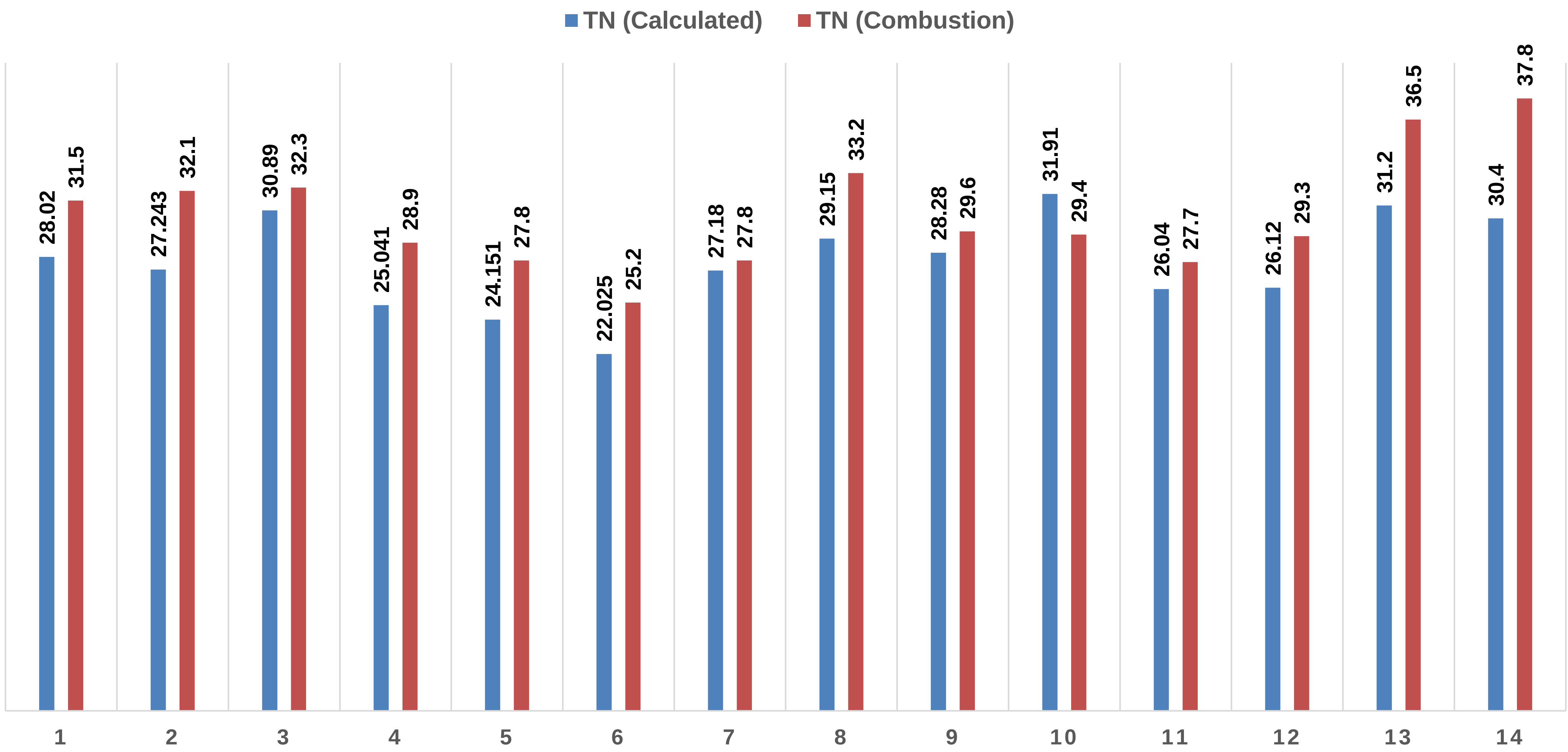
TKN and Catalytic Combustion Recovery of Various Compounds



Catalytic Combustion (TNb) comparison with persulfate

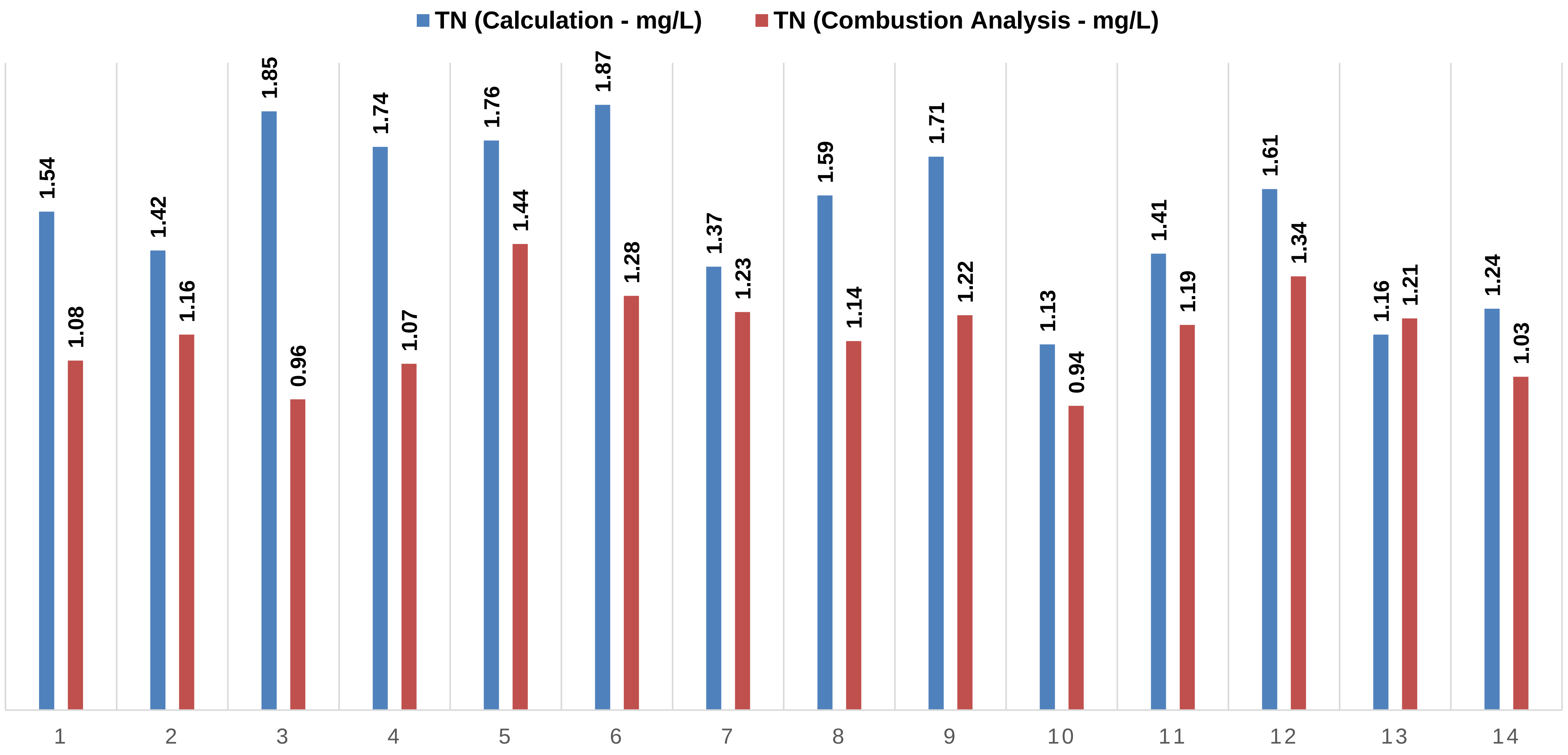


Comparison of Calculated TN with combustion TN



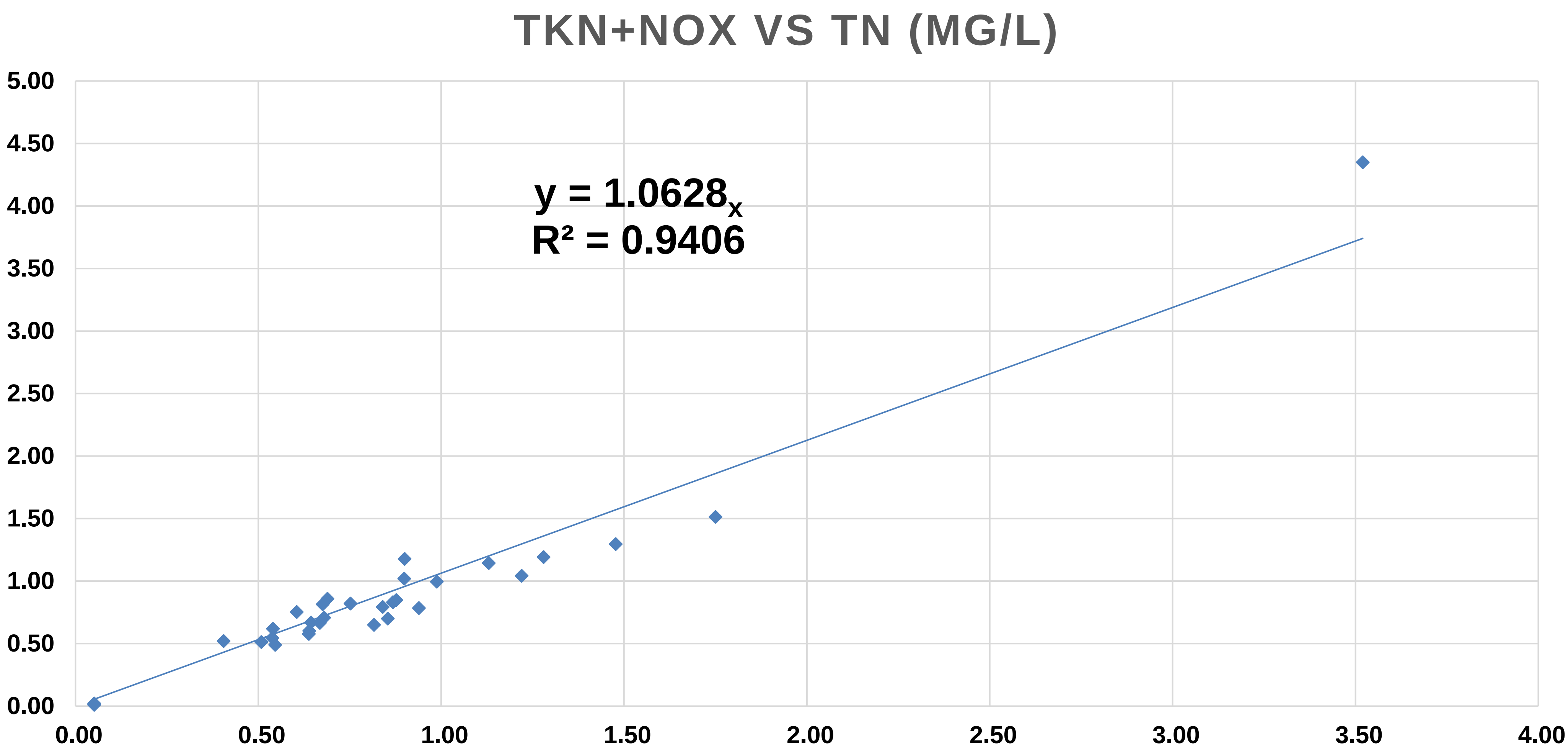
Combustion trends higher

Comparison of Calculated TN with Combustion TN



Combustion trends lower

Comparison of Calculated TN and Combustion TN



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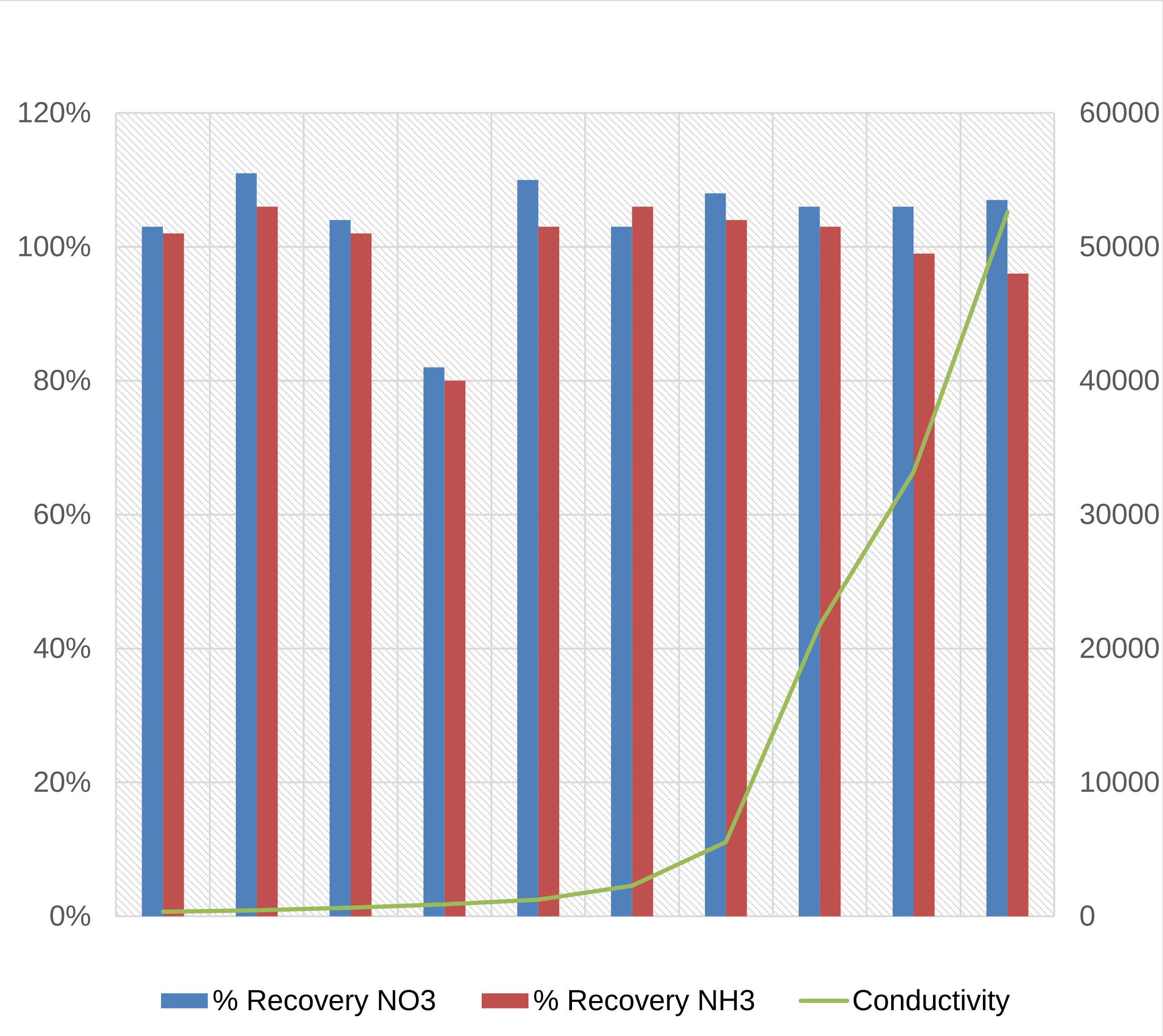
Study data for SM 4500 –N E total Nitrogen Method (combustion)

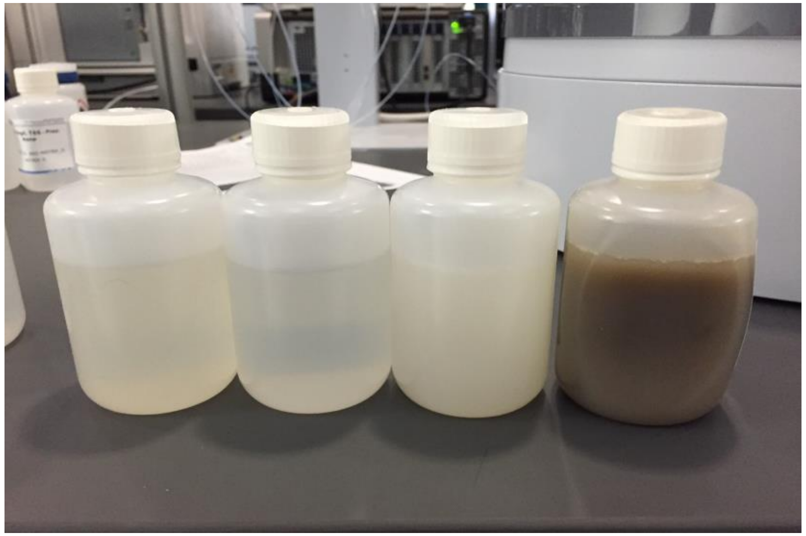


Lab ID	Level of N (mg/L)	Experimental Average of N in mg/L (SD)	Deviations from Grand Average
1	4.61	4.55 (0.06)	0.52
	4.46		
	4.58		
2	4.01	4.00 (0.02)	-0.03
	4.02		
	3.98		
3	3.98	3.96 (0.02)	-0.07
	3.97		
	3.94		
4	3.64	3.67 (0.03)	-0.36
	3.67		
	3.71		
5	4.04	4.00 (0.03)	-0.03
	3.99		
	3.97		
6	4.05	4.02 (0.03)	-0.01

ASTM D8083-16 Inter-Lab Study data

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%

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



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Pros and Cons of the TKN procedure

- Uses hazardous reagents
- Must run NO_3 + NO_2 separately, then add to TKN to get TN
- Positive bias at low concentrations (< 1 mg/L)

Digestion – very vigorous, time tested

Digestion of particulates is no problem

Digestion vessels enable larger volume samples

- Macro in flask
- Micro in block

Can distill or separate interferences

No “study” of method, but a lot of historical data

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Pros and Cons of the TN Persulfate procedure

- Safe reagents, small quantity
- Standardized digestion
- Sensitive detection
- Extensively studied by USGS
- Any nitrate method

Particulates cause low results

High organic carbon (> 150 mg/L) causes low results

May need to filter after digestion

Different ways to determine NO_3-N?

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Pros and Cons of Combustion procedures

- Safe reagent, added by instrument
- All samples treated equally (automated)
- Efficient digestion of refractory compounds
- ASTM and SM methods and ILS

Particulates may cause low results

Results may vary by combustion tube packing

Dedicated instrumentation

Why should we have a new TN parameter and these new methods?

- Better data (one result)
- Faster results
- Safer for lab personnel
- No addition or subtraction (of method results)
- TKN + NO_x result may not be reliable (bias high or low?)

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Any Questions?

Contact Information

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