Automated, Accurate pH and Conductivity Measurements Using a Discrete Photometric Analyzer with an ECM Module

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Introduction

In this study pH and electrical conductivity (EC) were measured from water samples using an Electro Chemical Measurement (ECM) unit integrated into an automated discrete photometric analyzer. Integrated ECM unit is capable of simultaneously measure both pH and conductivity alongside the photometric testing. Accuracy of the results was verified by parallel testing with manual conductivity and pH meters.

Conductivity test has been developed to cover a measurement range from 20 µS/cm to 112 mS/cm. The pH test measures a pH range from 2 to 12. Results show very good precision, below 1.0 %, and good correlation to the manual methods with an R^2 value ranging from 0.977 to 1.000.

Methods

In the ECM unit, the conductivity measurement is performed via two electrodes. pH is measured using a two-electrode galvanic cell consisting of an indicator pH electrode and a reference electrode.

Temperature compensation

Both conductivity and pH are measured at 37 °C. However, results can be reported in different temperatures, e.g., at 25 °C, because the discrete analyzer software has a robust system with which the sample result may be correlated to a reference analyzer result automatically.
Published correction factor values for conductivity measurements are available for a variety of sample types.

Instruments

Thermo Scientific™ Gallery™ Plus analyzer with the ECM unit.

Thermo Scientific™ Orion™ 3 Star benchtop pH meter with Orion ROSS™ Combination Glass pH Electrode.

Radiometer™ CDM 80 Conductivity meter.

Calibration

Calibration in the Gallery analyzer is performed using point-to-point calibration type. With a point-to-point calibration separate linear equations are generated between each set of two calibrators. For example if the calibration is done using five calibration levels, four separate equations are generated for the four linear segments.

FIGURE 1. Conductivity calibration.

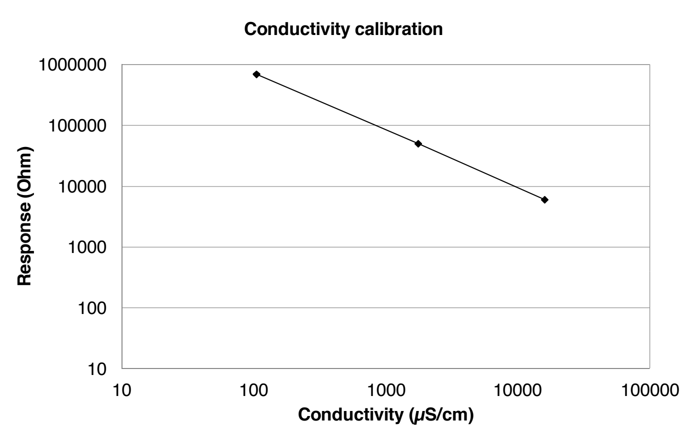
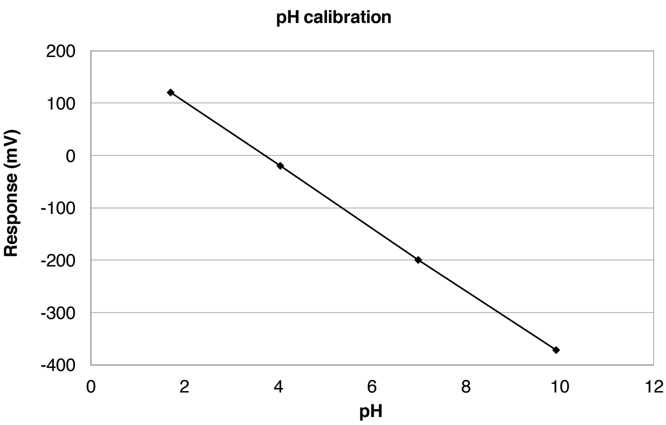


FIGURE 2. pH calibration.



Results

All measurements were done simultaneously with the Gallery Plus discrete analyzer and the manual pH or conductivity meter. Figures from 3 to 6 shows the method comparison results. Temperature compensation is not included in the graphs, but correction factors and biases for different matrices are calculated to the Table 1.

FIGURE 3. Method comparison of natural water samples containing surface and ground water samples. Samples were measured at +37°C using Gallery temperature compensation with the correction factor of 0.793 (from literature).

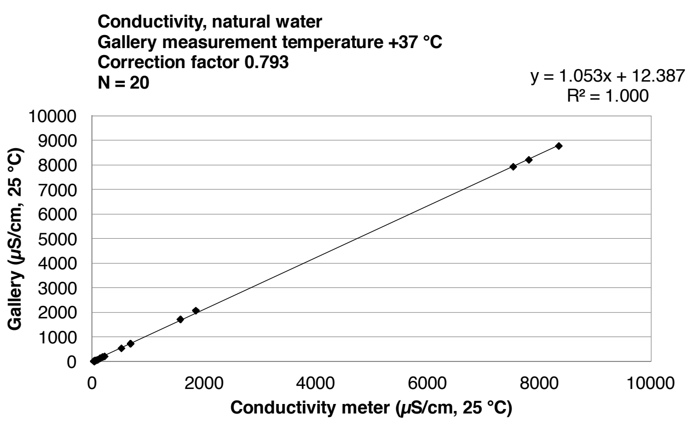


FIGURE 4. Method comparison of surface water samples.

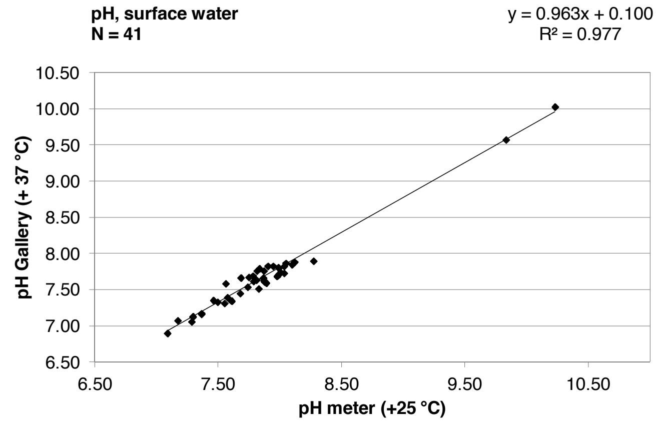


FIGURE 5. Method comparison of ground and well water samples.

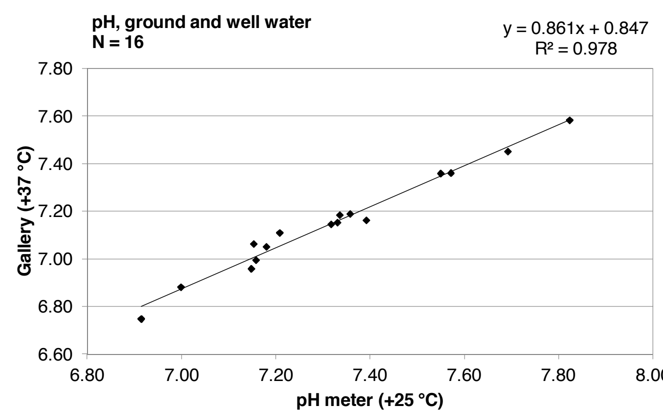


FIGURE 6. Method comparison of waste water samples containing influents, effluents and industrial waste waters.

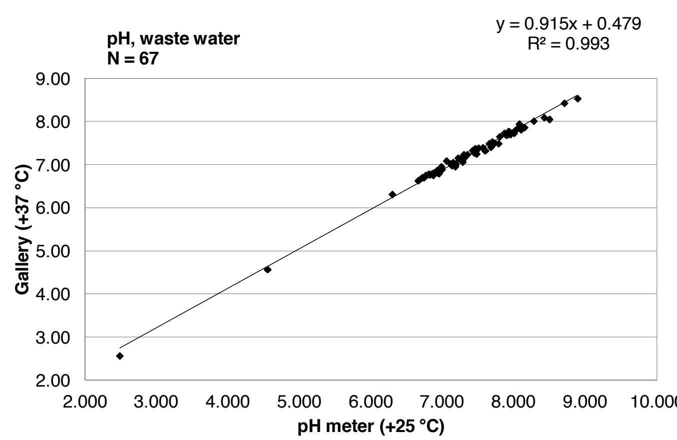


TABLE 1. Calculated correction factors and biases for different matrices based on method comparison results. C_{factor} is the inverse of the slope and C_{bias} is the unmodified y-intercept.

	C_{factor}	C_{bias}
Surface water	1.038	0.100
Ground and well water	1.161	0.847
Waste water	1.093	0.479

TABLE 2. Precision results of conductivity and pH.

	Natural water			
	Conductivity		pH	
	N	20	**N**	20
	Mean (µS/cm)	194.13	**Mean**	7.80
	SD	**CV %**	**SD**	**CV %**
Within Run	0.709	0.37 %	0.061	0.78 %
Between Run	1.410	0.73 %	0.007	0.09 %
Total	1.578	0.81 %	0.062	0.79 %

Conclusion

The automated pH and conductivity methods correlate well with the manual methods. Although measurement temperature in the ECM unit is higher, the temperature compensation can be done automatically with the software and the results can be reported at +25°C.

References

1. Laxen, D.P.H., A specific conductance method for quality control in water analyses. In: Water Research, Vol 11, 1977, pp 91-94.
2. SFS-EN 27888:1985, Suomen Standardisoimisliitto SFS. Water quality. Determination of electrical conductivity.

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