Development and Validation of Fast and Highly Selective MRR Method for Simultaneous Quantitation of Multiple Polar Impurities in Gas Mixtures

Introduction

Molecular Rotational Resonance (MRR) spectroscopy is a powerful alternative to Gas Chromatography (GC) for analysis of hard-to-separate polar analytes in light hydrocarbon and other industrial gas streams. The extraordinary resolving power of MRR enables analysis without chemical separation to significantly decrease analysis cycle time comparing to GC and eliminate any potential analyte co-elution problems. In addition to fast analysis, MRR offers fast and straightforward method development, easy and infrequent calibration, ability to selectively adjust analysis sensitivity and detection limits for each analyte independently from other analytes, requires essentially no consumables, and can be readily used online.

As an example, we develop and validate an MRR method for quantitation of three chemically diverse polar impurities - chloromethane, propyne, and trimethylamine - in a propane matrix. We selected analytes that are challenging for GC and cannot be adequately analyzed at low-ppm levels using the same column or method.[1-4] In contrast to GC, MRR is capable of accurate quantitation of all these impurities and the main component (propane) in one measurement. With the gas-flow inlet sampling, the presented analysis can be performed as frequently as every 10 seconds. With the direct injection port sampling utilized in this application note, the analysis cycle time is about 2 minutes including sample injection, 2 seconds per analyte targeted MRR measurements, and sample chamber purge and cleaning.

Similar MRR analytical methods can be readily developed and validated for quantitation of various polar impurities in various industrial gas mixtures or streams including hydrocarbons. Since MRR analysis is free from chemical separation challenges and does not require use of different types of columns or detectors to adequately separate and quantify all the chemically-diverse analytes of interest, one fast and simple MRR measurement can replace several lengthy and labor-intensive GC analyses to enable dramatic time and labor savings. Furthermore, since MRR analysis is also consumable-free and, thus, can be executed continuously without human intervention, it can be readily utilized for online process monitoring and control.

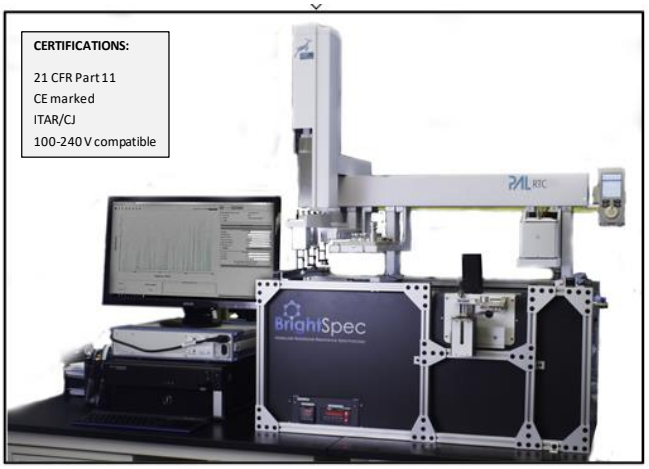

Figure 1. A picture of the BrightSpec-ONE spectrometer. Default sampling options include the online-capable gas sampling manifold (GSM) and direct injection (DI). Additional sampling and automation options include static headspace sampling module (HSM) and PAL-RTC autosampler for analysis of volatile impurities in solutions and volatilizable solids.

Experimental

BrightSpec-ONE Instrument. The measurements described here were performed using a BrightSpec-ONE spectrometer (Figure 1). This instrument is optimized for the quantification of polar molecules with molecular weights up to 150 amu. Sampling injection can take place either through a gas sampling flow inlet or gas-tight syringe injection.

Sample Preparation. Gas mixture samples were prepared in Tedlar® gas sampling bags, which are prefilled with 2 liters of 99.97% pure propane (Aldrich). Known amounts of the polar impurities were injected into these bags using gas-tight syringes. The analyte concentration ranges in the prepared mixtures were 0 to 900, 0 to 2250, and 0 to 36000 ppmv for chloromethane, propyne, and trimethylamine, respectively.

Targeted MRR Measurements. 40 µL of each prepared gas mixture was injected into the BrightSpec-ONE's direct injection port (DIP) using a clean 50 µL syringe. Each injection was immediately followed by the targeted MRR measurement. Three consecutive injections of each gas mixture have been performed to

MRR Method Development: low-ppm quantitation of chemically diverse analytes in one measurement

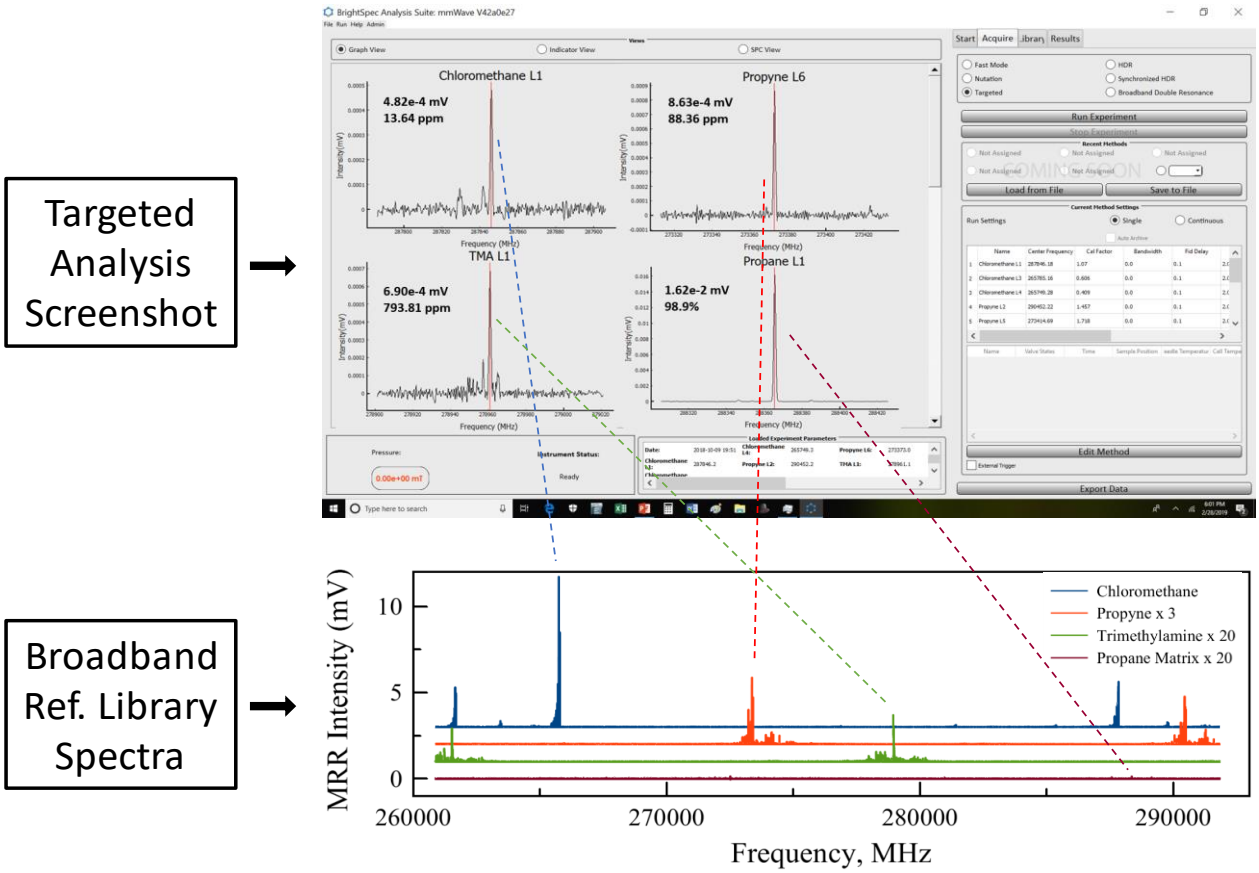

Figure 2. Simultaneous measurements of chloromethane, propyne, and trimethylamine (TMA) in propane (C3) matrix using MRR. Broadband spectra (bottom plot) from the BrightSpec Spectral Library are used to select overlap-free analyte peaks for fast and highly sensitive targeted analysis (top plot).

evaluate the DIP-MRR method analysis repeatability for each gas. MRR measurement times were 2 seconds per analyte.

MRR Method Development

Selecting Suitable Transitions for Each Analyte. Suitable transitions of each analyte can be selected using the BrightSpec spectral library (Figure 2, bottom plot). It can be seen that due to the high resolution of the MRR spectrum, there are no overlaps between the strong features of each analyte or the matrix (Figure 2, top plots). Therefore, quantitative analysis can be performed without chemometrics, using a simple and robust univariate calibration model.

The reference spectral library is user-expandable to include additional analytes of interest. Furthermore, if pure analytes are not available during the method development to directly measure their reference spectra, it is possible to unambiguously extract the reference spectra of individual components from a mixture using a method described in our recent white paper.[5] The latter capability of MRR spectroscopy is enabled by the extremely precise two-way relationship between the experiment and theory for this technique.[6]

Once transitions of each analyte using the broadband MRR spectra are selected (Figure 2 bottom plot), the faster targeted mode is used, which achieves high sensitivity over small frequency ranges with known MRR transitions (Figure 2, top plot) to enable ppb to low-ppm detection limits for most of polar analytes. In addition, targeted analysis sensitivity for each analyte can be selectively adjusted independently from other analytes to eliminate any detector or column saturation issues and enable quantitation of all impurities and main components in one measurement, with the shortest possible analysis time for a specific sample matrix.

Frequency Calibration. Frequency calibration is fully automated. Frequencies are verified using a Rb atomic standard to yield extremely low uncertainty of ±2 parts in 10^{10}. Therefore, this approach achieves essentially absolute frequency accuracy.

Intensity Calibration. For a gas-phase MRR measurement, the observed signal intensity depends only on three factors: the intensity response of the instrument at each frequency, the dipole moment projection of the corresponding rotational transition of a molecule (can be denoted as a 'scaling factor'), and the molecular concentration.

MRR Method Validation: Low-ppm quantitation of chemically diverse analytes in one measurement

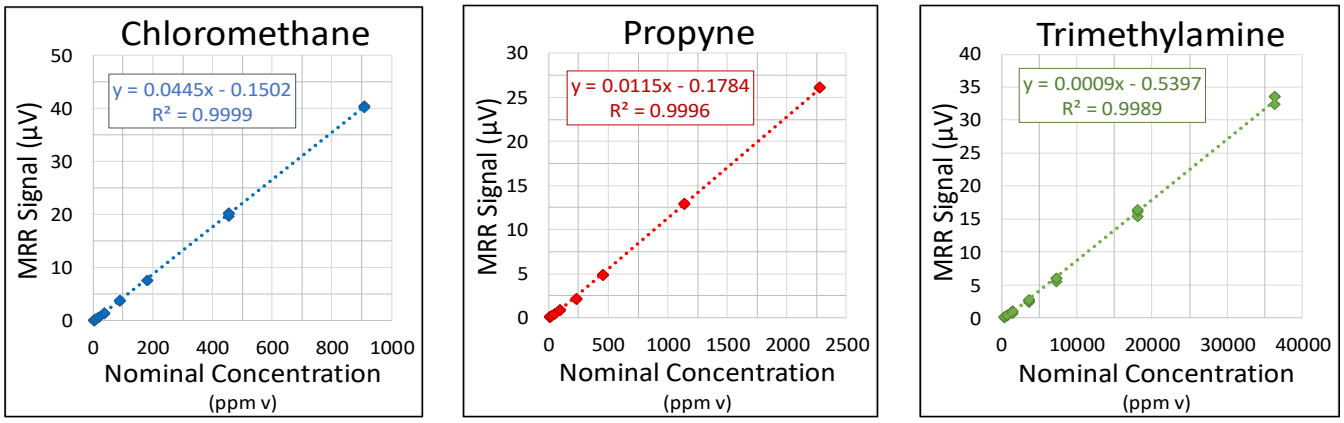

Figure 3. Method validation data for simultaneous quantitation of chloromethane, propyne, and trimethylamine (TMA) in propane (C3) matrix. Targeted MRR analysis demonstrated excellent linearity, sensitivity, and repeatability.

Table 1. Validation of targeted DIP-MRR method for simultaneous detection of chloromethane, propyne, and trimethylamine in C3 matrix.

Analyte	Linearity (R^2)	Verified Linear Range (40 µL Injection Volume)		Expected Linear Range (40 µL Injection Volume)		MRR Low Detection Limit * (2 SECONDS)		Est. MRR Low Detection Limit * (200 SECONDS)		Est. Method Repeatability (between 3 individual injections, 2 second MRR measurements)		
		ppm v	nL	%	nL	ppm v	nL	ppm v	nL	at 10 ppm	100 ppm	1000 ppm
Chloromethane	0.9999	0 - 900	0 - 36	0 - 12%	0 - 5000	0.8	0.03	0.08	0.003	~ 4%	~ 1%	~ 0.5%
Propyne	0.9996	0 - 2250	0 - 200	0 - 30%	0 - 12000	2	0.09	0.2	0.009	~ 8%	~ 5%	~ 0.2%
Trimethylamine	0.9986	0 - 36000	0 - 3200	0 - 40%	0 - 16000	28	1	3	0.1	n/a for 2 s	~ 16%	~ 9%

** MRR low detection limits are estimated for 40 µL light hydrocarbon matrix injection volumes, and 2 and 200 second MRR measurements, respectively.*

The MRR intensity response measurement is a push-button procedure that is sample-free and takes about 3 minutes. Our experience is that the instrument response factors barely change with time. Nevertheless, this procedure can be run as frequently as desired to ensure that the instrument performance is consistent.

Scaling factors for every analyte of interest can be determined using a conventional approach, with a set of standards with known concentrations of analytes. Alternatively, modern quantum chemistry methods can calculate the dipole moment projections for many important molecules in a gas-phase within less than 1% accuracy. Therefore, use of reference standards to determine the scaling factors is not always necessary.[5]

On top of all that, MRR measurements are background free. Therefore, knowledge of just one linear scaling factor per molecular line (or per analyte) is sufficient for accurate concentration calibration.

As a result, after the initial MRR method is developed, the routine MRR analysis becomes essentially calibration-free. Only the periodic intensity response measurements are required to compensate for potential signal and/or calibration drifts. Therefore, typical MRR analysis includes only one run – the analysis run itself. In contrast to MRR, the conventional chromatography analysis may require execution of several runs every time when analysis is needed including the calibration runs, blank runs, and analysis runs.

MRR Method Validation

Specificity. Figure 2 (top subplots) show MRR spectral lines selected for quantitative targeted analysis during the method development step. As can be noticed, the selected peaks are well resolved, and there is no spectral overlap between the analytes and other components present in the mixture. Thus, the selected MRR lines can be used to unequivocally assess the analytes.

MRR Repeatability. The MRR method repeatability (short-term precision) was roughly estimated as a relative standard deviation between 3 independent MRR determinations at about 10, 100, or 1000 ppm concentration levels of each analyte in propane, respectively, where applicable (Table 1). The individual MRR determination included the sample injection that was immediately followed by 2-second-long MRR measurement.

Linearity and Range. Linearity was assessed by preparing gas mixture standards at 10 different concentration levels within 0 to 900, 0 to 2250, and 0 to 36000 ppmv for chloromethane, propyne, and trimethylamine in propane, respectively. Three individual sample injections have been made at each concentration level. As can be noticed from Figure 3 and Table 1, MRR shows the excellent linearity of >0.998 for all three analytes within the specified concentration ranges.

Expected Linearity Range. Expected MRR linearity range (Table 1) is estimated from the linearity data of pure analytes (data not shown), and assuming 40 µL light hydro-carbon matrix injections into the DIP port of the instrument.

Low Detection Limits. The MRR low detection limits (LDLs) are determined from the Figure 3 linear response slopes and the MRR detector noise levels measured at 2 and 200 seconds, respectively, using the following formulas:

LDL = 3 x Detector Noise (2 or 200 s, n=6, 1σ) / Slope

Data are summarized in Table 1. Since MRR in targeted mode measures each selected rotational transition separately, these detection limits can be independently adjusted in any direction by shortening or increasing the measurement time for a specific analyte, as needed to optimize the method.

Accuracy. Table 2 shows the results of targeted MRR analysis of the pre-made gas mixtures, at four lowest concentrations of each analytes in the propane matrix. As can be noticed from this table, there is a good agreement between the nominal and measured values for these three analytes, even at 2 seconds per analyte MRR measurements.

Table 2. Concentrations of three polar impurities in propane measured by BrightSpec-ONE unit versus their nominal concentrations.

Chloromethane		Propyne		Trimethylamine	
Measured (ppm v)	Nominal	Measured (ppm v)	Nominal	Measured (ppm v)	Nominal
2.9	2.3	7.1	5.7	109	91
4.4	4.6	10.2	11.4	208	182
16.4	18.2	42.3	45.4	655	757
35.2	36.4	91.6	90.9	1481	1455

Conclusions

We have developed and validated a rapid, highly selective, easy-to-use, and consumable-free MRR method that is capable of simultaneous quantitation of chemically diverse polar impurities in light hydrocarbon and other industrial gas streams. The developed method is online-capable and shows analytical validation metrics comparable to or exceeding that of conventional gas analysis methods, even with 2 seconds per analyte MRR measurements.

The key advantage of MRR is its extraordinary chemical specificity to eliminate a need for a chemical separation or chemometrics to resolve individual contributions. Therefore, the MRR calibration model is simple and robust, and the analysis is free from the common separation challenges including co-elutions, tailing peaks, reactivity, low-mass or high vapor pressure analytes, isomers, and others. With MRR, chemically diverse polar analytes, that otherwise would require multiple conventional analyses for their full characterization, can be unambiguously identified and accurately quantitated in just one fast and highly selective MRR measurement.

In summary, major benefits of MRR implementation include reducing analysis cycle time, streamlining analysis of gases and volatiles, and reducing consumable costs. If implemented for online process monitoring, MRR is likely to enable tighter control over critical process parameters due to the analytical power of this technique, and/or reduce number of analytical instruments required for process control.

In addition, MRR can serve as an orthogonal method for analysis verification or certification purpose. Furthermore, due to a direct and highly precise two-way relationship between the experiment and theory,[5,6] MRR can also be used as a fast and convenient screening tool for unambiguous identification and accurate quantitation of unexpected analytes in process gas streams.

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For more information

Please contact us at sales@brightspec.com or +1 (434) 202-2391, or visit us on the Web at: http://www.brightspec.com/