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Rapid Analysis of Acids in Wines Using Automated Discrete Analyzers

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Introduction

Acids (such as acetic, lactic, malic, citric, and tartaric acids) contribute to the flavor, stability, color, and pH of wines. Measurements for acids are performed during process control, raw material inspection, or for quality control. In this paper, Thermo Scientific™ Gallery™ discrete analyzers are used and the methods for the associated system reagents are described. Automated bench-top Gallery instruments can simultaneously measure several acids from a single sample and homogenous samples can be measured without pretreatment using colorimetric or enzymatic methods. Applications are optimized requiring small reagent volumes and resulting in a low cost per test.

Measuring ranges and performance data are presented. The correlation graph illustrates the quality control sample concentration plotted against a theoretical calculated concentration. Precision studies demonstrate the repeatability and reproducibility of the methods used.

Discrete cell technology offers faster, reproducible results where multiple tests can be done on a single sample without the need for additional method changeover time. All necessary analysis steps are automated, providing true walk-away time for the operator. In less than ten minutes after the insertion of samples into the analyzers, results are obtained.

Materials and Methods

Thermo Scientific system reagents are ready-to use. Some reagents are available in lyophilized or powdered format which requires reconstitution and ensures a longer shelf life. Reagent volumes are optimized for the system application; an average of 300 test results can typically be reported from each kit.

Ready-to-use and single use reagent vials are bar-coded. Embedded in the barcode is the material lot number and expiration date. As part of its programming, the instrument sounds an alarm when the reagent is almost finished and can automatically calibrate after the insertion of a new reagent vial. In addition to the reagent's on-board stability, the instrument has the capability to fully trace reagents and store results, including associated calibrations and reagent lot data.

Instruments and Application

Thermo Scientific Gallery and Gallery Plus analyzers are pre-programmed with the methods to test various acids in their application menu. Application parameters are adapted to test less than 300 µL of total volume where the sample and first reagent are usually blanked to eliminate any color interference.

Measuring Range

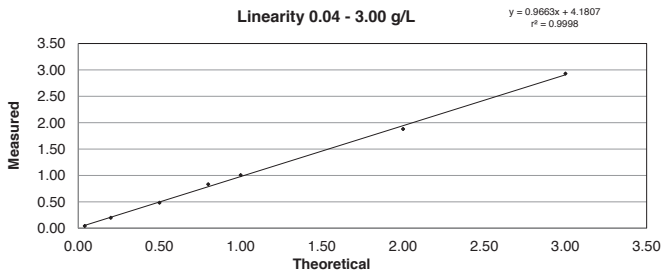
Measuring ranges for each acid kit are shown in Table 1. Applications are designed to incorporate automated dilutions that achieve these ranges.

Table 1. Measurement ranges of acid kits.

Kit	Test limit low	Test limit high
Acetic acid (ACS)	0.04 g/L	3.0 g/L
Citric acid	15 mg/L	5000 mg/L
D-Lactic acid	25 mg/L	1600 mg/L
L-Lactic acid	20 mg/L	1600 mg/L
L-Malic acid	0.05 g/L	20 g/L
Tartaric acid	0.5 mg/L	12 mg/L
Total acids (Wine pH 7)	1 g/L as tartaric acid 0.5 g/L as sulfuric acid	18 g/L as tartaric acid 12 g/L as sulfuric acid

Results and Discussions

Linearity performance curves for each method using water based solutions are presented in Figures 1—7. The analyzers are designed with an automated dilution function, allowing for easy insertion of additional calibration points if required. The image plots linearity comparing both measured and theoretical values.



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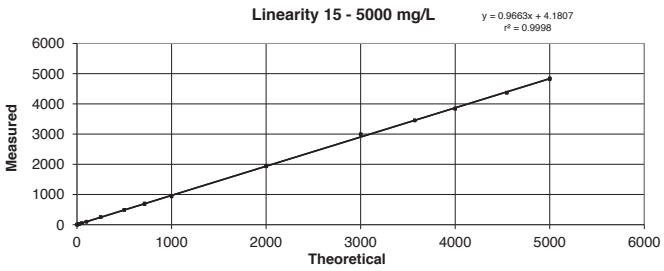

FIGURE 2. Citric acid.

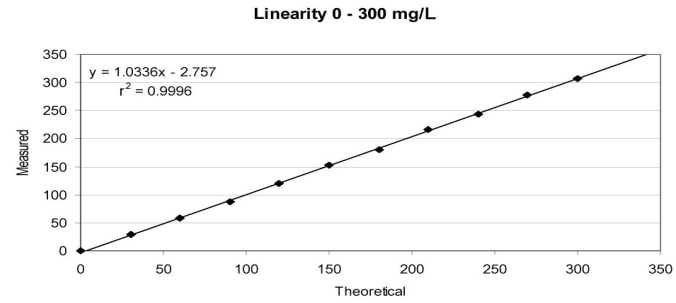

FIGURE 3. D-Lactic acid.

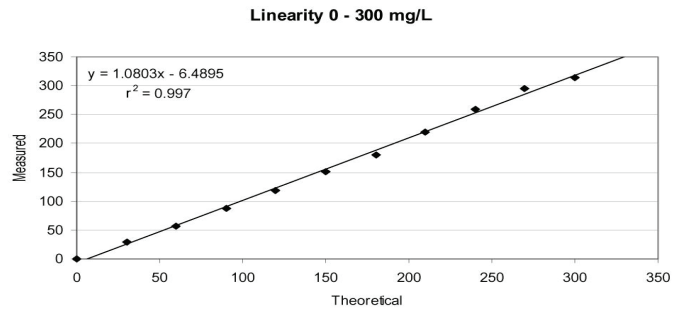

FIGURE 4. L-Lactic acid.

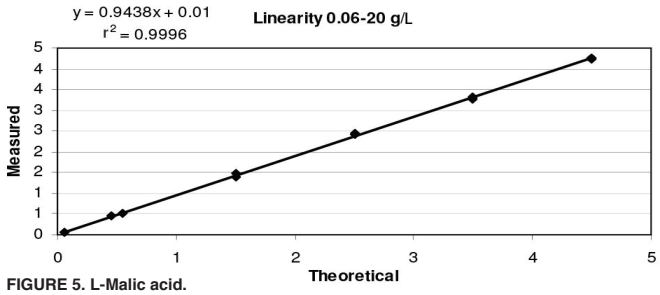

FIGURE 5. L-Malic acid.

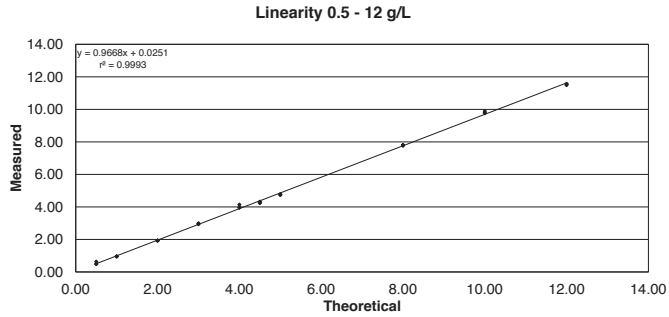

FIGURE 6. Tartaric acid.

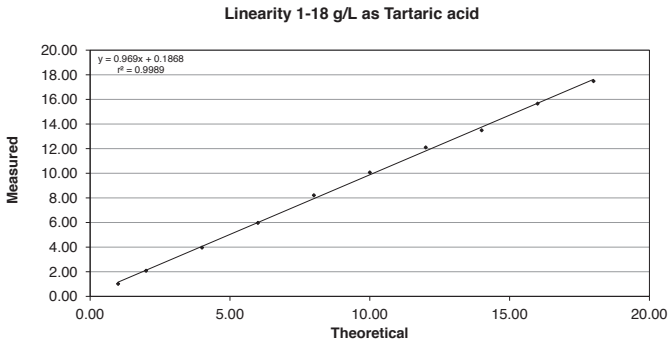

FIGURE 7. Total acids (Wine pH7).

Table 2. Method precision data for Gallery analyzers.

Acetic acid (ACS)	Mean 0.44 g/L		Mean 0.92 g/L	
	SD	CV %	SD	CV %
Within run	0.003	0.7	0.005	0.6
Between run	0.010	2.3	0.013	1.5
Total	0.010	2.4	0.014	1.6

D-Lactic acid	Mean 31		Mean 77		Mean 172	
	SD	CV %	SD	CV %	SD	CV %
Within run	0.791	2.6	0.884	1.1	5.049	2.9
Between run	0.872	2.8	1.143	1.5	0.426	0.2
Total	1.177	3.8	1.445	1.9	5.067	2.9

L-Malic acid	Mean 1.19		Mean 2.44		Mean 3.83	
	SD	CV %	SD	CV %	SD	CV%
Within run	0.011	0.9 %	0.023	0.9 %	0.024	0.6
Between run	0.017	1.4 %	0.035	1.4 %	0.065	1.7
Total	0.020	1.7 %	0.042	1.7 %	0.069	1.8

Total acids (Wine pH 7)	Mean 4.15		Mean 5.15		Mean 6.81	
	SD	CV %	SD	CV %	SD	CV %
Within run	0.036	0.9 %	0.047	0.9 %	0.052	0.8 %
Between run	0.087	2.1 %	0.032	0.6 %	0.032	0.5 %
Total	0.094	2.3 %	0.057	1.1 %	0.061	0.9 %

Citric acid	Mean 61 mg/L		Mean 126 mg/L		Mean 3779 mg/L	
	SD	CV %	SD	CV %	SD	CV %
Within run	1.4	2.2	1.2	1.0	20.8	0.5
Between run	0.4	0.6	1.0	0.8	60.8	1.6
Total	1.4	2.3	1.6	1.3	64.3	1.7

L-Lactic acid	Mean 26 mg/L		Mean 125		Mean 182 mg/L	
	SD	CV %	SD	CV %	SD	CV %
Within run	0.662	2.0	1.605	1.3	2.681	1.5
Between run	0.789	3.0	1.570	1.3	1.631	0.9
Total	1.029	4.0	2.246	1.8	3.138	1.7

Tartaric acid	Mean 2.76		Mean 2.11	
	SD	CV %	SD	CV %
Within run	0.045	1.6 %	0.052	2.5 %
Between run	0.043	1.5 %	0.042	2.0 %
Total	0.062	2.2 %	0.067	3.2 %

Analysis Speed

An automated operating systems allow laboratories to simultaneously measure multiple analytes while reducing total analysis time and increasing efficiency. The Gallery Plus analyzer is capable of performing an acid test panel for 100 samples in 4 hours and 20 minutes. The panel includes tests for acetic, citric, D-lactic, L-lactic, L-malic, tartaric, and total acids from each sample. First results are available in less than 14 minutes. In comparison, if acetic, L-lactic, and L-malic acids are tested for 100 samples, the Gallery Plus instrument completes the panel in 2 hours and 25 minutes and if only tartaric acid is tested, the Gallery Plus instrument completes 100 tests for tartaric acid in 77 minutes with the first results available in less than 6 minutes.

Conclusions

Thermo Scientific Gallery and Gallery Plus automated discrete analyzers have the capability to measure several acids from a single sample without the need for extra method changeover time. Since the analyzer can automate sample dilutions, methods are designed to accurately measure large concentration ranges. Methods were repeatable; a within run CV% as low as 0.5% can be achieved for citric acid analysis. When comparing the calculated concentration to the measured concentrations, an $r^2 = 0.997$ or better was obtained.

All necessary analysis steps are automated, providing true walk-away time for the operator. Results are fully traceable and designed for ease of use. Optimized applications ensure the use of very low volumes of reagents which result in low costs per test. Discrete cell technology offers rapid process and quality testing for wine samples. The analysis of 100 samples using the acetic acid, L-lactic acid and L-malic acid tests are completed less than 2 hours and 30 minutes.

References

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2. Compendium of International Methods of Analysis, Citric acid, Method OIV-MA-AS313-09 : R2009 1
3. Beutler, H. O. Methods of Enzymatic Analysis. L-Ascorbate and L- Dehydroascorbate. 3rd ed; Bergmeyer, H. U., Ed.; VCH Publishers (UK) Ltd., Cambridge, UK, 1988: Vol. VI, pp 376-385.

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