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Efforts to Standardize TKN Measurements and Add Total Nitrogen to 40 CFR Part 136.

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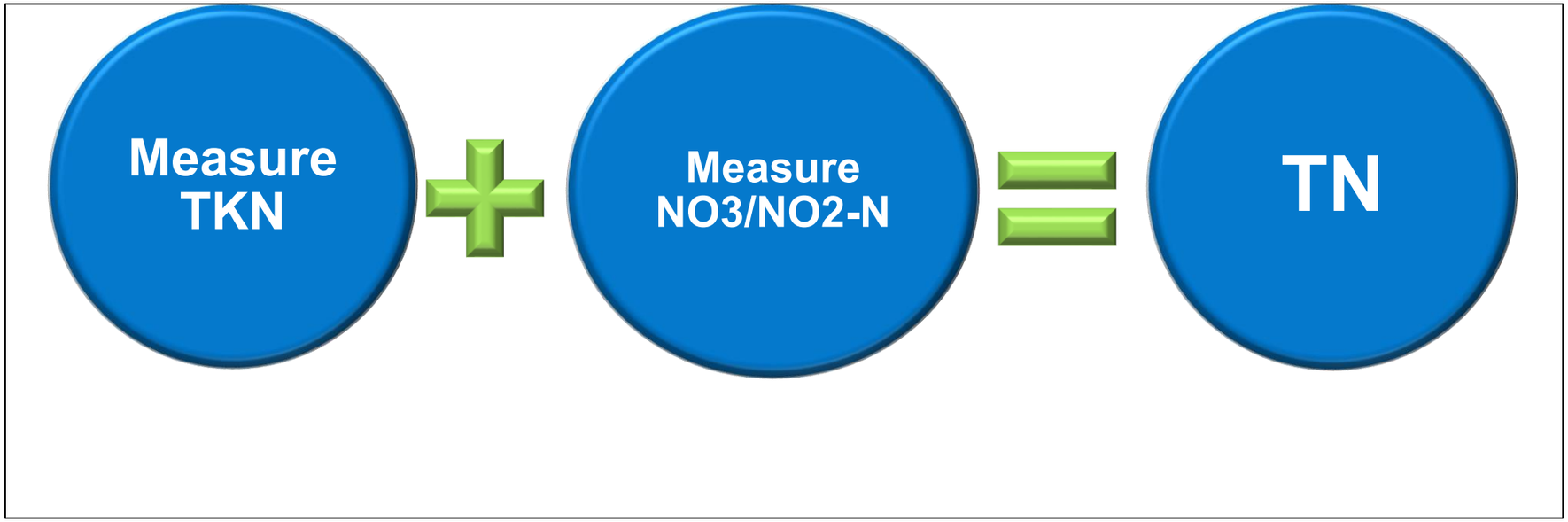
The current “EPA” definition for Total Nitrogen is TKN plus nitrate/nitrite

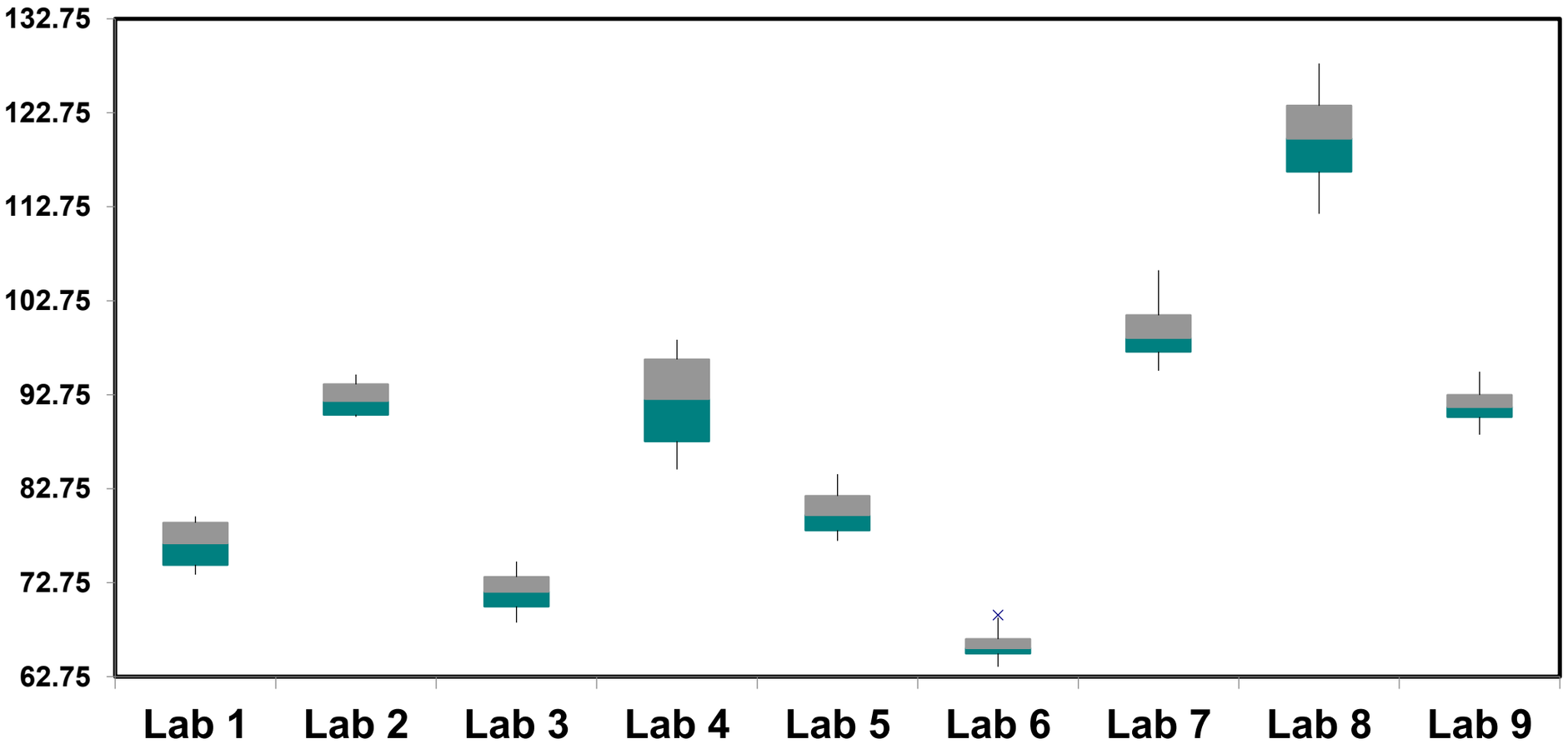


- Not standardized = unknown accuracy and precision
- Approved method

- Accurate and standardized
- Approved method

- Accurate and standardized
- No Approved method

For example, these are the results of an Inter-lab study on a TKN LCS (ammonia spiked in reagent water)



Standard Methods conducted a survey to compare how people run TKN

- Sample collection and preservation
- Sample digestion volume
- Digestion vessel
- Digestion reagent
- Evaporation time and temperature
- Digestion time and temperature
- Distillation or no distillation
- Analytical step
- For titration – what acid and indicator
- For colorimetry – what reagents
- Determination of clearing time?
- What QC?
- What is the MDL or MRL?
- What is used for the LCS?
- Do you map the block?
- Any other comments

Sampling and sample preservation

Lab	Response	Final
A	1 L with 5 ml 25% H_2SO_4	100 – 1000 mL at pH ~ 2 (check with paper) and cool from above freezing to 6 °C.
B	1 L with 5 ml 25% H_2SO_4	
C	0.5 L with 1 ml H_2SO_4	
D	0.1 L with 1:1 H_2SO_4 to pH < 2	
E	1 L with H_2SO_4 at pH < 2 and stored at 4°C	
F	0.25L	
USGS	0.1 L with H_2SO_4 at pH < 2	
ISO 5663	pH < 2 at 2 – 5°C	

Sample digestion volume and vessel

Lab	Volume	Vessel	Final
A	100 mL	250 mL tube	Varies by method. 25 mL for block
B	50 mL	250 mL tube	
C	25 mL	100 mL tube	
D	25 mL	tube	
E	50 mL	tube	
F	20 – 250 mL	Not provided	
USGS	10 mL	75 ml tube	
ISO 5663	100 mL	500 mL flask	

Digestion reagent and amount added per ml sample

Lab	Response	Final
A	0.24 g K2SO4 per ml 0.08 ml H2SO4 per ml 0.006 g CuSO4 per ml	0.0268 g K2SO4 per ml 0.0268 ml H2SO4 per ml 0.00146 g CuSO4 per ml
B	0.0536 g K2SO4 / ml 0.0536 ml H2SO4 /ml 0.00292 g CUSO4 / ml	
C	0.0268 g K2SO4 per ml 0.0268 ml H2SO4 per ml 0.00146 g CuSO4 per ml	
D		
E		
F	Not provided (copper catalyst)	
USGS	0.0268 g K2SO4 per ml 0.0268 ml H2SO4 per ml 0.0004 g Hg per ml	
ISO 5663	0.05 g K2SO4 / ml 0.1 ml H2SO4 / ml 0.05 g Se / ml	

Evaporation temperature and time

Lab	Temperature (°C)	Time	Final
A	160	1 hour	Varies by method. 180± 20°C for 1 hour or < 3 mL for block
B	160	1 hour	
C	200	1 hour	
D	200	1 hour	
E	200	1 hour	
F	160 200	1 hour 1 hour	
USGS	220	30 minutes (to < 3 ml)	
ISO 5663	Boil to fumes	1 hour	

Digestion temperature and time

Lab	Temperature (°C)	Time	Final
A	380	1 hour	Varies by method. 380 °C for 30 minutes or “clearing + 15 minutes”
B	380	1 hour	
C	380	30 minutes	
D	380	1 hour	
E	380	1 hour	
F	380 380	30 minutes 1 hour	
USGS	370	15 minutes (to < 0.5 ml)	
ISO 5663	fumes	1 hour	

Clearing time for some potential QC compounds

Compound	Time (minutes)
Glycine	15
Lysine	15
Nicotinic Acid	20
Urea	10
ASTM wastewater (flour)	15

Digest until clear, the 15 minutes more?

Distill or bring to known volume?

Lab	Response	Final
A	Add 70 ml Water, then distill	Distillation, ~ 200 ml Block, dilute to 25 ml
B	Add 50 ml water for direct colorimetry	
C	Bring to 25 ml for colorimetry	
D	Bring to 25 ml for colorimetry	
E	Distill to 200 ml	
F	Steam distill or bring to volume	
USGS	Bring to 10 ml for colorimetry	
ISO 5663	Distill to 200 ml	

Titration reagents

Lab	Response	Final
A	4% Boric Acid with bromocresol green-methyl red. Assume titrate with 0.01 N H_2SO_4	2% boric Acid with methyl red and methylene blue. Titrate with 0.02 N H_2SO_4
B	NA	
C	NA	
D	NA	
E	Assume into boric acid and titrate with 0.01N H_2SO_4 with methyl orange	
F	Methyl Orange or Bromocresol green	
USGS	NA	
ISO 5663	0.02 M HCl methyl red with methylene blue.	

Colorimetric Reagents

Lab	Response	Final
A	NA	No Standard Method with salicylate (except Lachat). Revise method in 4500-NH_3 Allow any NH_3 method after distillation. Allow salicylate after gas diffusion Allow salicylate by direct if prove distillation or diffusion not needed
B	Salicylate via discrete analyzer	
C	Salicylate	
D	Salicylate via CFA	
E	NA	
F	NA	
USGS	Salicylate via CFA with diffusion	
ISO 5663	NA	

What QC samples are run per batch

Lab	Response	Final
A	20 samples per batch, LOQ each batch, LCS, MS, MSD one every 20 samples.	20 per batch MRL, MB, LCS, MS/MSD (or duplicate) LCS must be organic
B	Method blank/CCB and CCV are 1 per 10 samples. LOQ each batch but if it fails once occasionally, we let it go since SM really says at least quarterly. LCS, MS, MSD one every 20 samples.	
C	ICV,ICB,MDRL.MB.LFB,MS, MSD,CCV,CCB,FCV,FCB.	
D	LCS Low 2.5 mg/L (Control range 85-115%); LCS High 7.5 mg/L (Control range 85-115%); Method Blank; sample duplicates; Matrix Spike at 1.8 mg/L (Control range 70-130%).	
E	NA	
F	NA	
USGS	blk, organic check (glycine), spikes, duplicates	
ISO 5663	NA	

What do you use as an LCS?

Lab	Response	Final
A	NH_3-N	Use Glycine or nicotinic acid Indicates clearing time May need NO_3-N as interference check
B	NH_3-N	
C	NH_3-N	
D	Glycine	
E	NH_3-N	
F	NH_3-N or Glycine	
USGS	Glycine	
ISO 5663	None mentioned	

How do you know when the digestion is completed?

Lab	Response	Final
A	time	Use clearing time + 15 minutes. Verify recovery
B	time	
C	time	
D	Glycine recovery 85-115%	
E	Solution clears	
F	Block temperature	
USGS	Solution clears, verify glycine recovery	
ISO 5663	Solution clears	

Do you map the block?

Lab	Response	Final
A	On commissioning and verify one position annually	Map block on commissioning, verify one position annually, or again if major spill.
B	On commissioning and verify one position annually	
C	yes	
D	yes	
E	380	
F	yes	
USGS	yes	
ISO 5663	NA	

Additional Comments

Comment	Response
1	Address what type of boiling chips are optimal (teflon vs. glass beads etc.) Perhaps address flow rate of cooling water during digestion, to pull off vapors (i.e., how to check it if there is a way, and how fast should the water rate be.) Address when to bring digestate up to volume (like while still warm to prevent crystallization or will have to reheat to dissolve crystals). Address overnight storage of digestate if needed, covered with parafilm and refrigerated.
2	We do not use teardrop stoppers. We did a study and the results showed there were no significant difference with/without teardrop stoppers. All results were comparable.

Conclusions from the survey

- TKN is a “legacy” method that many labs run, differently
- Blind samples of NH3-N in reagent water vary a lot
- In a small survey the variability in crucial steps varies a lot

Why does this matter?

- The concept of a standard method is everyone does the crucial steps the same.
- There is high variability between labs, probably due to non-standardized methodology
- When introducing TN methods, results will be compared to TKN + NO_3/NO_2 – N
- Comparisons may not compare because the TKN results may not be accurate

Next steps for TKN

- Standardize the digestions in 4500-Norg
  - Macro Kjeldahl
  - Semi- automated with steam distillation
  - Block digestions

- Separate FIA method in 4500-Norg and move to 4500-NH_3
  - Add NH3 methods as needed, for example gas diffusion
  - Manual salicylate

- Propose digestion with any NH_3 method, or as referenced.

- Provide all 4500-NH_3 with 4500-Norg purchase.

New TN methods we intend to propose

- ASTM D8083 and SM 4500-N E (HTCC with CLD)
- ASTM D8003 (alkaline persulfate with IC)
- SM alkaline persulfate with any NO_3 + NO_2 method
- New SM strong alkaline persulfate with dimethylphenol
- Others?

Any Questions?

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