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Application News

SSI-LCMS-139

Liquid Chromatography Mass Spectrometry

Quantitation of Smoke Taint Markers in Wine using the Triple Quad LCMS-8050

Liquid Chromatograph Mass Spectrometer
LCMS-8050

■ Summary

Guaiacol rutinoside and 4-methylguaiacol rutinoside are smoke taint markers that are found in grapes and wine that have been exposed to smoke from forest fires. Four different white and red wine samples were analyzed for the two smoke taint markers.

■ Background

As the frequency and intensity of wildfires increases around the world, smoke taint has become a growing global concern for winemakers. When grapes are exposed to smoke in a vineyard due to a nearby forest fire, volatile phenols like guaiacol and 4-methylguaiacol can permeate the grape skin, bond with the sugars (glycosylation), and accumulate inside the grapes. Due to their reduced volatility, the resulting glycosides can no longer be detected by smelling or tasting the grapes. However, fermentation breaks down those bonds again and the released compounds often give the wine a burnt or "ash tray" flavor .

To allow detection of smoke taint in the grapes, certain glycosides of the volatile phenols, such as guaiacol rutinoside and 4-methylguaiacol rutinoside, have been identified as smoke taint markers. For this application, four wine samples were analyzed. An LCMS-8050 triple quadrupole mass spectrometer was used to quantitate these smoke taint compounds.

■ Method

Two white wine samples and two red wine samples were filtered through a 0.45 µm PTFE filter. No dilutions were made prior to injection for analysis.

An LC-40 Nexera HPLC system was coupled to an LCMS-8050 triple quadrupole mass spectrometer with an ESI source. A 15-minute chromatographic method was developed to quantify 4-methylguaiacol rutinoside (464.2>147.1) and guaiacol rutinoside (450.2>147.0) by MRM. Additional LC and MS parameters used in this analysis are shown in **Table 1**. **Figure 1** shows chromatograms of each analyte in unspiked and 10 ng/mL spiked White Wine A.

One white wine (White Wine A) and one red wine (Red Wine A) sample were selected to be the matrices for the matrix matched calibration curves. Since the concentrations of the two smoke taint compounds were unknown in these two wine samples, a standard calibration curve was created in both White Wine A and Red Wine A to determine the native concentrations. After the native concentration adjustment, matrix matched calibration curves in both white and red wine were obtained. The two matrix matched calibration curves, ranging from 0.5-100 ng/mL, were then used to quantify analytes in the other wine samples with corresponding matrices. All samples and calibrators were analyzed on an LCMS-8050 in duplicate.

Table 1: LC and MS parameters used.

LC Parameters		MS Parameters	
Injection Volume (µL)	15	**Nebulizing Gas (L/min)**	2
Column Oven Temperature (°C)	40	**Drying Gas (L/min)**	10
Chromatography	Reversed Phase	**DL Temperature (°C)**	250
Elution	Gradient	**Heat Block (°C)**	400
		Heating Gas (L/min)	10

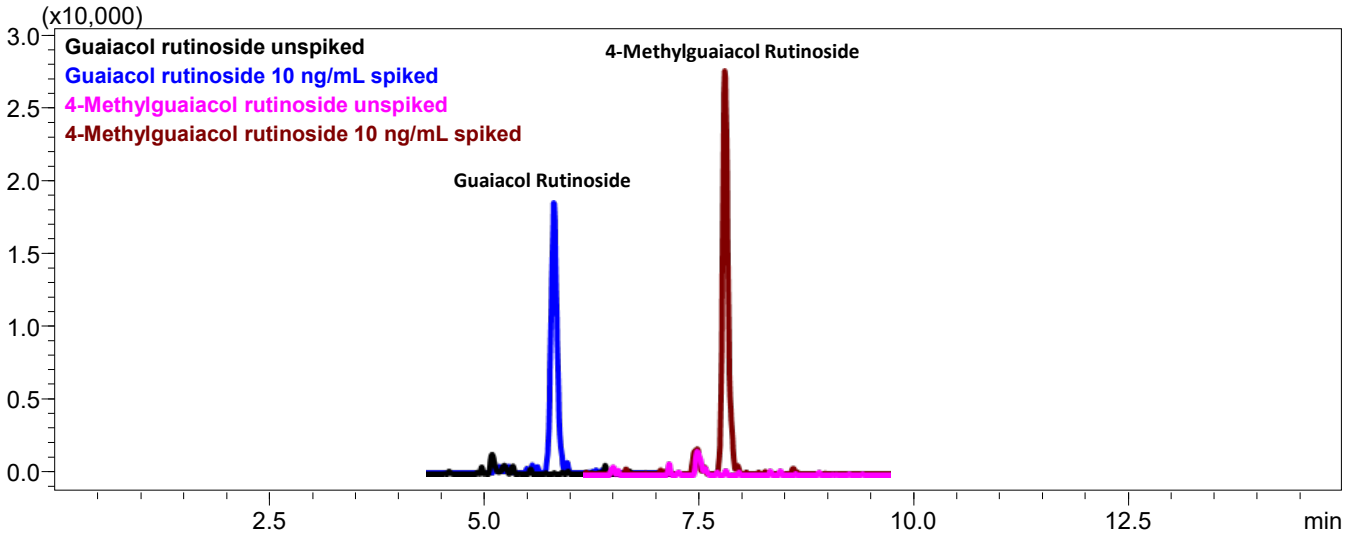


Figure 1: Example chromatograms of unspiked and spiked (10 ng/mL of guaiacol rutinoside and 4-methylguaiacol rutinoside) White Wine A overlaid.

■ Results and Discussion

Standard addition calibration curves (**Figure 2 and 3**) were generated in representative white and red wine (White Wine A and Red Wine A) to quantify native guaiacol rutinoside and 4-methylguaiacol rutinoside concentrations. (**Table 2 and 3**). Since Red Wine A already contains 13.2 ng/mL of guaiacol rutinoside, a matrix matched calibration curve in Red Wine A for guaiacol rutinoside was adjusted accordingly. Linear matrix matched calibration curves (R^2>0.999) were obtained with high accuracy at all levels (80-120% accuracy). Concentrations of guaiacol rutinoside and 4-methylguaiacol rutinoside in all wine samples were determined according to the calibration curve in corresponding matrices (**Figure 4 - 7**).

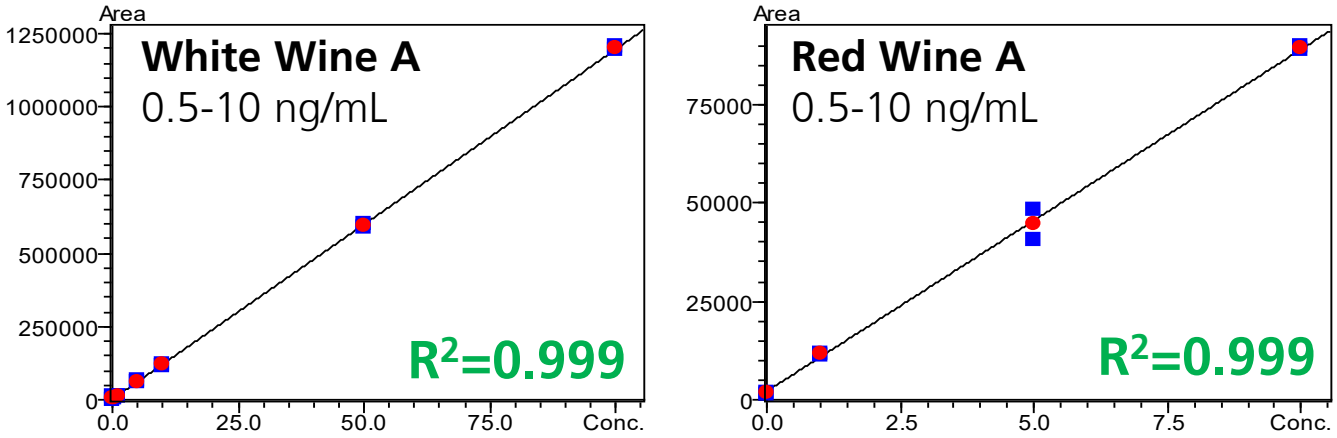


Figure 2: Standard addition curves of 4-methylguaiacol rutinoside in White Wine A and Red Wine A. Standard addition curve range and R^2 are shown for each curve.

Table 2: 4-methylguaiacol rutinoside concentration in unspiked White Wine A and Red Wine A based on standard addition results.

Sample	4-Methylguaiacol rutinoside concentration (ng/mL)
White Wine A	<0.5
Red Wine A	<0.5

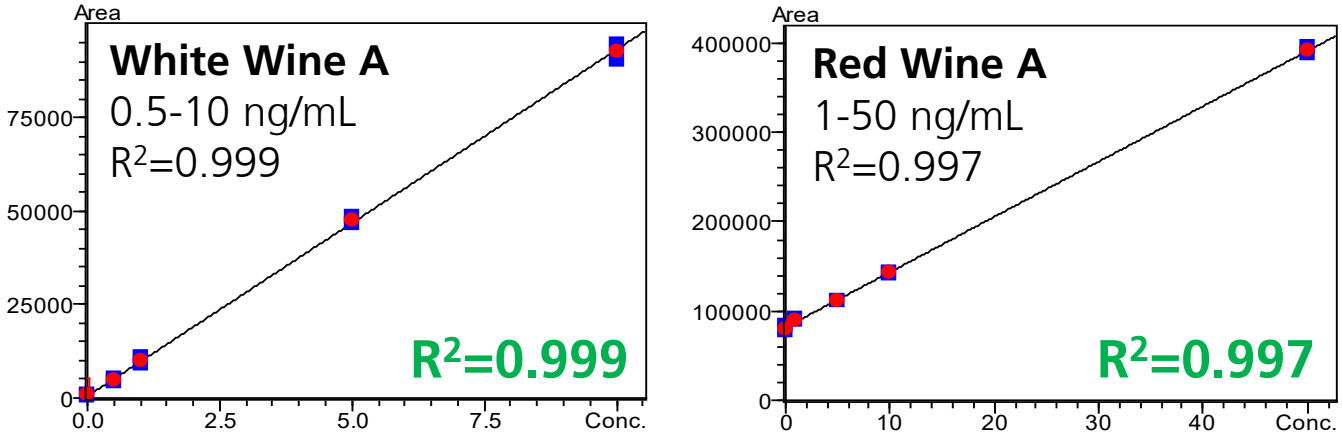
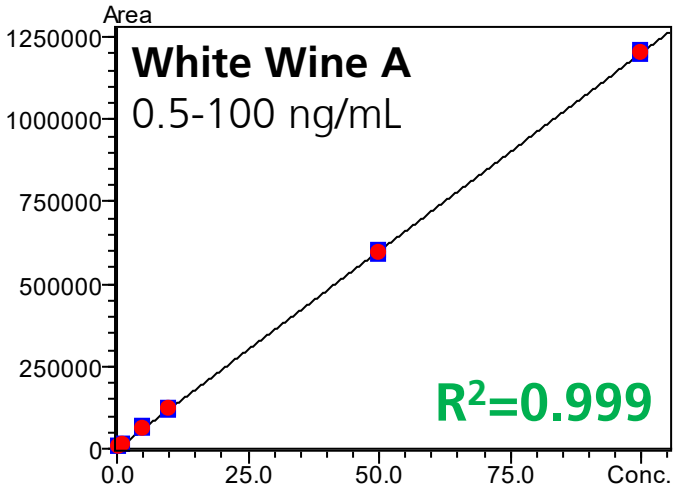


Figure 3: Standard addition curves of guaiacol rutinoside in White Wine A and Red Wine A. Standard addition curve range and R^2 are shown for each curve.

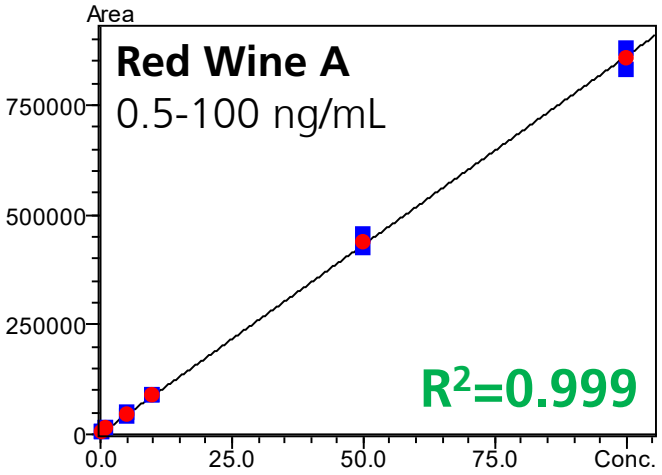
Table 3: Guaiacol rutinoside concentration in unspiked White Wine A and Red Wine A based on standard addition results.

Sample	Guaiacol rutinoside concentration (ng/mL)
White Wine A	<0.5
Red Wine A	13.2



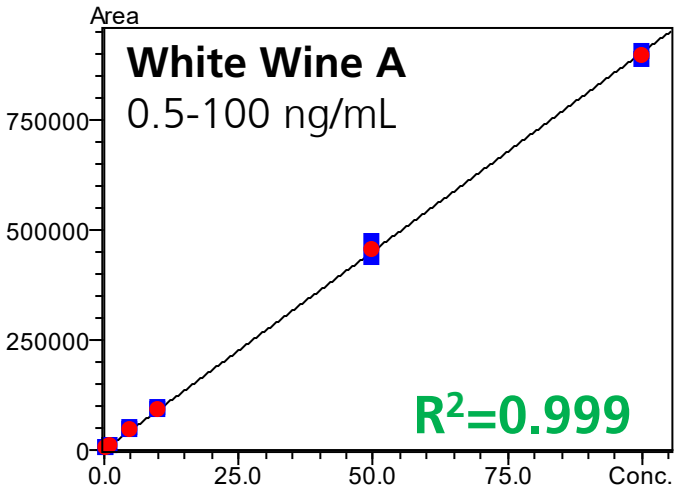
Wine Sample	4-Methylguaiacol rutinoside concentration (ng/mL)	% Accuracy
White Wine B	0.13 (<0.5)	-
White Wine B + 1 ng/mL	1.3	115%
White Wine B + 10 ng/mL	11.5	114%

Figure 4: Calibration curve of 4-methylguaiacol rutinoside in White Wine A with R^2 >0.999. Concentrations of 4-methylguaiacol rutinoside in White Wine B were determined according to the calibration curve in White Wine A. Since White Wine B quantified at 0.13 ng/mL (<0.5 ng/mL), 4-methylguaiacol rutinoside was spiked in to show a quantifiable amount.



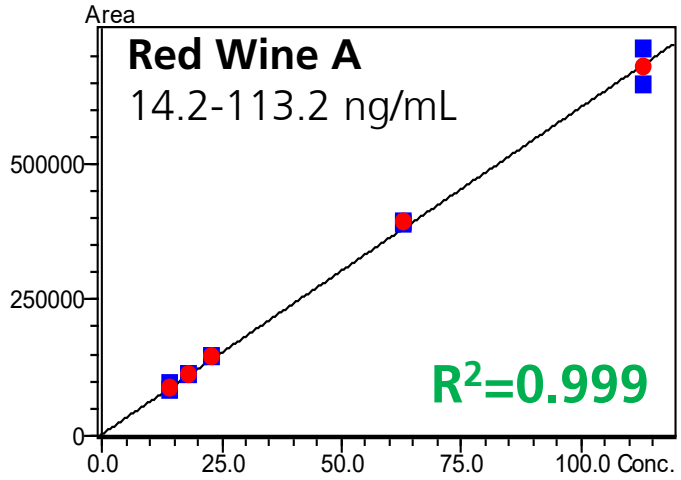
Wine Sample	4-Methylguaiacol rutinoside concentration (ng/mL)	% Accuracy
Red Wine B	6.1	-
Red Wine B + 1 ng/mL	6.8	96%
Red Wine B + 10 ng/mL	16.1	100%

Figure 5: Calibration curve of 4-methylguaiacol rutinoside in Red Wine A with R^2 >0.999. Concentrations of 4-methylguaiacol rutinoside in unspiked and spiked Red Wine B samples were determined according to the calibration curve in Red Wine A.



Wine Sample	Guaiacol Rutinoside concentration (ng/mL)	% Accuracy
White Wine B	0.49 (<0.5)	-
White Wine B + 1 ng/mL	1.4	94%
White Wine B + 10 ng/mL	12.1	115%

Figure 6: Calibration curve of guaiacol rutinoside in White Wine A with R^2 >0.999. Concentrations of guaiacol rutinoside in White Wine B were determined according to the calibration curve in White Wine A. Since White Wine B quantified at 0.49 ng/mL (<0.5 ng/mL), guaiacol rutinoside was spiked in to show a quantifiable amount.



Wine Sample	Guaiacol Rutinoside concentration (ng/mL)	% Accuracy
Red Wine B	9.5	-
Red Wine B + 1 ng/mL	9.7	92%
Red Wine B + 10 ng/mL	20.1	103%

Figure 7: Calibration curve of guaiacol rutinoside in Red Wine A with the lowest calibration point at 14.2 ng/mL (adjusted according to the standard addition result of guaiacol rutinoside concentration in Red Wine A) and R^2 >0.999. Concentrations of guaiacol rutinoside in in unspiked and spiked Red Wine B samples were determined according to the calibration curve in Red Wine A.

■ Conclusion

Two white wine samples and two red wine samples were analyzed quantitatively by an LCMS-8050 triple quadrupole mass spectrometer. Concentrations of smoke taint markers (4-methylguaiacol rutinoside and guaiacol rutinoside) were determined according to the matrix matched calibration curves. Linearity (R^2) was higher than 0.999 for all calibration curves and accuracy was between 80-120% for each calibrator. Quantitation result of the spiked wine samples (92-115% accuracy) also demonstrated the high quantitation accuracy of the method.

ULTRA FAST MASS SPECTROMETRY


LCMS-8040


LCMS-8045


LCMS-8050


LCMS-8060NX


LCMS-2020


Q-TOF LCMS-9030

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