WHITE PAPER

Detection of Methanol in Methanol/Ethanol Mixtures

Summary

A study was performed for the detection of methanol in methanol-ethanol mixtures. The scope of the study was to determine at what level methanol can be detected and what the characteristics are of the methanol-ethanol mixtures.

The study was undertaken based on the requirement that contamination of ethanol by methanol can be quickly and effectively detected based on the common adulteration levels. The contamination of methanol in ethanol poses a health risk, especially in the case of alcohol adulteration for liquor sales and off-vendor sales, and also for safety checks in reliable vendors. This study was done to assess the best levels for detection of methanol by using pure methanol and ethanol solutions and looking for characteristic spectral qualities. In addition to assessing the ability of Progeny ResQ handheld Raman to detect and identify the components of the mixtures.

Procedure

A series of solutions of methanol in ethanol were made. Triplicate samples were obtained from the stock samples. Table 1 shows the range of solutions used. All samples are based on wt/wt%. Ethanol and methanol were obtained from Sigma Aldrich and all are reagent grade.

Sample	Sample ID, % MeOH	MeOH, wt%	EtOH, wt%
1	5%	6.26	93.74
2	10%	9.78	90.22
3	15%	17.98	82.02
4	20%	19.52	80.48
5	30%	31.62	68.38
6	40%	40.64	59.36
7	50%	51.30	48.70
8	60%	58.48	41.52
9	70%	68.87	31.13
10	80%	80.04	19.96
11	90%	89.05	10.95
12	95%	94.24	5.76
13	100%	100	0.00
14	0%	0	100.00

Table 1. The range of samples used based on wt/wt%.

All samples were tested on the Progeny ResQ, after optimization on a methanol sample. The instrument settings were: AutoCollect, Master Library, Rigaku Mixture and focal point from optimization of 2. Performance Verification was done prior any testing.

Results

Material Identification Testing

The first round of testing was done on the instrument using AutoCollect and Rigaku Mixture mode. Each replicate sample was scanned and the identification and correlation was recorded.

Sample	Sample ID, % MeOH	Instrument Identification	CC, Average
1	5%	Ethanol	0.99
2	10%	Ethanol	0.99
3	15%	Ethanol	0.99
4	20%	Ethanol	0.99
5	30%	Ethanol/Methyl alcohol	
6	40%	Ethanol/Methanol	
7	50%	Ethanol/Methanol	
8	60%	Ethanol/Methanol	
9	70%	Methanol/Ethanol	
10	80%	Methanol/Ethanol	
11	90%	Methanol	0.98
12	95%	Methanol	0.98
13	100%	Methanol	0.99
14	0%	Ethanol	0.99

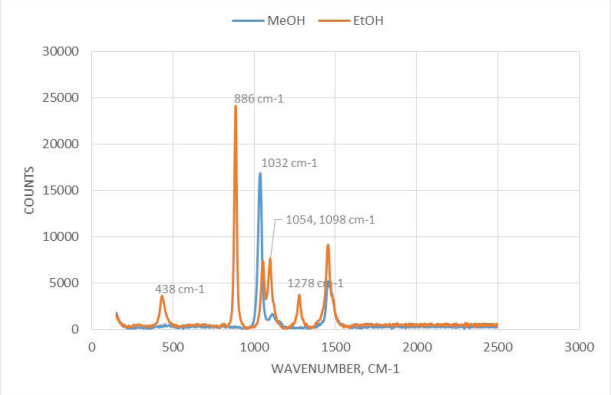
Table 2. Average results using AutoCollect and Rigaku Mixture mode.

Initial results are shown in Table 2 and indicate an interesting trend. As seen, up to 20% methanol contamination will give results of ethanol only. Then the results indicate that the correct result of a mixture of methanol and ethanol are returned up to 90% methanol. From then on, only methanol is returned as a result. There is an obvious discontinuity between the low and high end – where it appears that ethanol has a stronger effect and the spectral signature dominates over that of methanol.

To evaluate this in more detail, an examination of the spectra was performed to differentiate visually between methanol and ethanol. Again in the spectra, an interesting result is seen. The spectra of methanol and ethanol differ quite clearly in several peak regions – and such an obvious difference should in fact be more prevalent in the instrument identification than is observed.

Spectral Analysis

Figure 1 shows the plot scans of ethanol and methanol as pure components in order to clearly show the peak differentiation.



Ethanol peaks, cm^{-1}		Methanol peaks, cm^{-1}
438	CC oop	
886	CCO stretch	
1278	CH3 and CH2 deformation	
1054, 1098	C-O stretch (double peak)	1032
1450	CH3 deformation	1450

Figure 1. The table and the plot show the unique peaks associated with either ethanol or methanol, with approximate peak assignments.

It is perhaps not surprising that ethanol tends to predominate, as a spectral identification is focused on the presence of the ethanol peaks. Since methanol and ethanol share common peak areas, with only slight differences due to methanol shift from ethanol, the more subtle differentiation of methanol leads to a lower identification in the instrument.

This can be seen in the overlay of the spectra of all the different solutions.

Figure 2 shows the overlay plot of the lower methanol solutions – and the spectra are predominately ethanol peaks. The larger ethanol peaks are clearly present, and the identification returned from the instrument until 30% was following this spectral trend by an identification of ethanol only.

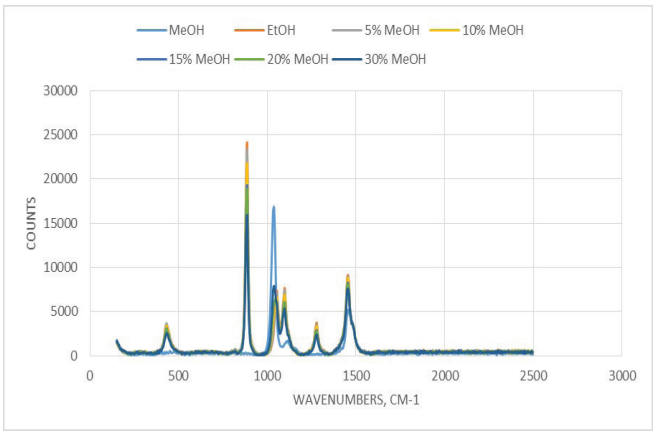


Figure 2. The plot shows the overlay plot of the lower methanol solutions.

If we then look at the higher end where the majority of the methanol is present we can start to see that the ethanol peaks start to disappear and we can then pick up the spectral features that are common to methanol instead. In Figure 3, we observe the spectral characteristics common to methanol so that the identification returned on the instrument is either correctly stated as an ethanol-methanol mixture or at the low end of ethanol – we observe an identification of purely methanol. The plot shows the diminishing size of the ethanol peaks and the corresponding rise of the smaller and more subtle spectral features that are due to the methanol. Specifically, as the very large peak at 886 cm^{-1} disappears with decreasing ethanol, it no longer dominates the spectra, and the peak (due to methanol) at 1032 cm^{-1} becomes more important.

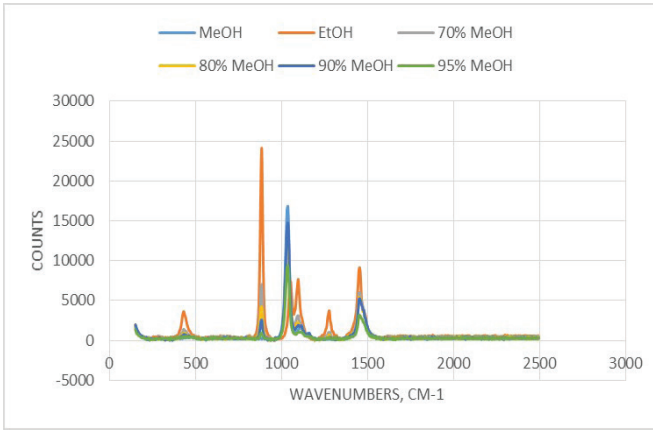


Figure 3. Spectral characteristics common to methanol.

Comparison of Mixture Analysis

A further examination was done in order to determine whether the mixture algorithm in the instrument could be challenged to pick up these spectral differences more quickly and thus determine the methanol contamination at a lower level. To do this we transferred the data set to an external Raman software package (BioRad Know It All), and used their SearchIt algorithm to determine at which point this software could identify two component mixtures of the methanol and ethanol.

Sample	Identified As:	CC
EtOH	Ethanol	91.63
5% MeOH	Ethanol	92.06
10% MeOH	Ethanol	92.68
15% MeOH	Ethanol	92.71
20% MeOH	Ethanol	92.53
30% MeOH	Ethanol	90.12
40% MeOH	Ethanol	86.53
50% MeOH	Ethanol	81.97
60% MeOH	Ethanol	80.34
70% MeOH	Methanol/Ethanol	84.2
80% MeOH	Methanol/Ethanol	90.68
90% MeOH	Methanol	94.33
95% MeOH	Methanol	94.63
MeOH	Methanol	94.52

Table 3. Results of using SearchIt algorithm of BioRad Know It All external Raman software.

As seen in Table 3, the results are very similar to the results obtained in the Rigaku Mixture analysis. From the cc match results, the correlations are very similar to about the 30% methanol – paralleling the similar spectra observed in the Rigaku mixture. It is only past the 30% methanol that we observe any significant changes in the correlation as we start to see more of the spectral features associated with the methanol. In the case of the results noted above, the mixture algorithm is working differently from the Rigaku mixture as it is only at 70 to 90% methanol that the algorithm reports 2 components. Prior to the 70% methanol, only a single component result of ethanol was reported. At the high end of the methanol mixture the same results are observed for both the algorithms, and also observed in the changes in spectral features on the plots.

Effect of Adding Methanol-Ethanol to Library

The next stage was to add the actual methanol-ethanol mixture to the library and see if that would allow us to find the methanol contamination at a lower level than observed. To do this both the 15% and the 20% methanol in ethanol were added as Methanol_Ethanol to the Master Library. Then the samples were run again using the same conditions of AutoCollect as before.

The results are shown in the Table 4. The first column indicates what the sample is composed of, the second column is the instrument ID when both the 15- and the 20% methanol/ethanol mixtures are in the library, and; the last column is when only the spectra for the 20% methanol in ethanol is used. The results look promising – especially when only the 20% methanol is added into the library as a MeOH_EtOH mixture.

	Instrument ID	
Sample, % MeOH	With both 15% and 20% MeOH_EtOH added to Library	Remove 15% as Mixture; Keep 20% MeOH_EtOH
5%	MeOH-15-EtOH	MeOH_EtOH
10%	MeOH-15-EtOH	MeOH_EtOH
15%	MeOH-15-EtOH	MeOH_EtOH
20%	MeOH_20_EtOH	MeOH_EtOH
30%	MeOH-15-EtOH/MeOH	Ethanol/Methyl alcohol
40%	MeOH-15-EtOH/MeOH	MeOH_EtOH/ Methanol
50%	MeOH_20_EtOH/Methanol	MeOH_EtOH/ Methanol
60%	MeOH_20_EtOH/Methanol	MeOH_EtOH/ Methanol
70%	Methanol/MeOH_15_EtOH	MeOH/MeOH_EtOH
80%	Methanol/MeOH_15_EtOH	MeOH/MeOH_EtOH
90%	Methanol	Methanol
95%	Methanol	Methanol
100%	Methanol	Methanol
0%	MeOH-15-EtOH	Ethanol

Table 4. Results of using SearchIt algorithm of BioRad Know It All external Raman software.

In both cases, when we add a mixture MeOH/EtOH spectra to the library, we correctly return the mixture result for the low methanol levels. We then correctly return the mixture results as shown previously where we have a two component result. For the 90% and more methanol in ethanol, we are returning an identification of only methanol – again similar to before. With the 15% and 20% components included in the library, we did get a false result at the pure ethanol level – as it returned a mixture result. However, when the 15% mixture was removed, and only the 20% methanol in mixture was kept as a MeOH_EtOH sample, then the pure mixtures were identified correctly and the remaining results were still showing the mixture results. This is a promising result in order to get around the low spectral contribution that methanol tends to have.

Summary

The initial testing indicated that while differentiation of methanol and ethanol mixtures was possible, the levels of methanol contamination tended to be higher than expected based on the methanol and ethanol spectral features. It was found that ethanol features tend to predominate in the spectra.

To counteract the high methanol levels required, a lower methanol solution (20% methanol in ethanol) was added to the library. The resulting testing on the samples indicated that this was adequate to return the correct identification of a mixture at the lower levels of methanol. This shows a positive indication for the subsequent identification of methanol contamination in ethanol.