

Recent Advances in Discrete Analysis Technology for Automated Simultaneous Multi-parameter Wet Chemistry Testing in Drinking Water, Wastewater, and Soil Samples

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Agenda

1 *Limited lab resource vs. demand for improved throughput?*

2 *Limitations of traditional wet chemistry workflow*

3 *Improve lab productivity by workflow automation*

4 *Recent advances of Gallery Aqua Master systems*



Water analysis

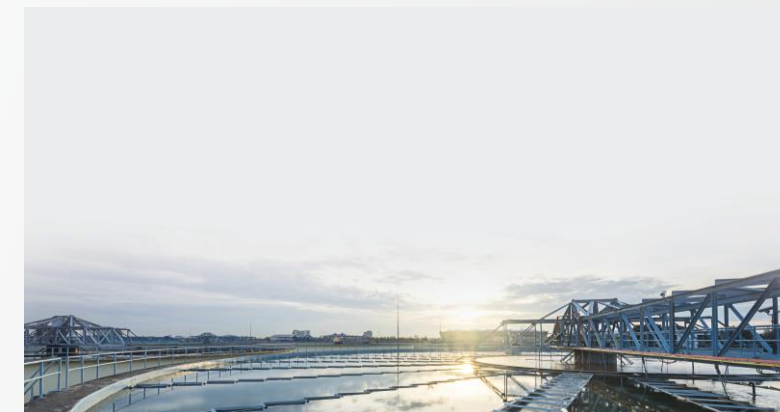
Same analytics – Different purpose



- Drinking water
 - Safe drinking water
 - Regulatory compliance



- Process water
 - Protect process equipment from corrosion, scaling
 - Energy efficiency
 - Regulatory compliance



- Wastewater
 - Environmental Protection Agency – clean water act
 - Reuse – Repurpose
 - Regulatory compliance

Water analysis is critical across all industries, water utilities and contract testing labs

Soil analysis

Same analytics – Different purpose



- Environmental soil samples
 - to check pollution e.g. after flooding.
 - Contaminants near ground water area



- Agricultural nutrient
 - Soil samples analysis to instruct the quantity of fertilizers needed for enhanced crop yield



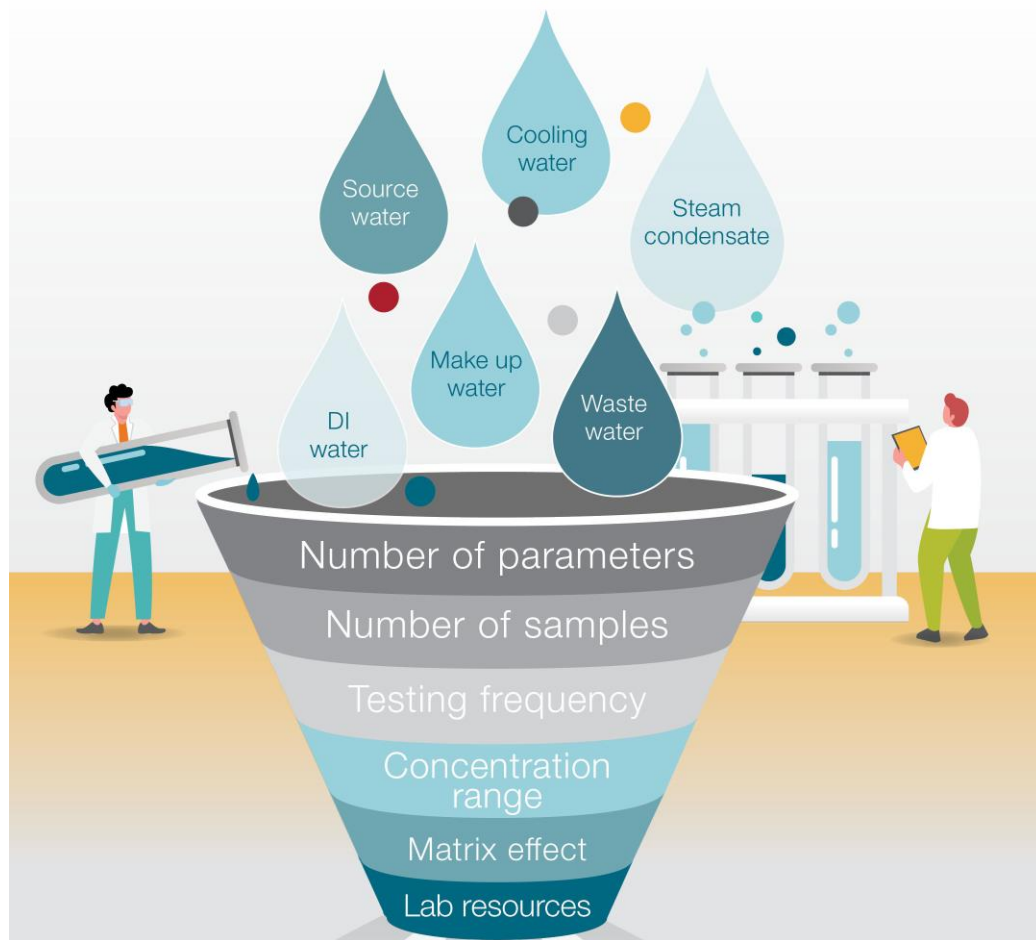
- Animal nutritional value
 - Farm animal manure for nutritional values and to give advice on animal feeding
 - Cows, hogs etc.

Soil analysis is critical for the determination of nutrients and contaminants

How does routine water and soil testing impact laboratory operations?

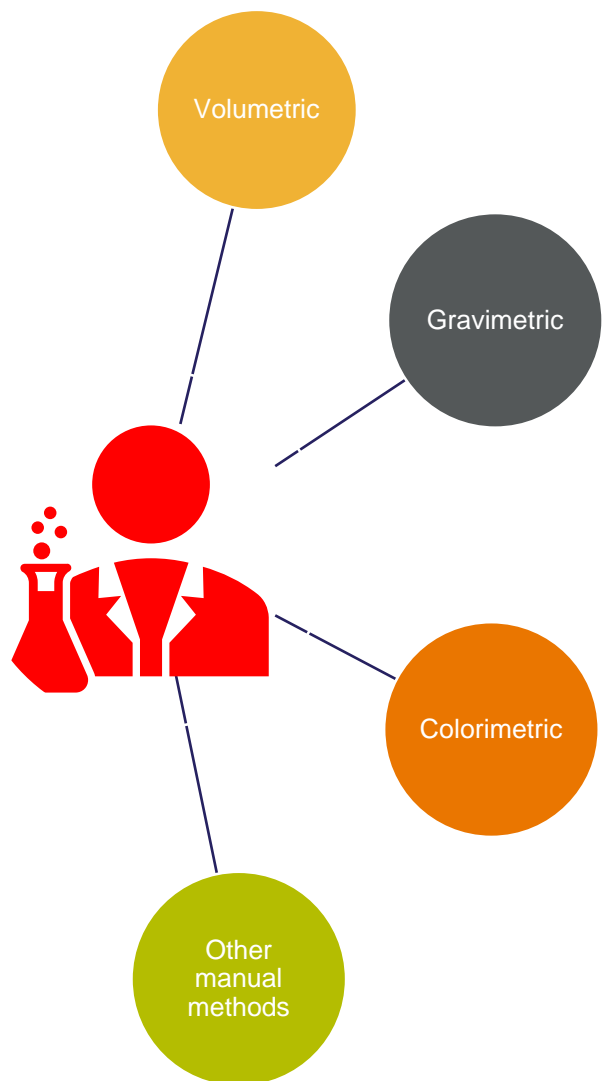
Many analytes, and diverse samples and concentrations

- Testing many samples for diverse parameters and concentrations can create a bottleneck with limited lab resources.
- Traditional analytical methods are slow, only process one parameter at a time—resulting in low throughput.



Analyte concentration varies from very low to high depending on the purpose and process

Wet chemistry analysis techniques and challenges



Spectrophotometers



Auto titrators



Flow injection analyzers
(FIA)



Segmented flow analyzers
(SFA)



- Manual techniques
- Visual detection
- Labor intensive
- Time consuming
- Large volume of reagent consumption per test
- Large waste generated

Water and soil testing can create a bottleneck for laboratories with limited resources

Consolidate water and soil analysis parameters

Basic water testing: pH, conductivity, alkalinity, total hardness

Comprehensive waste water testing as per regulatory methods: Total Kjeldal Nitrogen (TKN), total phosphate, total phenol, Total Oxidizable Nitrogen (TON), phosphate, nitrite, nitrate, boron, aluminium

Corrosive anions: Fluoride, chloride, sulfate, sulfide, nitrite, nitrate, phosphate, thiocyanate

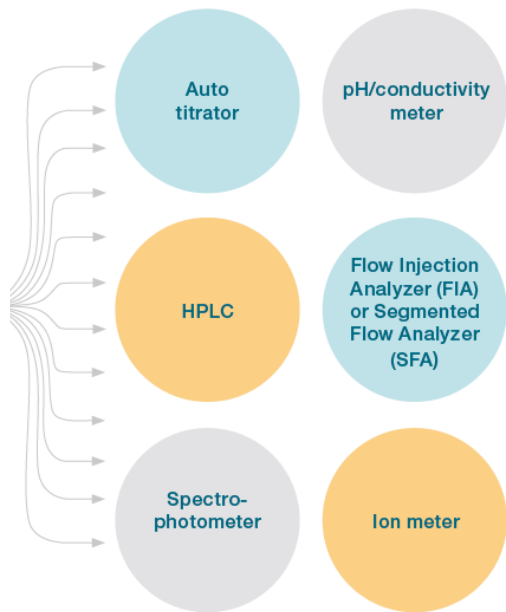
Scale formers: Silica, calcium, magnesium

Corrosion inhibitors: Ammonia, zinc, molybdenum, nitrite

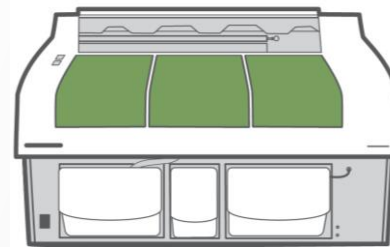
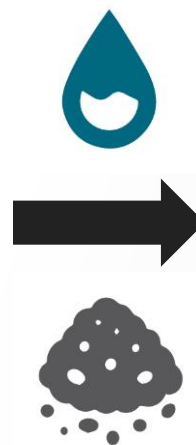
Corrosion indicators: Total iron, hexavalent chromium, zinc

Free and total cyanide

Regulatory fulfillment: Waste water analysis as per U.S. EPA and other standard methods



Multiple parameters –
Multiple instruments – Multiple operators



Basic water testing: pH, conductivity, alkalinity, total hardness

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Multiple parameters –
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What is wet chemical colorimetric analysis?

For a basic assay, in this case sulphate

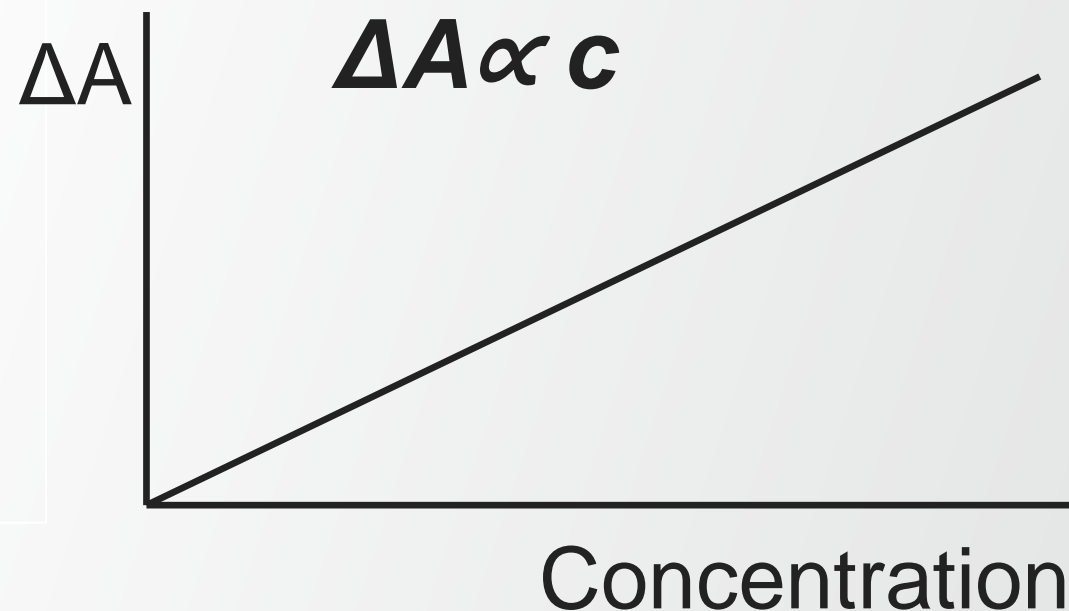
- Add an aliquot of sample (100µl)
- Shine light (420 nm) through the sample and measure the intensity in absorbance units (Au)
- Add an aliquot of barium chloride reagent (40 µl)
- Wait for the reaction to occur (300 s)
 $[\text{SO}_4^- + \text{BaCl} = \text{BaSO}_4 + \text{Cl}^-]$
- Shine light (420 nm) through again and the difference in intensity is the change in absorbance ΔA



Beer–Lambert law

$$\Delta A = \epsilon \times l \times c$$

$$\Delta A \propto c$$



Discrete analyzers in a nutshell

Photometric detection

- Colorimetric
- Enzymatic
- Electrochemistry



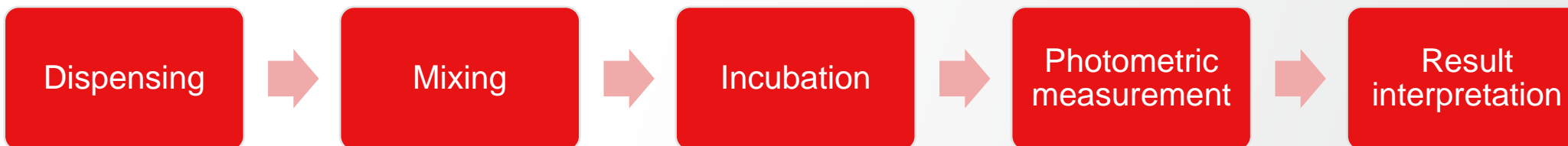
Liquid handling

- Sample aspiration
- Reagent addition
- Mixing and washing
- Calibration, QC, spiking, and dilution
- Incubation



Automation

- Random access
- Parallel analysis
- Auto-dilutions on overrange samples
- High throughput



High throughput photometric analyzer

Simplified workflow solution

Gallery Aqua Master discrete analyzer workflow



Load cuvettes



Insert samples



Insert reagents



Run analytes
Quick startup
Create run table
Start analysis



Fully-automated
water and nutrient analysis
Automated calibration, QC
scheme, spiking, dilution
Parallel pH & conductivity
measurement



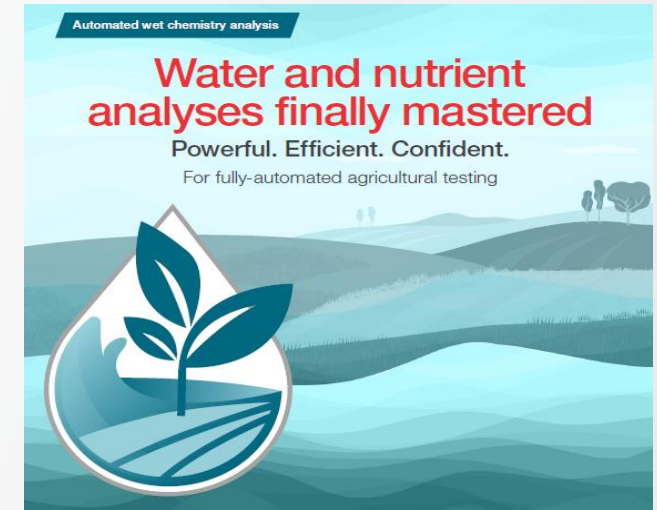
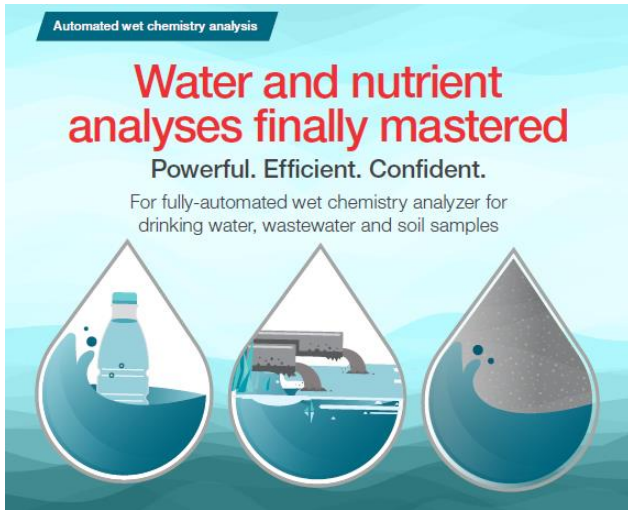
Consolidated report
Flexible reports by tests
PDF
LIMS export
Spreadsheet

Walk away from Gallery system



Highly automated workflows built for regulatory compliance

Recent advances of Gallery Aqua Master systems



Software features for regulatory (EPA) compliance

- ✓ Choice of calibration order and relative standard error calculation (RSE)
- ✓ Automated spiking procedure for easy identification of sample-matrix-related interferences
- ✓ More flexibility for automated QC procedures
- ✓ More flexible results reporting
- ✓ Easy dilution rerun of multiple samples

New automation features reduce manual workarounds and risk of errors

Choice of calibration order, relative standard error calculation (RSE)

- Comprehensive calibration commands and flexibility
- Ascending or descending concentration calibration orders
- Automated RSE calculation with user-defined limits and automated error flagging if a limit is exceeded
- Instant feedback for calibration and goodness-of-fit — industry preferred

The screenshot shows the 'Calibration' tab in the software. The 'Calibration order' dropdown is set to 'Ascending' and is highlighted with a red box. Below it is a table with the following data:

Nbr	Calibrator	Cu	Dilution 1 +
1	Cal1	Defa	0
2	Cal2	Default	0

The 'QC' section on the right has a red box around the 'RSE max. (%)' field, which is currently empty. Other fields in the 'QC' section include 'Abs. error (A)', 'Rel. error (%)', 'Factor limit min.', 'Factor limit max.', 'Bias limit min.', 'Bias limit max.', and 'Coeff. of det. min.'.

Choosing the calibration order to meet method requirements—either ascending or descending—is fast and easy using the Gallery Aqua Master discrete analyzer software.

Automated spiking procedure for easy identification of sample-matrix-related interferences

The screenshot displays the software interface for the Gallery Aqua Master discrete analyzer. The top navigation bar includes function keys F1 through F5. Below this, a menu bar contains options: 1 Test status, 2 Reagents, 4 Test definition (selected), 5 Reagent definition, 6 Wash definition, and 7 Profile definition. The main content area has tabs for Info, Flow, Dilution, Limits, Reflex/Screening, Calibration, QC, and Spiking (selected). The Spiking configuration screen includes the following fields:

- Standard for the preparation cell: Spike ratio (%) 2,00
- Calibrator name: CI-High
- Volume (µl): 4
- Extra volume (µl): 10
- Sample for the preparation cell:
 - Volume (µl): 196
 - Extra volume (µl): 50
- Recovery limit min. (%): 90,00
- Recovery limit max. (%): 110,00
- RPD limit max. (%): 10,00
- Spike on interval: Yes
- Request interval: 10

The Gallery Aqua Master discrete analyzer software provides for automated sample spiking that can streamline identification of sample-matrix-related interferences, including minimum and maximum limits for percent recovery and maximum limit for percent RPD

- Spiking series can be automatically and repeatedly performed at user-specified intervals
- Saves time and reduces error compared to manual sample spiking
- Automated calculation of the concentration of native and spiked samples, recovery for both spiked samples, and the Relative Percent Difference (RPD) between spiked samples
- User-defined minimum and maximum limits for percent recovery and maximum limit for RPD

More flexibility for automated QC procedures

- User-configurable QC elements and procedures can be set to run 1) at defined intervals, and 2) at the start or end of a run
- If multiple QC procedures must be run, their sequence is user definable

The screenshot shows the 'QC' configuration tab. On the left, a list of procedures is shown with 'Procedure2' selected. On the right, the 'Trigger' section has several checkboxes: 'Manual', 'Calibration', 'Interval', 'Reagent lot change', 'Reagent vial change', 'Start of run', and 'End of run'. Below this is a table titled 'Controls and rules'.

Control	Current Lot	Conc.	SD	Req. count	Run group
LRB	Default	0,00	0,005	1	All
NO3N-LFB 1	Default	1,00	0,050	1	1
NO3N-LFB 4	Default	4,00	0,200	1	2

This screenshot is similar to the one above but highlights the 'Start of run' and 'End of run' checkboxes in the 'Trigger' section with a red circle. The 'Manual' checkbox is also highlighted with a dashed box.

The screenshot shows the 'Configuration' tab with various system settings. A red box highlights the 'Perform QC in start and end of run' setting, which is set to 'Yes'. Other settings include 'Use barcode checkdigit' (Yes) and 'Report result outside of test limits' (Procedure specific).

Run group for controls

- Controls of a QC procedure have a new setting: Run group
- Controls can be defined to be part of a specific, or of all, run groups.
- Each time a QC procedure is run, the software will run the controls appropriate for the current run group
- The Run group setting provides flexibility for automatically alternating the controls that are run each time the procedure is run

The screenshot shows the 'QC' configuration page for 'Procedure1'. The 'Controls and rules' table is as follows:

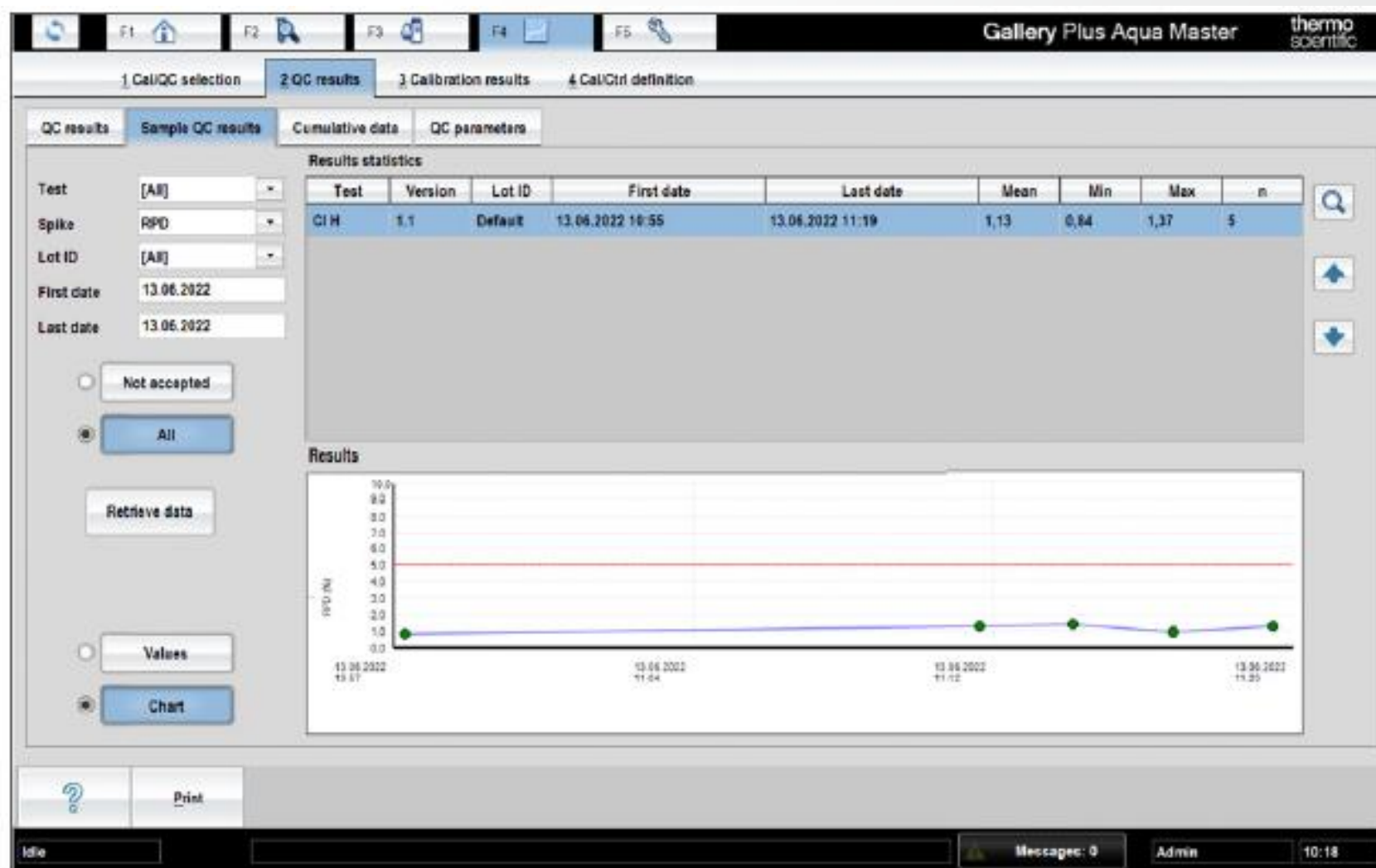
Control	Current Lot	Conc.	SD	Req. count	Run group
High-CL-QC	Default	50,00	5,000	1	1
Low-CL-QC	Default	5,00	0,250	1	2
CL-QC20	Default	20,00	2,000	1	All

The 'Run group' column is circled in red. To the right, the 'Usage' section shows 'In use' set to 'Yes', 'Acceptance' set to 'Manual', and 'Requests' set to 20.

*Example above: The first time the procedure 1 is run, the control High-CL-QC belonging to **Run group 1** is run. The next time the procedure1 is run, the control Low-CL-QC belonging to **Run group 2** is run. As there are no more run groups defined, on the third round it starts again from run group 1. The control CL-QC20 is run every time the procedure1 is run, as it belongs to **Run group "All"**.*

More flexibility for automated QC procedures

- Automated transfer of QC data into the Gallery Aqua Master discrete analyzer's QC charts to visualize trends
- Saves time compared to manually transferring data to LIMS or Shewhart control charts



Flexible results reporting

Test results report

Sample/ctrl ID	Test	Accepted	Result time	Result
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Sample report	Default 1
Test report	Custom
Spreadsheet report	Default
Archive window list report	Default
Results window list report	Default
Archive window spreadsheet report	Default

The report editor includes versatile capabilities to report test results, including report templates that can be easily customized to meet laboratory needs.

- Versatile results reporting, including predefined and easily customizable report templates available by test
- Environmental laboratories can report by tests, samples and or batches
- The report editor also allows customization of the header texts and logos used

Easy rerun of samples with new dilution factors

- Multiple samples can be rerun without having to individually define a new dilution factor for each
- Important usability improvement makes life a lot easier and enables time saved each day

The screenshot displays the '4 Results' tab of the software interface. At the top, there are navigation tabs: 1 Samples, 2 Rack disk, 3 Racks, 4 Results (selected), 5 Reports, 6 Requests, 7 Archive, and 8 Request counter. Below the tabs, there are search and filter fields for Test name (CI H), Sample ID ([All]), Group ID ([All]), Group name ([All]), and Request type (Sample, Control). The main area contains a table with the following columns: Test name, Sample/ctrl ID, Result, Unit, Status, Note, Dil. 1+, and Errors. The table lists various test results, with rows 14 and 15 highlighted in blue. A dialog box titled 'Enter dilution for rerun' is open over the table, showing a list of 'Test dilutions (1 +)' with values 0, 3, 9, 29, and 99. The 'Enter dilution (1 +):' field contains the value 3. The dialog has 'OK' and 'Cancel' buttons. At the bottom of the interface, there are buttons for '?', Print, Accept page, Accept selected, Reject selected, and Rerun selected.

Test name	Sample/ctrl ID	Result	Unit	Status	Note	Dil. 1 +	Errors
CI H	1 MD	57,08	mg/l	calc		0	Spike recovery high
CI H	CCVB	-11,46	mg/l	calc		0	Outside calibration
CI H	CCV CI 59	52,36	mg/l	calc		0	
CI H	10	0,33	mg/l	calc		0	
CI H	10 M	56,48	mg/l	calc		0	
CI H	11	1,11	mg/l	calc		0	
CI H	12	0,53	mg/l	calc		0	
CI H	10 MD	57,00	mg/l	calc		0	
CI H	CCVB	-11,49	mg/l	calc		0	
CI H	CCV CI 59	52,08	mg/l	calc		0	
CI H	14	0,45	mg/l	calc		0	
CI H	15	0,46	mg/l	calc		0	
CI H	13 MD	57,09	mg/l	calc		0	
CI H	CCVB	-11,53	mg/l	calc		0	
CI H	CCV CI 59	52,28	mg/l	calc		0	

To rerun samples using a new dilution factor simply select the samples to rerun and then enter the new dilution factor.

Built for regulated analyses

Environmental labs are highly regulated environments, as such analysis techniques & methods used must be compliant with recognized regulatory methods or standards.

- ✓ New automation features further reduce manual workaround and risk of errors

Gallery discrete analyzers

U.S. EPA wastewater reference methods		U.S. EPA drinking water reference methods	
Analyte	Regulatory method	Analyte	Regulatory method
Alkalinity	EPA 310.2 (Rev. 1974)	Nitrate + Nitrite (TON) (Hydrazine reduction)	SM 4500-NO3-H
Ammonia	EPA 350.1 (Rev. 2.0 1993)	Nitrate + Nitrite (TON) (Vanadium reduction)	NEMI (Nitrate via manual Vanadium (III) reduction)
	SM 4500-NH3-F		
	SM 4500-NH3-G		
COD*	EPA 410.4 (Rev. 2.0 1993)	Nitrite	N07-0003 (Bypass enzymatic reduction)
Chloride	SM 4500-Cl-E		SM 4500 NO2-B
Chlorine (Total residual)*	SM 4500-Cl-G	Orthophosphate	EPA 365.1 (Rev. 2.0 1993)
Conductivity	EPA 120.1 (Rev. 1982)		SM 4500-P-E
Copper*	SM 3500-Cu-C	pH	EPA 150.2 (Dec. 1982)
Cyanide (Amenable)*	SM 4500-CN-G	Silica	SM 4500 SiO2-C
	EPA 335.4 (Rev. 1.0 1993)		SM 4500 SiO2-D
Cyanide (Total)*	SM 4500-CN-E	Sulfate	SM 4500 SO4-E
	SM 4500-CN-E		ASTM D516-16
Fluoride	SM 3500-F-D		Sulfide*
Total hardness	EPA 130.1 (Issued 1971)	Total Kjeldahl nitrogen (TKN)*	EPA 351.2 (Rev. 2.0 1993)
Chromium	SM 3500 Cr-B	Total phenol*	EPA 420.1 (Rev. 1978)
Iron	SM 3500 Fe-B	Total phosphorous (TP)*	EPA 365.1 (Rev. 2.0 1993)
			EPA 365.4 (Issued 1974)
			SM 4500-P-E

* Third party reagent

Methods compliant with U.S. EPA, NELAC, ASTM and other international standards

Overcome nitrate + nitrite (TON) measurement challenges

Using safer enzymatic methods in Gallery discrete analyzers

Limitations of traditional cadmium reduction coil methods



Carcinogenic health risk



Costly waste disposal



Time-consuming, manual methods

Advantages of enzymatic Nitrate + Nitrite method



Green chemistry

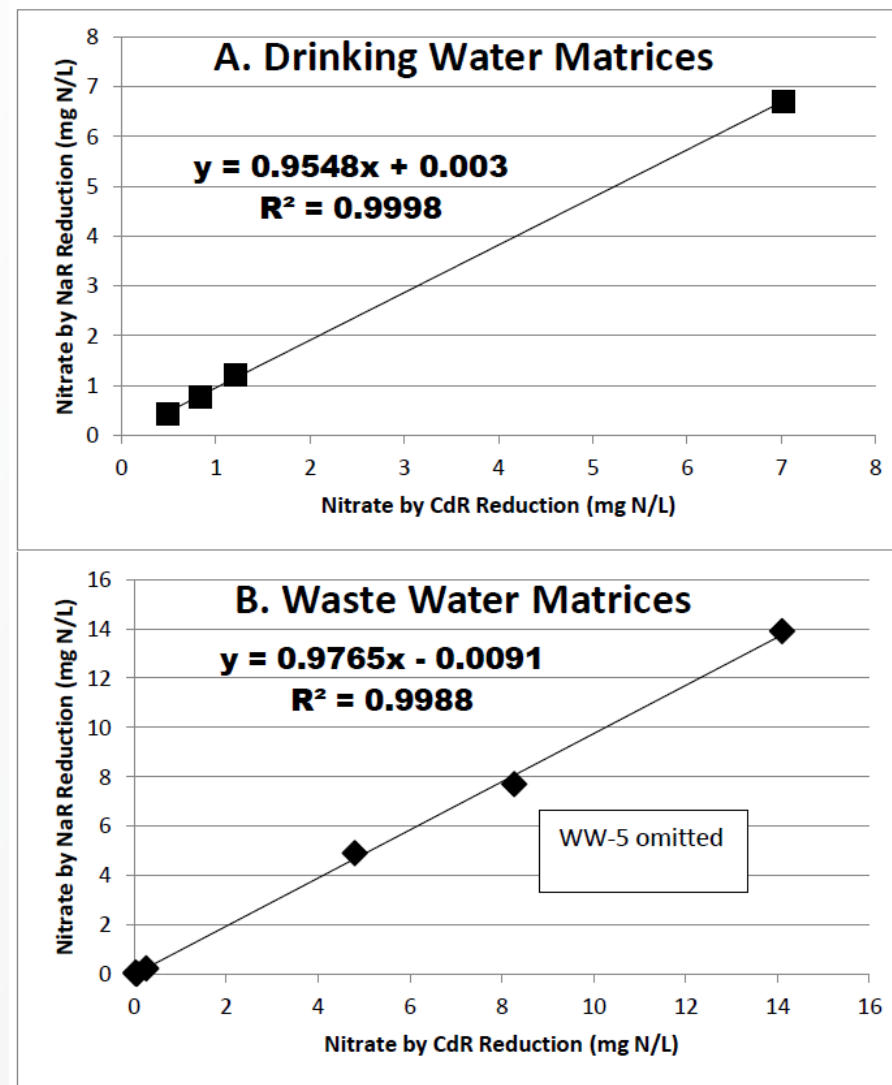


No sample preservation or pH adjustment



Cost effective

In compliance with 40 CFR Part 136, 40 CFR Part 141.23, 40 CFR Part 141, NECi-N07-0003, USGS I-2547-11, USGS I-2548-11 and, NECi Nitrate-Reductase regulatory standards.



Data courtesy to the NECi method report N07-0003

Figure 1A, 1B. Results comparison of cd reduction method and nitrate reductase method

Detecting nitrate + nitrite (TON) in drinking water

Official system method for EPA Safe Drinking Water Act (SDWA)



Automated method to detect the sum of nitrate + nitrite (TON) in drinking water using the Thermo Scientific Gallery discrete analyzer

Application benefits

- Meets requirements of regulated nitrate + nitrite total oxidized nitrogen methods
- Minimizes use of hazardous reagents and their associated costs and safety risks when carrying out nitrate + nitrite methods
- Automation and Thermo Scientific™ Gallery™ system reagents save time and reduce errors compared to manual approaches

Table 9. Performance of the Thermo Scientific drinking water method: drinking water nitrate + nitrite for Thermo Scientific Gallery discrete analyzer compared to reference method acceptance criteria

	QC acceptance criteria for reference method <i>Method for Nitrate Reductase Nitrate-Nitrogen Analysis of Drinking Water, Ver. 1.0 Rev. 2.0 Feb 2016</i>	Performance of nitrate + nitrite method for the Gallery Discrete Analyzer
MDL	To be determined by each laboratory according to 40 CFR Part 136 Appendix B. (MDL results in reference method validation were between 0.0066 and 0.0097 mg N/L)	MDL: 0.0038 mg N/L when done according to 40 CFR Part 136, Appendix B. MDL 0.009 mg N/L was applied*
MRL	NA	0.027 mg N/L
Reduction efficiency	90–110%	101–103%
Method blank	<MDL	*max. 0.0088 mg/L < MDL (0.009 mg N/L)
% Recovery initial calibration range (ICR)	±10% of true value, the equation between instrument responses and the nominal values of the standards must have regression coefficient (R ²) ≥ 0.999	9–110% for both primary and extended ranges (0.027–25 mg N/L). The R ² was 1.000 for both ranges.
% Recovery QCS	±10%	94–97%
Recovery initial precision and recovery (IPR)	From CRM certificate (ERA #698, lot: S234-698 acceptance limits 8.49–10.5 mg N/L) or ±10% of known value, whichever is more restrictive.	Recovery IPR: 8.70–8.95 mg N/L (91–93% recovery)
% Recovery ongoing precision and recovery (OPR)	±10%	91–102%
% Recovery spike sample	±10%	91–100%
% RSD IPR	NA	1.2%
% RSD OPR	≤10%	1.4–1.9%
Relative percent difference (% RPD) spike duplicates	≤10%	0.1–0.4%

*The method criteria state that the LRB sample should never be higher than the MDL. The highest individual LRB result of the test was 0.0088 mg N/L.

Conclusion:

The results demonstrated that the Gallery discrete analyzer-based automated method meets the QC acceptance criteria in the EPA-approved reference method for testing drinking water.

Detecting orthophosphate in drinking water

Official system method for EPA Safe Drinking Water Act (SDWA)



Automated method to detect orthophosphate in drinking water using the Thermo Scientific Gallery discrete analyzer

Application benefits

- Meets the requirements of regulated methods for orthophosphate testing in drinking water.
- Automation and ready-to-use reagents save time and reduce errors compared to manual approaches.

Table 10. Performance of the Thermo Scientific drinking water method: Drinking water orthophosphate for the Thermo Scientific Gallery discrete analyzer compared to the reference method acceptance criteria

	QC acceptance criteria for reference method: standard method 4500-P E.	Performance of drinking water ortho-PO4P method for the Gallery discrete analyzer
MDL	Minimum 7 replicates of MDL sample, conc. 1–5 x MDL estimate, analyzed in 3 days, ideally by different users. Recoveries should be 50–150% and % RSD ≤20%.	0.00036 mg P/L when the procedure in 40 CFR part 136, Appendix B was used. The procedure is similar to reference method.
MRL	Set at or above the lowest calibrator and verified with QC sample at 1 to 2 times the MRL conc. Result is acceptable if precision and accuracy meet laboratory method requirements.	0.0125 mg P/L. The MRL confirmation procedure was done per EPA requirements. ⁷
Method blank	<1/2 MRL	Max. 0.0035 mg/L
% Recovery continuing calibration verification (CCV)	±10%	100–105%
% Recovery QCS	±15%	97–98%
% Recovery spike sample	Laboratory specific	92–98%
% RSD CCV	Laboratory specific	1.3–1.9%

Conclusion:

The results demonstrated that the Gallery discrete analyzer-based automated method meets the QC acceptance criteria in the EPA-approved reference method for testing drinking water.

Learn more about Gallery Aqua Master systems

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Thank you