

Why we need new Total Nitrogen parameter and methods for CWA reporting



William Lipps

Chief Science Officer, Eurofins Eaton Analytical

August 2018

Full Service Laboratories



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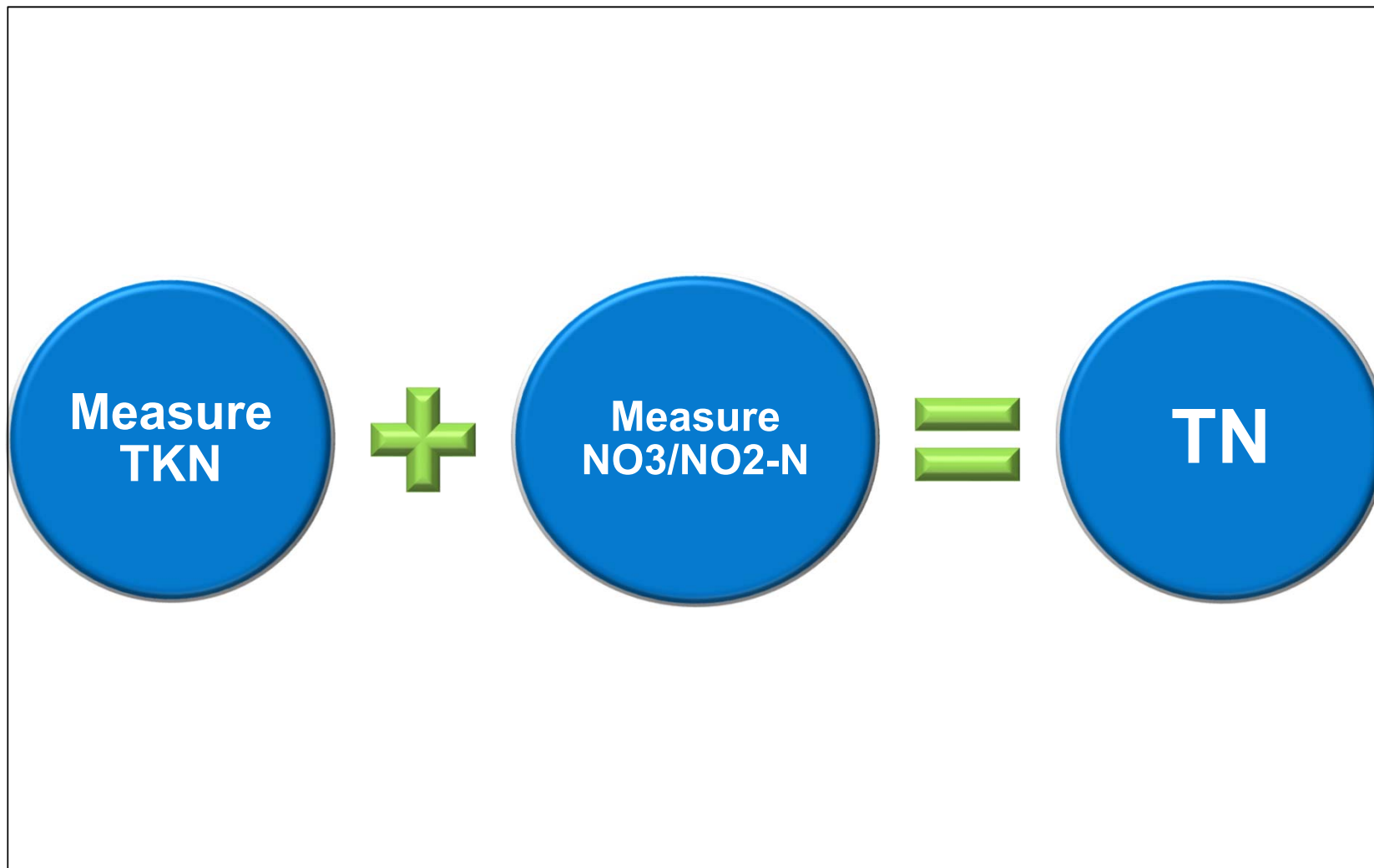


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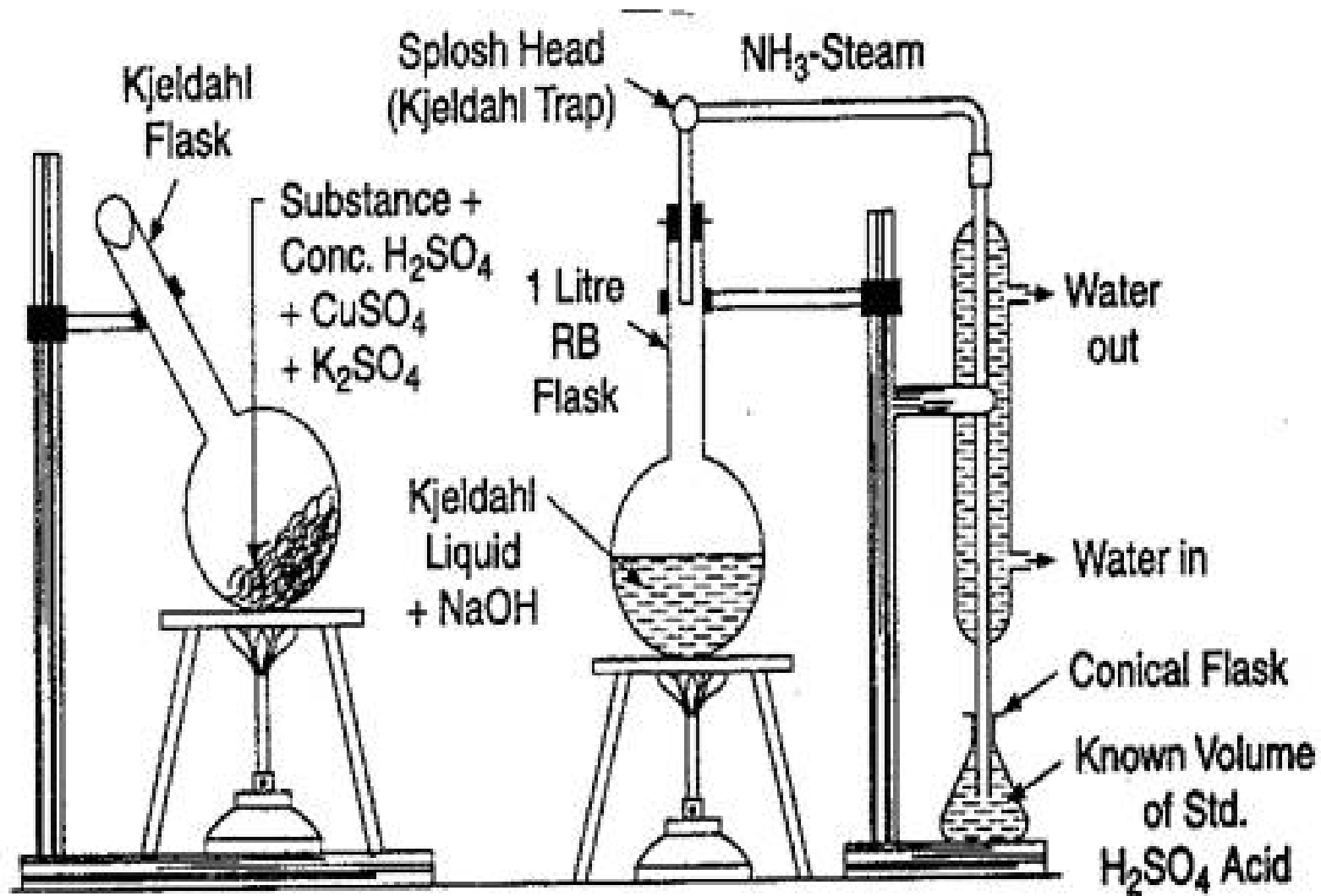


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The current “EPA” definition for Total Nitrogen is TKN plus nitrate/nitrite



TKN = modification of 1883 digestion/distillation



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	

Which TKN digestion procedure (Part 136 methods)?

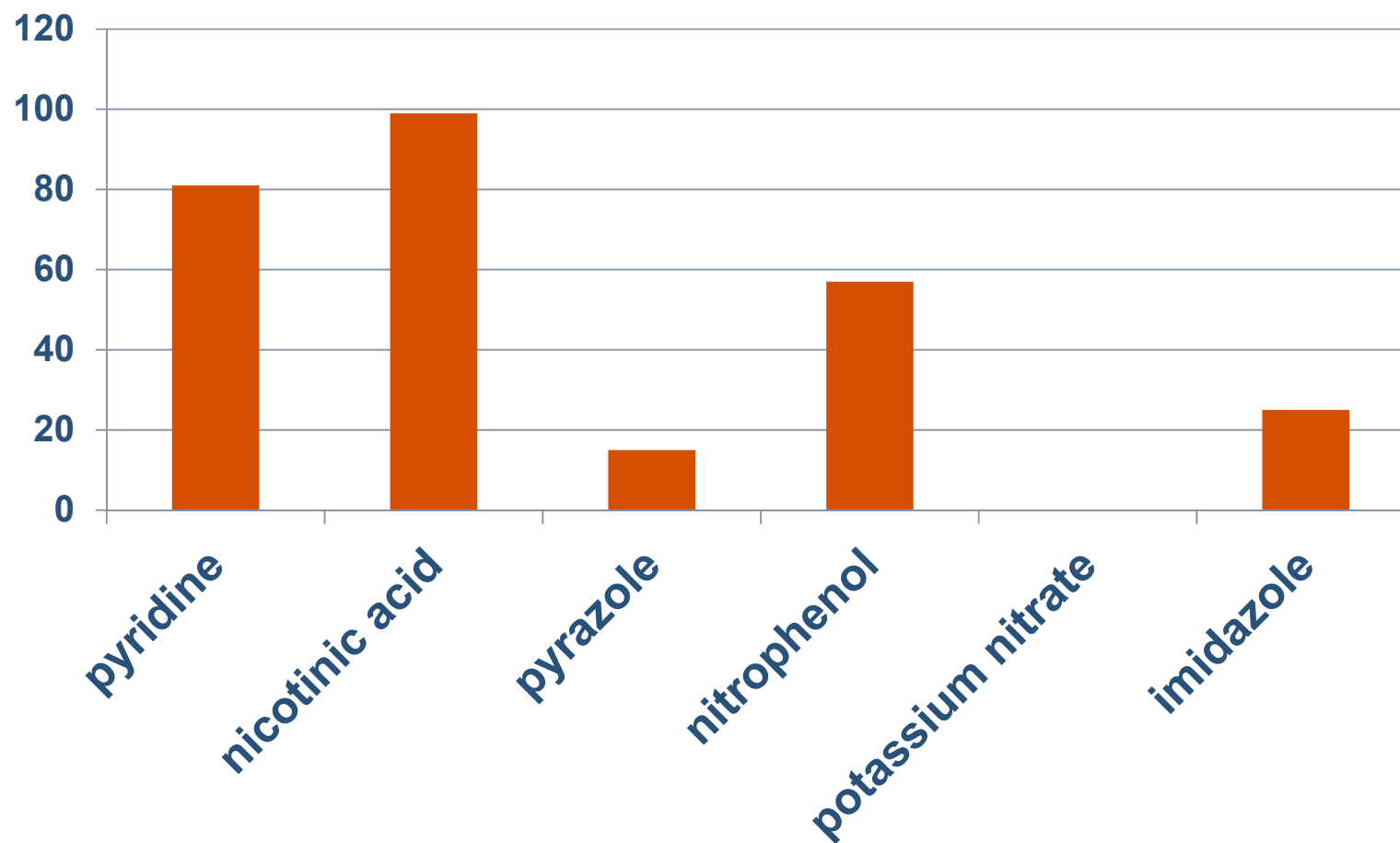


Sample Volume	Water Removal	Digestion
25 ml	160 °C for 1 hour	380 °C for 1.5 hour
10 ml	220 °C for 30 minutes	370 °C for 15 minutes
Up to 500 ml	Boil down to 25 – 30 ml	Heat to fumes at 375 – 380 °C then 30 minutes
5 – 50 ml	Boil 30 minutes	Heat to fumes at 375 – 380 °C then 30 minutes
25 ml	220 °C for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

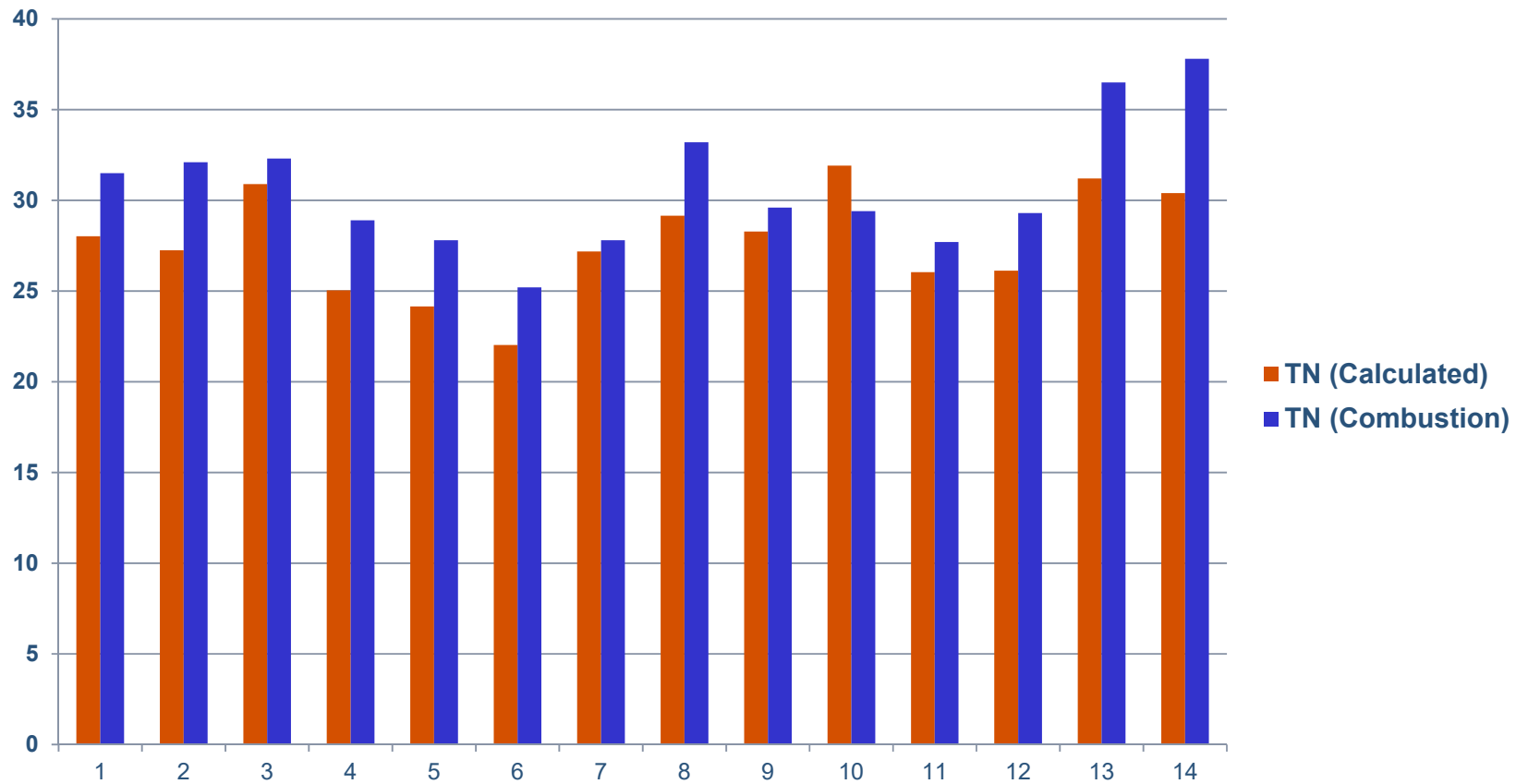
TKN suffers from low recovery of some organics



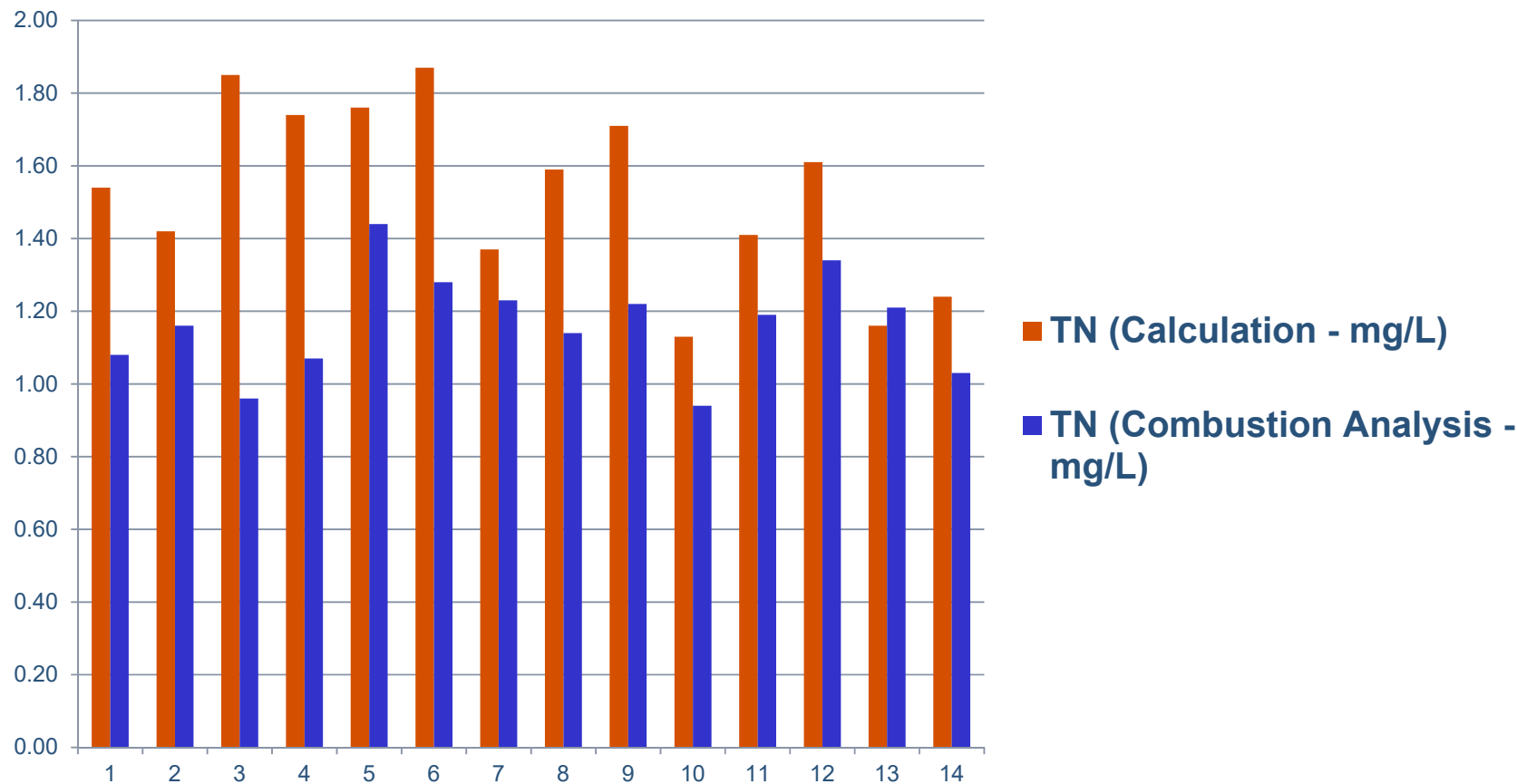
TKN Recovery in Various N compounds



EPA Calculated TN can be lower than combustion TN



EPA Calculated TN can be higher than combustion TN



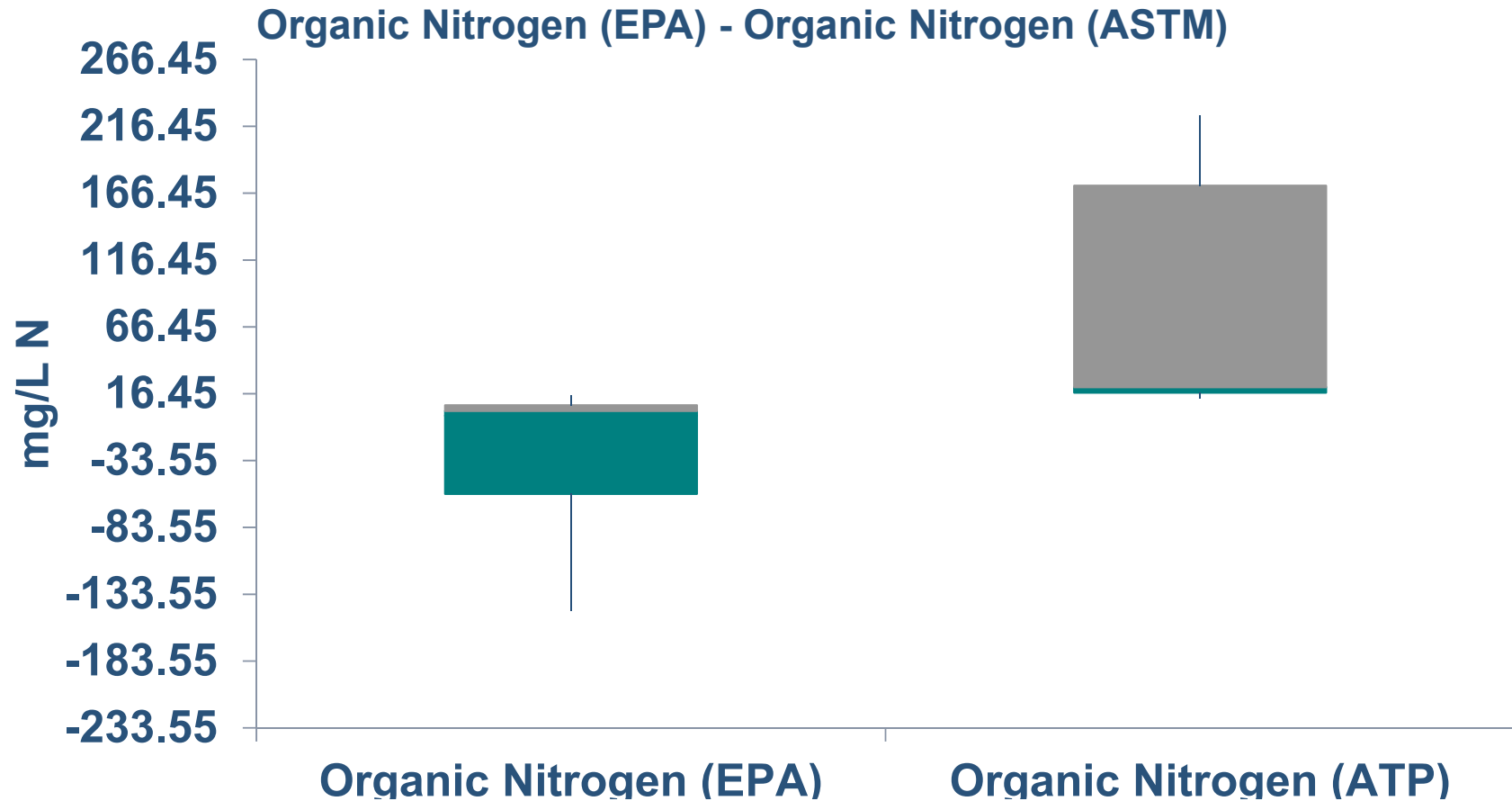
Sometimes EPA Calculated TN can be lower than measured $\text{NH}_3\text{-N}$



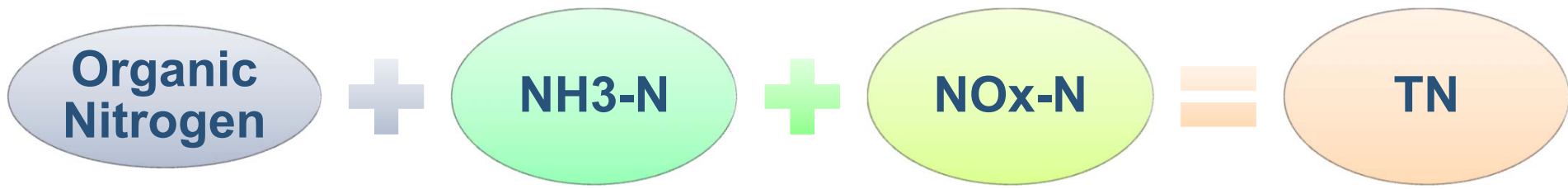
TKN	NO _x -N	TN (EPA-calc)	NH ₃ -N	TN (D8083)
790	0.077	790	910	1083
776	0.211	776	922	1093

TKN < NH₃-N ?

A low TKN results in low bias for Organic Nitrogen calculations (negative?)



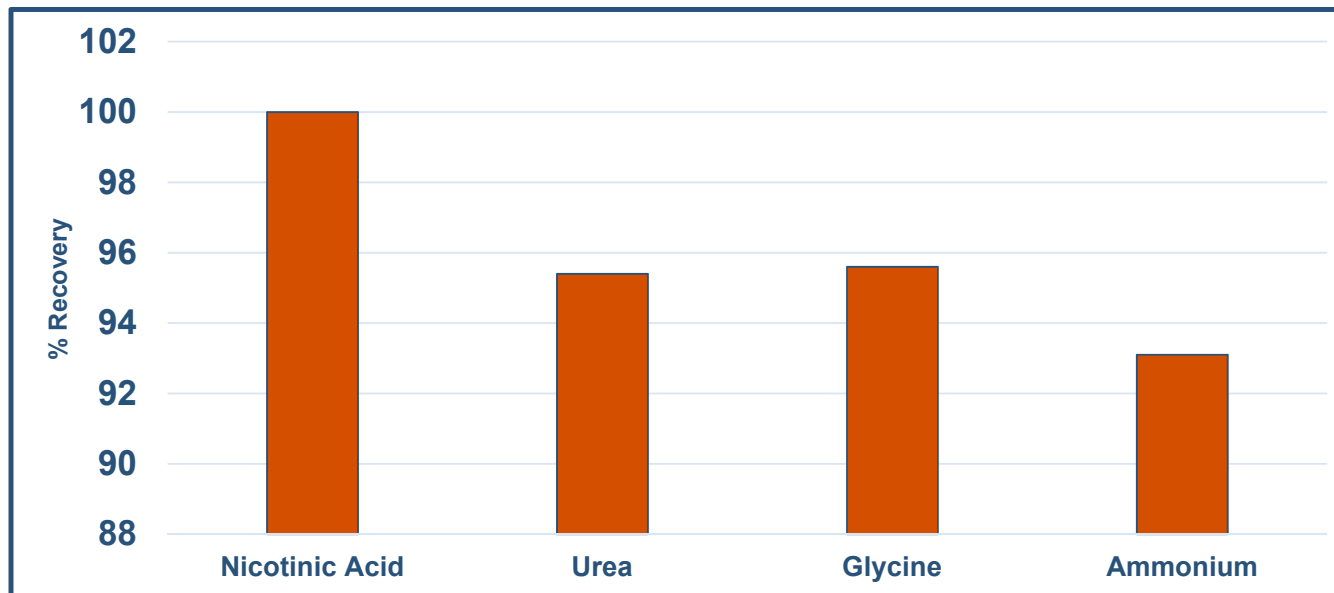
New methods are needed that measure Total Nitrogen as a single result, and not TKN



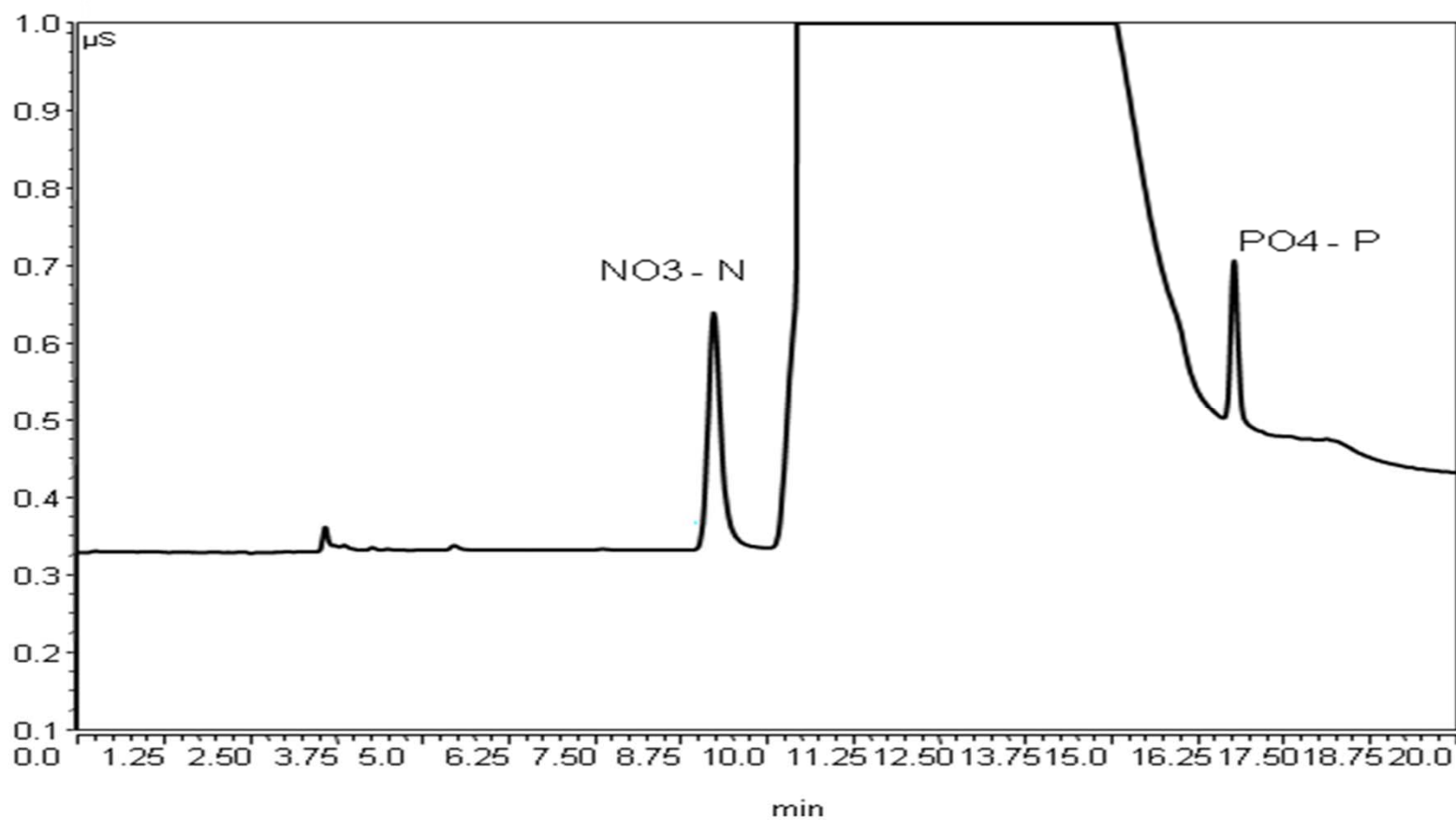
ASTM D8003 = TN (and TP) by 120 °C alkaline persulfate digestion and ion chromatography



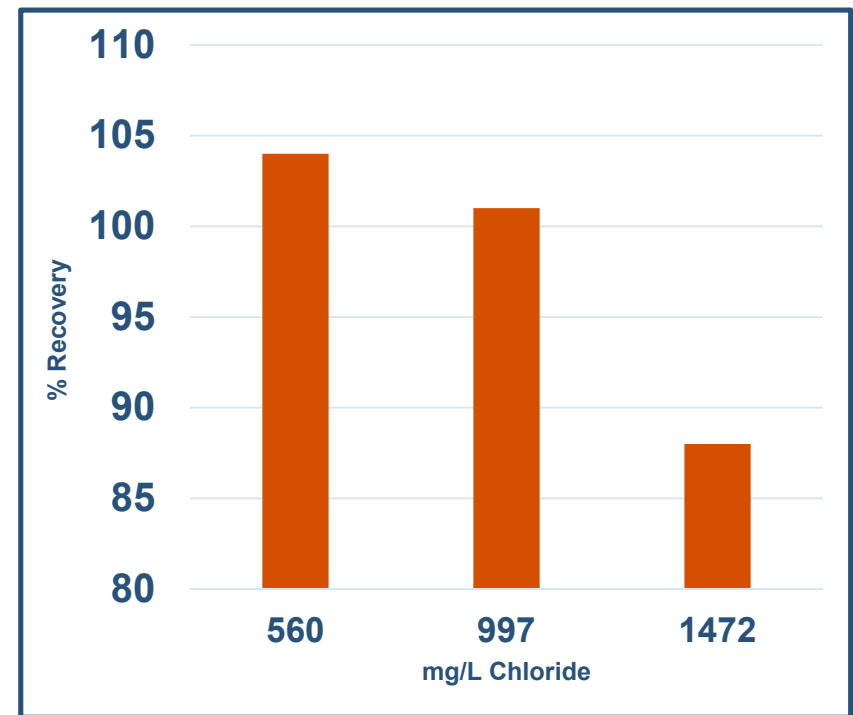
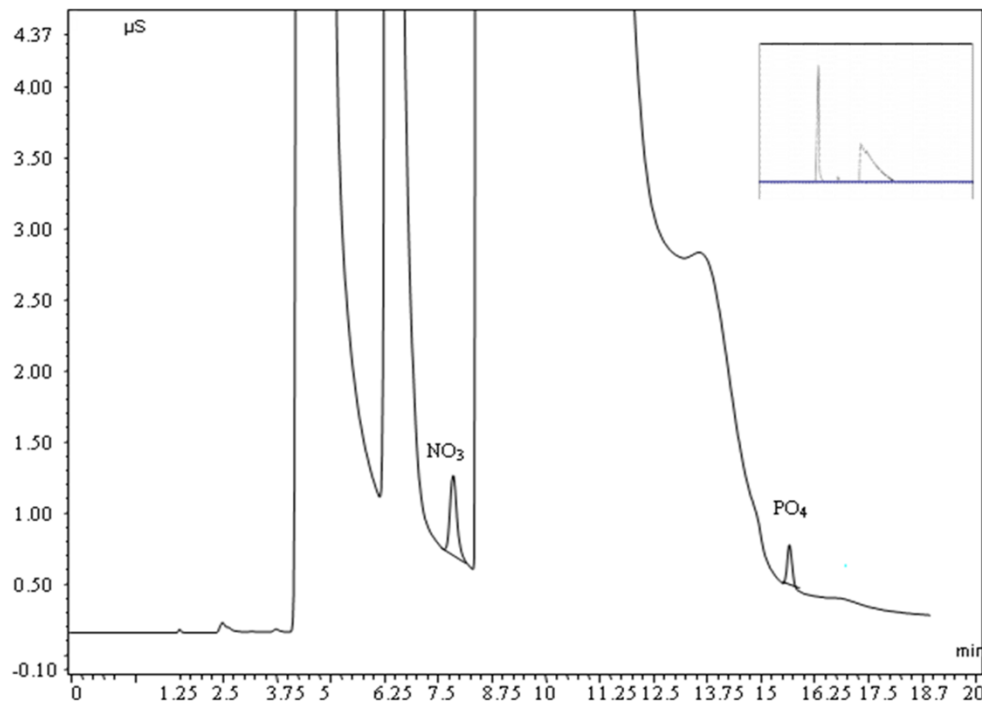
- Digest on your COD Block to Nitrate
- Only one hour digestion
- Safer reagents – less hazardous
- Nitrate (TN and $\text{NO}_3\text{-N}$) is measured by Ion Chromatography
- Calculate TKN by difference ($\text{TN}-\text{NO}_3\text{-N}$)



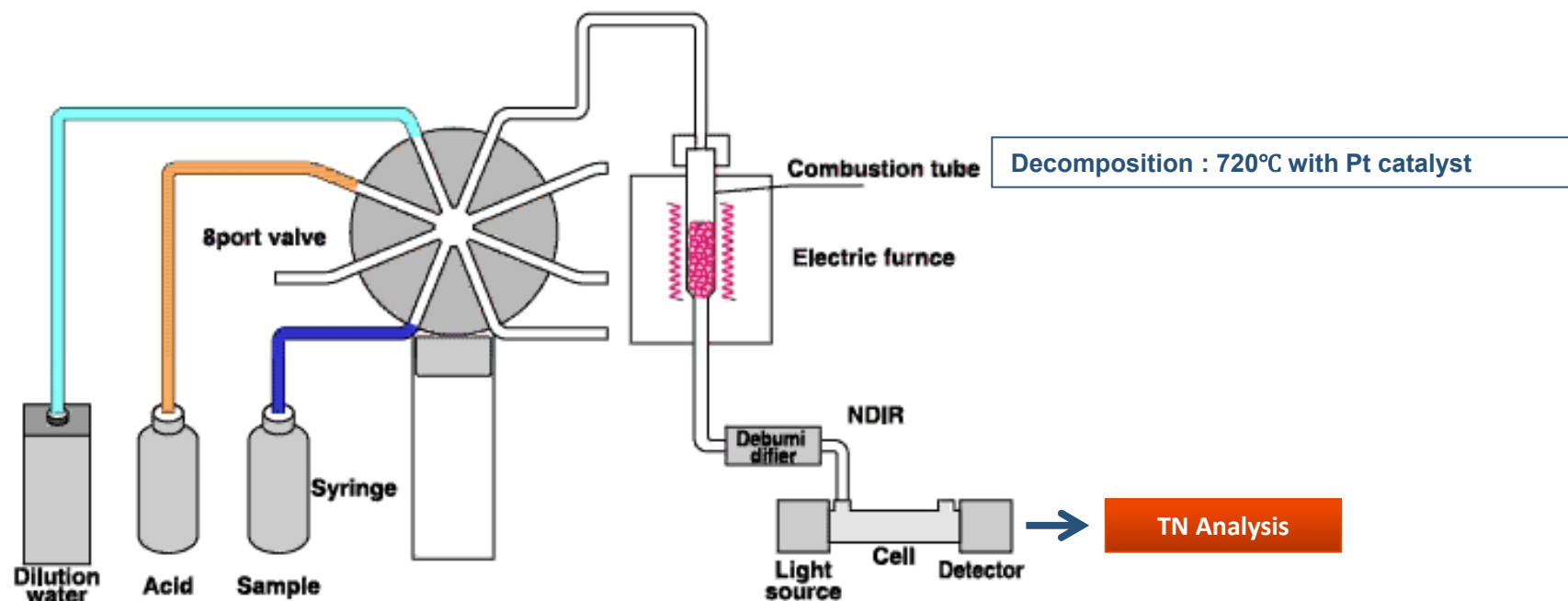
The method is capable of measuring analytes in the high sulfate matrix



Chromatogram and recovery with chloride present



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

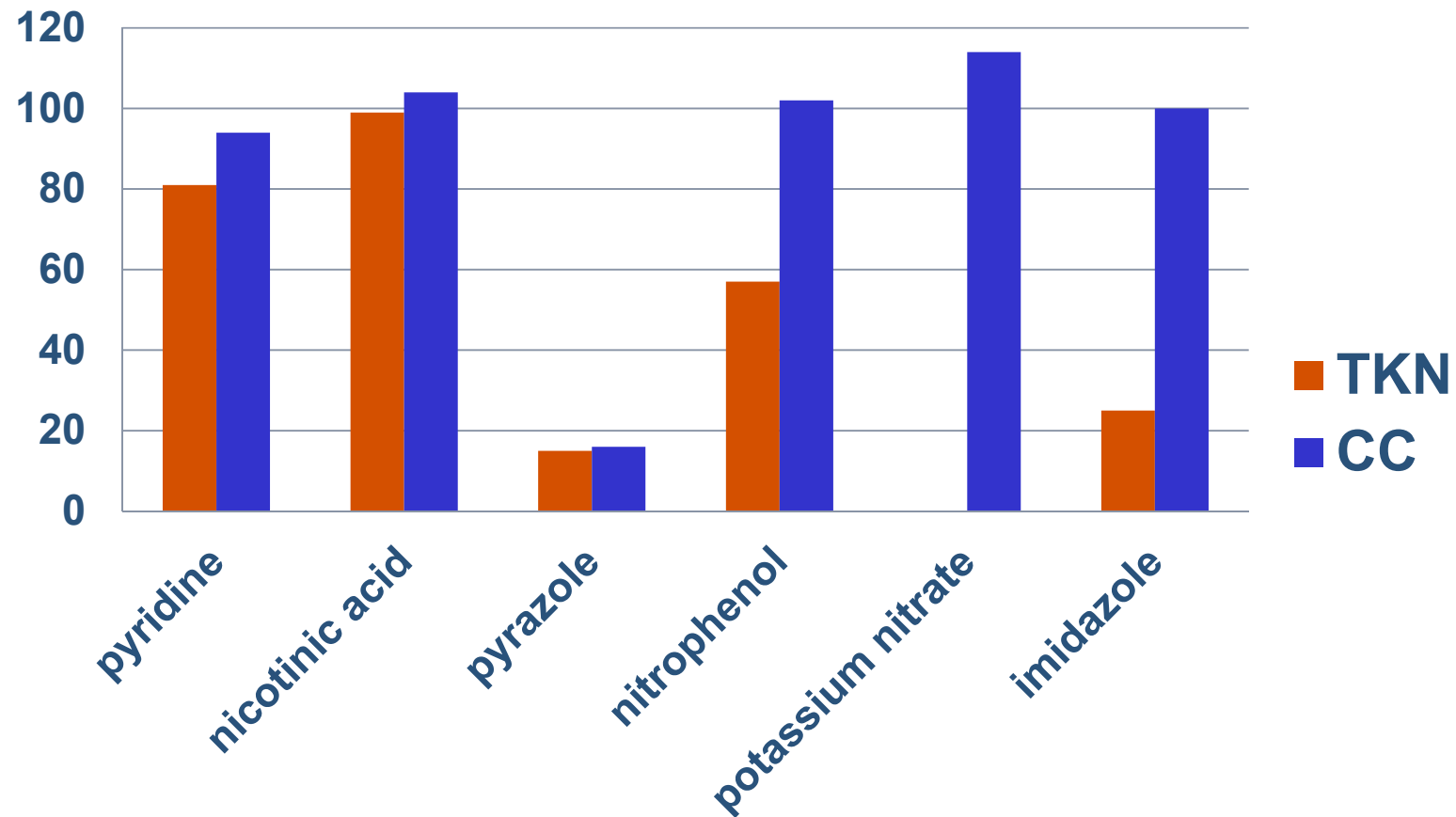


Formation of NO_2^* , $\rightarrow \text{NO}_2$, Photon Emission

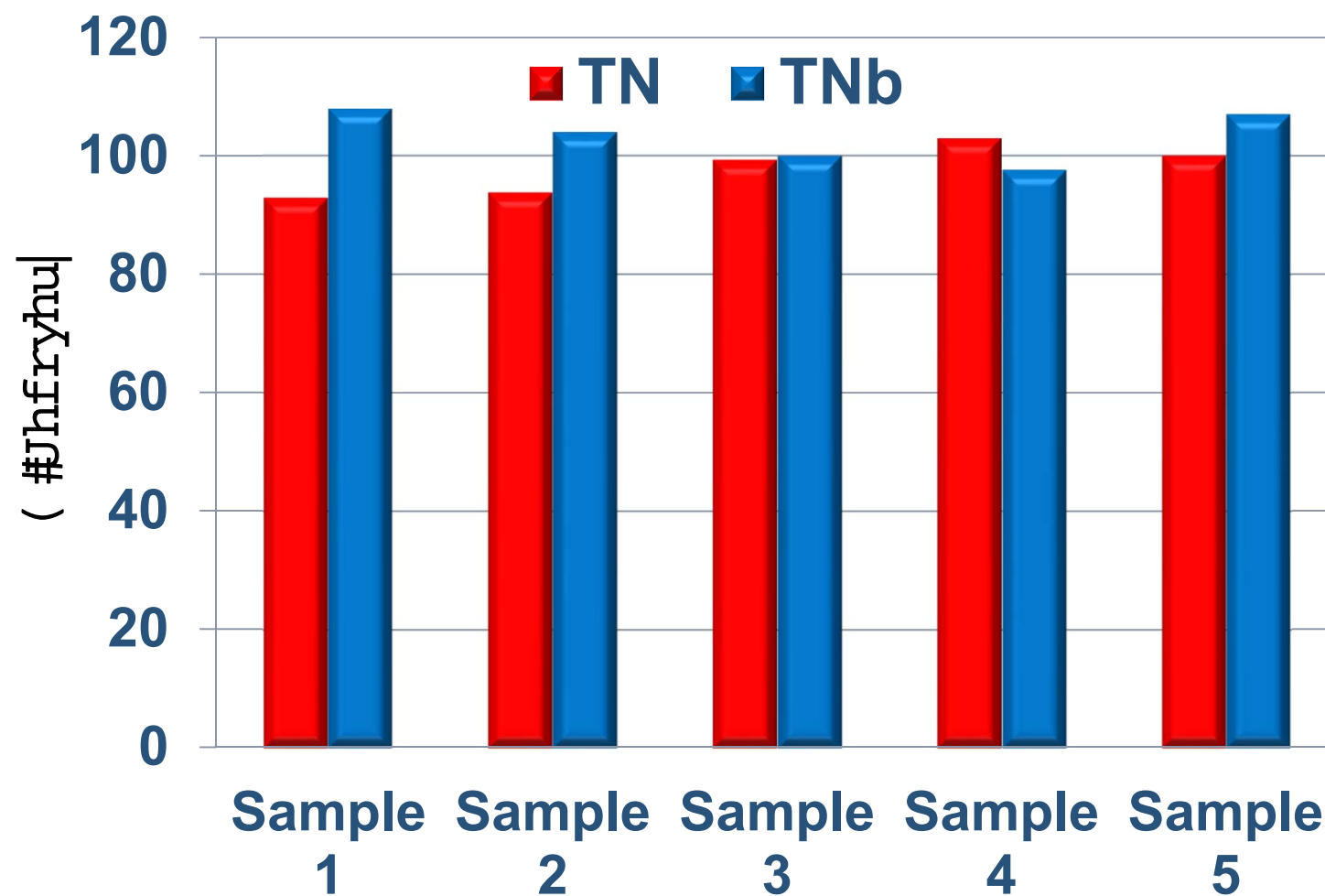
Obtain a TN Result (~ every 5 minutes)



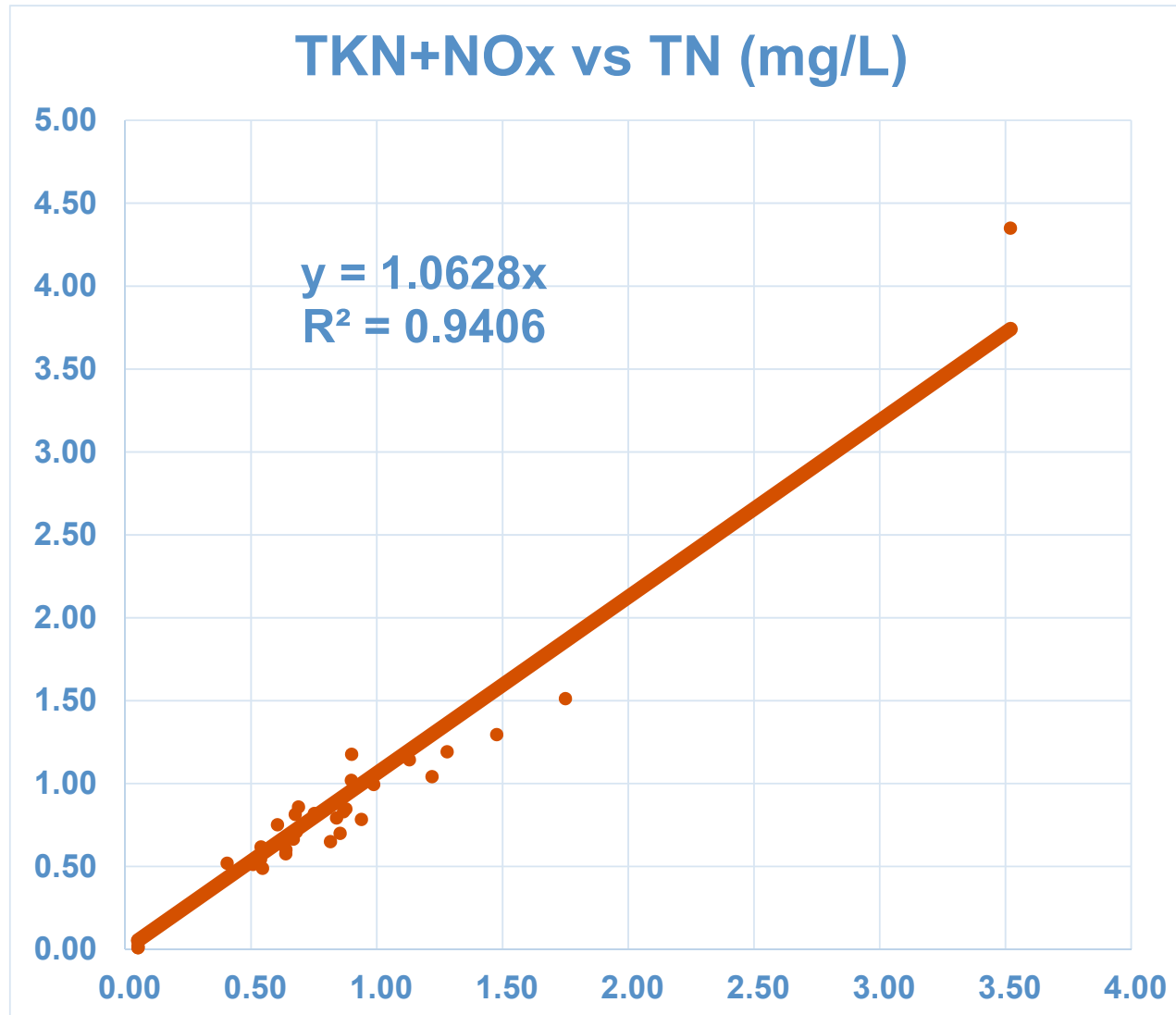
TKN and Catalytic Oxidation Recovery in Various N Compounds



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

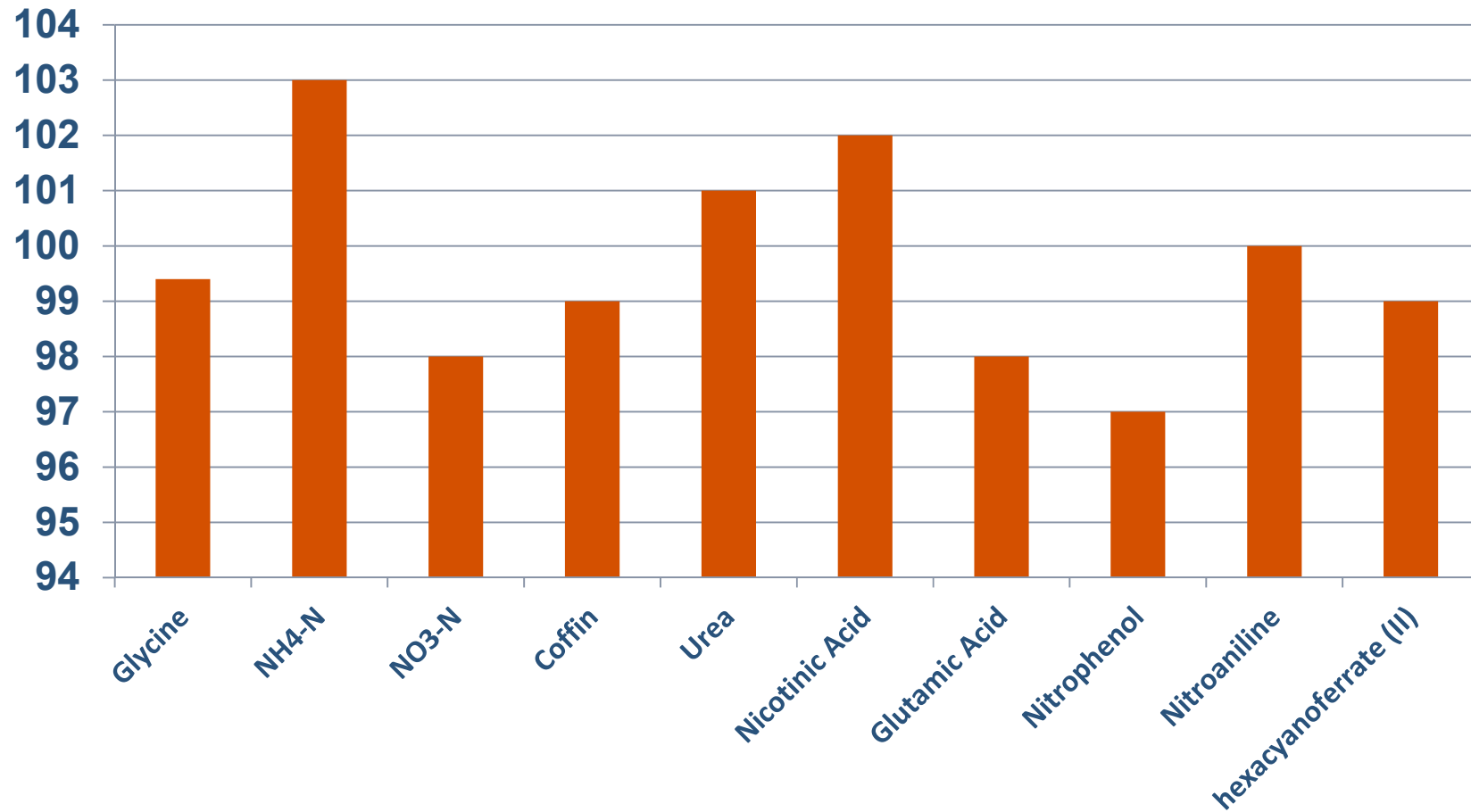


Comparison of "EPA" TN and new TN (SM)

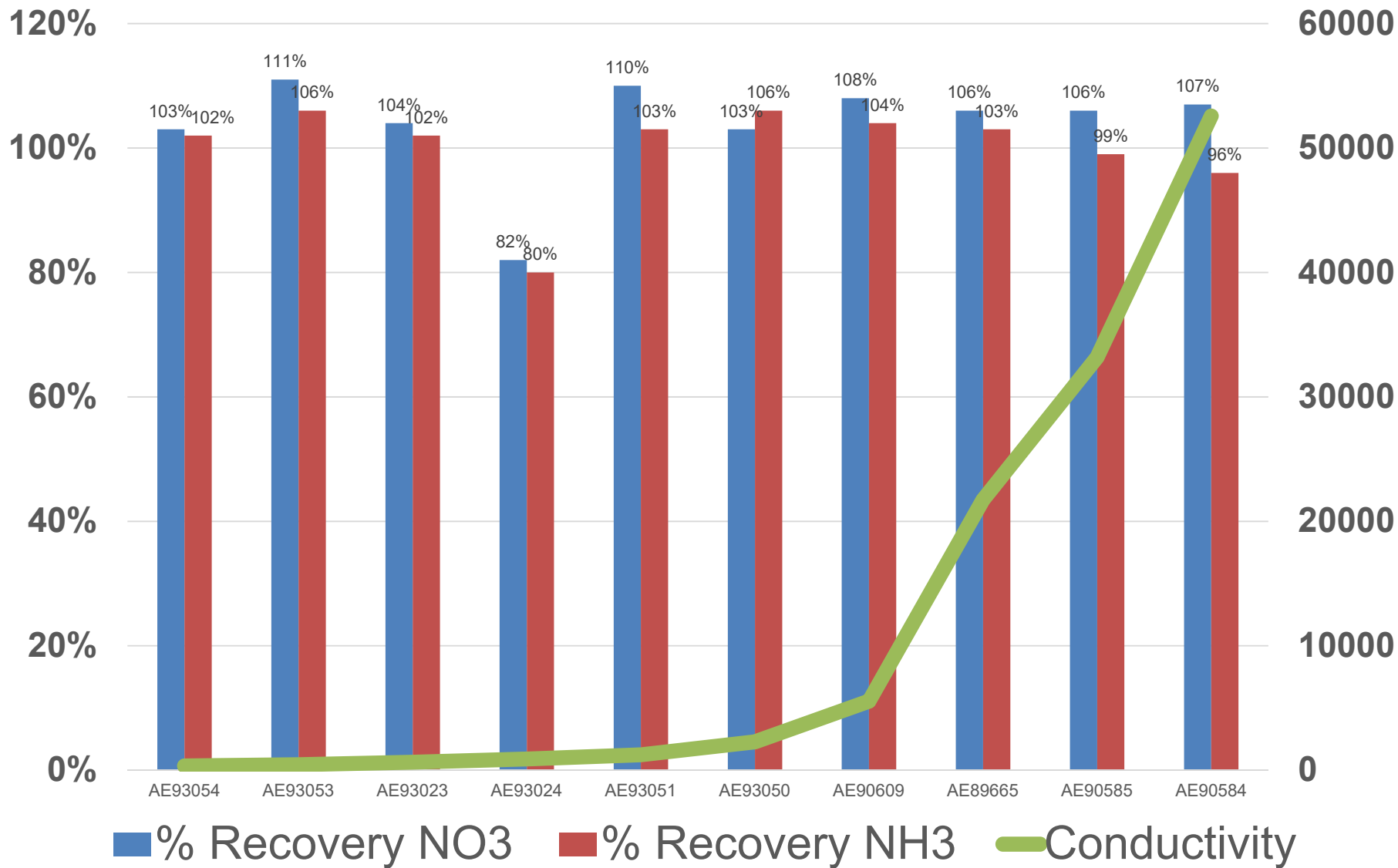




% Recovery of Various Nitrogen Compounds



MS Percentage Recoveries (%) and Conductivity using NO3 and NH3 STD's for TN analysis (SM study)



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%

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 (Hg, Cu, Se?)
- Must run NO_3 + NO_2 separately
- Not applicable to all N compounds

Issues with TKN procedure



- Digestion time – varies per lab
- Digestion temperatures – vary per lab
- Digestion vessels
 - Macro in flask
 - Micro in block
- To distill or not to distill?

- Where is the study that compares all these versions of the same method?

Why should we have a new TN parameter and methods?



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

Any Questions?



William Lipps

williamlipps@eurofinsus.com

Eurofins Eaton Analytical, LLC

www.eurofinsus.com