Better Chemistry, Better Work with Flow Injection Analysis

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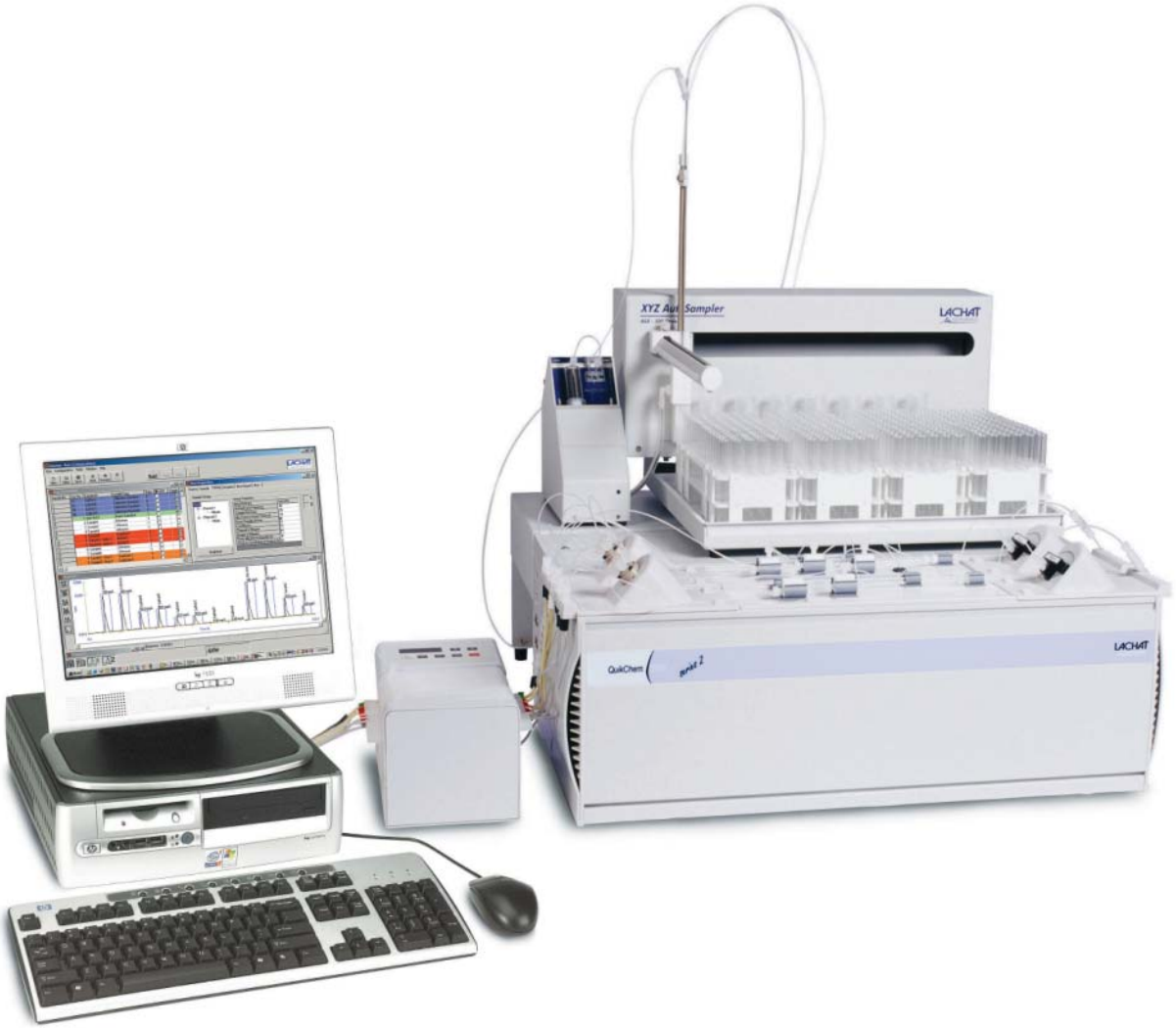
Introduction

- Advantages of Laboratory Automation
  - Increased throughput / productivity
  - Improved precision and accuracy
  - Simplification of Data Quality Management, data integrity, and audit trails
  - Decreased detection levels / sensitivity
  - Simplify difficult and time consuming manual extractions

Automation = Better Chemistry

Simplification with Automation



Simplification thru Automation

- **Extractions:**
  - In-line Extraction Application for Anionic Surfactants
- **Distillations:**
  - In-line Distillations for Phenolics, Cyanide, Sulfide, Ammonia, and TKN digests
- **Digestions:**
  - In-line Digestions for Total Nitrogen, Total Phosphate, Total Cyanide

Simplification thru Automation

- **Anionic Surfactant Extraction**
  - In-line chloroform extractions where ~ 30 samples can be analyzed per hour.
  - Lachat offers a dual and single in-line extraction. The dual extraction involves an alkaline and acidic extraction to remove the positive interferences from inorganic anions, such as nitrate and chloride.

Simplification thru Automation

- **Anionic Surfactant Extraction**
  - The manual surfactant extraction takes approximately 1 HOUR per sample or standard to extract and analyze.
  - Plus, multiple extractions are needed for each sample before being analyzed. This involves having multiple separatory funnels and consuming more reagents.
  - With Lachat's automated in-line method you can analyze 24 samples per hour.
  - Reagent consumption with the in-line method is very low:

    Methylene Blue = 7.5 mLs per sample

    Chloroform = 3.6 mLs per sample

Simplification thru Automation

- **In-line Distillation for Phenol, Cyanide, Sulfide, Ammonia and TKN Digests**
  - The sample is mixed with a releasing solution (acid or base), heated and distilled in-line. The distillate is then measured colorimetrically or amperometrically (CN^-).

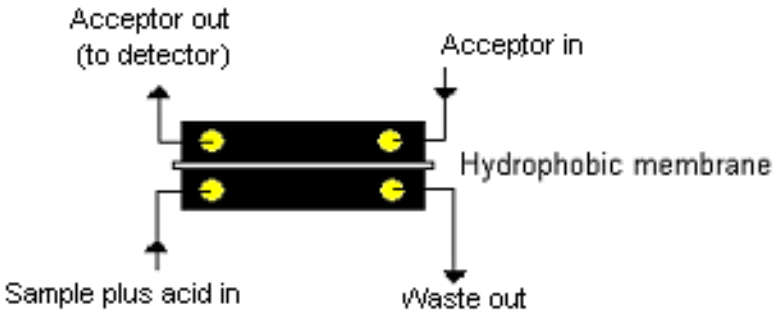
Simplification thru Automation

- **In-line Distillation for Phenol, Cyanide, Sulfide, and Ammonia**

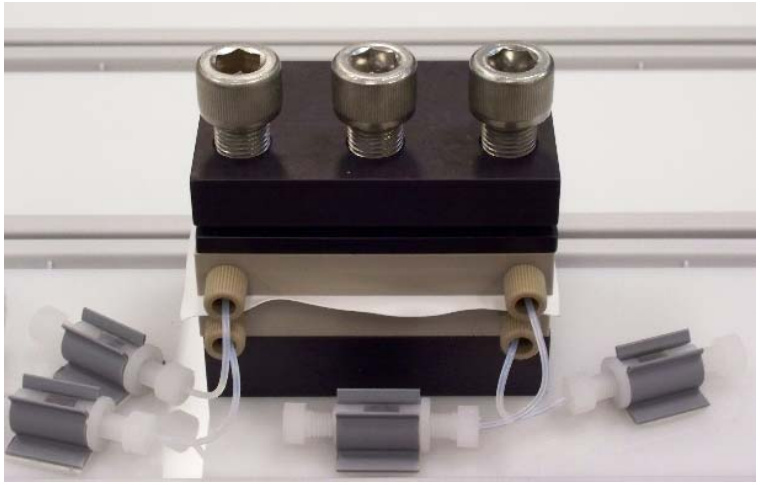
Analyte	Duration of Manual Distillation	Duration of In-Line Distillation And Analysis
Phenol	90 minutes per sample	5 minutes per sample
Cyanide	30 minutes per sample	5 minutes per sample
Sulfide	30 minutes per sample	4 minutes per sample
Ammonia	30 minutes per sample	3 minutes per sample

Simplification thru Automation

- Ammonia In-line Distillation
  - In-line ammonia distillation uses heat and a borate buffer to convert ammonia gaseous phase. In the diffusion cell the gas passes over the hydrophobic membrane into a dilute sulfuric acid acceptor solution. The distilled sample then reacts colorimetrically on the FIA manifold by either the phenolate or salicylate method. Simple, and no consumables other than the diffusion membrane.



Gas Diffusion Block



Simplification thru Automation

- **In-line Digestions for Total Nitrogen, Total Phosphate**
  - The sample is mixed with a digestion solution, heated, then irradiated by passing over a UV lamp. The digested sample is then measured colorimetrically.

Simplification thru Automation

- **In-line Digestions for Total Nitrogen, Total Phosphate**

Analyte	Duration of Manual Digestion	Duration of In-Line Digestion And Analysis
TN	30 minutes per sample	1.5 minutes per sample
TP	30 minutes per sample	1.5 minutes per sample

Simplification thru Automation

In-line Persulfate digestion for TP and TN:

- The in-line digestion for TP and TN save time and money
  - No need for separate digestion block or autoclave
  - No sample preparation; autosampler draws up sample, pumps it through the digestor, then injects it for the analytical measurement
  - For wastewater testing, these applications can be used for reporting through the MUR (Method Update Rule)

Simplification thru Automation

In-line Persulfate digestion for TN:

Waters

Method Number	Range, mg N/L	MDL, mg N/L
10-107-04-3-A	0.2 – 2.0	0.0056
10-107-04-3-B	0.5 – 30.0	0.1
10-107-04-3-C	0.5 – 10.0	0.011
10-107-04-3-D	Low Range: 0.05 – 5.0 High Range: 0.2 – 20.0	LR – 0.003 HR – 0.008
10-107-04-3-P	0.2 – 10.0	0.05

Brackish waters

Method Number	Range, mg N/L	MDL, mg N/L
31-107-04-3-A	0.1 – 1.0	0.005
31-107-04-3-B	0.5 – 5.0	0.078

Simplification thru Automation

In-line Persulfate digestion for TP:

Waters

Method Number	Range, mg P/L	MDL, mg P/L
10-115-01-3-A	0.1 – 10.0	0.007
10-115-01-3-B	0.1 – 4.0	0.01
10-115-01-3-C	0.05 – 1.0	0.0011
10-115-01-3-E	0.01 – 0.5	0.0014
10-115-01-3-F	0.002 – 0.10	0.00042

Brackish waters

Method Number	Range, mg P/L	MDL, mg P/L
31-107-04-3-D	0.05 – 1.0	0.002
31-115-01-3-F	0.002 – 0.10	0.00059

Simplification thru Automation

- **Lachat's multiple Sample Processing Modules (SPM) allow for analyte subtractions.**
  - Nitrate/Nitrite analysis: On one SPM measure combined nitrate/nitrite, on a subsequent SPM measure nitrite; subtract the nitrite from the combined form to report nitrate alone.

Simplification thru Automation

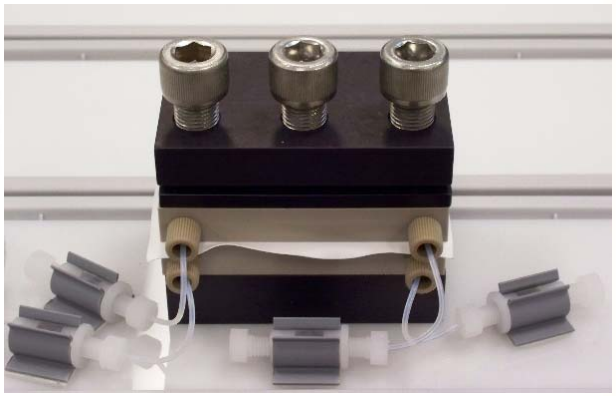
- **Lachat's multiple Sample Processing Modules (SPM) continued:**
  - Determination of free ammonia in chloraminated sample. Free ammonia + monochloramine are analyzed on the first SPM and monochloramine on the second SPM. By subtracting the NH_2Cl concentration from the combined NH_3 + NH_2Cl concentration, free NH_3 can be determined.

Simplification thru Automation

- **Lachat's multiple Sample Processing Modules (SPM) continued:**
  - Subtract out background color from your samples:
    - If your samples are colored, analyze your regularly, then on the subsequent SPM use the same exact manifold board plus reagents except for removing the color reagent. Subtract out the calculated concentration for the colored sample to achieve the analyte's true value.

Simplification thru Automation

Utilizing these in-line sample preparation steps save both the analyst's time and the laboratory money.



Simplification thru Automation

Cost Savings Compared to Manual Testing (Traditional Cuvette Tests)

Parameter	**Lachat Cost per test**	**Manual Cuvette Cost per test**
Ammonia	$ 0.034	$1.59
Nitrate	$ 0.014	$1.26
Ortho-phosphate	$ 0.019	$1.08
Total Phosphorus	$ 0.026	$1.59
Total Nitrogen	$ 0.021	$2.18

Costs for Lachat reagents are based on bulk ACS chemicals purchased from chemical manufactures. Manual cuvette tests are based on cost of specific reagent packages.

Green, Environmentally Friendly Applications

Lachat's Green Applications:

- Amperometric Cyanide
- Ion Chromatography
- Ultra Low Flow Applications
- UV Nitrate Reduction

Amperometric Detection for Cyanide

- Why use **Amperometric Detection**?
  - Cyanide, detected electrochemically:
    - Requires less reagents
    - Less labor
    - No hazardous pyridine or barbituric acid
      - Existing, accepted methodologies for cyanide are not only labor intensive, but require the use of hazardous compounds, such as pyridine and barbituric acid, a controlled compound, regulated in the U.S. by the D.E.A.

Amperometric Detection for Cyanide

There are a total of 5 cyanide methods, utilizing Amperometric Detection

Method Number	Range, µg CN^-/L	Comments
10-204-00-5-A	2-400	**Ligand Exchange**; Approximately equivalent to Cyanide Amenable to Chlorination (CATC)
10-204-00-5-B	2-500	**In-line total CN,** with UV Digestion. Recovers Ferricyanide and Ferro-cyanide
10-204-00-5-C	2-500	**Free Cyanide**
10-204-00-5-X	5-400	Used to measure **MicroDist™ Distillates** for **Total Cyanide**
10-204-00-5-WX	5-400	Used to measure **MicroDist™ Distillates** for **Weak Acid Dissociable Cyanide**

Ion Chromatography

- In addition to Flow Injection, Lachat Instruments also offers **Ion Chromatographic (IC)** methods
  - A patented software algorithm called the Shared Peripheral System (SPS) enables operation of FIA and IC simultaneously and independently on the same instrument
  - Alternatively, IC runs can be set to perform overnight, while FIA runs during the day!

Ion Chromatography

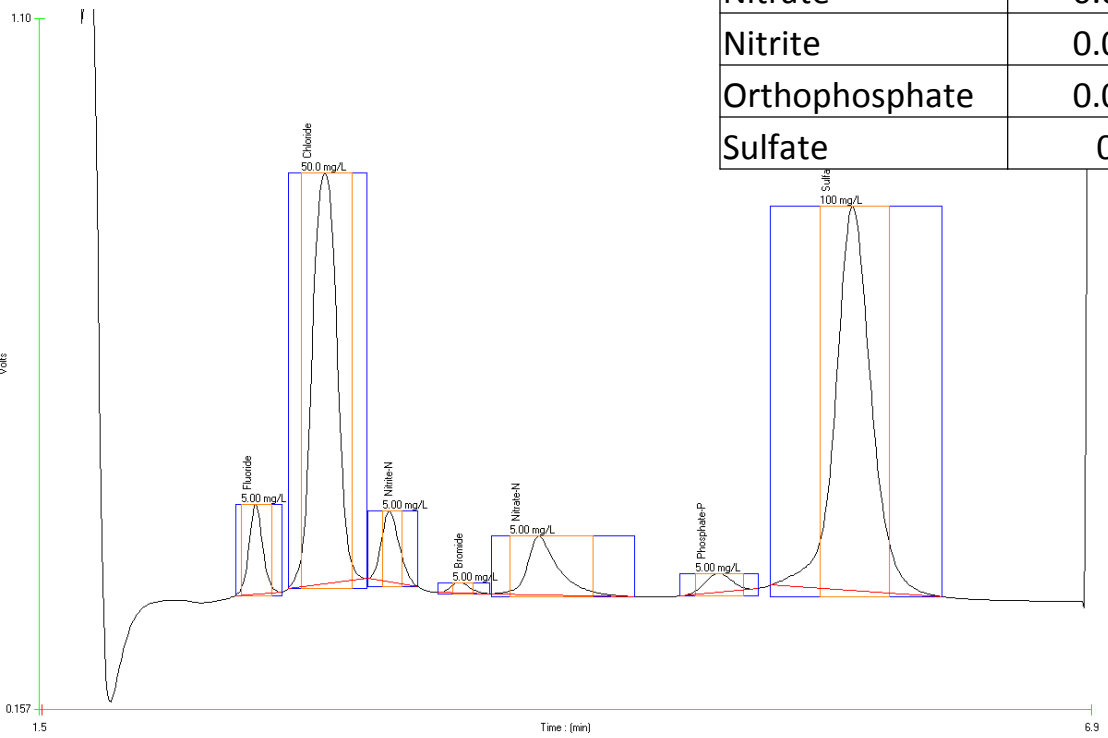
IC uses innocuous reagents that can be poured down the drain. Available applications:

- Anions
- Cations
- Disinfection By Products
- Organic Acids

Rapid Anions

Method number **10-510-00-1-E** allows separation of the seven common anions in about 7 minutes (dependent upon the ranges).

Analyte	Low Range, mg/L	Mid Range, mg/L	High Range, mg/L
Bromide	0.025 - 2.5	0.05 - 5	0.1 - 5.0
Chloride	0.015 - 25	0.5 - 50	2.0 - 100
Fluoride	0.025 - 2.5	0.05 - 5	0.2 - 10.0
Nitrate	0.025 - 2.5	0.05 - 5	0.2 - 10.0
Nitrite	0.025 - 2.5	0.05 - 5	0.1 - 5.0
Orthophosphate	0.025 - 2.5	0.05 - 5	0.2 - 10.0
Sulfate	0.5 - 50	1 - 100	4.0 - 200



Chromatogram of calibration standard A - Mid Range

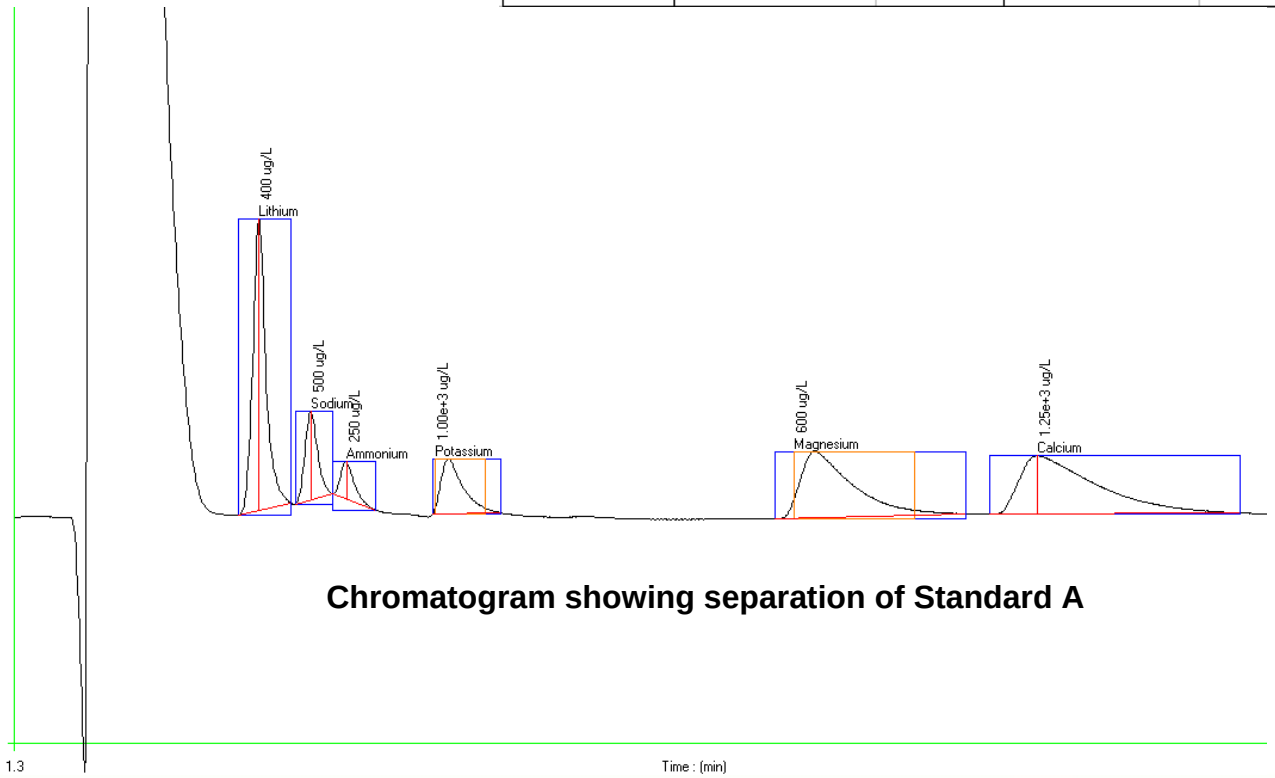
Time = 6.9 minutes

Method is an Acceptable Version of EPA 300.1 part A under NPDWR

Cations

Method number **10-520-00-1-D** allows separation of the six common cations in about 14 minutes (dependent upon the ranges).

Analyte	Range 1, **mg/L**	R1 MDL	Range2, **mg/L**	R2 MDL	Range 3, **µg/L**	R3 MDL
Lithium	0.25 to 10	**0.05**	0.05 to 1.0	**0.01**	8 to 400	**0.58**
Sodium	1.8 to 72	**0.4**	0.2 to 4.0	**0.04**	10 to 500	**1.44**
Ammonium	0.8 to 32	**0.14**	0.2 to 4.0	**0.045**	5 to 250	**3.49**
Potassium	1.6 to 64	**0.5**	0.2 to 4.0	**0.04**	20 to 1000	**5.74**
Magnesium	0.8 to 32	**0.13**	0.25 to 5.0	**0.05**	12 to 600	**2.6**
Calcium	1.6 to 64	**0.3**	0.25 to 5.0	**0.05**	25 to 1250	**7.44**



Chromatogram showing separation of Standard A

Ion Chromatography

Disinfection By Products

Analytical Range:

Chlorite - 5 to 50 μg/L

Bromate - 5 to 50 μg /L

Chlorate - 20 to 200 μg/L

Bromide - 10 to 100 μg/L

Method cycle period = 38 minutes

Organic Acids

Analytical Range:

3 to 300 mg oxalic acid/L

3 to 300 mg succinic acid/L or lactic acid/L

3 to 300 mg citric acid/L

3 to 300 mg formic acid/L

3 to 300 mg tartaric acid/L

3 to 300 mg acetic acid/L

3 to 300 mg malic acid/L

3 to 300 mg fumaric acid/L

3 to 300 mg malonic acid/L

4.5 to 450 mg adipic acid/L

Method cycle period = 22 minutes

Ultra Low Flow (ULF) Methods

- **ULF Methods** were developed to provide maximum efficiency in reagent usage
- Advantages:
  - 70%+ reduction in reagent consumption vs. traditional Lachat methods
  - Maintain efficient throughput of up to 60 samples per hour
  - Equivalent performance to other FIA methods (as well as to alternative techniques)

Ultra Low Flow (ULF) Methods

- Traditional vs. ULF methods
  - Example of reagent consumption advantages:

Parameter	Traditional Cyanide	ULF Cyanide	Traditional NO_x	ULF NO_x	Traditional Chloride	ULF Chloride
Methods	10-204-00-1-A 10-204-00-1-X	80-204-00-1-A 80-204-00-1-X	10-107-04-1-J	80-107-04-1-A	10-117-07-1-A	80-117-07-1-A
Throughput	55 samples / hr	80 samples / hr	60 samples / hr	60 samples / hr	60 samples / hr	60 samples / hr
Reagent use (mL per sample):						
Carrier	2.21	0.77	DI water		DI water	
Buffer	0.96	0.45	1.45	0.42	NA	
Reagent 1	0.96	0.15	0.76	0.42	2.47	0.50
Reagent 2	1.85	0.40	NA		NA	
Total	5.98	1.77	2.21	0.83	2.47	0.5
Reagent Reduction		70%		62%		80%

- Available parameters: Ammonia, Chloride, Cyanide, Nitrate-Nitrite, Nitrite, Orthophosphorus
  - More to come soon!

UV Nitrate Conversion

Nitrate is quantitatively photo converted to a detectable form of nitrogen using traditional colorimetric methods by the passage of the sample over a germicidal UV lamp. Conversion of both nitrate and nitrite are controlled allowing for quantification of nitrate/nitrite mixtures.

The method requires the sample to be injected into a buffered carrier stream that passes over a low-pressure mercury lamp through PTFE tubing. Nitrate and nitrite in the sample are photo-converted to a detectable form using UV light at 254 nm.

The extent of the reduction is managed utilizing the EDTA compounds in the buffer allowing for the conversion efficiency to reach 100% without over reducing the nitrogen to oxidation states that cannot be detected with traditional colorimetric methods.

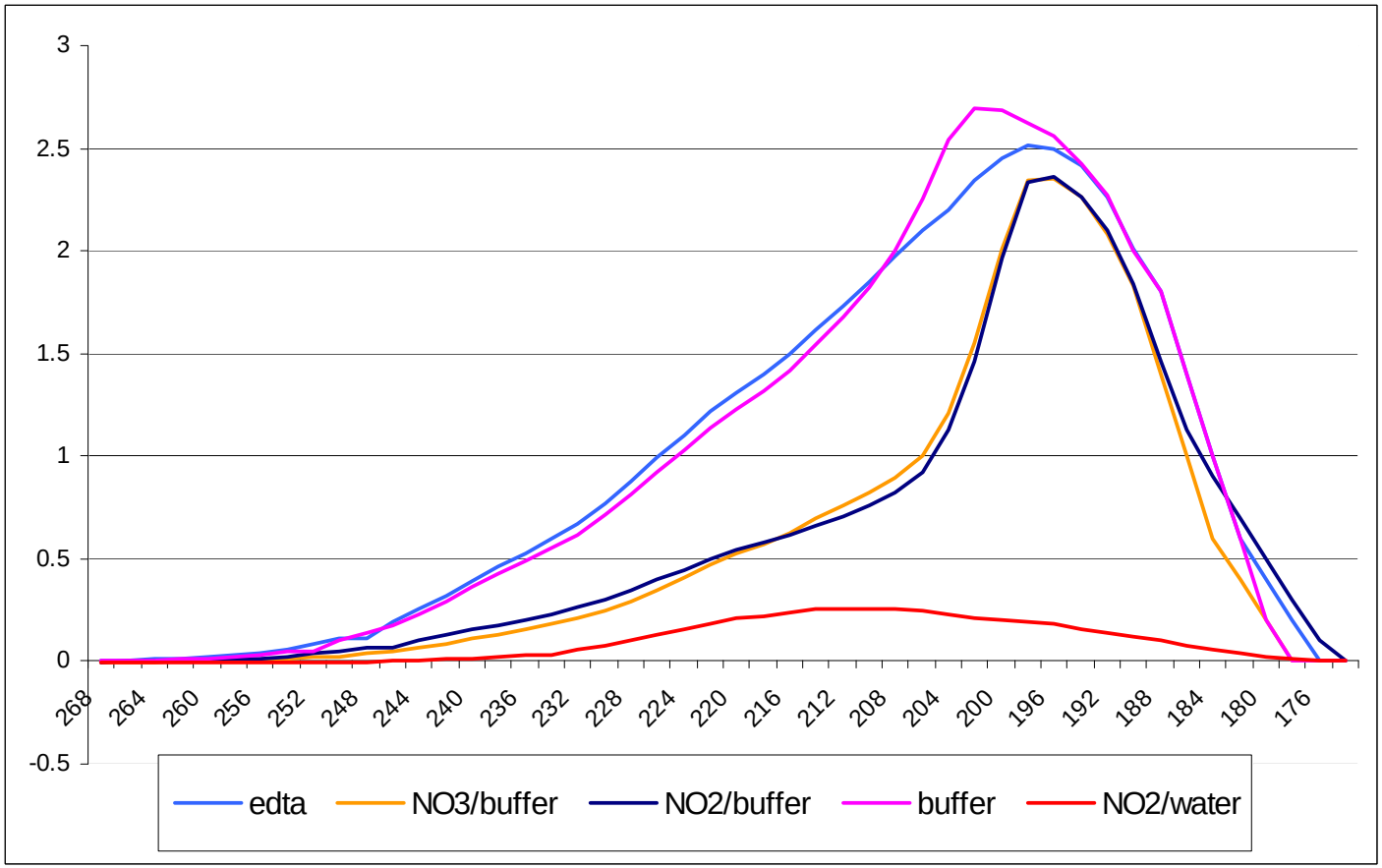
UV Nitrate Conversion

There are no toxic compounds used in the method's chemical reaction. Therefore, the waste generated can be disposed of down the drain.

The reduction efficiency of NO_3 to NO_2 is calculated at 100%, the same efficiency achieved by the cadmium and hydrazine reduction without the aid of toxic compounds.

This is also the same reduction efficiency as the enzymatic nitrate reductase method, however the chemical reaction for the UV reduction is completed in a shorter period, and more cost effective.

UV Nitrate Conversion



Passed the different solutions over the UV lamp, collected and scanned at a wavelength range of 268 – 176 nm. With the correct buffer formulation, both the 10 mg/L nitrate and nitrite standards are converted to exactly the same UV absorbance; and thus produce the same absorbance at 540 nm with the Griess reagents.

UV Nitrate Conversion

Nitrogen Species and their Oxidation States

Species	Name	Oxidation State
NH_3, NH_4^+	Ammonia, ammonium ion	-3
N_2H_4	Hydrazine	-2
NH_2OH	Hydroxylamine	-1
N_2	Nitrogen	0
N_2O	Nitrous oxide	+1
NO	Nitric oxide	+2
HNO_2, NO_2^-	Nitrous acid, nitrite ion	+3
NO_2	Nitrogen dioxide	+4
HNO_3, NO_3^-	Nitric acid, nitrate ion	+5

Once the sample is mixed with the ammonium chloride buffer (at the correct pH and amount of EDTA) and is irradiated by the UV lamp, the nitrite and nitrate in the sample are reduced to NO and / or N_2O. These nitrogen species also react with the Griess reagents to absorb at 540 nm.

UV Nitrate Conversion

This UV reduction of nitrate to nitrite is applicable for waters (drinking, surface, waste, brackish, and seawaters) as well as 2 M KCl soil extraction solutions.

10-107-04-6-A = Concentration range for the waters method:

High Range: 0.2 to 20 mg N/L as NO_3^- or NO_2^-

Low Range: 0.05 to 5.0 mg N/L as NO_3^- or NO_2^-

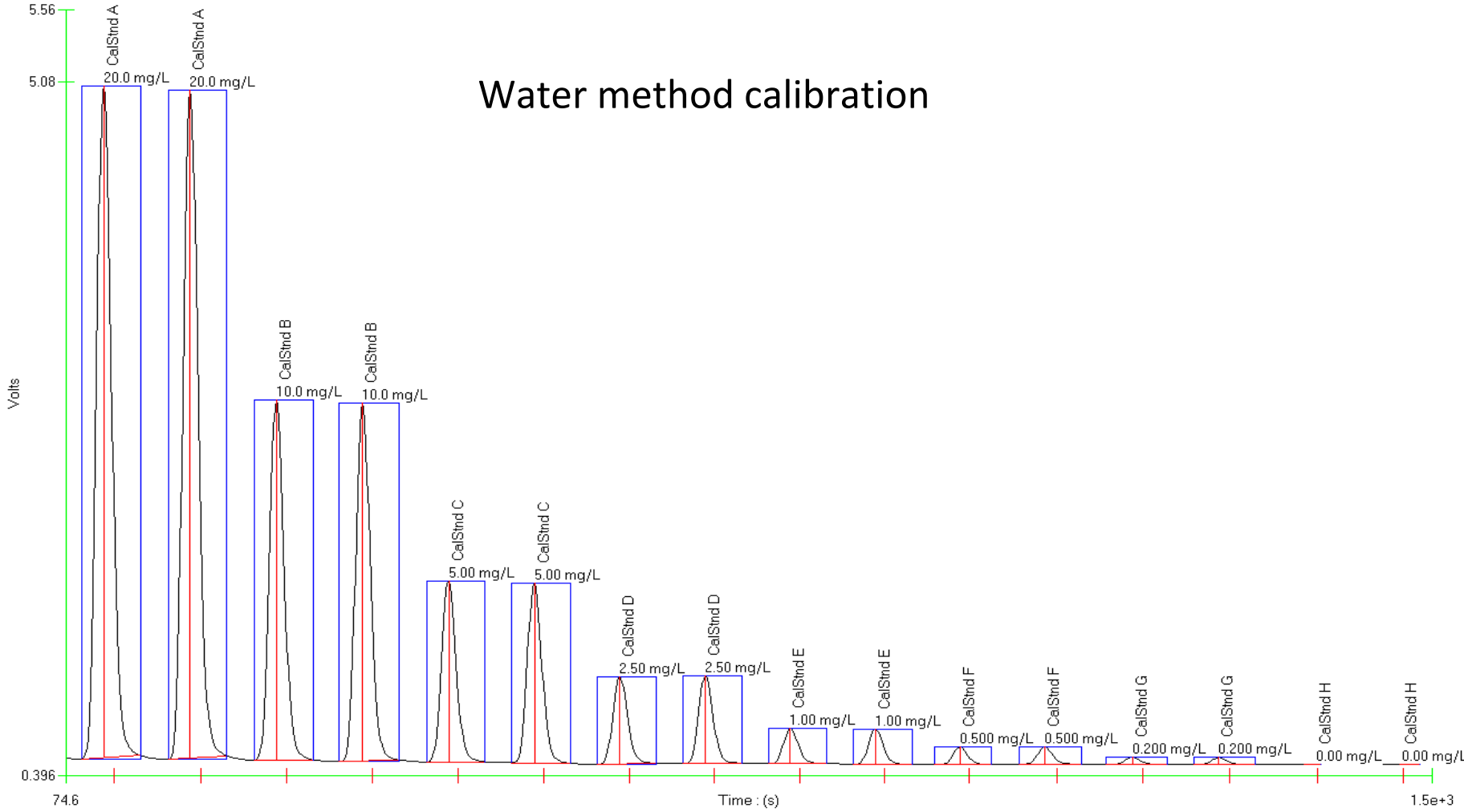
31-107-04-6-A = Concentration range for brackish/seawater method:

High Range: 0.2 to 20 mg N/L as NO_3^- or NO_2^-

Low Range: 0.05 to 5.0 mg N/L as NO_3^- or NO_2^-

12-107-04-6-A = Concentration range for 2 M KCl soil extraction solution method: 0.2 to 20 mg N/L as NO_3^- or NO_2^-

UV Nitrate Conversion

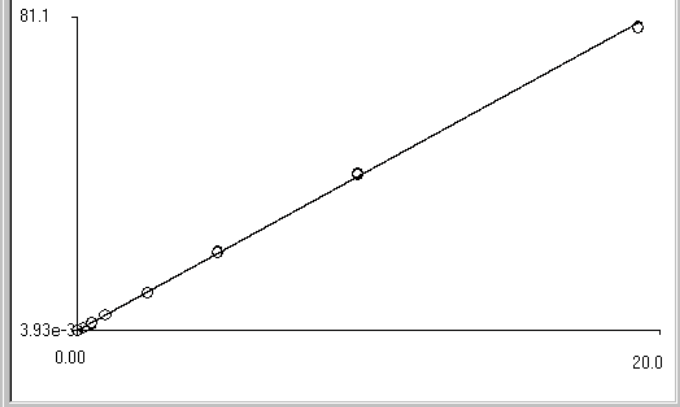


UV Nitrate Conversion

Calibration Results - Channel 1

NO3

	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	20.0	1	81.1	4.54	0.2	1.3	☐	19.7	5/14/2009	1:35:28 PM
2	20.0	2	80.9	4.51	0.2	1.6	☐	19.7	5/14/2009	1:36:57 PM
3	10.0	1	42.2	2.43	0.6	-2.5	☐	10.2	5/14/2009	1:38:25 PM
4	10.0	2	41.8	2.41	0.6	-1.7	☐	10.2	5/14/2009	1:39:52 PM
5	5.00	1	21.0	1.22	0.4	-1.9	☐	5.09	5/14/2009	1:41:20 PM
6	5.00	2	21.1	1.22	0.4	-2.4	☐	5.12	5/14/2009	1:42:48 PM
7	2.50	1	10.2	0.590	0.0	0.8	☐	2.48	5/14/2009	1:44:15 PM
8	2.50	2	10.2	0.594	0.0	0.9	☐	2.48	5/14/2009	1:45:43 PM
9	1.00	1	4.14	0.239	0.3	-0.2	☐	1.00	5/14/2009	1:47:09 PM
10	1.00	2	4.16	0.239	0.3	-0.6	☐	1.01	5/14/2009	1:48:36 PM
11	0.500	1	2.00	0.117	3.1	3.9	☐	0.480	5/14/2009	1:50:02 PM
12	0.500	2	2.09	0.117	3.1	-0.3	☐	0.502	5/14/2009	1:51:28 PM
13	0.200	1	0.867	0.0487	2.0	-2.5	☐	0.205	5/14/2009	1:52:58 PM
14	0.200	2	0.843	0.0474	2.0	0.3	☐	0.199	5/14/2009	1:54:26 PM
15	0.00	1	3.93e-3	1.88e-3			☐	-4.69e-3	5/14/2009	1:55:55 PM
16	0.00	2	0.0161	3.76e-4			☐	-1.72e-3	5/14/2009	1:57:24 PM



Area = 4.11 * Conc + 0.0239
Conc = 0.243 * Area - 5.64e-3
Correlation Coefficient (r) = 0.99998

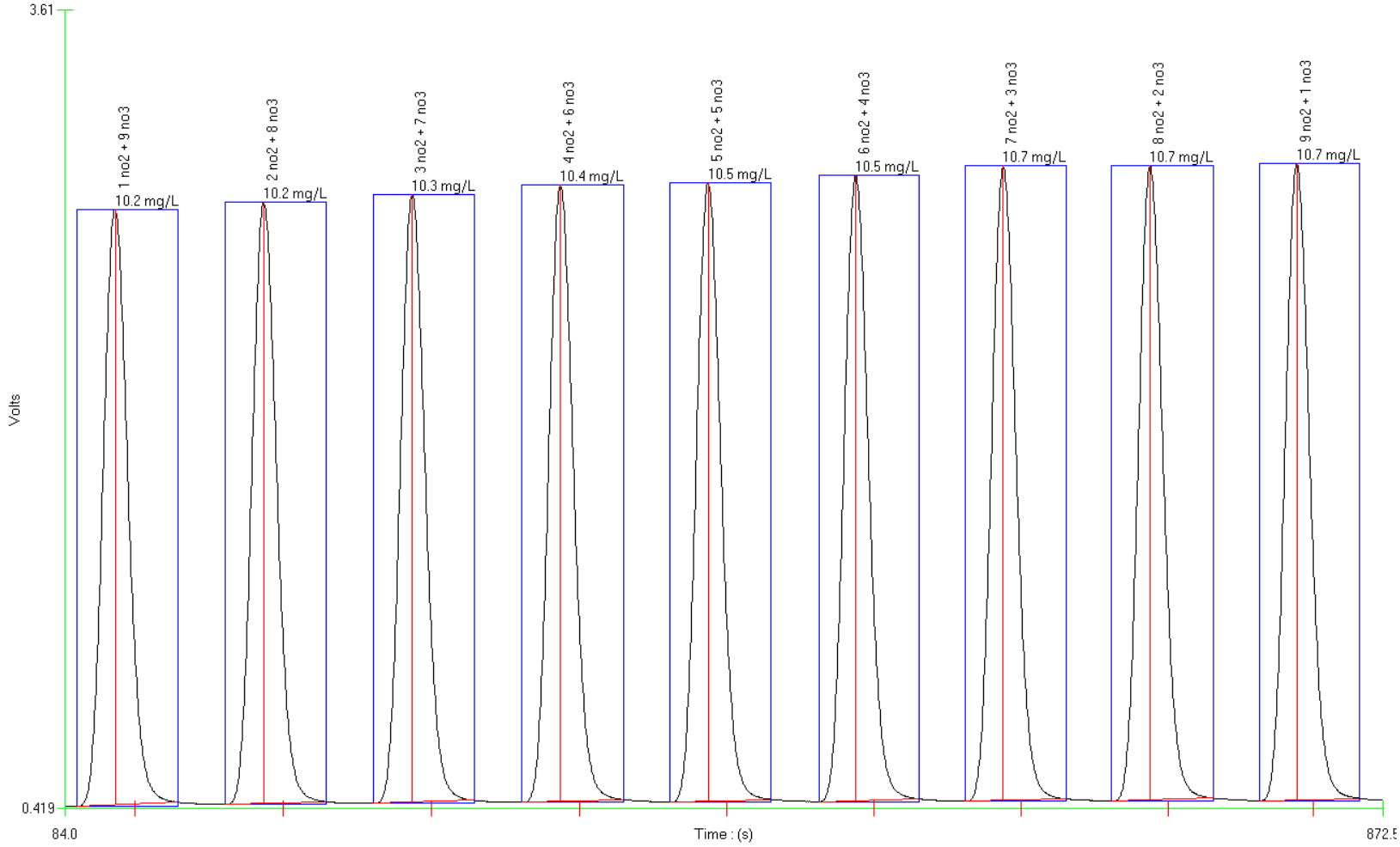
Weighting : 1/x

Settings

Water Method Calibration Graph and Statistics

UV Nitrate Conversion

Nitrate to Nitrite concentration ratios



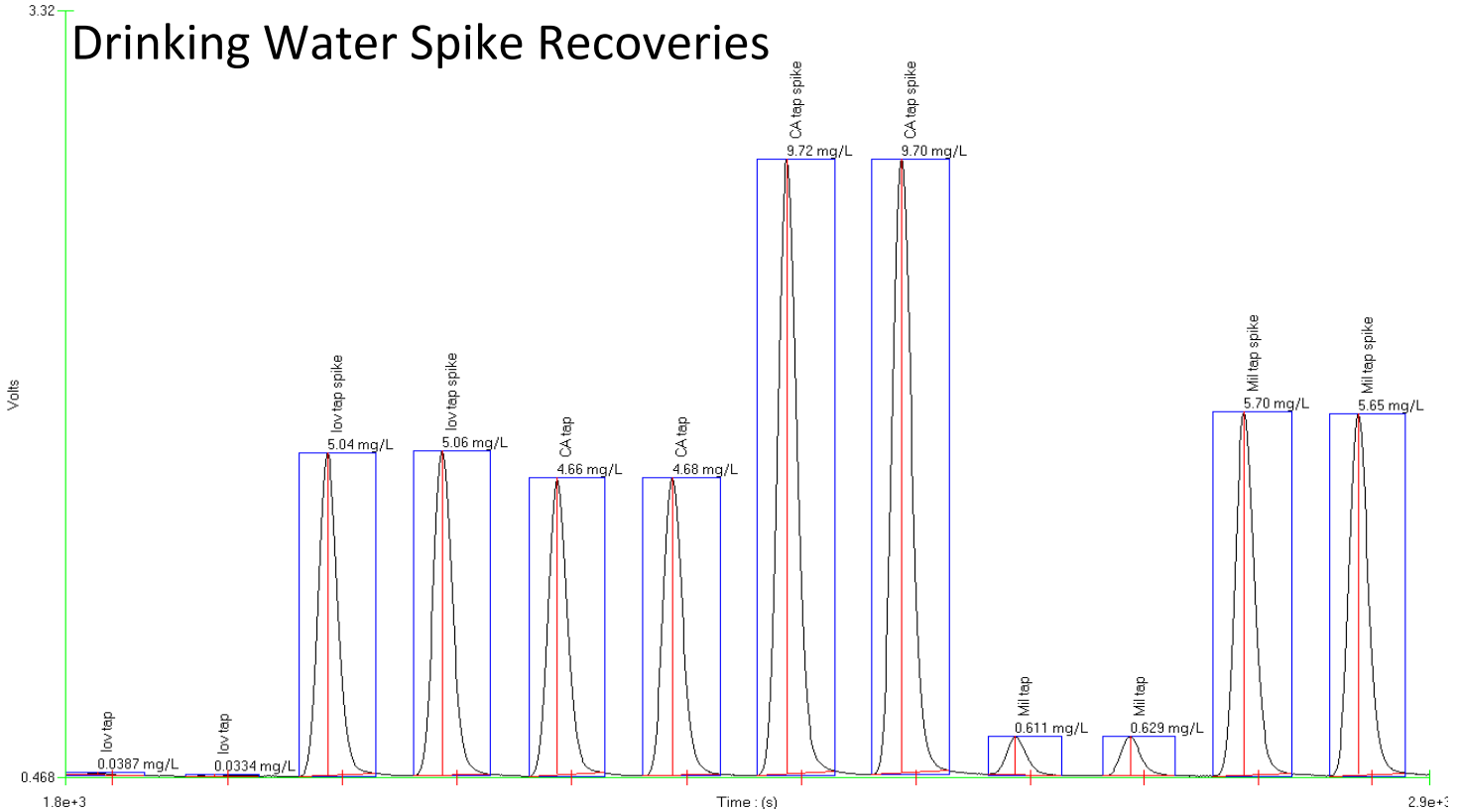
UV Nitrate Conversion

Nitrate to Nitrite concentration ratios

Nitrogen compound ratio	Concentration (mg/L)	Nitrogen compound ratio	Concentration (mg/L)
1 ppm NO_2 + 9 ppm NO_3	10.2	6 ppm NO_2 + 4 ppm NO_3	10.5
2 ppm NO_2 + 8 ppm NO_3	10.2	7 ppm NO_2 + 3 ppm NO_3	10.7
3 ppm NO_2 + 7 ppm NO_3	10.3	8 ppm NO_2 + 2 ppm NO_3	10.7
4 ppm NO_2 + 6 ppm NO_3	10.4	9 ppm NO_2 + 1 ppm NO_3	10.7
5 ppm NO_2 + 5 ppm NO_3	10.5		

UV Nitrate Conversion

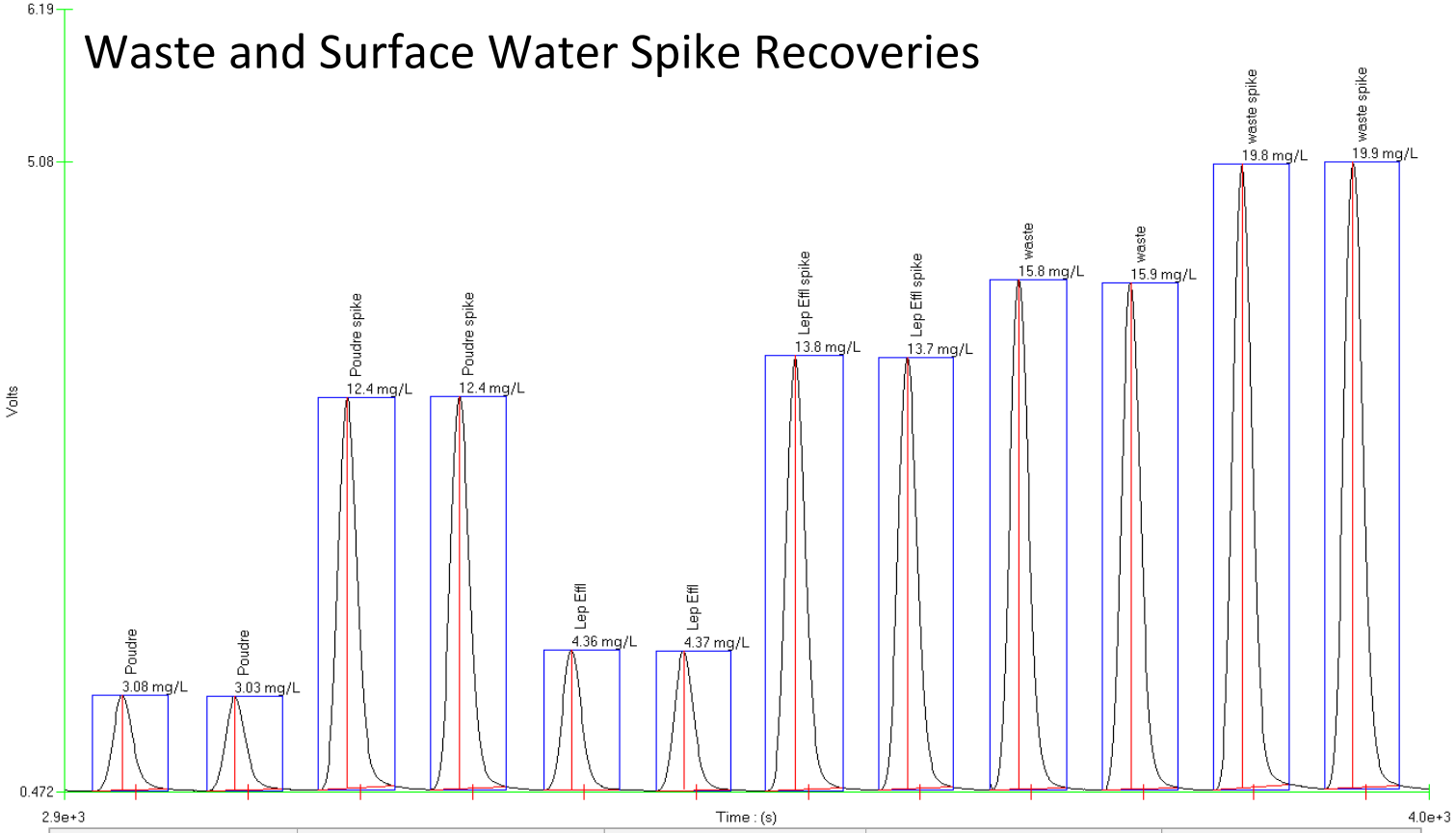
Drinking Water Spike Recoveries



Sample ID	Unspiked conc (mg/L)	Spiked conc (mg/L)	Spiked amount (mg/L)	% Recovery
Loveland Tap	0.036	5.05	5.0	100.3%
CA Tap	4.67	9.71	5.0	100.8%
Milwaukee Tap	0.62	5.68	5.0	101.1%

UV Nitrate Conversion

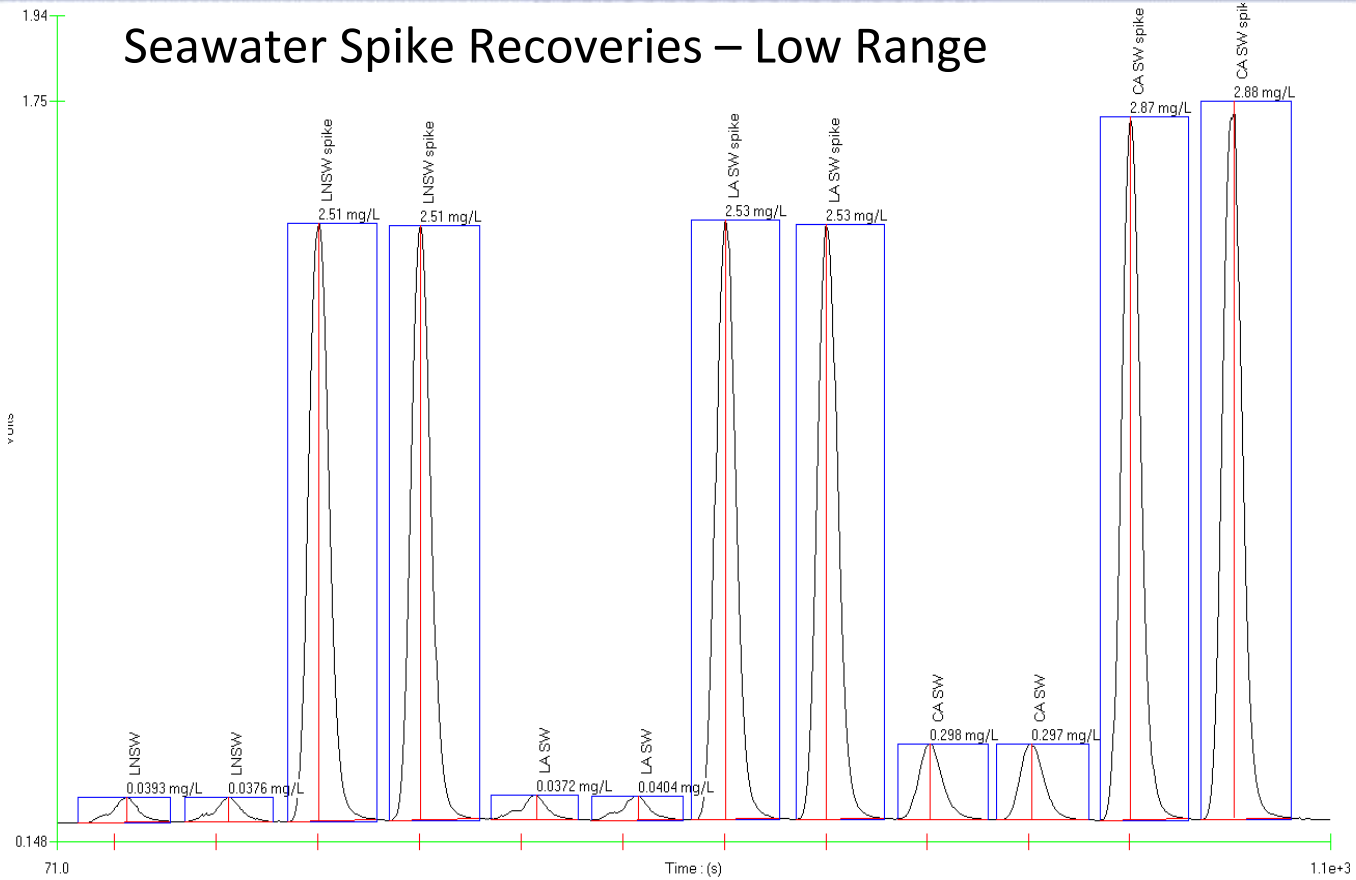
Waste and Surface Water Spike Recoveries



Sample ID	Unspiked conc (mg/L)	Spiked conc (mg/L)	Spiked amount (mg/L)	% Recovery
Poudre River	3.06	12.40	10.0	93.5%
LEP Effluent	4.36	13.75	10.0	93.9%
Wastewater	8.02	12.95	10.0	98.7%

UV Nitrate Conversion

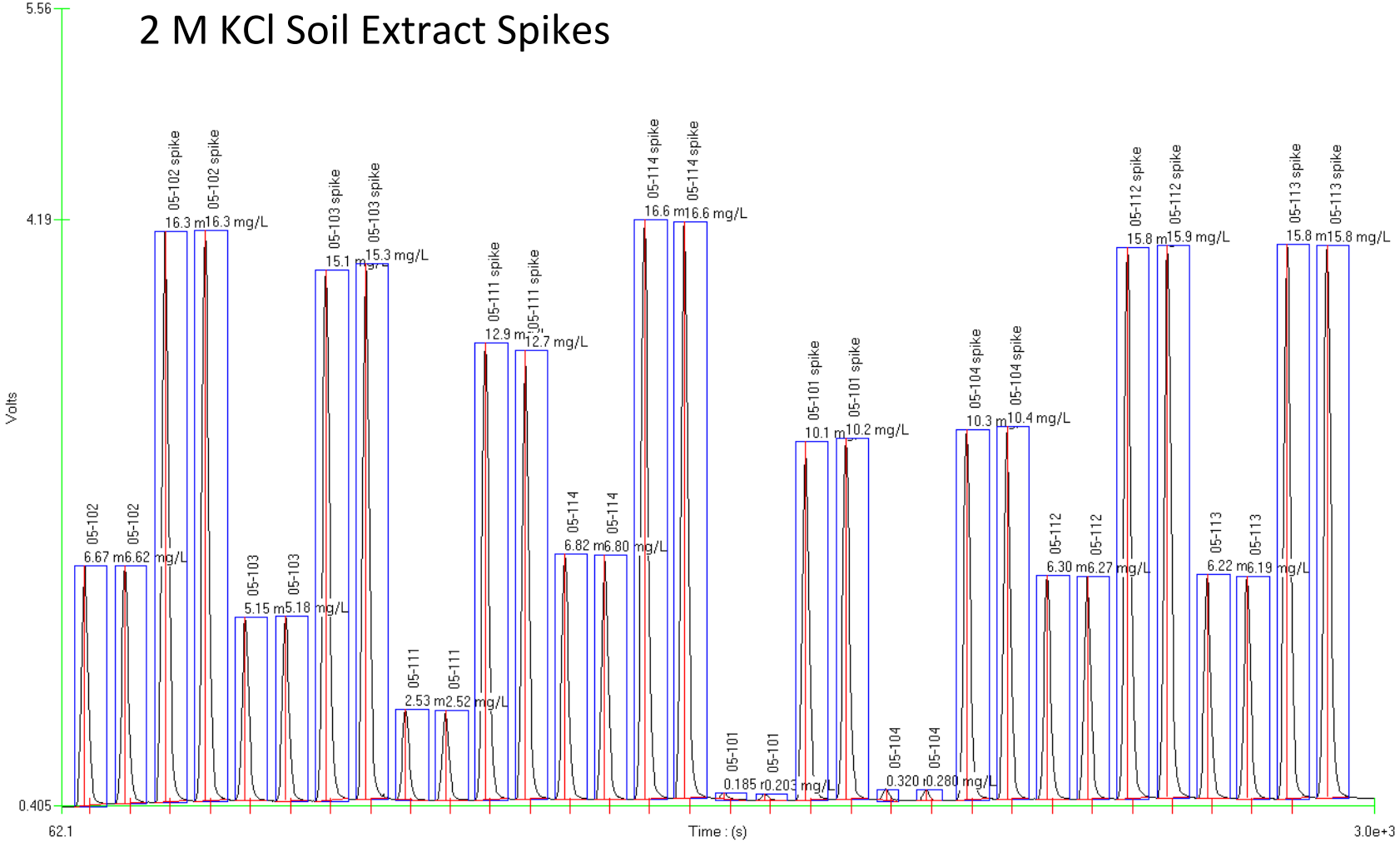
Seawater Spike Recoveries – Low Range



Sample ID	Unspiked conc (mg/L)	Spiked conc (mg/L)	Spiked amount (mg/L)	% Recovery
Low Nutrient SW	0.038	2.51	2.50	98.86%
Louisiana SW	0.039	2.53	2.50	99.65%
California SW	0.298	2.88	2.50	103.1%

UV Nitrate Conversion

2 M KCl Soil Extract Spikes



UV Nitrate Conversion

2 M KCl Soil Extract Spikes Recoveries

Sample ID	Unspiked conc (mg/L)	Spiked conc (mg/L)	Spiked amount (mg/L)	% Recovery
05-101	0.19	10.12	10.0	99.56%
05-102	6.65	16.30	10.0	96.55%
05-103	5.17	15.20	10.0	100.4%
05-104	0.30	10.35	10.0	100.5%
05-111	2.53	12.80	10.0	102.8%
05-112	6.29	15.85	10.0	95.65%
05-113	6.21	15.80	10.0	95.95%
05-114	6.81	16.60	10.0	97.90%

Custom Method Development

- Lachat Applications does **custom** method development
  - FREE evaluations of method feasibility with the CPQ (Customer Profile Questionnaire) process
    - Form available from any Lachat representative or at www.lachatinstruments.com
  - The custom work can be simple (range change) or complicated (current work on colorimetric arsenic method)
  - Turnaround can be **QUICK** if needed and feasible

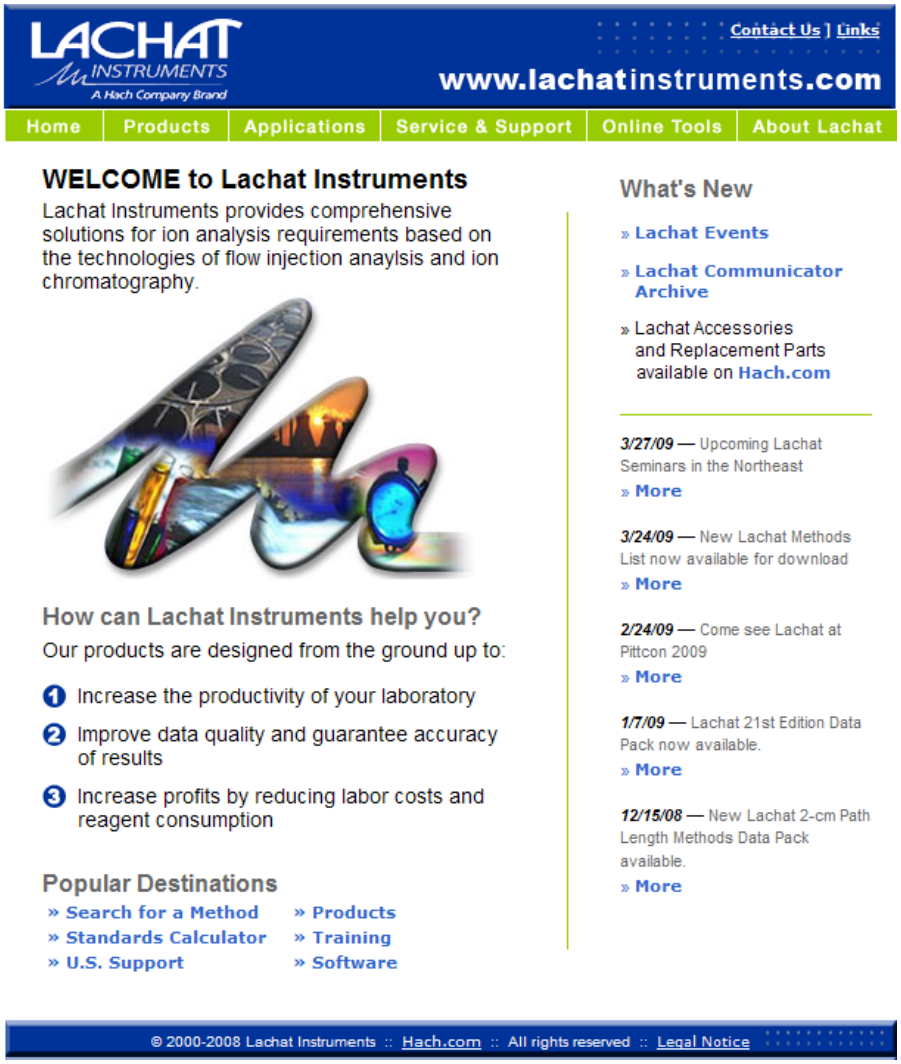
www.lachatinstruments.com

Lachat Applications does custom method development.

Often our best ideas come from YOU!

Thank you for your time and interest!

Download this presentation and the current Lachat Methods List at www.lachatinstruments.com



Questions?