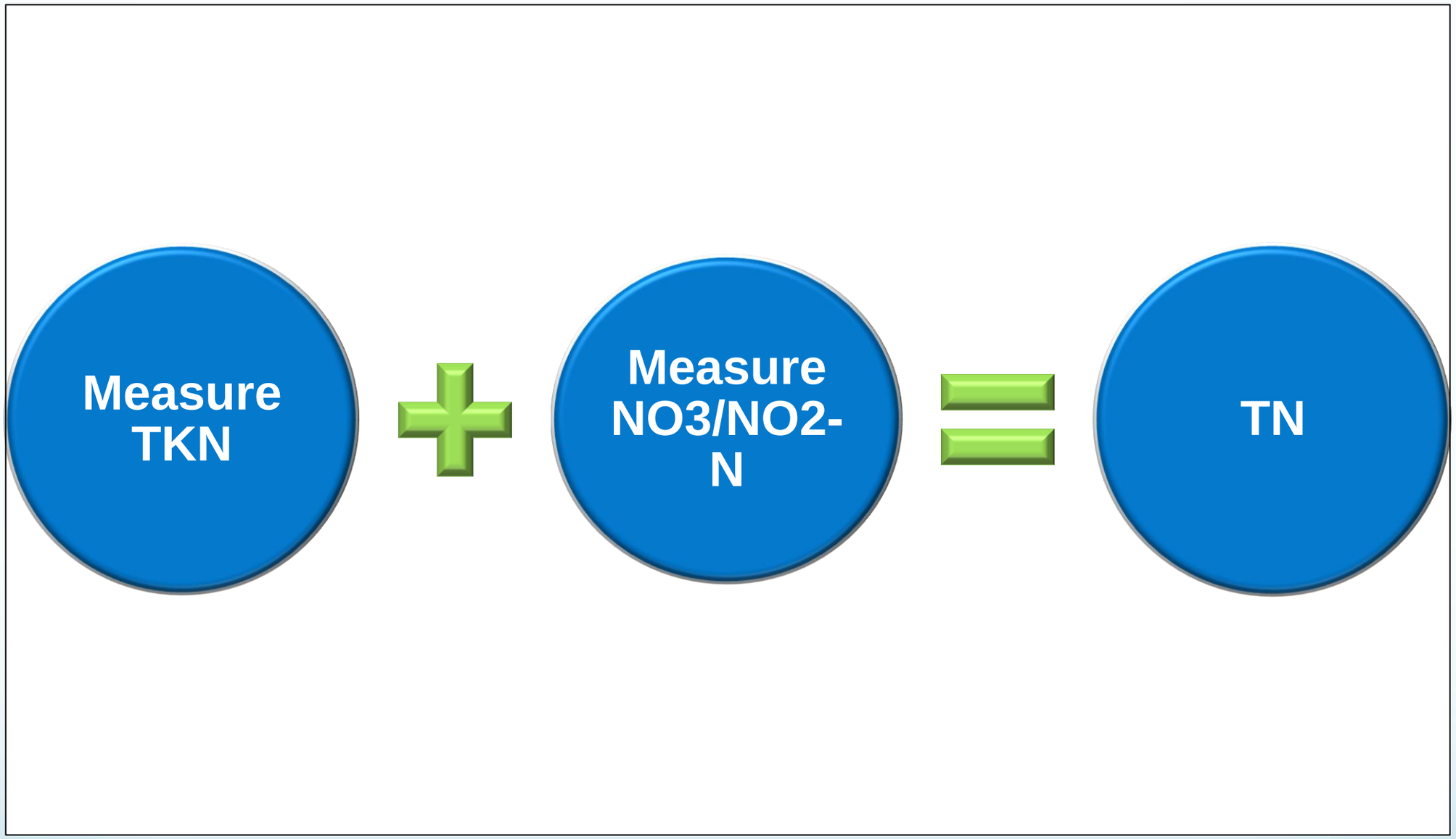
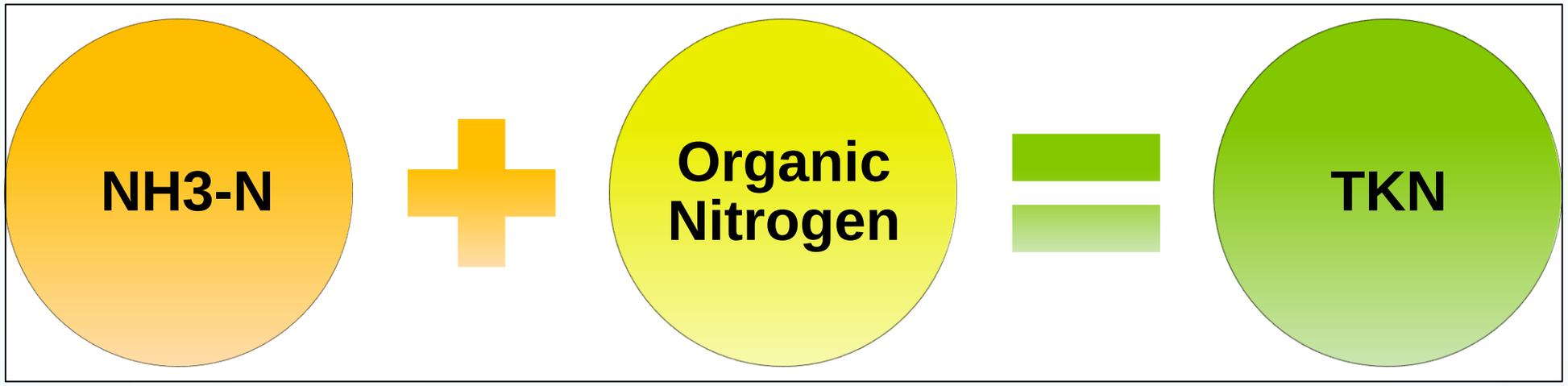
Automated Digestion of Total Nitrogen and Total Phosphorus in Environmental Samples

William Lipps
OI Analytical

EPA definition of total nitrogen



Measuring organic nitrogen requires a TKN and ammonia analysis



TKN is a “classical” analysis of total nitrogen

- **TKN includes**
  - **Organic Nitrogen**
  - **Ammonia Nitrogen (NH_3-N)**
- **TKN does not include**
  - **Nitrate Nitrogen (NO_3-N)**
  - **Nitrite Nitrogen (NO_2-N)**

Must use 40 CFR Part 136 methods

TKN Methods	• Manual digestion • Manual distillation • Nessler, IC, Titration, ISE, phenate
TKN Methods	• Manual digestion • Automated distillation/diffusion • Direct Colorimetry
NO3/NO2 –N Methods	• IC, Reduction colorimetry

The “classical” Kjeldahl Reactions distilled and titrated ammonia

Digestion

- $H_2SO_4 + 2(NH_2)_2CO \rightarrow (NH_4)_2SO_4 + 2\ CO_2$

Distillation

- $(NH_4)_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O + 2NH_3$

Capture

- $H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 + H_2O$

Titration

- $H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$

Present Day TKN methods can either distill (diffuse) or measure NH_4^+ in the matrix

Manual Digestion

- $H_2SO_4 + (NH_2)_2CO \rightarrow (NH_4)_2SO_4 + 2CO_2$
  - Must use catalyst

Distillation (required for some methods)

- $(NH)_4SO_4 + NaOH \rightarrow NaHSO_4 + H_2O + 2NH_3$

Detection

- Titration, ISE, manual colorimetry, automated colorimetry

The block digester methods for TKN do not require distillation

- Sodium Citrate is a better complexing agent
- Salicylic acid method
- Blue color measured at 640 – 660 nm
- Continuous Flow or Discrete Analyzer methods.

Digest multiple samples on a block and analyze them automatically

- Faster than titration
- Results in minutes
- Easy repeat of questionable results
- Dilute off scale samples
- No distillation
- Smaller volumes (25 ml)

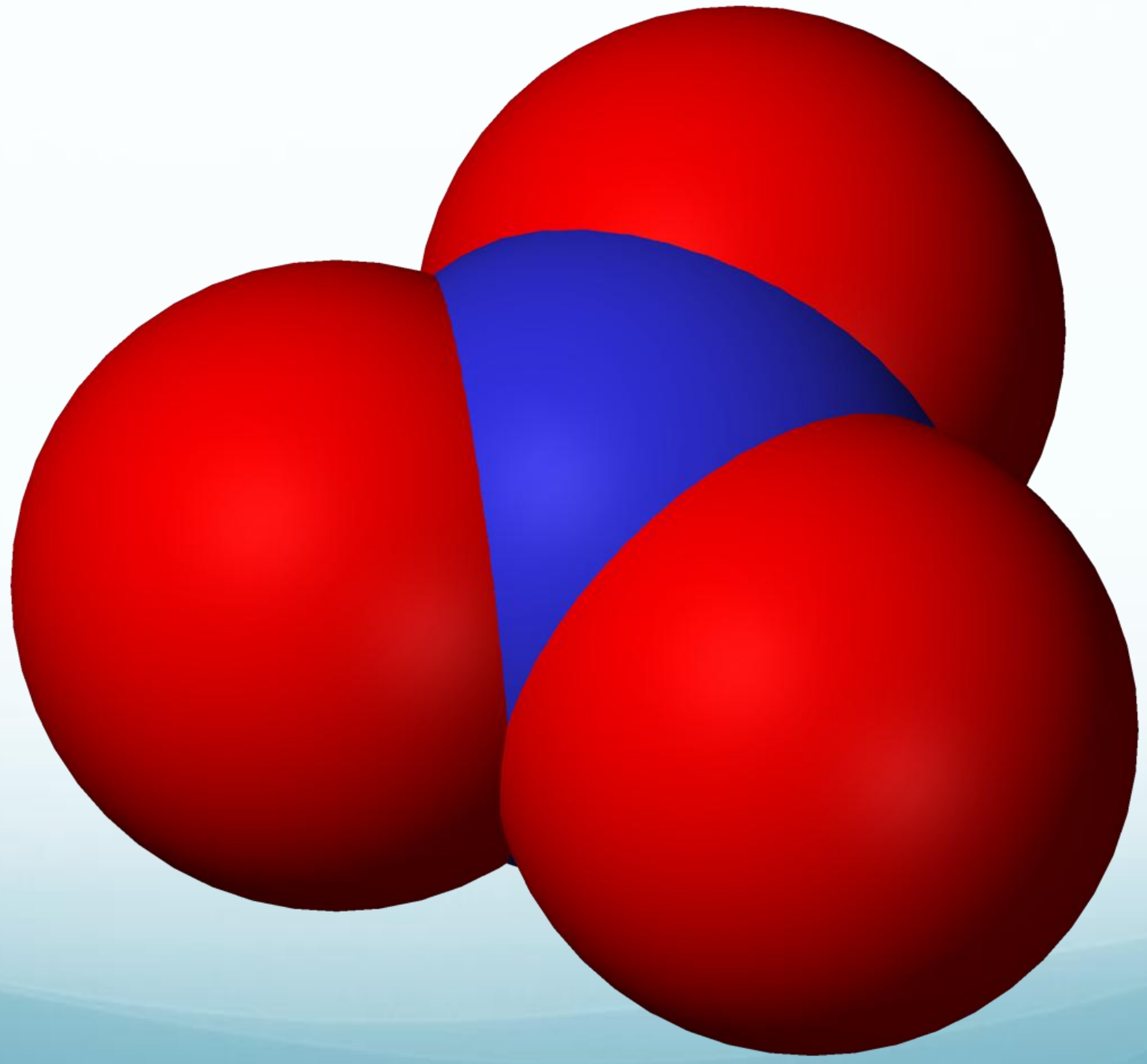
Operational Comparison of TKN methods

Manual Digestion & Distillation Followed By:	Require final digest volume	Require final distillate volume
Titration	no	no
Ion Selective Electrode	no	yes
Manual Phenate	no	yes
Automated Phenate	no	yes
Block Digestion		
Automated Salicylate	yes	N/A

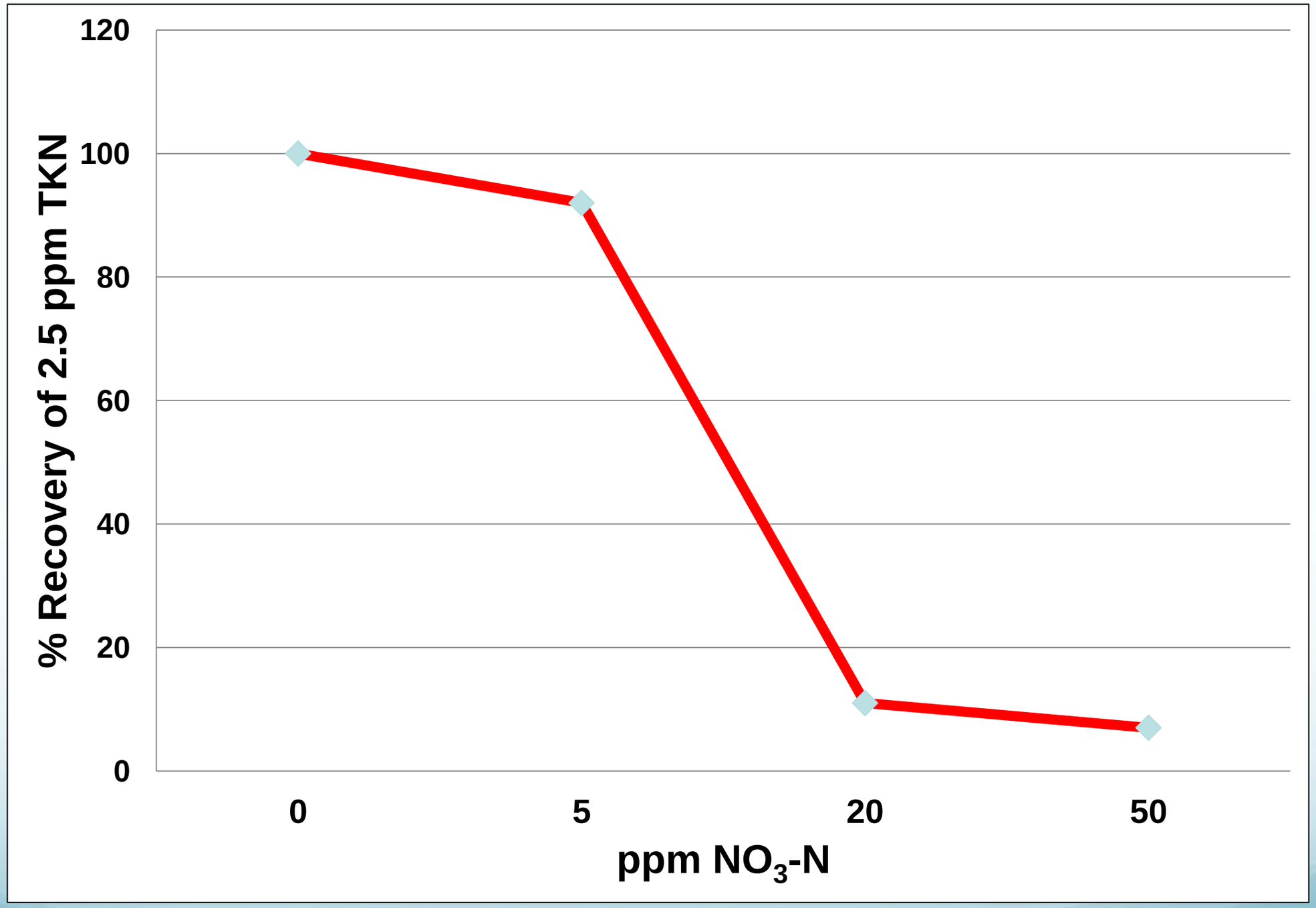
Techniques for the analysis of Total Nitrogen (EPA only approves TKN)

Manual Digestion & Distillation Followed By:	MDL (mg/L)
Titration	1.0
Manual Phenate	0.05 ?
Ion Selective Electrode	0.03
Automated Phenate	0.01
Block Digestion	
Automated Salicylate	0.1
Auto-GD/pH colorimetry	0.2
Auto-GD/Salicylate	0.02

Problem -TKN does not measure nitrate, and total nitrogen includes nitrate plus nitrite



Low Recovery of TKN in presence of NO_3-N



Schlueter 1977

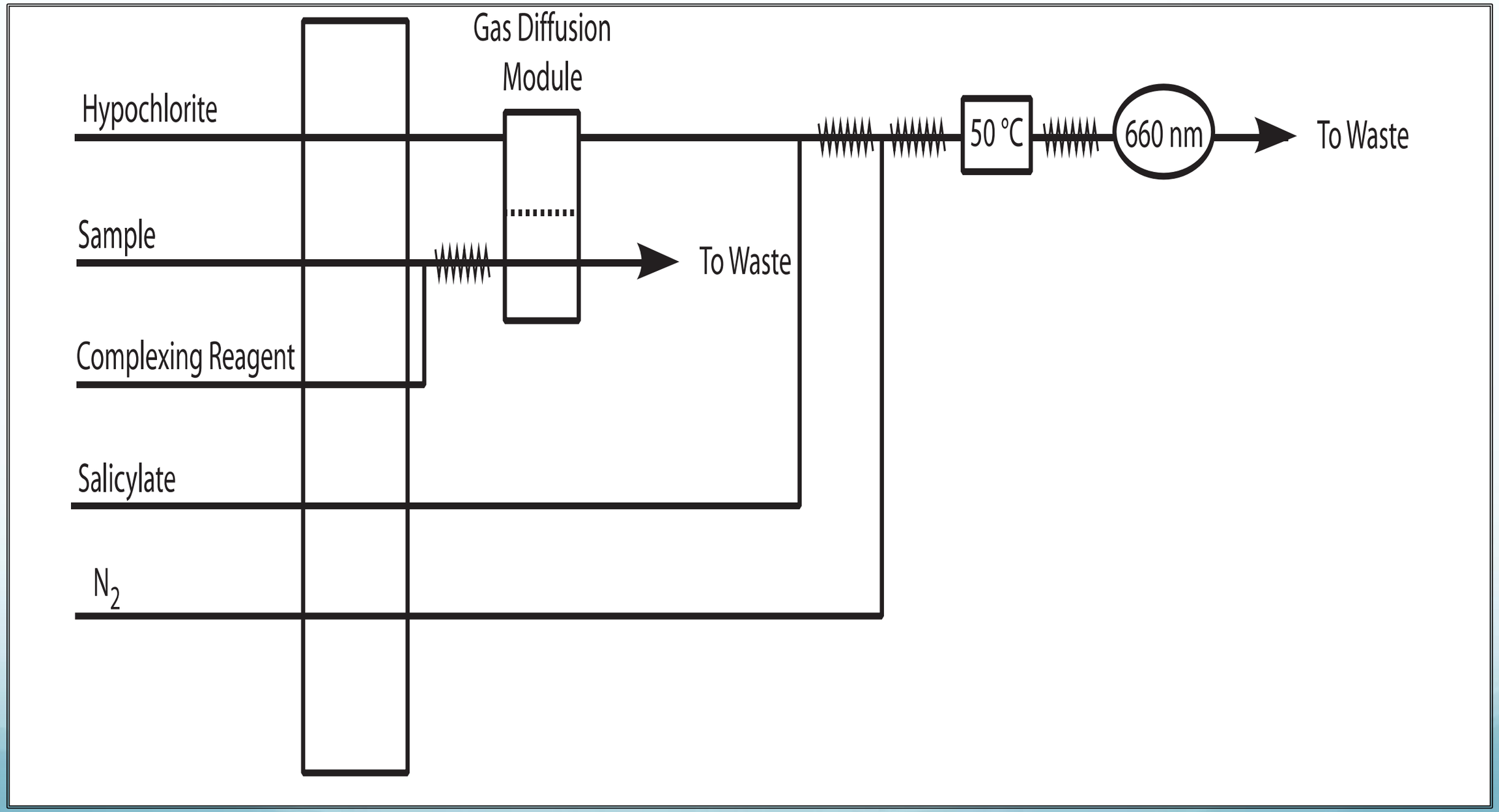
Typical N in influent and effluent

	Influent	Effluent
TKN (mg/L)	30	2
NO_3-N (mg/L)	0	17
TN (mg/L)	30	19

Minimize digestion time to maximize recovery when nitrate is present

1. 25 mL sample
2. 10 mL digestion reagent
3. 5 stones
4. 160° C for 1 hour
5. 380° C for 30 minutes
6. Cool, rinse sides, cool
7. Dilute to 25 mL (or 50 mL)

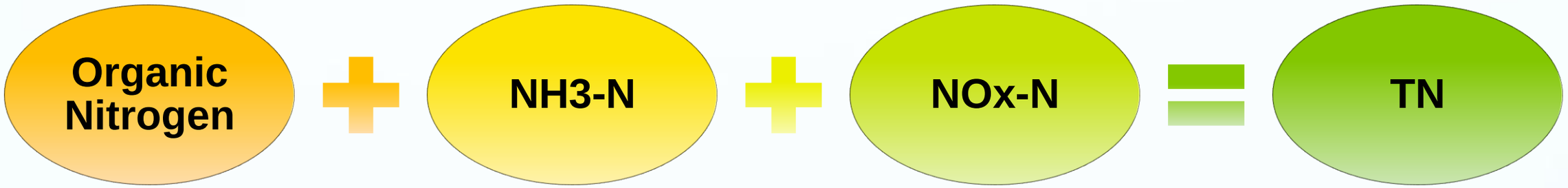
With EPA allowed method modifications, both ammonia and TKN can be determined with the same CFA method



EPA 351.2 TKN by Gas Diffusion Colorimetry

EPA	Modified
Direct Colorimetry	Automated Diffusion
Salicylate	Salicylate
Tartrate	Citrate
0.01 – 2.0 ppm	0.01 – 20 ppm

Low Level Organic Nitrogen Requires a TN analysis, not TKN

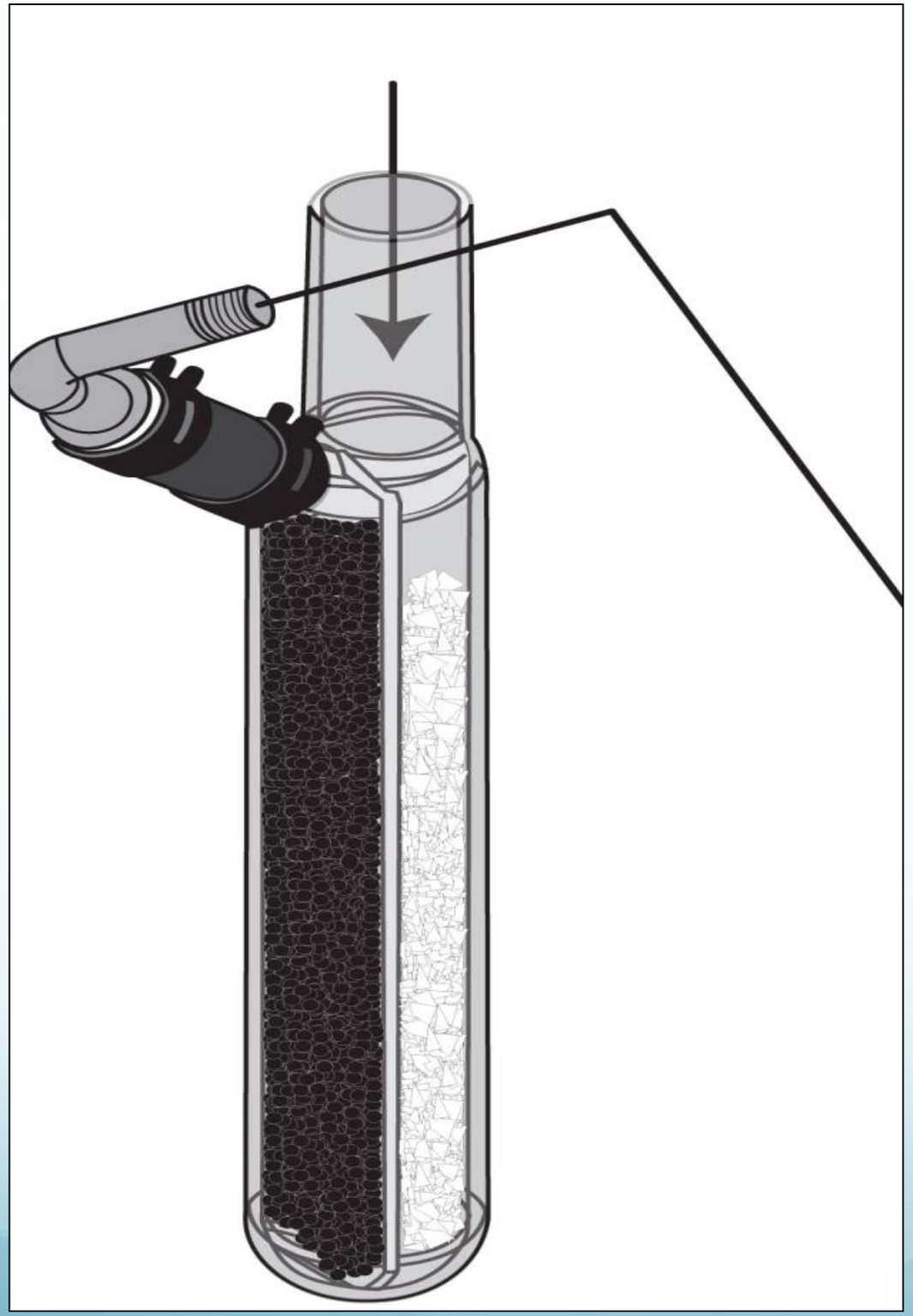


$$NO_x\text{-}N = NO_3\text{-}N + NO_2\text{-}N$$

Analysis of Total Nitrogen Compounds

- Filter preserved sample for DIN
- Do Not filter preserved sample for TN
- Analyze TN
- Analyze DIN (DIN=TIN)
  - NO3 + NO2
  - NH4
- TON = TN - DIN

HTCO Total Nitrogen Bound (TNb)



720° C reactor

TOC & TNb

Total Nitrogen Bound, or TNb is measured on a TOC analyzer

Oxidation

- $2(NH_2)_2CO + 7O_2 + catalyst \rightarrow 4NO_2 + 4H_2O + CO_2$

Reduction

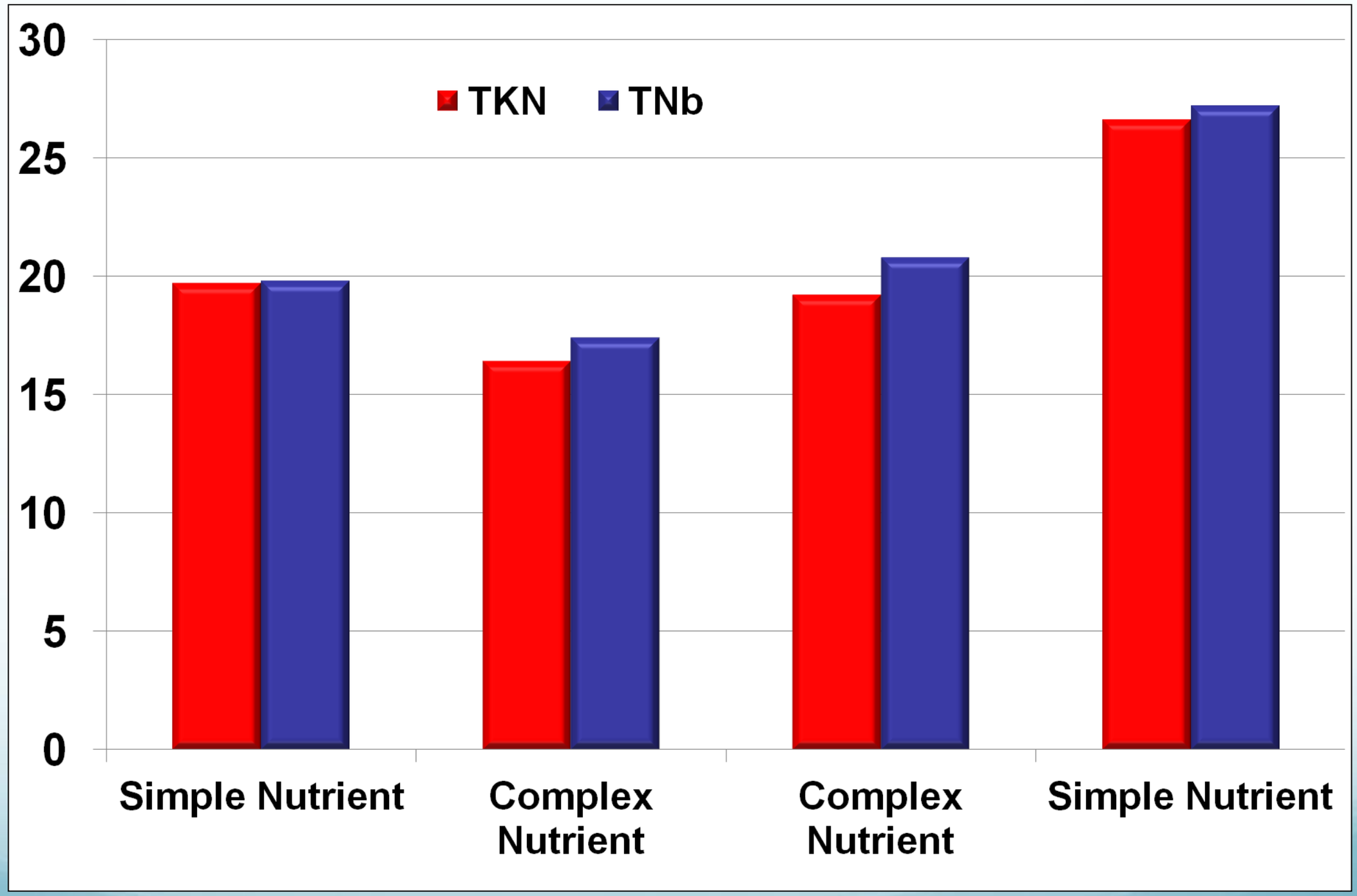
- $2NO_2 + catalyst \rightarrow 2NO + O_2$

Detection

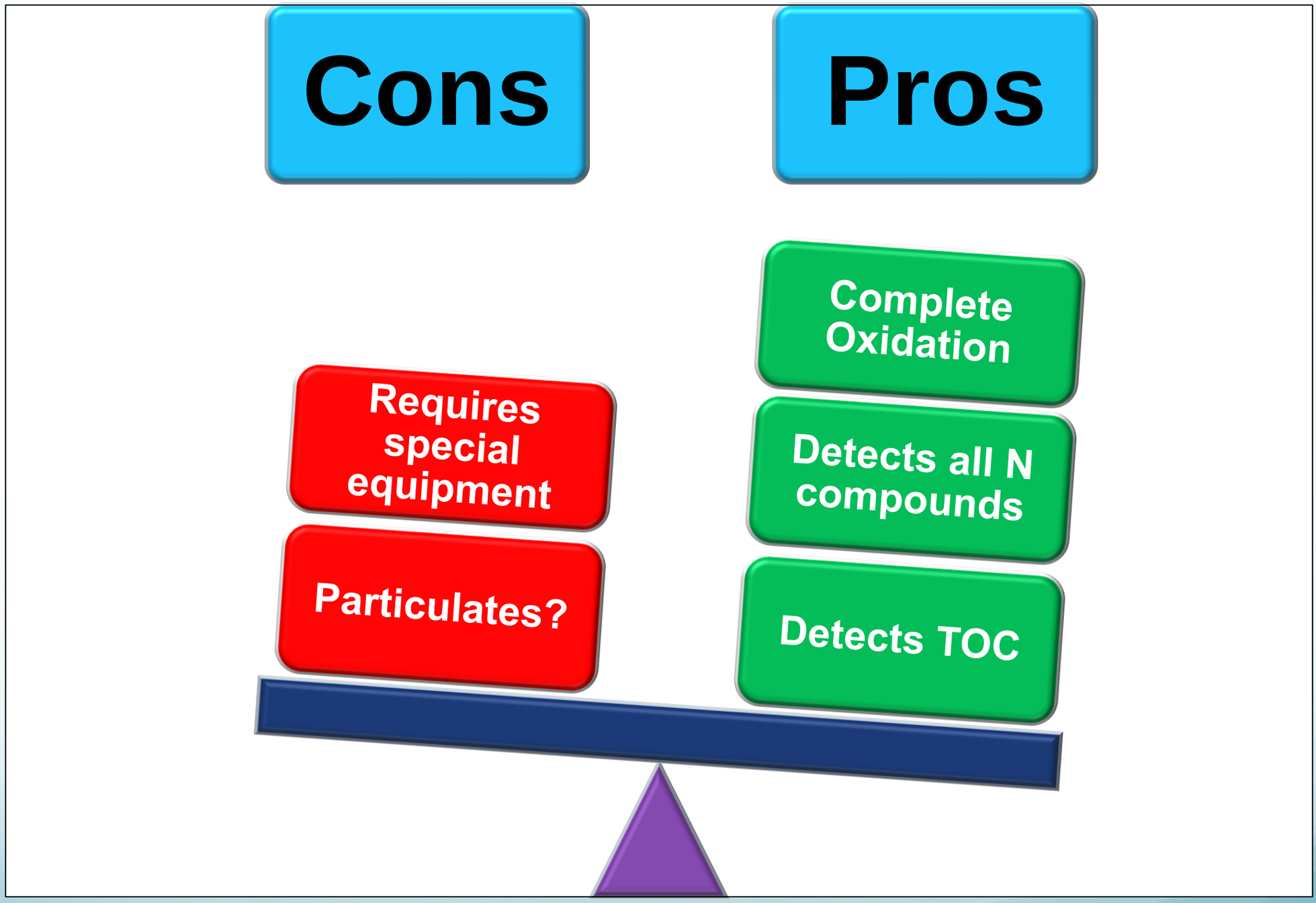
Chemiluminescence

Electrochemical

Comparison of TNb to TKN (QC samples)



Advantages and disadvantages of TNb



Alkaline Persulfate Digestions for TN do not require specialized equipment

Manually digest

Determine NO_3-N

Measures all TN

Manual Alkaline Digestion for TN can be done in an autoclave or with test tubes

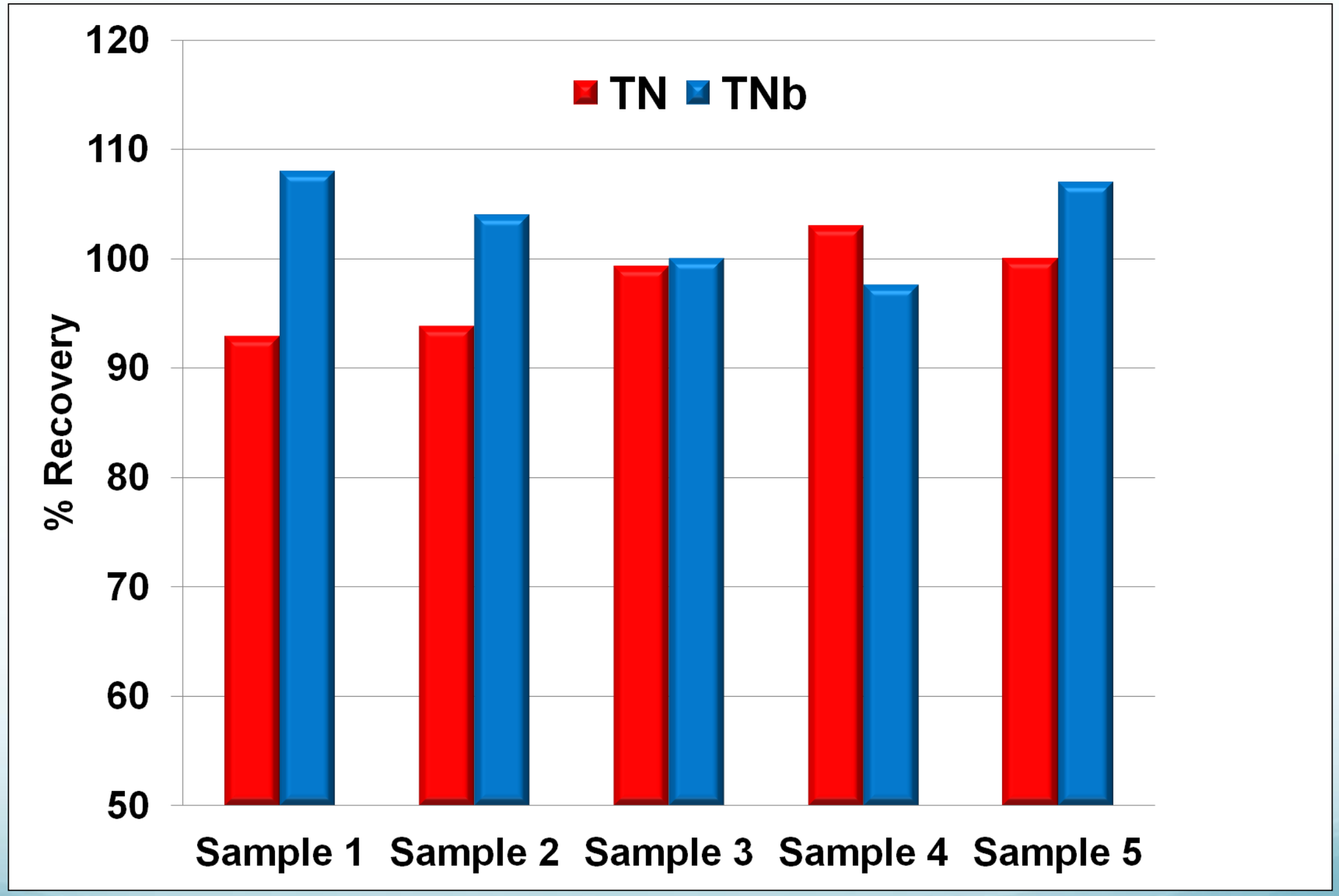
Alkaline Digestion

- $(NH_2)_2CO + 8\ S_2O_8^{-2} + 18\ OH^- \rightarrow 2\ NO_3^- + CO_2 + 16\ SO_4^{-2} + 11\ H_2O$

Colorimetry

- Any Nitrate or Nitrate + Nitrite method

Comparison of TN to TNb illustrates equivalent results on samples tested



Doyle 2004

Comparison of TN to TKN + NO_3/NO_2 -N

	TOC (mg/L)	TKN + NOx (mg/L)	TN (mg/L)
Cecil	17.5	2.9	2.9
Greenville 1	36.0	3.1	3.5
Hiwassee 2	59.0	8.8	8.9
Irwin	108	17.7	16.0

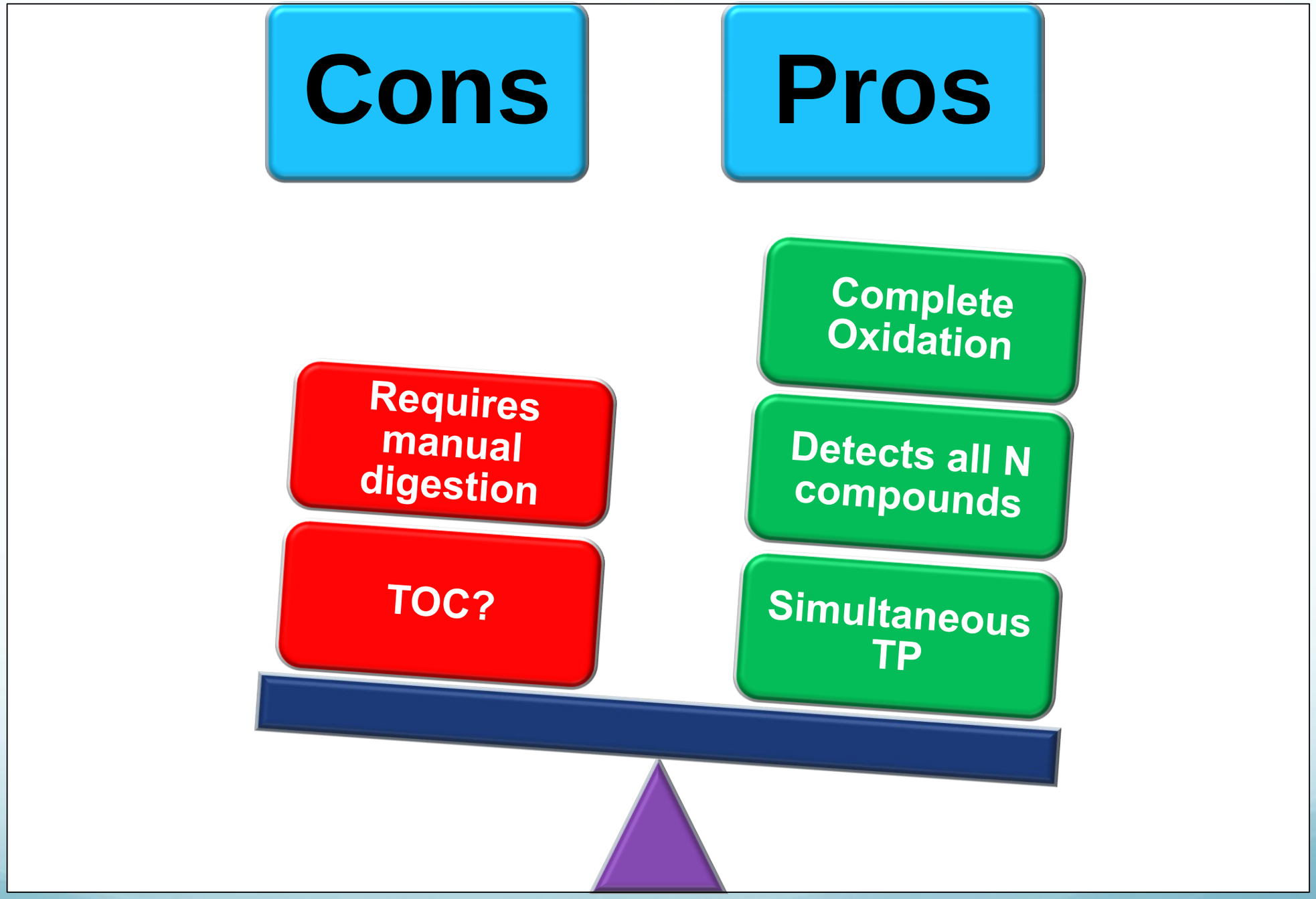
Cabrera 1993

Comparison of TN to TKN with % RSD

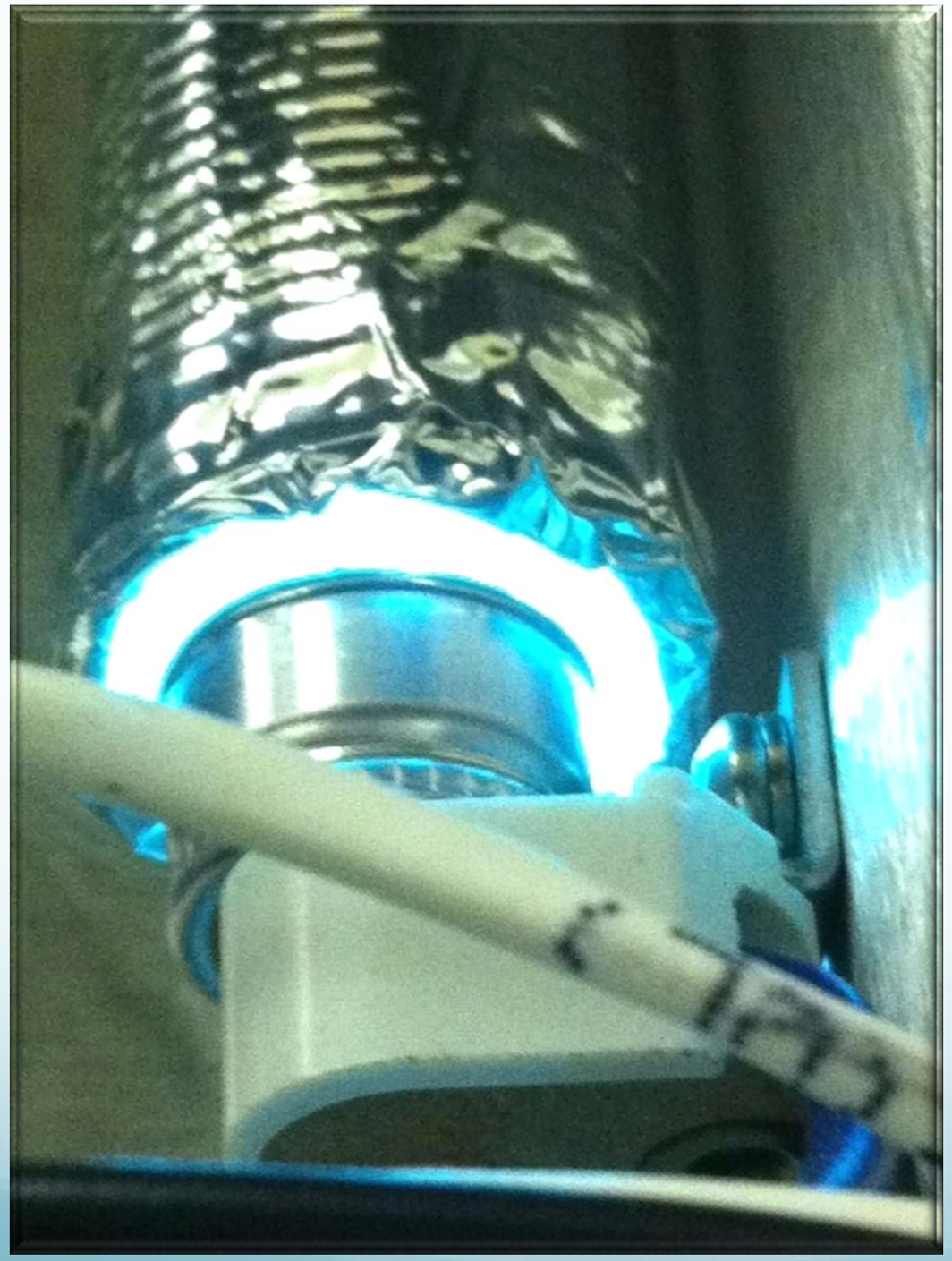
	TKN (mg/L)	TKN (%RSD)	TN (mg/L)	TN (%RSD)
Bear Creek	0.18	10.65	0.22	5.72
Silver Fork	0.36	19.29	0.41	6.49
Salt River	0.59	25.31	0.76	3.23
Ted Shanks	0.61	25.25	1.05	6.04

Smart 1981

Advantages and disadvantages of manual TN persulfate methods



Automated Alkaline UV Persulfate Digestions increase throughput

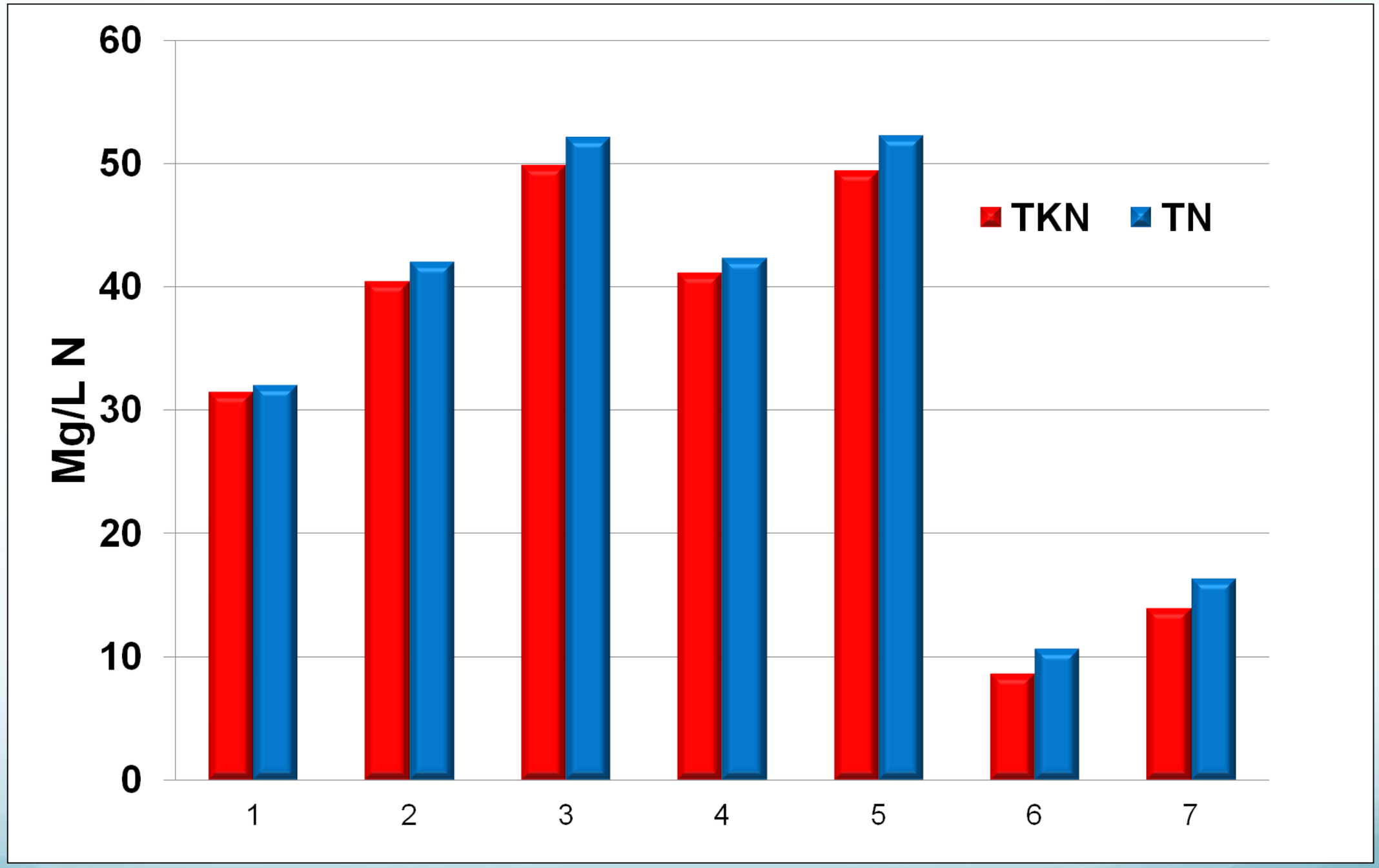


Automated digest

Determine NO_3-N

Measures TDN

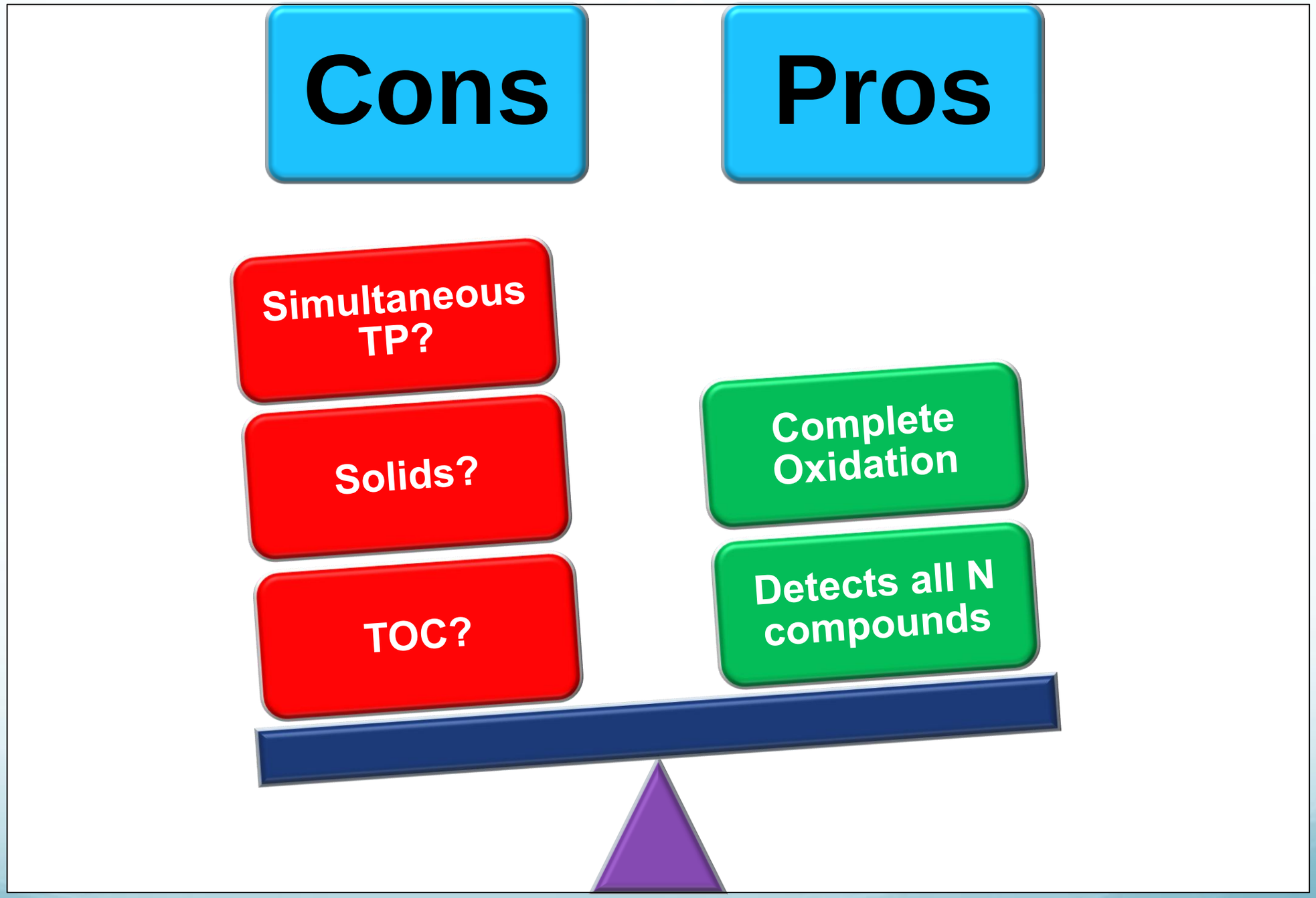
Comparison of Automated TN with TKN



Unknowns regarding the efficiency of Automated UV Alkaline Digestion

Particulates?

Advantages and disadvantages of automated TN persulfate methods



What samples for Total Nitrogen may look like

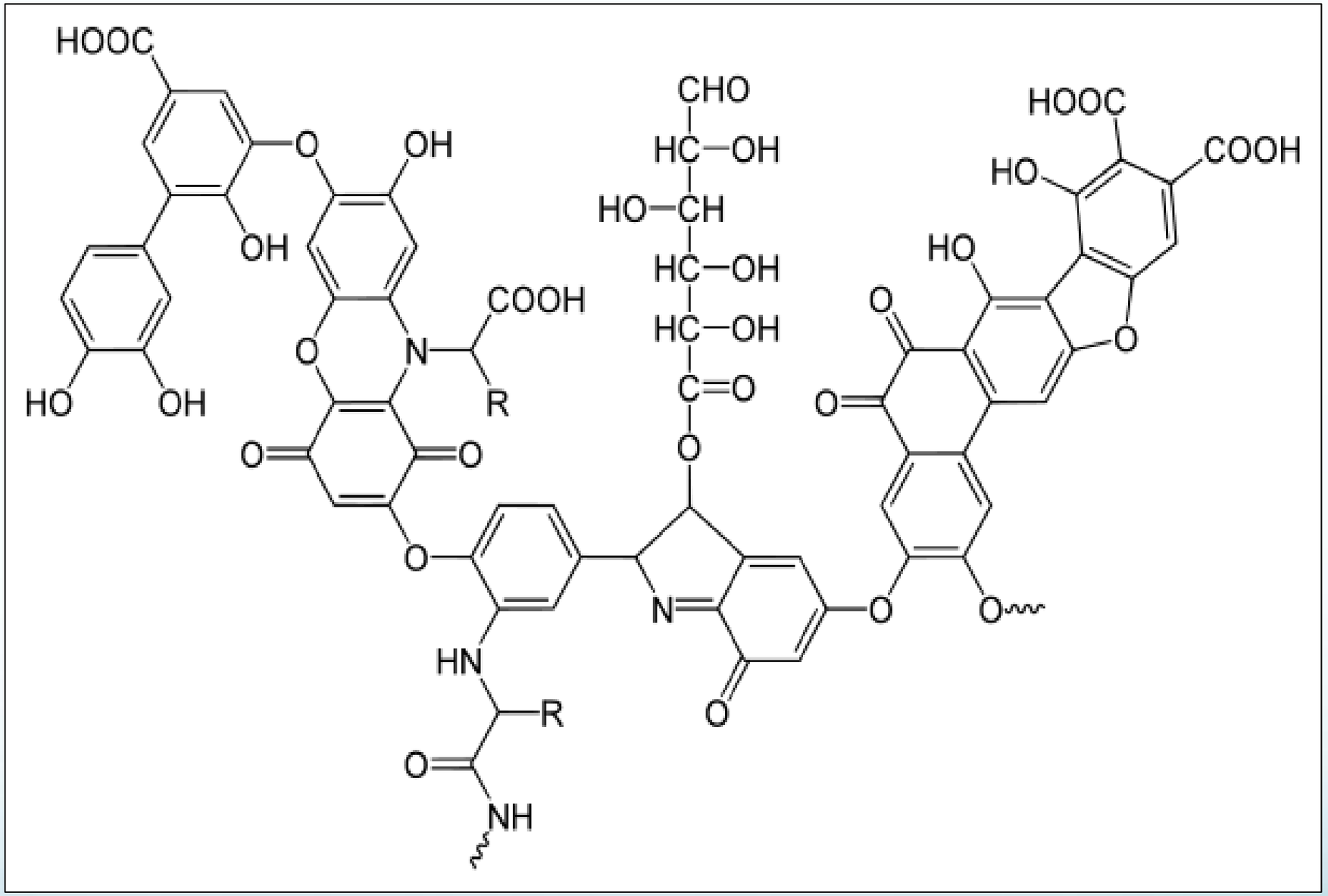
Organic matter consumes persulfate too

$$(NH_2)_2CO + 8\ S_2O_8^{-2} + 18\ OH^- \rightarrow 2\ NO_3^- +$$

$$CO_2 + 16\ SO_4^{-2} + 11\ H_2O$$

About 100 ppm C upper limit

A Humic acid molecule



Particulates consume persulfate and are hard to sample

~ 15 - 20% N attached to particulates

Particulates > ~ 30 ppm TSS N/A by CFA

Non quantitative transfer of particulates to HTCO

Fe^{+2} to Fe^{+3} = 1 e^{-}

Total Phosphorus Digestion Methods

Acid Persulfate (beaker or autoclave)

Kjeldahl (block digestion)

Both convert inorganic and organic phosphorus to orthophosphate

Acid persulfate digestion for total P can be done in a beaker, autoclave, or test tubes

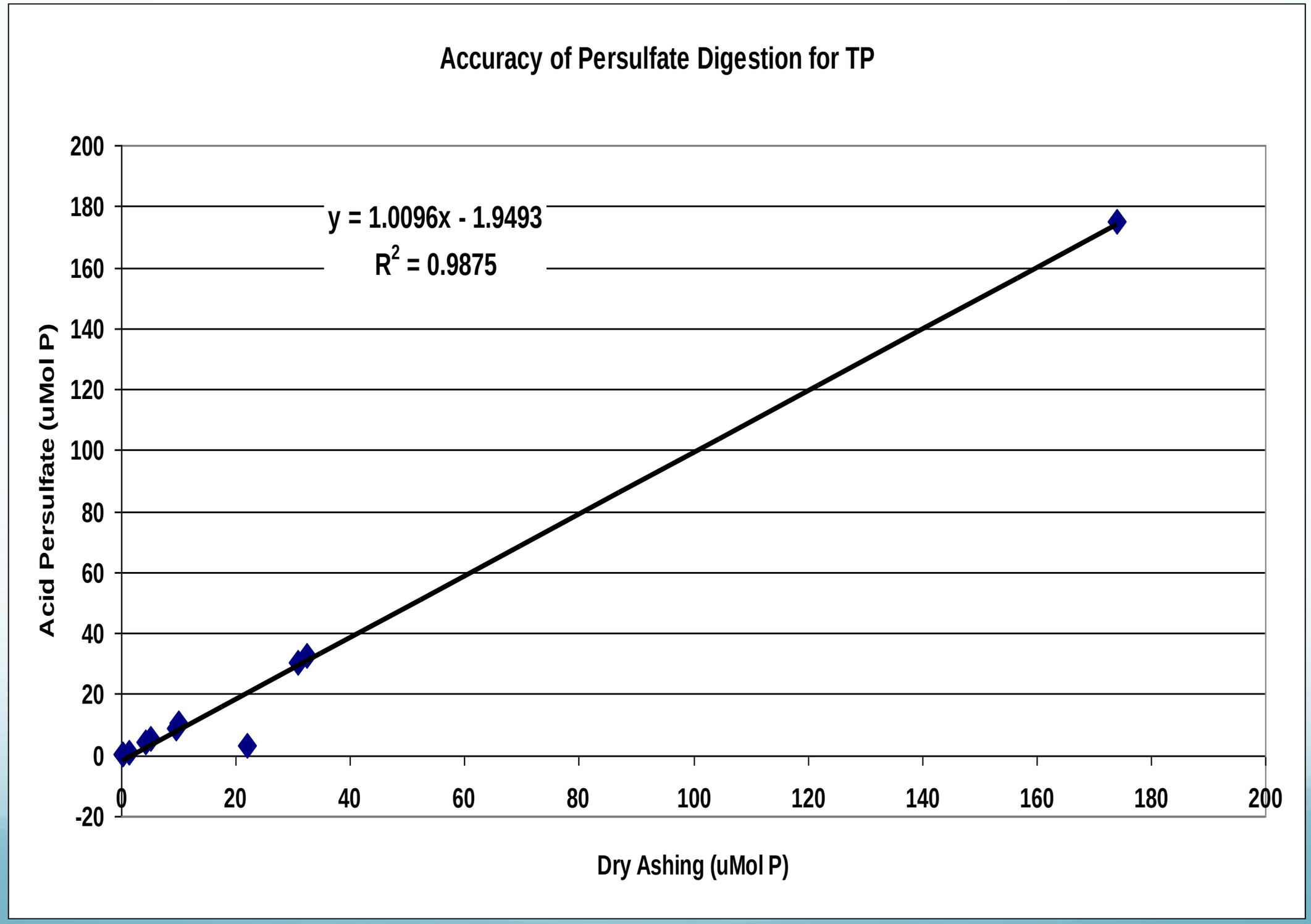
Acid Persulfate Digestion

- R-HPO4 + $S_2O_8^{-2}$ + H2SO4→ H3PO4 + nCO_2 + nHSO_4^- + n H_2O

Colorimetry

- Any Phosphate method

Comparison of Dry Ashing and Acid Persulfate for Total P



Outlier data on persulfate and wet oxidation comparison for TP digestion

Material tested	Dry Ash uMol P	Persulfate uMol P
Montmorillonite	1.44	1.00
Kaolinite	22.0	3.04

Suzamura, Limnol. Oceanogr. Methods 6 2008, 619-629

Potential problems with acid persulfate digestions for total phosphorus

Too much acid

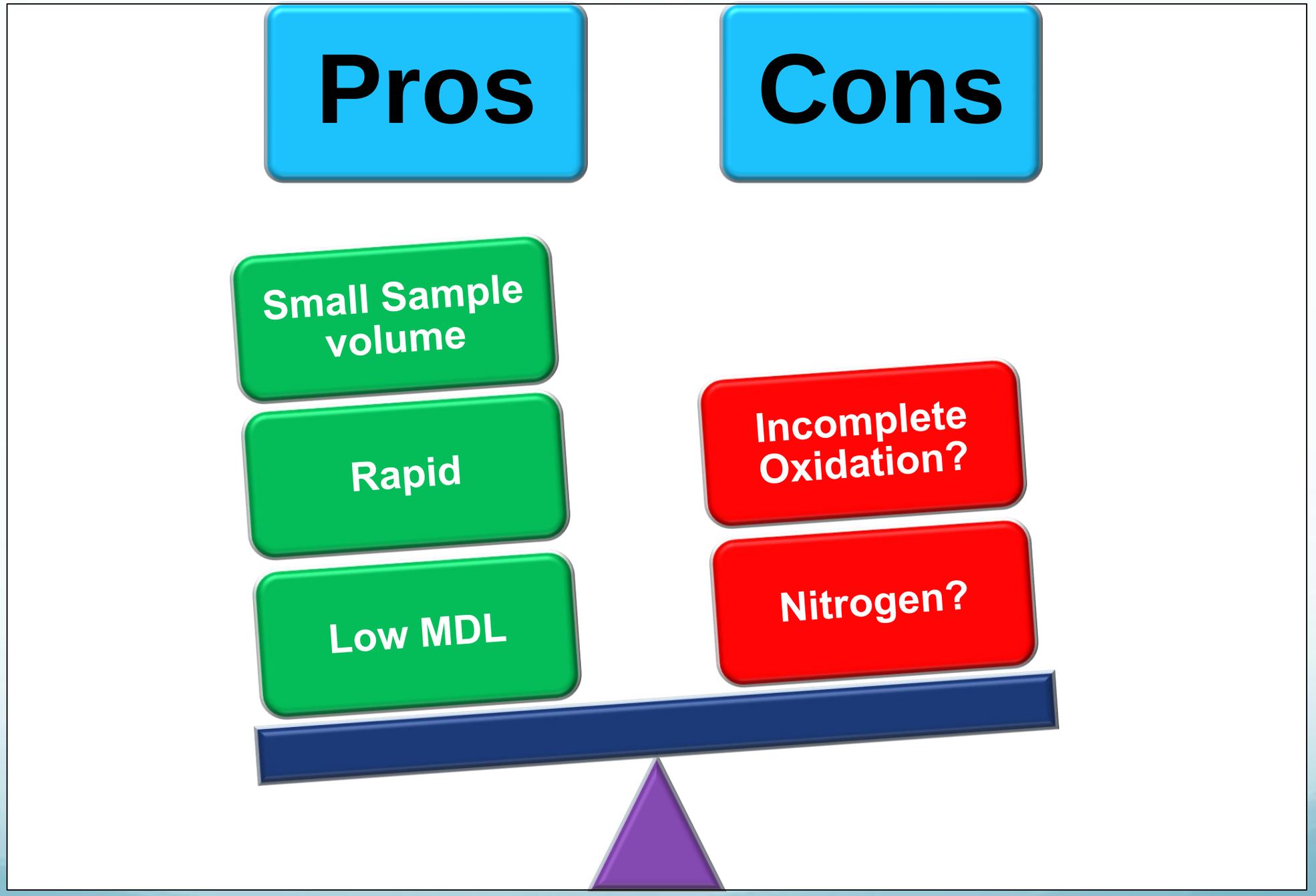
High chloride

Organic Matter

Excess particulates

Contamination

Advantages and disadvantages of manual acid persulfate methods for TP



“Kjeldahl” Digestion for TP

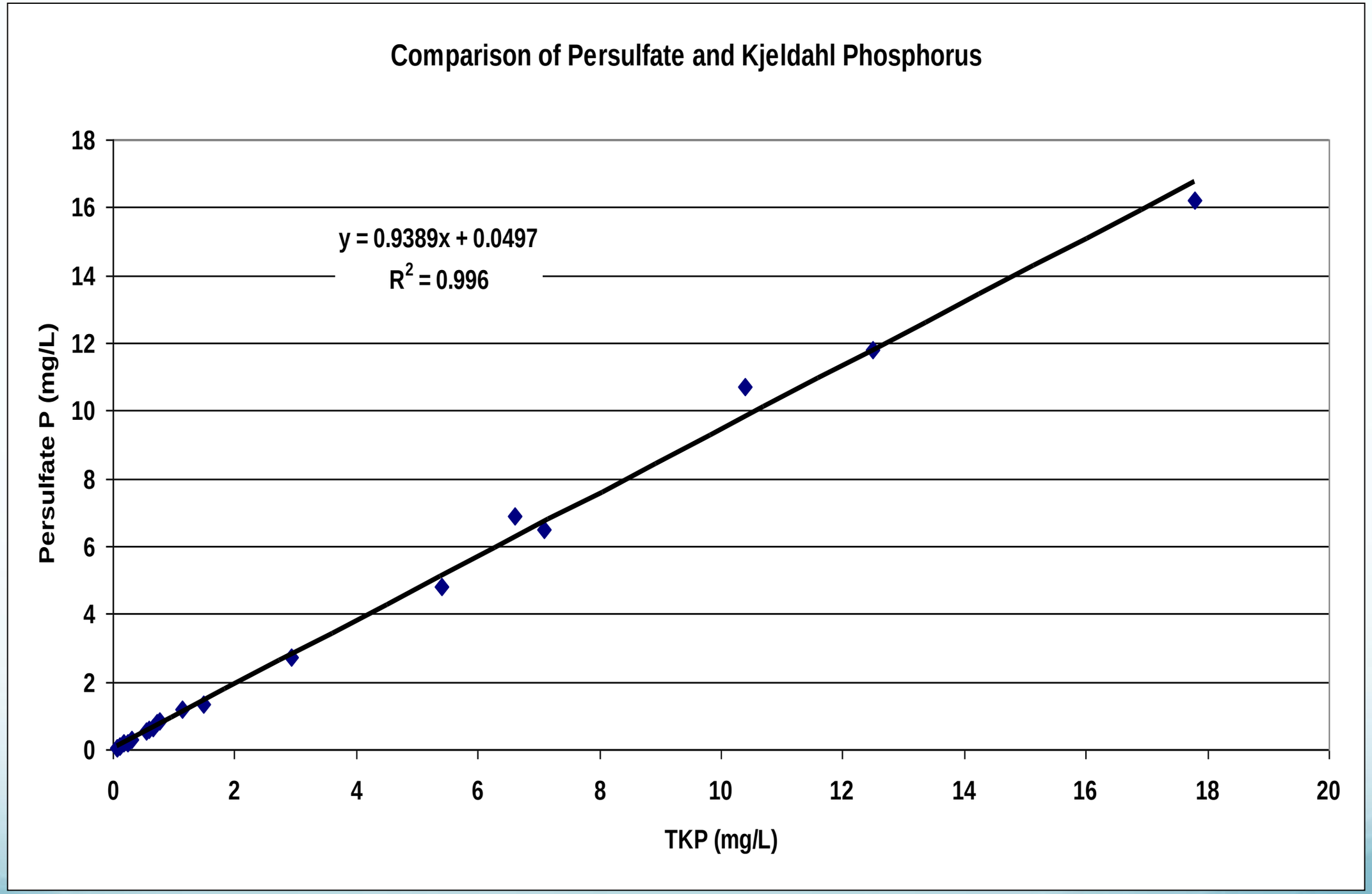
Kjeldahl Digestion

- R-HPO4 + H2SO4→ H_3PO_4 + nCO_2 + nSO_2 + n H_2O + H_2SO_4
- Contains catalyst

Colorimetry

- Any Phosphate method
  - High Acid concentration
  - Catalyst

Comparison of persulfate and Kjeldahl for TP



Potential problems with Kjeldahl digestions for total phosphorus

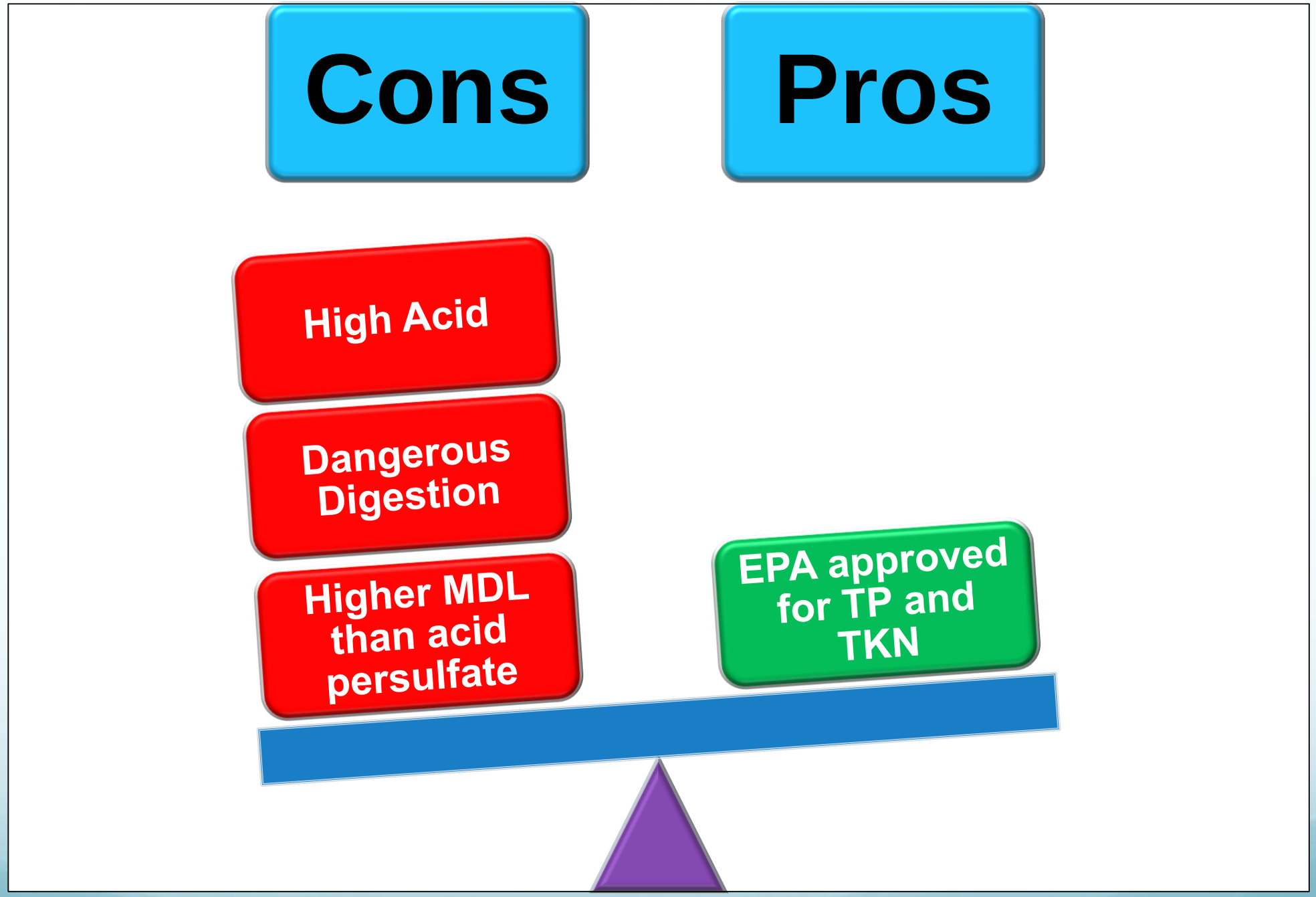
High Acid Concentration

Hazardous Digestion

Catalyst

May require dilution of acid

Advantages and disadvantages of manual acid persulfate methods for TP



Using USGS I-4690-91 to overcome problems with normal Kjeldahl phosphorus methods

Uses Dialysis

includes On-line dilution

Includes On-line filtration

Controls acid concentration

Low Detection Limit

Alkaline Persulfate Digestions for Total P

Manually digest

Determine PO_4^{-3}

Measures TP

Manual Alkaline Persulfate Digestion for TP

Alkaline Digestion

- $R\text{-}HPO_4$ + excess $S_2O_8^{-2}$ + 18 OH^- → H_3PO4 + CO_2 + HSO_4^{-2} + n H_2O

Colorimetry

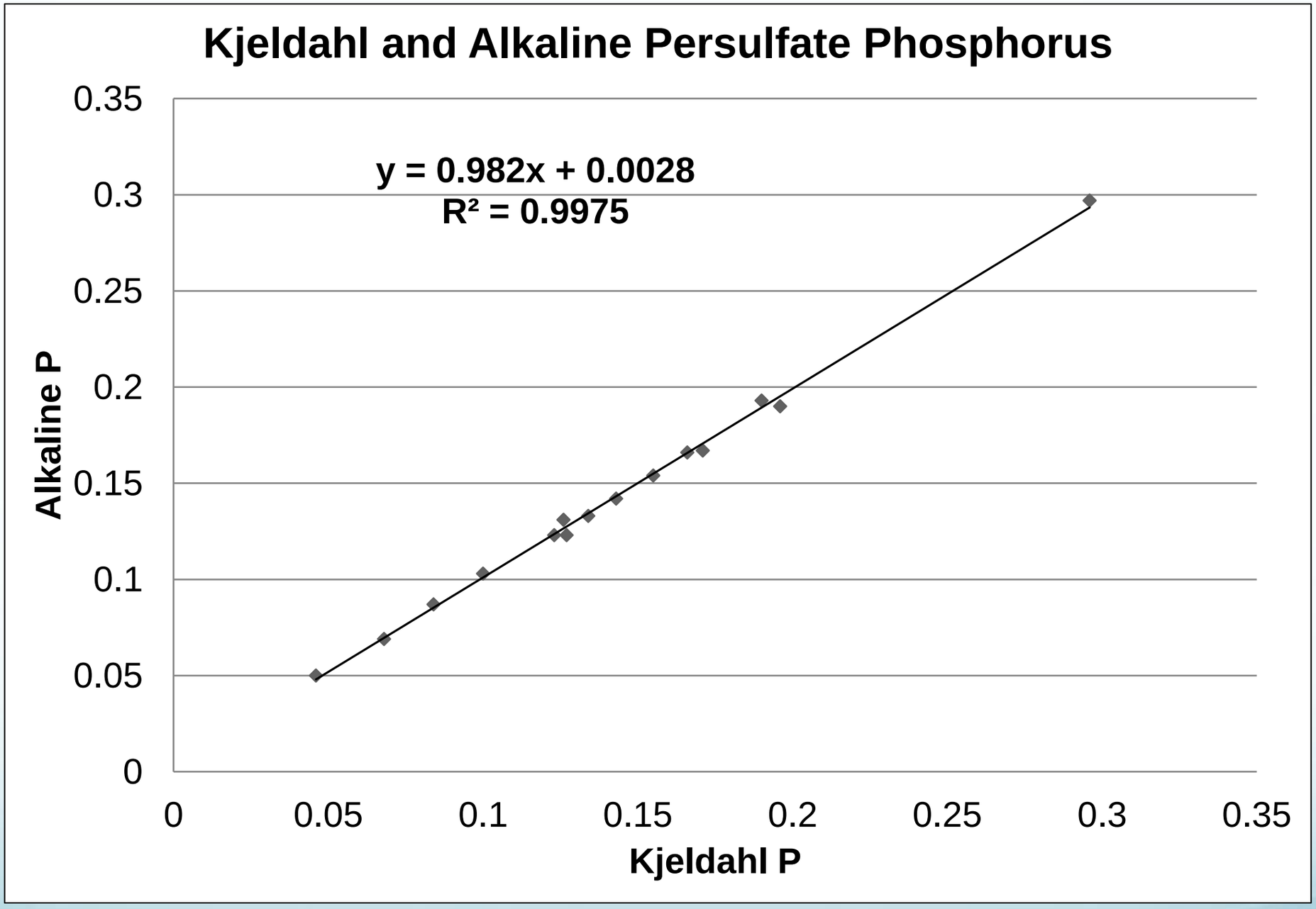
- Any phosphate method

Comparison of Alkaline Persulfate and Acid Persulfate Total Phosphorus

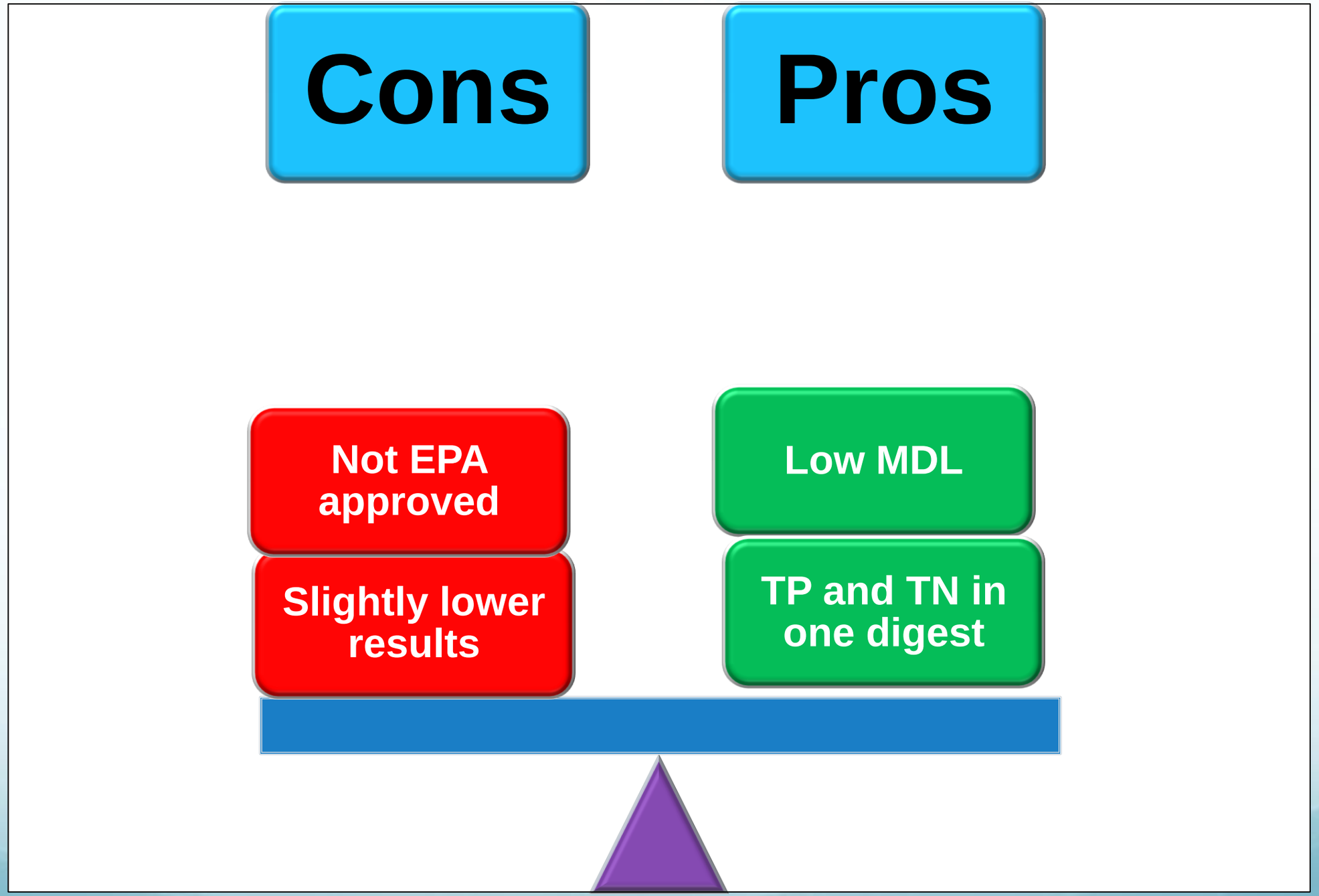
Compound	Alkaline (mg/L P)	Acid (mg/L P)
Adenosine tri-phosphate (ATP)	0.166	0.176
Glycerophosphate	0.196	0.204
Phenyl Phosphate	0.168	0.179
Phytic Acid	0.177	0.180

USGS Water Resources Investigative Report 03-4174 (2003)

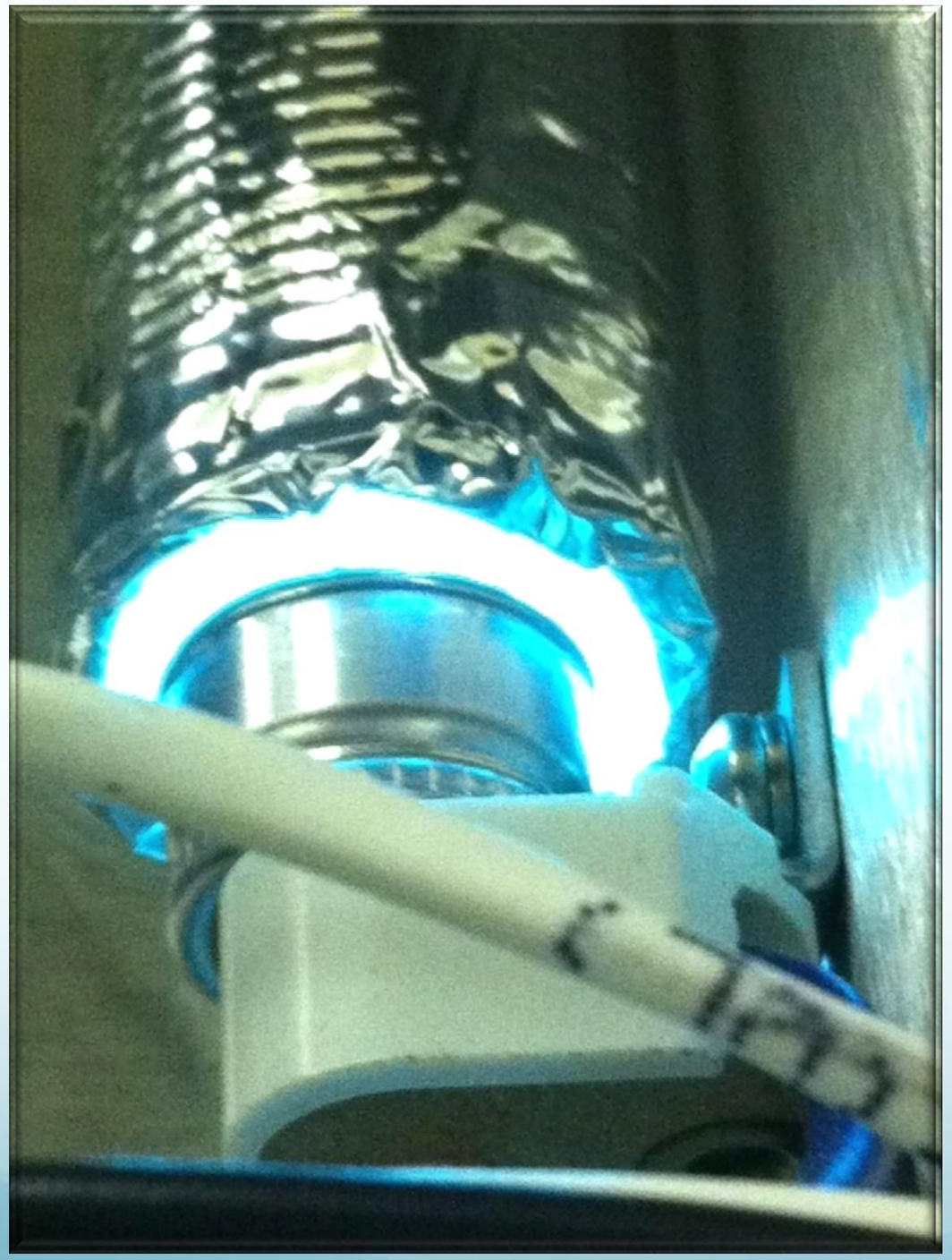
Comparison of TKP and Alkaline Persulfate



Advantages and disadvantages of manual Alkaline persulfate method for TP



Automated Alkaline UV Persulfate Digestions

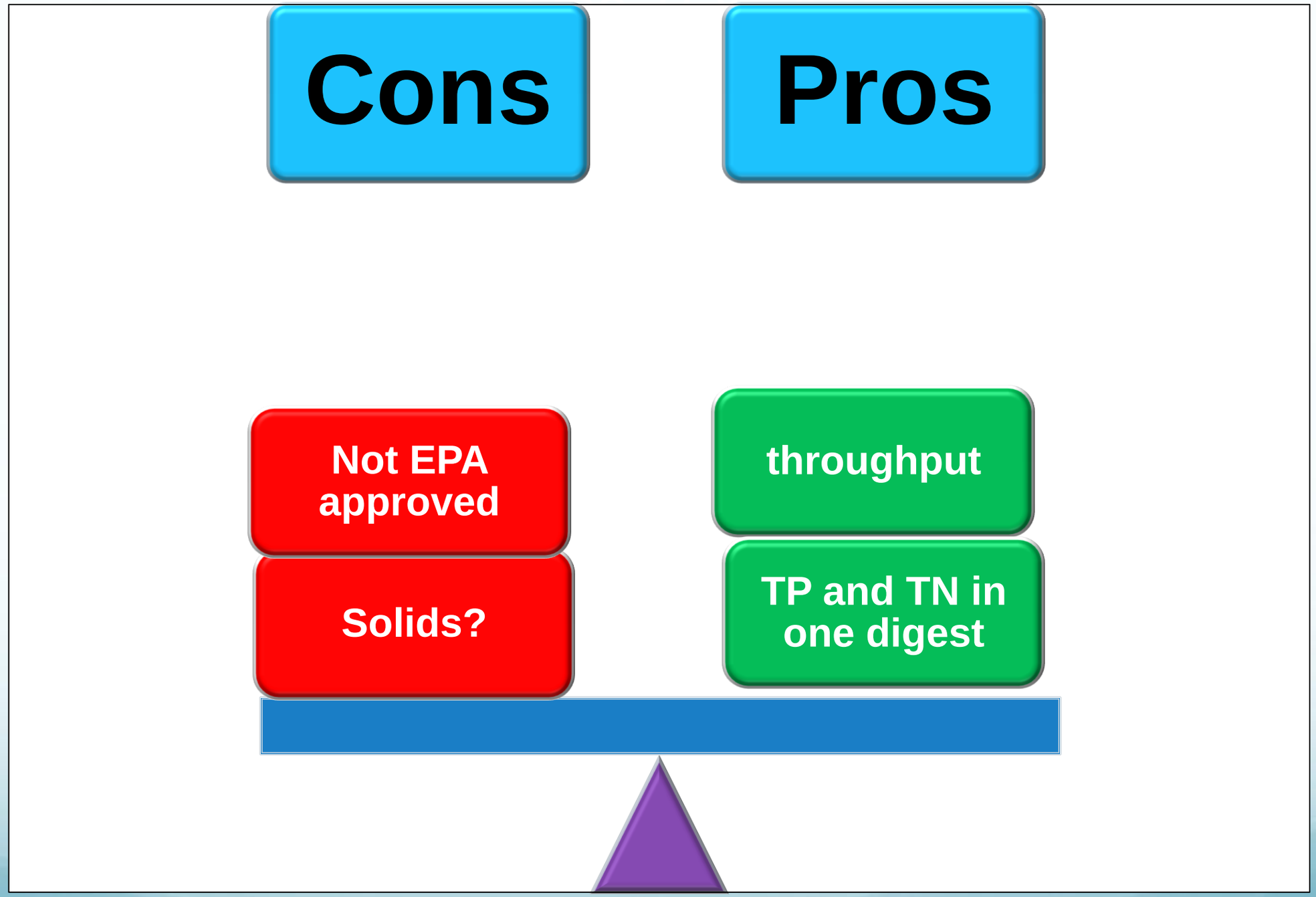


Automated digest

Determine PO_4^{-3}

Measures TDP

Advantages and disadvantages of automated persulfate method for TP



Thank You!!

William Lipps
OI Analytical
William.lipps@xyleminc.com