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ASTM D19 Method Validation Procedures

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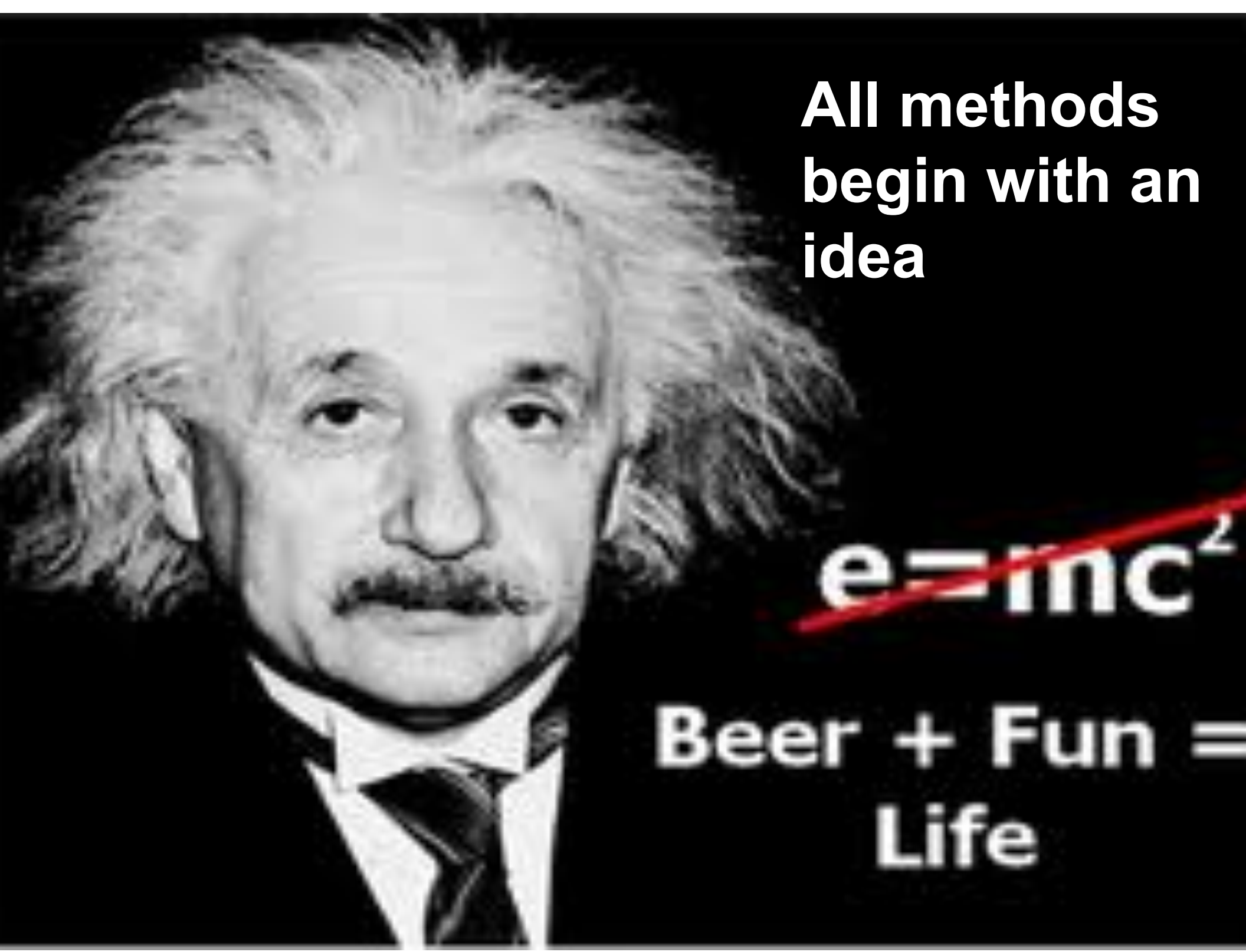
- **This presentation is the opinion of the author.**
- **The author is a volunteer member of ASTM**


All methods begin with an idea
e=mc²
Beer + Fun =
Life

An idea can be introduced by anyone at a sub committee meeting

- Determine if new standard is needed
- Identify and gather key stakeholders
- Appoint a Task Group Chair
- Register a Work Item
- Subcommittee decides on title and scope

By registering as a Work Item, ASTM:

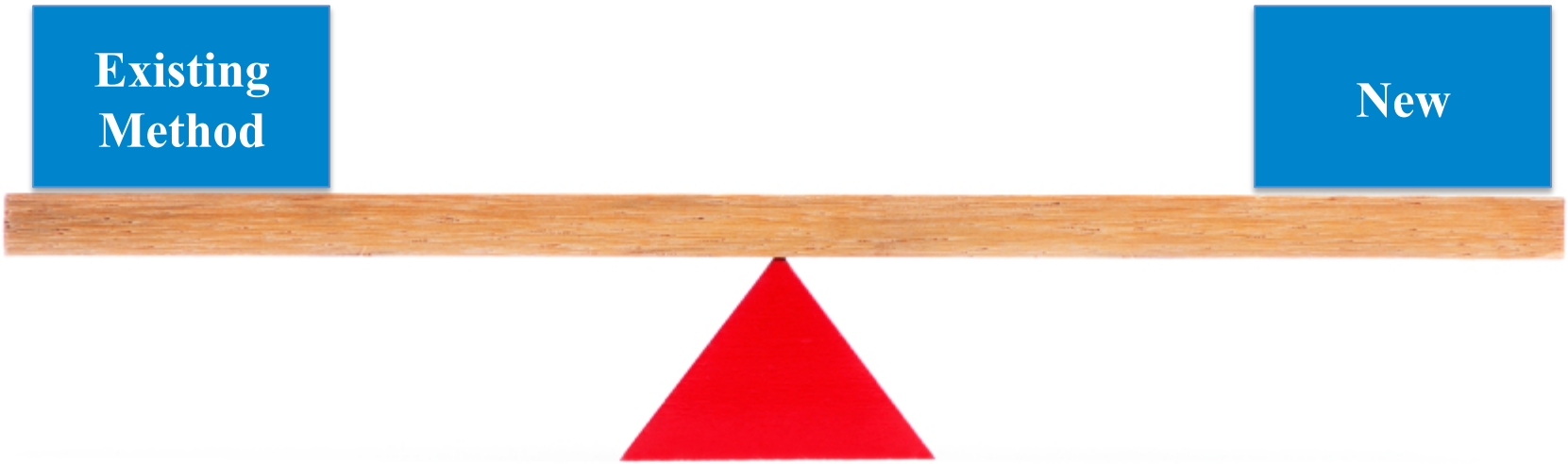
- Provides a tracking number, “WK5432”
- Alerts other members
- Initiates a time table and process

In this presentation we are referring to “Standardized ” Methods

- **Technique**
  - Scientific Principle, such as GCMS
- **Method**
  - Adaptation of a technique to a measurement problem
- **ASTM Method**
  - A method of known precision issued by ASTM

Validation of methods that measure the same analyte as other methods needs to establish:

- Equivalency
  - Same result as approved method (interference free)
  - Same QC
  - Same detection (wet chemistry)
  - Same extraction (GC)



Validation of the method must include

- Calibration
- MDL
- DOC
- Single Lab Study (matrices)
  - Precision
  - Spike Recoveries
- Multi-Lab study
  - Precision

Validation of a New Method

- Preliminary Literature Search
- Design Phase
- Development Phase
- Validation Phase
- Evaluation Phase

The design phase occurs before significant amounts of data are collected:

- Literature search
- Draft “method”
  - Scope
  - Summary
  - Technique
  - Matrices
  - Concentration Range (estimate)

  - Optional vote at Subcommittee level

The Development phase collects preliminary data

- Single or two lab studies
  - Proof of concept
  - “preliminary data”

- Vote at Subcommittee level

The Validation phase includes collection of the following information:

- **Selectivity**
  - Correctly ID analyte in matrices
- **Calibration**
  - Technique and model
- **Repeatability**
  - At a range of concentrations
  - In numerous matrices
- **Bias**
  - Compare to known matrices
  - Spike samples
  - Compare to other techniques
- **Ruggedness**
  - What can change results

Before an inter-laboratory study is carried out the draft must pass subcommittee balloting

- Evaluation Phase
  - Prefer 9 labs
  - Prefer 9 matrices for CWA
  - Minimum 3 matrices for SDWA
  - 3 Youden Pairs (optional)

Validation of ASTM D7781 Test Method For Nitrite-Nitrate in Water by Nitrate Reductase

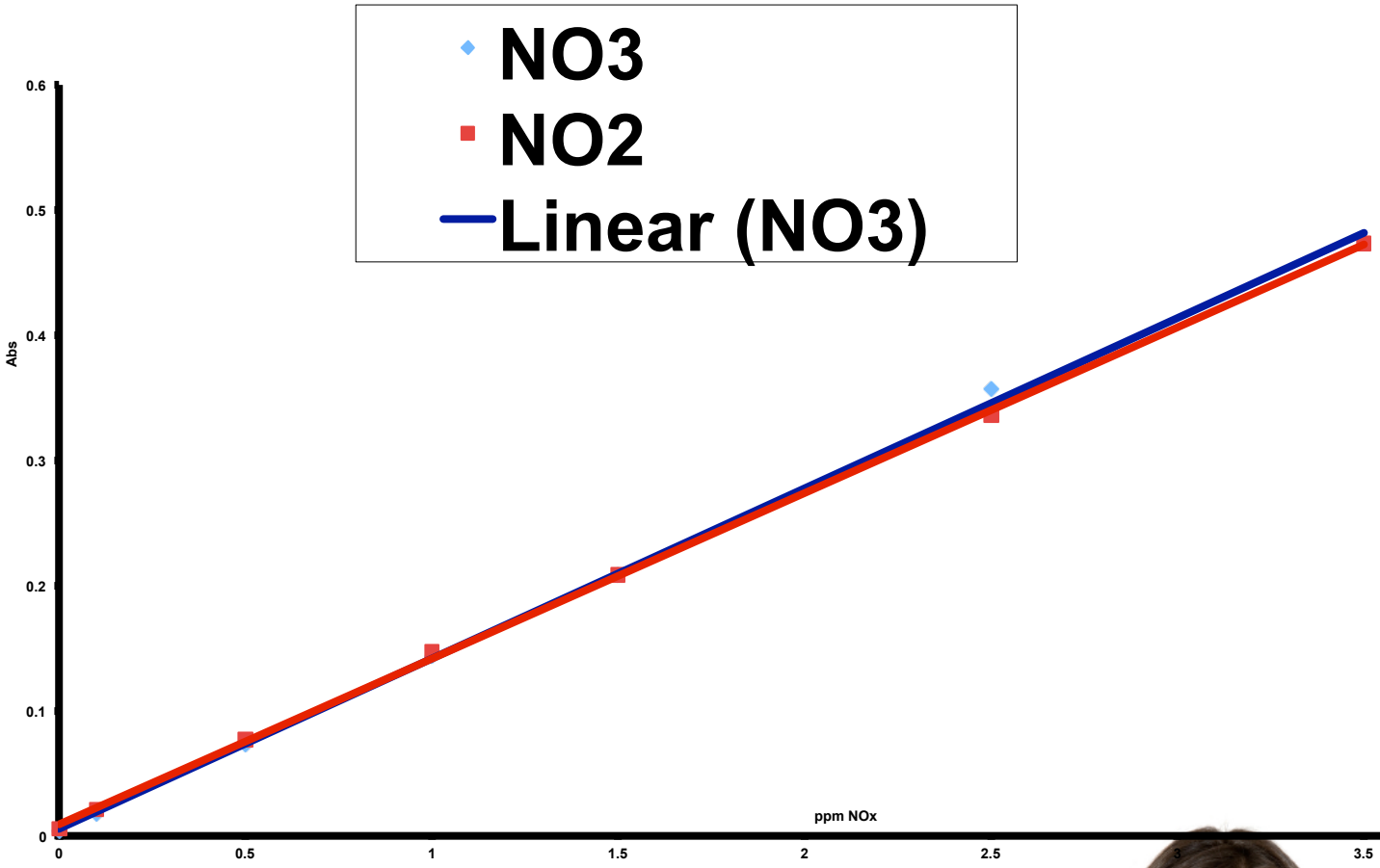
- **Literature Search - justification**

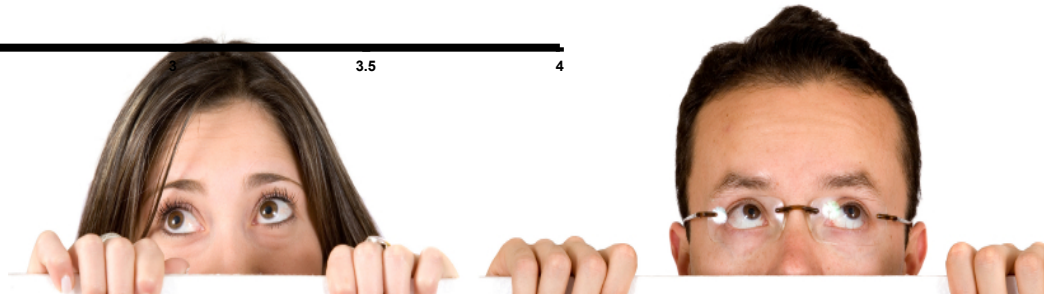
  Analytical methods using nitrate reductase have been previously reported,[11] however, these investigators limited testing to surface and ground waters without evaluating complex matrices such as wastewater

A specific “technique” was chosen

- This new ASTM nitrate method is a discrete analyzer method.
- Discrete analyzers are defined in the standard

Selectivity was verified by showing nitrite and nitrate are recovered equally





Comparison with another method and evaluation of preservatives was made

Sample #	Commercial Laboratory Results, Analysis Method EPA 335.2 (mg NO_3+NO_2-N/L)	Analysis by Reductase (mg NO_3+NO_2-N/L)	Analysis by Reductase (mg NO_3+NO_2-N/L) Non-Preserved
1	0.8	0.94	0.88
2	<0.1	0.05	0.06
3	<0.1	0.24	0.55
4	0.66	0.68	0.58
5	11.8	11.6	Lost
6	0.78	0.79	0.77
7	2.4	3.11	2.88

Since the method is for an existing EPA pollutant (nitrate plus nitrite) with established sampling and preservation guidelines, D19.05 did not perform a holding time study.

Potential interferences were evaluated (partial list)

Species	Added (mg/L)	Unspiked Sample Result (mg/L)	Spiked Sample Results (mg/L)	Spike Added (mg/L)	% Recover
Cl^-	500	0.02	0.23	0.200	105
		0.17	2.54	2.50	95
F^-	500	0.01	0.22	0.200	105
Br^-	500	<0.01	0.21	0.200	100
		0.15	2.65	2.50	100
PO_4^{-3}	500	0.01	0.22	0.200	105
		0.14	2.54	2.50	96
SO_4^{-2}	500	<0.01	0.21	0.200	105
		0.14	2.53	2.50	96

Inter-Laboratory study carried out after successful subcommittee ballot

- 10 laboratories
- Four different discrete analyzer manufacturers
- One manufacturer had several different models

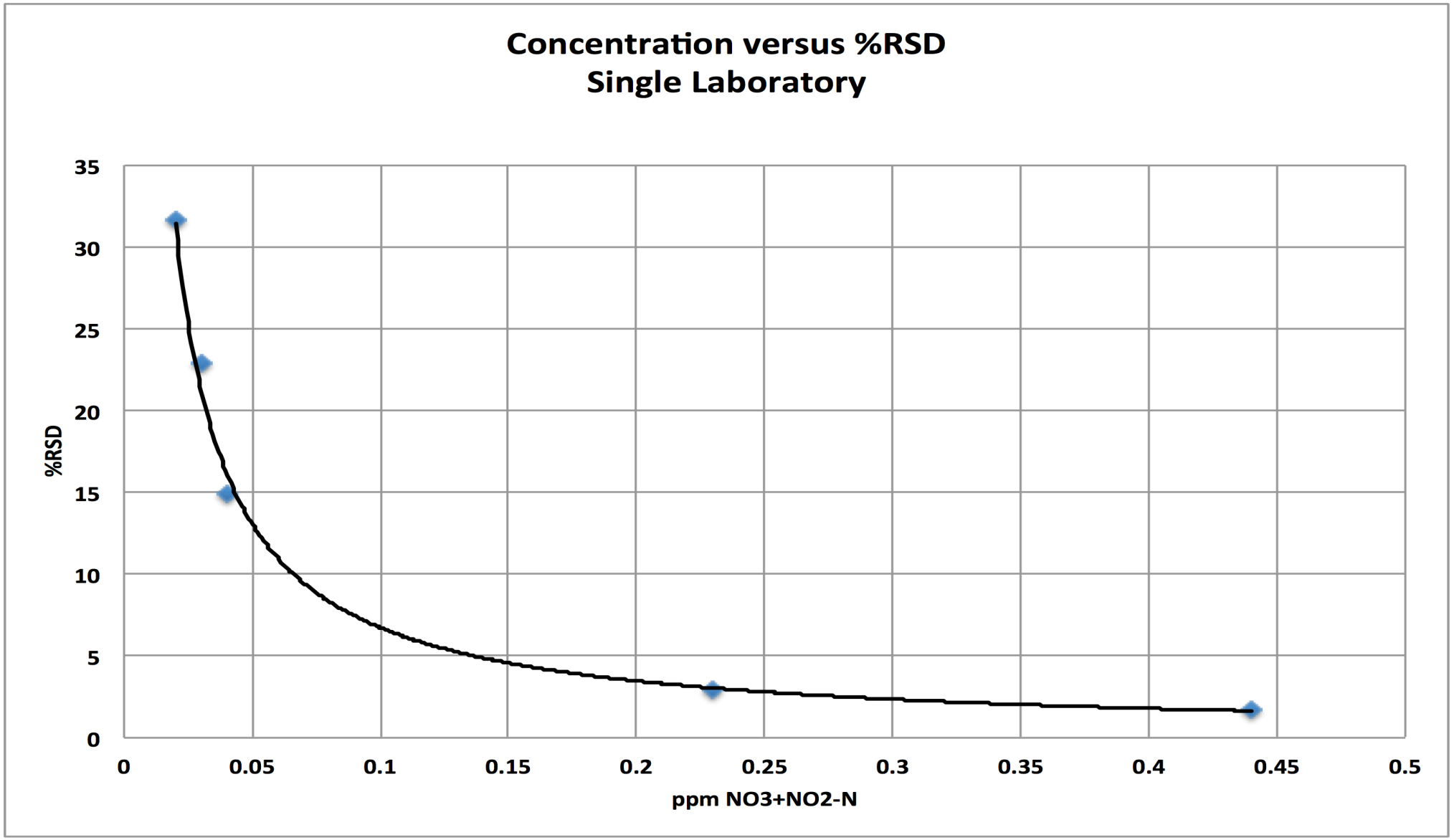
Each lab calculated reduction efficiency

Lab	Mg/L NO2-N (Found)	Mg/L NO3-N (found)	% Efficiency
1	2.46	2.51	102
2	2.45	2.48	101
3	2.38	2.55	107
4	2.22	2.59	117
5	2.48	2.62	106
6	2.46	2.56	104
7	2.42	2.51	104
8	2.43	2.49	102
9	3.04*	3.00	98.7
10	2.48	2.60	105

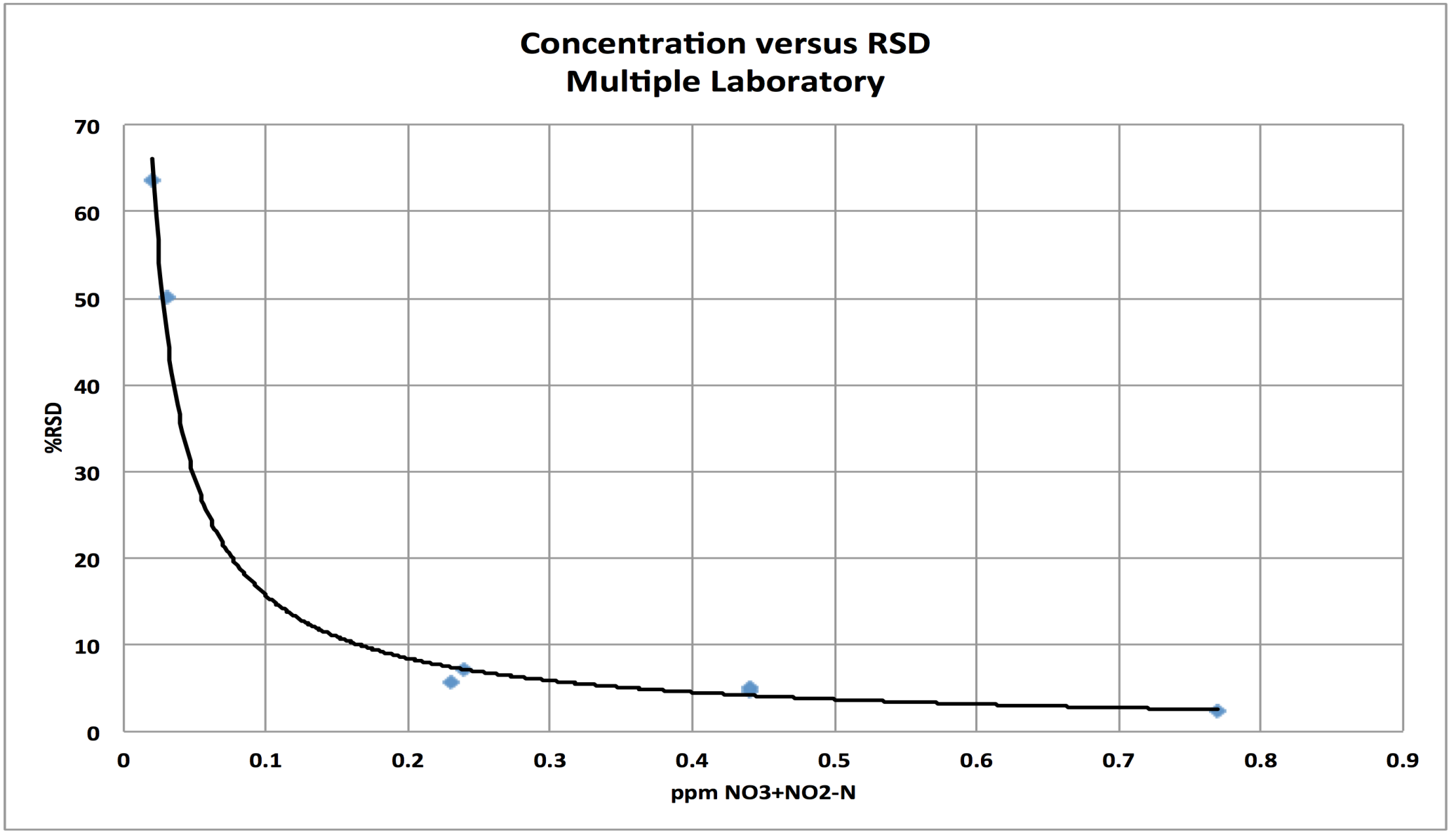
Each lab evaluated an LCS and control limits were established

average	101	1.23
Standard Deviation	2.66	0.67
Lower Limit (99% CI)	92.9	0
Upper Limit (99% CI)	109	3

Single Lab precision was plotted



Multiple Lab precision was plotted



ample atrix	Mean (mg/ L)	Standard Deviation	No. of Laboratories	No. of Results	Multi-laboratory %RSD
igh TDS 00 ppm)	0.77	0.02	5	35	2.28%
igh TOC (2 ppm)	1.12	0.02	5	35	1.36%
RA #698 WS	6.59	0.17	4	28	2.51%
SGS 116	0.44	0.02	6	42	5.09%

Sample Matrix	Mean (mg/L)	Standard Deviation	No. of Results	Single Operator %RSD
WW treatment	0.03	0.0131	30	22.9%
reatment plant ffluent #1	7.73	0.3181	30	1.03%
reatment plant ffluent #2	0.23	0.0126	30	2.92%
Paper Mill waste tream effluent	0.04	0.0156	30	14.9%
netal finisher vastewater effluent	273	10.234	24	24.3%
ommercial laundry vastewater effluent	4.90	0.2123	30	13.3%
ERA #507 Hardness	0.02	0.0144	30	36.8%
Confined Animal Feeding Operation CAFO) effluent	13.9	0.4623	30	12.6%
Low Nutrient Seawater	0.02	0.0112	30	31.7%

ASTM method validation procedures produce methods of defined precision and accuracy

Thank You, for more information contact me

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