



**Inorganic Anion Analysis of
Wastewater Using Discrete Analyzers**

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Outline

- Wastewater
 - Sources
 - Reasons for analysis
 - Analytical challenges
- Common anions in wastewater
- Anion measurement instrumentation
- Discrete analysis
 - Automated photometric assays
 - Accurate, precise measurement
- Conclusion

Wastewater

- Municipal or household waste
 - Sewage effluent
 - Raw sewage
 - Treated effluent
 - Leachates
 - Surface run-off
- Industrial
 - Production effluents
 - Process and cooling waters
- Agriculture
 - Soils - leached/extracted into solution



Reasons to Perform Wastewater Analysis

- Monitoring discharge
 - Regulatory limits
- Nutrient Analysis
 - Excessive plant growth in aqueous environments
- Known samples
 - Historical analysis
 - E.g., High chloride level from a treatment facility with a water inlet near the sea/estuary
- Unknown samples
 - Investigative, pollution incident, farm run-off, milk spill, or industrial discharge due to plant failure

Wastewater Analytical Challenges

- The content of wastewater samples is often unknown
- Accurate, rapid results are needed
- Samples out of calibration range will have to be rerun
 - Ability to automatically perform dilutions pre- or post-run is advantageous
- Samples can contain disparate analyte concentrations
 - May need to run multiple dilutions depending on the analytes of interest

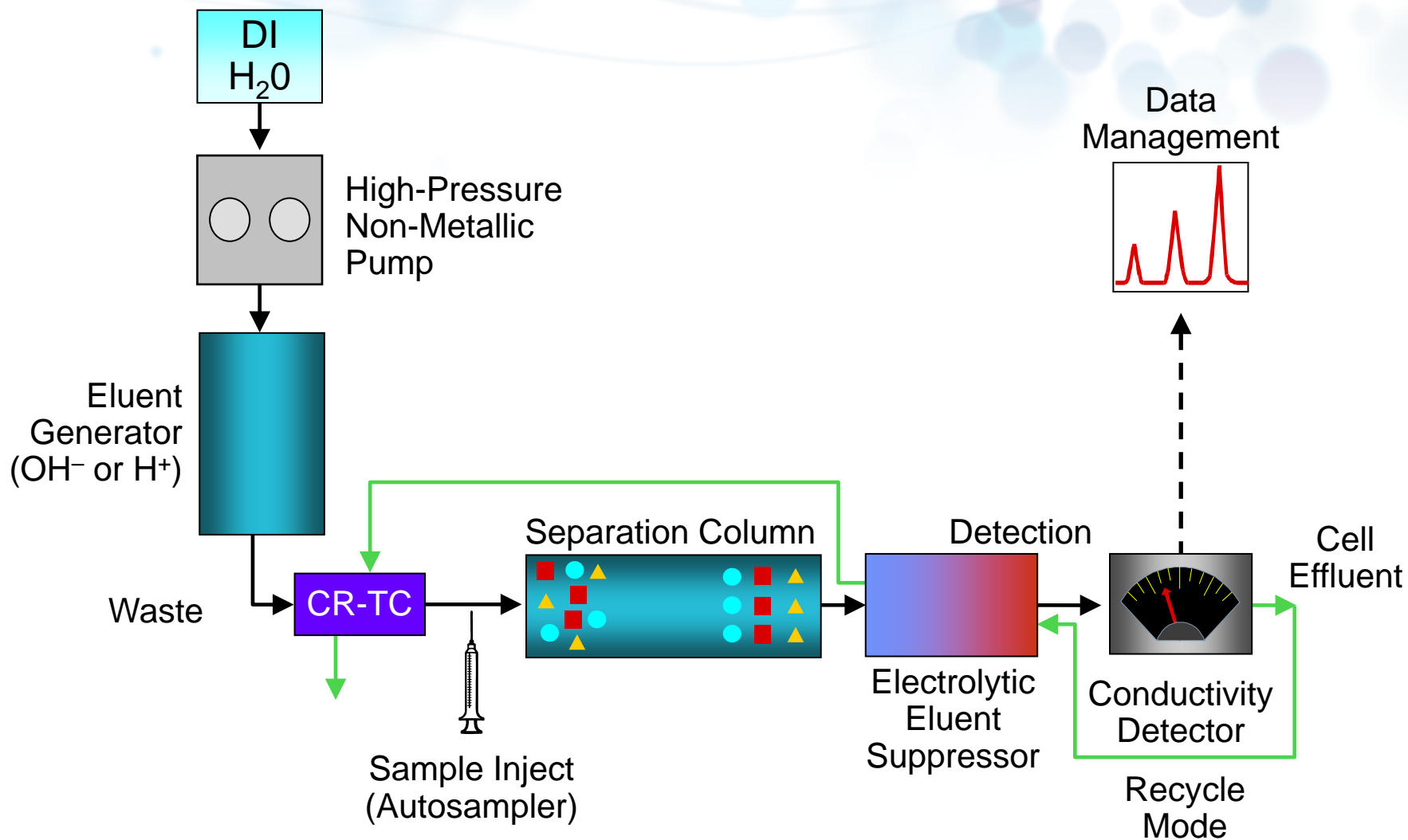
Common Anions in Wastewater

- Inorganic anions
 - Chloride
 - Disrupts nitrification process (treatment)
 - Sulfate
 - Disrupts anaerobic digestion process (treatment)
 - Phosphate, nitrate, nitrite
 - Plant nutrients; phytoplankton blooms
 - Bromide
 - Ozonation, chlorination -> Disinfection by products: brominated trihalomethanes, bromate (carcinogens)
- Organic acids
 - Formic, acetic, propionic acids
 - pH balance

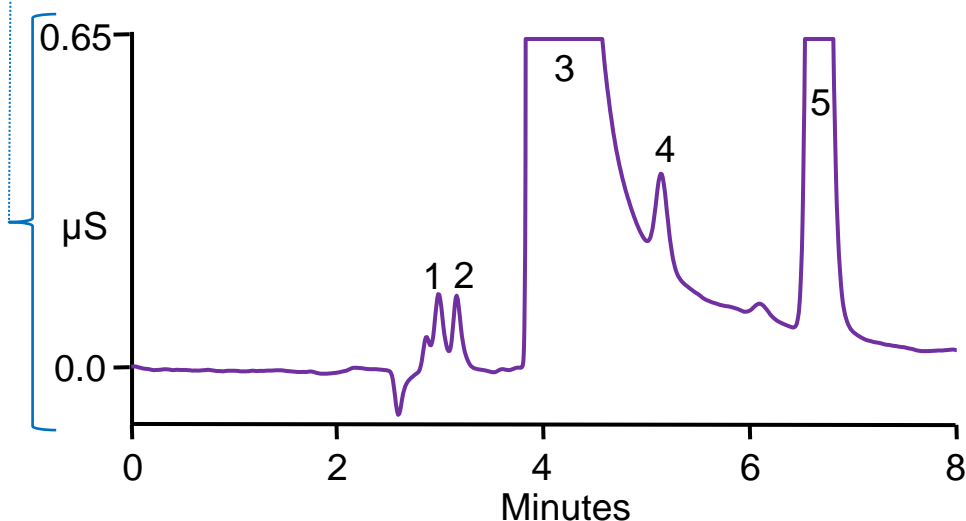
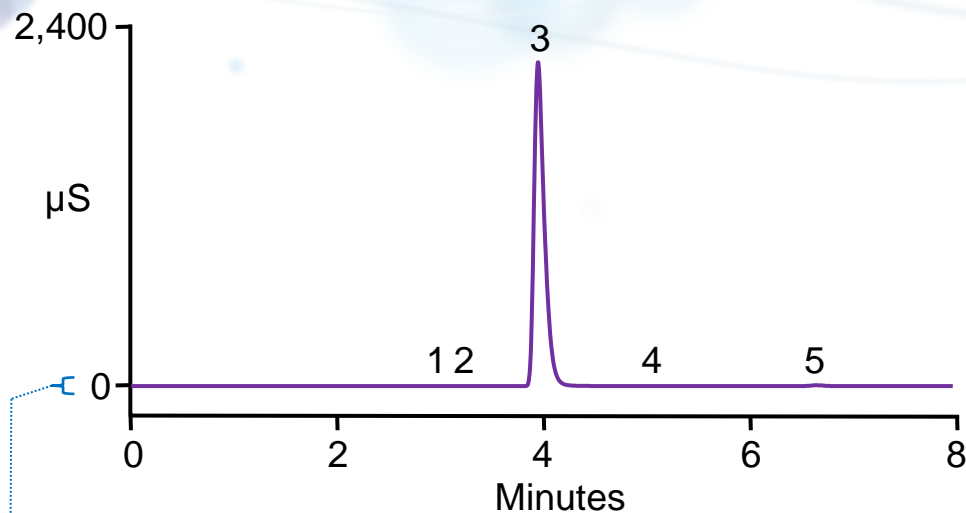
Measurement of Anions in Wastewater

- Ion chromatography (IC)
 - Sample separated into its constituents
 - Automated; conductivity detection
- Manual, wet chemical assays
 - Photometric (spectrometer)
- Continuous flow analysis (CFA)
 - Segmented flow analysis (SFA); flow injection analysis (FIA); sequential injection analysis (SIA)
 - Semi-automated; photometric
- Discrete analysis
 - Individual tests for specific analytes
 - Automated; photometric

Ion Chromatography System



Anions in Hydraulic Fracturing Flowback Wastewater



Column: Thermo Scientific™ Dionex™ IonPac™ AG18/AS18 columns , 4 mm i.d.

Eluent Source: Thermo Scientific Dionex EGC III KOH cartridge

Eluent: 39 mM KOH

Flow Rate: 1 mL/min

Inj. Volume: 25 μL

Col. Temp.: 30 °C

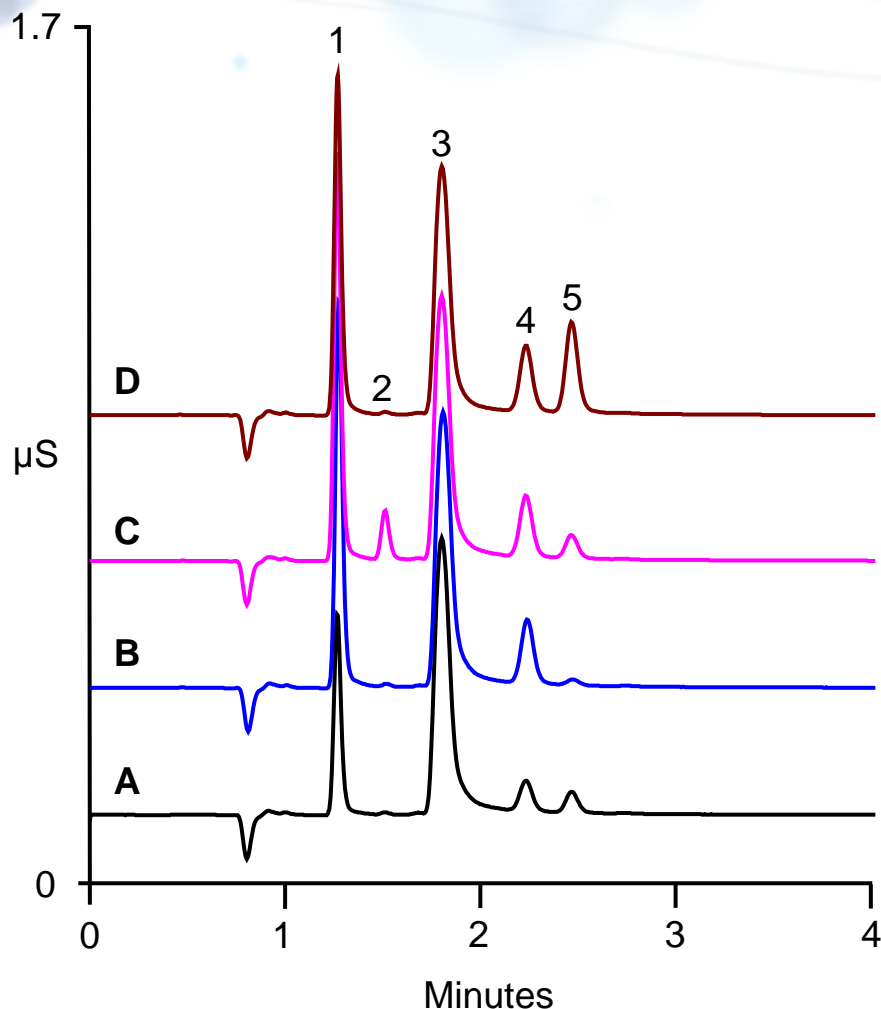
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor, recycle mode

Sample: 100-fold fracking flowback, filtered, 0.2 μm

Peaks:

	Measured	Undiluted
1. Acetate	< 0.05 mg/L	< 5
2. Formate	< 0.05	< 5
3. Chloride	940.0	94,000
4. Sulfate	0.12	12
5. Bromide	8.90	890

Fast Determination of Inorganic Anions in Municipal Wastewater



Column: Dionex IonPac AG18-4µm,
 Dionex IonPac AS18-4µm,
 0.4 mm i.d.
Eluent Source: Dionex EGC-KOH Cartridge
 (Capillary)
Eluent: 23 mM KOH
Flow Rate: 0.025 mL/min
Inj. Volume: 0.4 µL
Column Temp.: 30 °C
IC Cube Temp.: 15 °C
Detection: Suppressed conductivity,
 Thermo Scientific™ Dionex™
 ACES™ 300 Anion Capillary
 Electrolytic Suppressor, recycle mode
Sample Prep: Diluted 1000-fold, filtered, 0.2 µm
Samples: A: Influent
 B: Primary effluent
 C: Trickle effluent
 D: Final effluent

Peaks:

	A	B	C	D
1. Chloride	76.5	146	154	130 mg/L
2. Nitrite	1.5	2.1	37.4	1.6
3. Carbonate	--	--	--	--
4. Sulfate	41.6	88.9	84.8	91.8
5. Nitrate	28.8	7.2	31.7	128

A Complete Family of Ion Chromatography Systems



Thermo Scientific
Dionex ICS-900
IC System



Thermo Scientific
Dionex ICS-1100
IC System



Thermo Scientific
Dionex ICS-1600
IC System



Thermo Scientific
Dionex ICS-2100
IC System



Thermo Scientific
Dionex
ICS-4000
HPIC System



Thermo Scientific Dionex
ICS-5000+ HPIC System



Anion Determinations Using Photometric Assays

- Manual wet chemistry assays
 - Labor intensive
 - Wastes reagents
 - Error prone
- Continuous flow analyzers
 - Relatively slow
 - Generates a lot of waste
- Discrete analyzers
 - Rapid, automated, efficient

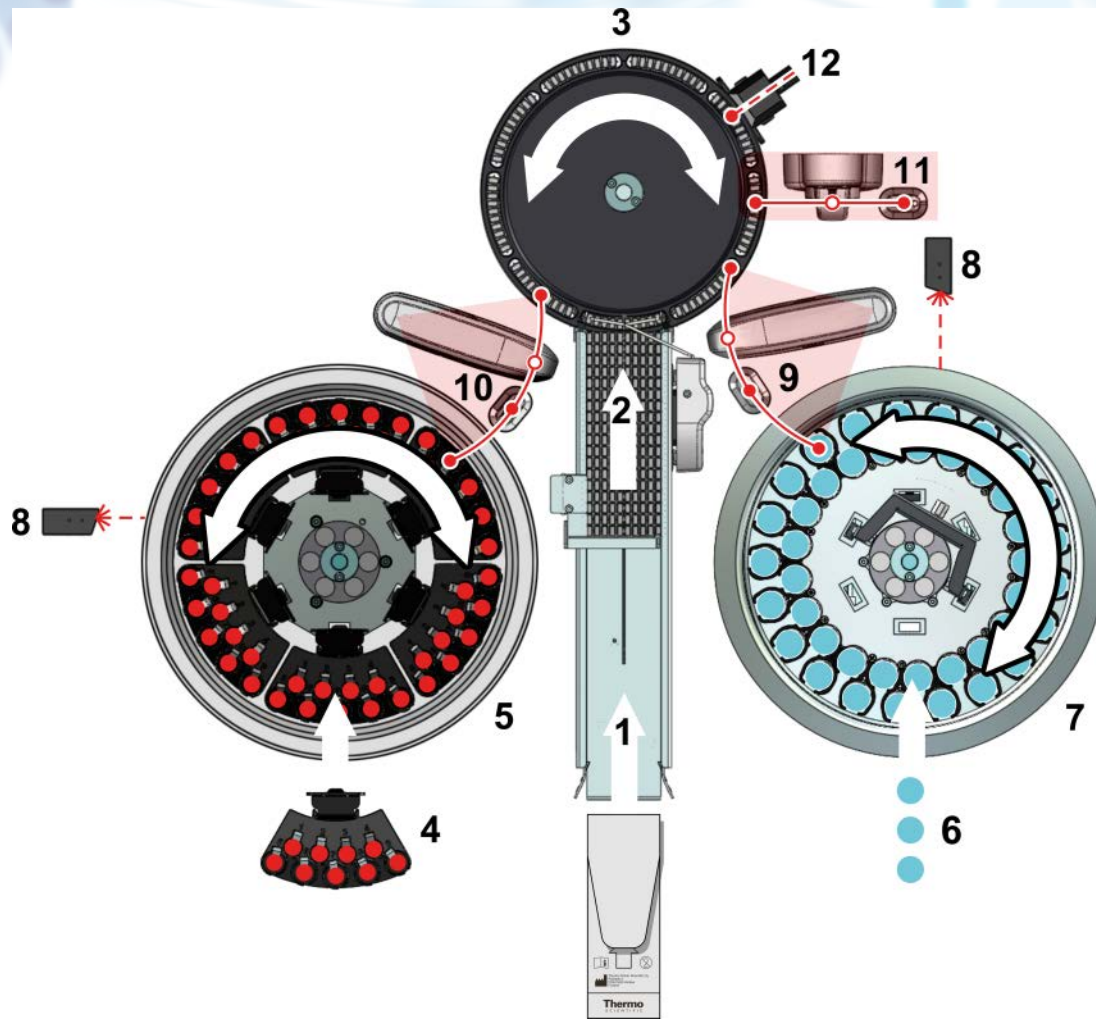


Benefits of Automated Discrete Analysis



- Flexible – various tests can be performed on each sample; there is no limitation on number of tests
- Fast – ready for immediate analysis, no reagent priming, no method changeover time
- Precise – specific measurements with high reproducibility, achieves low detection levels
- Minimal carry-over – each reaction takes place in its own reaction cuvette

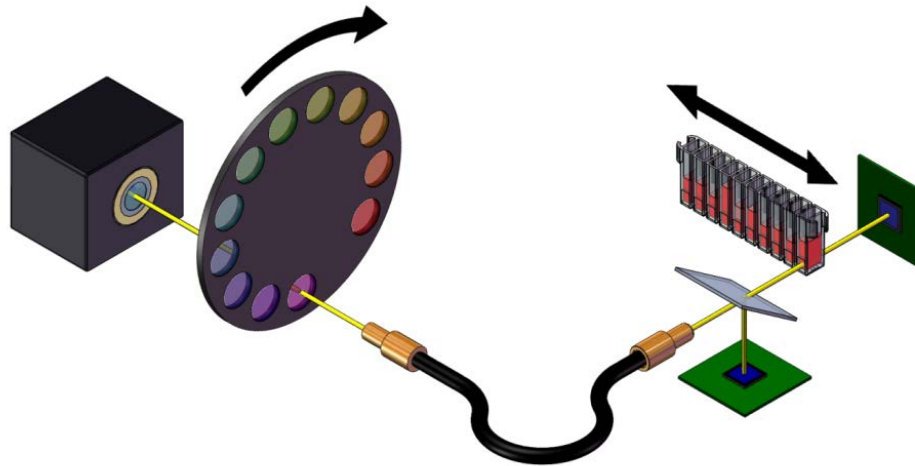
Discrete Analysis Process



1. Cuvette entry point
2. Cuvette loader
3. Incubator
4. Sample racks
5. Sample disk
6. Reagents
7. Reagent disk
8. Barcode reader
9. Reagent dispenser
10. Sample dispenser
11. Mixer
12. Photometer unit

Fast Photometric Measurement

- Spectral range 275 – 880 nm
 - 12 filter positions
- Fast measurement with a flash lamp
 - Main and side wavelengths measured at the same time
 - Water blank measured in all wavelengths at the same time



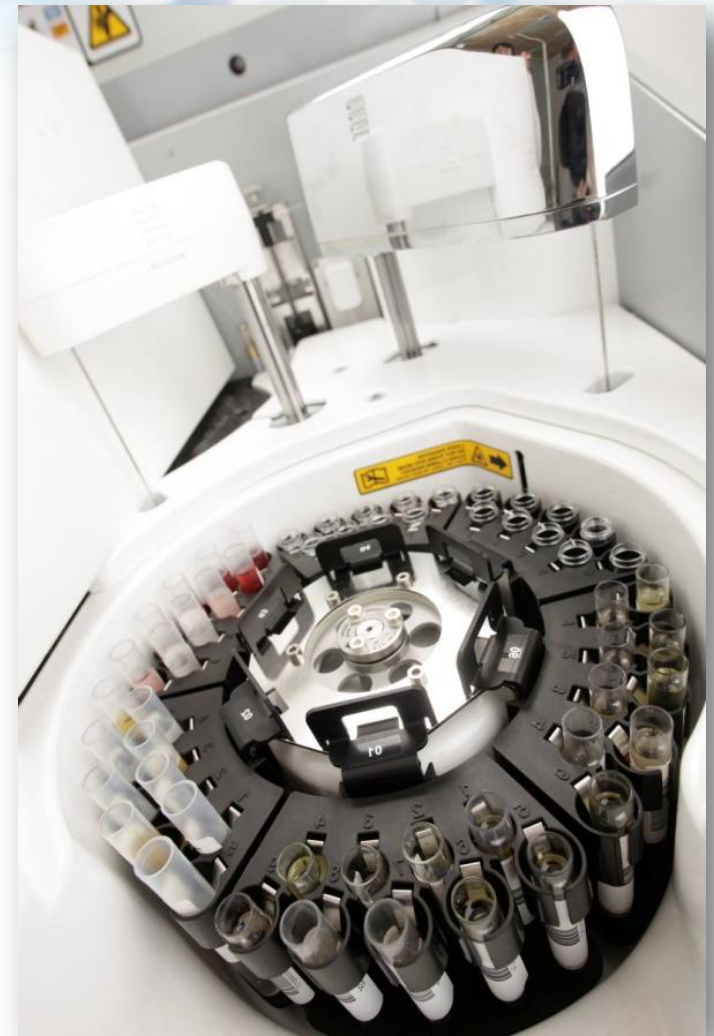
Flexible, Reliable, Temperature-Stabilized Measurement

- Several calibration options
 - Factor, Bias, Linear, Logit-log, Spline, Polynomial, Point-to-point
- Possibility to add up to four reagents per test
 - Automation even for the most complex methods
- Real-time QC program assures reliable performance
- Measurement temperature can be adjusted between 25 °C and 60 °C



Flexible Sample Management

- Sample volumes from 2 to 120 μL
- Any mix of sample containers
 - 0.5, 2.0 and 4.0 mL sample cups
 - 5.0, 7.0 or 10.0 mL sample tubes
- Automatic identification via internal barcode reader
- Tests can be requested individually or using a profile



Easy Reagent Handling

- Reagent volumes from 2 to 240 μL
- Reagent containers
 - 10 and 20 mL vials
- Barcoded system reagent containers are automatically identified
 - Non-system reagents can be entered without barcodes
- Clearly displayed
 - Real-time reagent volume
 - Remaining test capacity
 - Expired reagents flagged automatically



Comprehensive Data Handling

- Application parameter values readable from barcode or electronically from a file
- Results
 - Calculated from both measured and off-line results
 - Automatically flagged in case of
 - Abnormal values
 - Repeats
 - Out-of-limit control values
- Long term storage of results
 - Associated calibrations
 - Reagent lot data



Reporting Options

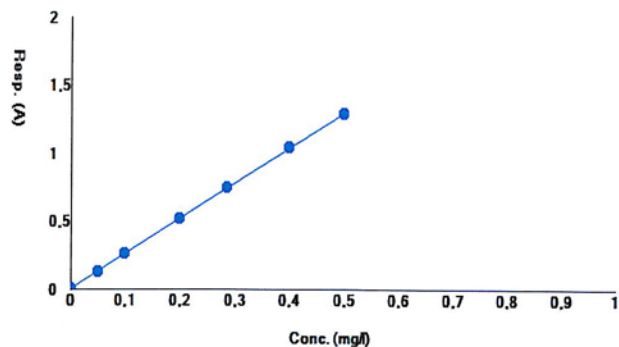
- Reports available
 - Spreadsheet export for further calculations
 - Export to LIMS
 - Printouts
 - PDF files

Calibration results
NO2 2mg/l Version number 1.4

Date 2014-02-17 User Dealer
Time 12:53:25 Software version: 4.1.1

Test	NO2 2mg/l	Coeff. of deter.	0,999956
Status		Total factor	0,387
Accepted	2014-02-13 10:36		
Checked	2014-02-13 10:36		
User name	Dealer		
Comment			
Errors			
Factor	0,387		
Bias	0,003		

Cal/Ctrl	Response	Calc. conc.	Given conc.	Lot	Errors
NO2-0	0,001	-0,001	0,000	Default	
NO2-STD	0,130	0,049	0,050	Default	
NO2-STD	0,260	0,100	0,100	Default	
NO2-STD	0,522	0,201	0,200	Default	
NO2-STD	0,743	0,287	0,286	Default	
NO2-STD	1,038	0,401	0,400	Default	
NO2-STD	1,288	0,498	0,500	Default	



Intuitive User Interface

- Graphical user-interface
 - Provides fast guidance
 - Includes context-sensitive help
 - Available in different languages
- Secure and traceable data handling
 - Different user groups can have different access rights
- Touch screen option



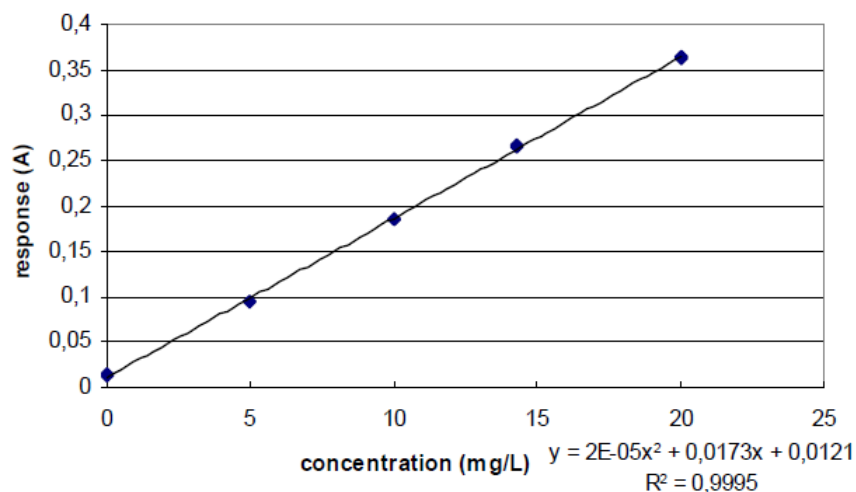
Wide Selection of Tests Optimized for Anions

- Chloride
- Fluoride
- Nitrate - Hydrazine
- Nitrate - Enzymatic
- Nitrate - Vanadium
- Nitrite
- Ortho-Phosphate
- Sulfate
- T.O.N
- TKN as N
- TP as P
- Additional analytes
 - Alkalinity
 - Ammonia
 - Calcium
 - Chromium (VI)
 - Magnesium
 - Silica
 - Total Hardness
 - Urea
 - pH
 - Conductivity

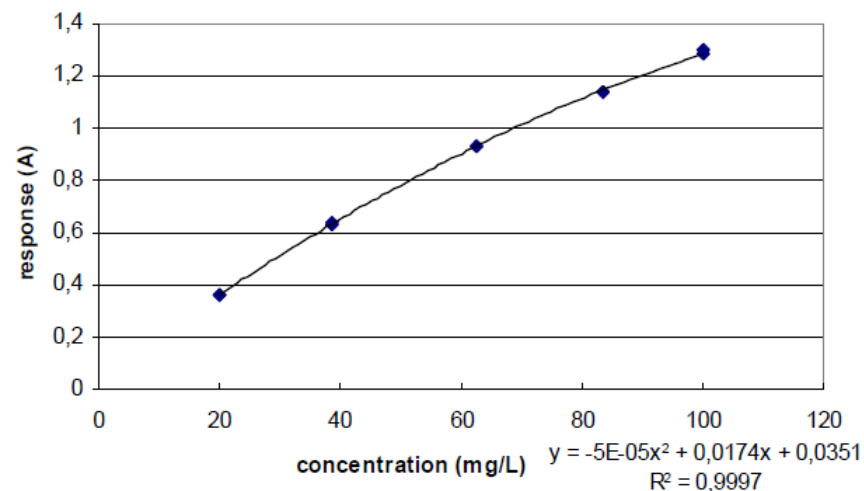
Chloride: Calibration Curves

- Using Thermo Scientific Chloride R1 reagent

Low Chloride (0–20 mg/L)



High Chloride (20–100 mg/L)



Chloride: Precision and Accuracy

Sample	Avg* Result (mg/L)	Std. Dev.	Avg* % Recovery	Std. Dev.	Accuracy
Cl_Low_10	10.01	100.1	100.1	1.52%	1.00
Cl_High_80	83.18	0.56	104.0	0.70%	1.04

*n = 20

Chloride: Method Detection Limit

Sample	Result (mg/L)	% Recovery
Cl_Low_0.5	0.503	101
Cl_Low_0.5	0.514	103
Cl_Low_0.5	0.485	97
Cl_Low_0.5	0.474	95
Cl_Low_0.5	0.482	96
Cl_Low_0.5	0.410	82
Cl_Low_0.5	0.407	81
Avg.	0.468	94
Std. Dev.	0.043	
MDL	0.14	

Chloride: Matrix Spiking

Sample	Result (mg/L)	% Recovery	RPD
Wastewater*	443.0		
Wastewater_MS50	489.0	101	
Wastewater_MSD50	489.8	103	0.2
Saline water (dil)*	140.4		
Saline water (dil)_MS50	187.3	103	
Saline water (dil)_MSD50	186.9	102	0.2

50 mg/L chloride spike; Saline water was diluted 100-fold;
RPD = relative percent difference





* Corrected for volume

Thermo Scientific System Reagents

- Optimized system solution
 - System applications for water analysis
 - Loadable application data from 2D barcode
 - Optimized kit sizes and on-board stability
 - Wide range of calibrators
- Productivity and efficiency
 - Ready-to-use liquid reagents eliminate reagent preparation
 - Minimal reagent waste
 - Bar-coded reagent vials provide easy and reliable identification
 - lot, expiration date, vial size
 - real-time reagent monitoring



Range of Discrete Analyzers for Wastewater Analysis

	Thermo Scientific™ Gallery™/ Thermo Scientific™ Aquakem™ 200	Aquakem 250	Gallery Plus	Aquakem 600
				
Capacity (tests/hr)	Up to 200	Up to 250	Up to 350	Up to 600
Incubation temperature	25 to 60 °C (Gallery) 37 °C (Aquakem)	37 °C	25 to 60 °C	37 °C
Optional units	pH and Conductivity (Gallery) Cadmium reduction(Aquakem)	Cadmium reduction	pH and Conductivity	Cadmium reduction and automation

Conclusions

- Determination of anions in wastewater is critical to verify its suitability for discharge
- Ion chromatography measures the conductivity of separated molecules while discrete analyzers use photometric assays that are specific for individual analytes
- Discrete analyzers
 - Automate photometric assays for fast, specific, high-throughput anionic measurements of up to 600 tests/hour
 - Assays produce accurate, precise data even from challenging matrices such as wastewater

Thank You!



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