**Application Note: 51558**

# Use of the DXR SmartRaman Spectrometer for Quantitative Analysis of Solvent Mixtures

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**Key Words**

- **Partial Least Squares (PLS) Quantitative Method**
- **Quality Control (QC)**
- **Quantitative Analysis**
- **Raman Spectroscopy**
- **Solvent Mixture Analysis**

## Introduction

Although Raman spectroscopy is now taking its place as a powerful analytical tool, it is only recently that it has started to be considered for use as a routine instrument for quality control. It has some attractive features for this type of application. Raman measurements can be made directly through glass and plastic containers. In addition, there is minimal interference from water and the technique is insensitive to peak broadening caused by solvent interactions, making the technique particularly well-suited to liquid samples.

The DXR SmartRaman spectrometer is designed to be reliable and reproducible and to accept a broad range of sample configurations. The instrument is configured with OMNIC™ software, which includes powerful algorithms for quantification and for the calibration and validation of analytical methods. This application note describes results obtained with a series of solvent mixtures and demonstrates the suitability of Raman spectroscopy for quantitative analytical applications.

## Experimental

For this application note we used a series of 31 samples graciously provided by Dave Haaland of Sandia National Lab. The samples, sealed in glass cuvettes, consist of varying mixtures of chlorobenzene and toluene with trace amounts of heptane. Spectra were collected on a DXR SmartRaman spectrometer equipped with a Universal Platform Sampling accessory (UPS) configured with the Universal Plate (UP) toolhead. For data collection the samples were placed on the UP toolhead. The Raman signal was maximized using autofocus, a standard feature in OMNIC. The DXR SmartRaman was configured with a 532-nm wavelength laser and a full-range grating.[1] Each data point consisted of four 1-sec exposures.

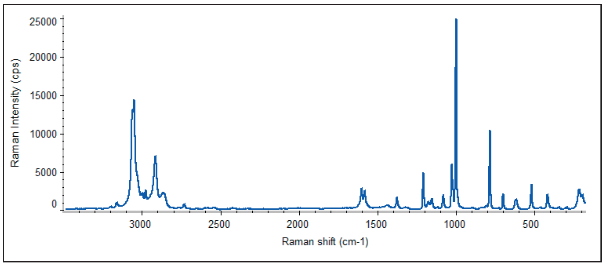

Figure 1: Typical Spectrum of a chlorobenzene, toluene, and heptane mixture (532-nm laser, full-range grating, 4 1-sec exposures)

## Results

A typical spectrum of a chlorobenzene, toluene, and heptane mixture is shown in Figure 1. The spectrum was collected using the full-range 532-nm grating which permits the collection of the full spectrum in a single exposure. This offers a benefit in terms of speed and avoids spectral stitching artifacts which may interfere with quantitative analysis.

The calibration was performed by setting up a PLS (Partial Least Squares) quantitative method using TQ Analyst™ software.[2] The fingerprint spectral region of 375 $cm^{-1}$ to 1650 $cm^{-1}$ was selected. Twenty of the samples were used for calibration and the remaining eleven for validation. The RMSEC (Root Mean Square Error of Calibration) and RMSEP (Root Mean Square Error of Prediction) were plotted. The results for chlorobenzene are shown in Figure 2 and the results for all three components are summarized in Table 1.

| Component | Spectral Range used for Calibration | RMSEC | RMSEP |
|---|---|---|---|
| Toluene | 375 – 1650 $cm^{-1}$ | 0.587 | 0.645 |
| Chlorobenzene | 375 – 1650 $cm^{-1}$ | 0.591 | 0.598 |
| Heptane | 375 – 1650 $cm^{-1}$ | 1.06 | 1.07 |

Table 1: Calibration data for solvent mixture calculated over the fingerprint spectral region

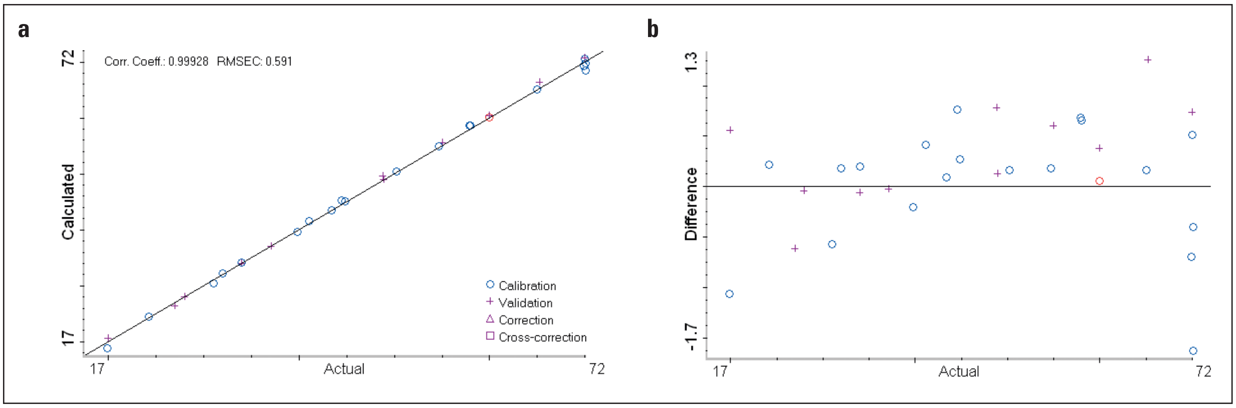

Figure 2: Results from PLS quantitative method of analysis for chlorobenzene in the solvent mixtures calibrated using the fingerprint region of the Raman spectrum. (a) RMSEC = 0.591; (b) RMSEP = 0.598

The results for toluene and chlorobenzene are similar, indicating that there is sufficient peak differentiation between the two major components in the fingerprint region to generate a reliable quantitative method. The initial results for heptane are not as good, however addition of the C-H stretch spectral region (2800 – 3225 cm$^{-1}$) to the PLS method improves the results for this component, as shown in Table 2. The addition of the C-H stretching region also significantly improves the results for chlorobenzene and toluene.

| Component | Spectral Range used for Calibration | RMSEC | RMSEP |
|---|---|---|---|
| Toluene | 375 – 1650 cm$^{-1}$ and 2800 – 3225 cm$^{-1}$ | 0.339 | 0.409 |
| Chlorobenzene | 375 – 1650 cm$^{-1}$ and 2800 – 3225 cm$^{-1}$ | 0.338 | 0.297 |
| Heptane | 375 – 1650 cm$^{-1}$ and 2800 – 3225 cm$^{-1}$ | 0.130 | 0.181 |

Table 2: Calibration data for solvent mixture calculated over the fingerprint and CH stretch spectral regions

## Conclusion

By using a series of solvent mixtures as a model for a typical quality control method, this application note demonstrates the ability of Raman spectroscopy to perform quantitative sample analysis in a QC environment. Although good quantitative results for toluene and benzene were obtained using a narrow spectral range, the benefit of being able to collect the full-range spectrum is demonstrated by the improvement in the heptane results. The DXR SmartRaman spectrometer is well-suited to this application. Instrument ruggedness, OMNIC software and the ability to perform routine full instrument calibration as a standard operating procedure contribute to the robustness of these results.

## References

1. Standard options for the DXR SmartRaman include 532-, 633- and 780-nm wavelength lasers. The full-range grating permits acquisition of a full spectrum from 50 – 3500 cm$^{-1}$ in a single exposure. The spectral resolution is nominally 5 cm$^{-1}$. A high-resolution grating (nominal 3 cm$^{-1}$) is also available.
2. A PLS quantitative method using 4 factors with a Standard Normal Variate scaling function was employed. This is generally recommended for Raman spectra to compensate for spectral intensity dependence on incident laser power variations, sampling variances and focusing. The scaling function is still useful, even though with the Laser Power Regulator and Autofocus these intensity variances are minimized with the DXR SmartRaman.

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