Simultaneous Trace-Level Analysis of Volatile Amines, Halocarbons, and Hydrocarbons in Gas Mixtures by MRR

Introduction

The accurate, quantitative analysis of polar impurities in gas mixtures is critically important for controlling and optimizing numerous industrial processes. However, this task can still present major challenges for gas analysis instrumentation such as gas chromatography (GC).

For example, small amines can react with active sites of GC columns to produce broad tailing peaks that are hard to accurately integrate, and so can require the use of specially designed columns.[1] Halocarbons may suffer from reactivity and separation issues, depending on the GC column and method.[2] Many small, polar molecules have poor sensitivity in the widely used flame ionization detector (FID) due to their low number of C-H bonds, requiring the use of alternative detectors, which may have less general applicability.[3] And finally, many of these analyses can be subject to matrix interference issues, posing extreme challenges in developing robust methods for quantification at trace levels.

The key advantage of MRR spectroscopy is its extraordinary chemical specificity and resolution, eliminating the need for separation prior to analysis and, therefore, overcoming common chemical separation challenges. MRR can measure all small molecules with dipole moments in a single, fast measurement. As a result, MRR is capable of quantifying multiple polar impurities from different chemical classes directly in one measurement, with analysis cycle time from a few seconds to a few minutes.

This application note demonstrates the ability of MRR to simultaneously quantify chloromethane, propyne, and trimethylamine in one fast analysis. Propane was selected as an example matrix to represent gaseous hydrocarbons, as a matrix that can pose co-elution challenges with other low-molecular weight analytes. Excellent linearity, reproducibility, and precision are observed, with fast cycle times of about 2 minutes and simple operation.

Experimental

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 about 150 amu. Sample introduction can take place either through a gas sampling flow inlet or gas-tight syringe injection. Compounds with molecular weight higher than 150 amu can be analyzed using other BrightSpec's MRR instruments.

Method Development and Validation

Preparation of Validation Standards. Gas mixture validation standards were prepared in Tedlar® gas sampling bags, which were pre-filled 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. 40 µL of each prepared gas mixture was injected into the BrightSpec-ONE's direct injection port (DIP) using a clean 50 µL syringe.

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

Method Development. Suitable transitions of each analyte are selected using the BrightSpec reference 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 and each other or the matrix. The spectral library is user-expandable to include additional analytes.

Alternatively, if neither reference spectra nor pure analytes are available during the method development, it is possible to unambiguously extract the reference spectra of individual components directly from a mixture using a method described in our recent white paper.[4] Furthermore, due to the extremely precise two-way relationship between the experiment and theory for MRR,[5] it may even be possible to generate accurate MRR reference spectra theoretically using the modern quantum chemistry methods.[4]

Targeted DIP-MRR Measurements. Once transitions of each analyte are selected, the faster targeted mode is used, which achieves high sensitivity over small frequency ranges with known MRR transitions (Figure 2, top plots). The targeted MRR measurement times were only 2 seconds per analyte. The total DIP-MRR analysis cycle time (including sample injection, measurement, sample chamber purge and evacuation) was about 2 minutes.

Method Validation. Table 1 summarizes a few basic DIP-MRR method validation parameters for simultaneous quantitation of chloromethane, propyne, and trimethylamine in propane. The MRR low detection limits (LOD) are determined from the linear response slopes and the MRR detector noise levels measured at 2 seconds (data not shown). The MRR method repeatability (short-term method precision) was estimated as a relative standard deviation between 3 independent MRR determinations at about 100 ppm concentration levels of each analyte in propane, respectively.

Example: Low-ppm quantitation of chemically diverse analytes in one measurement

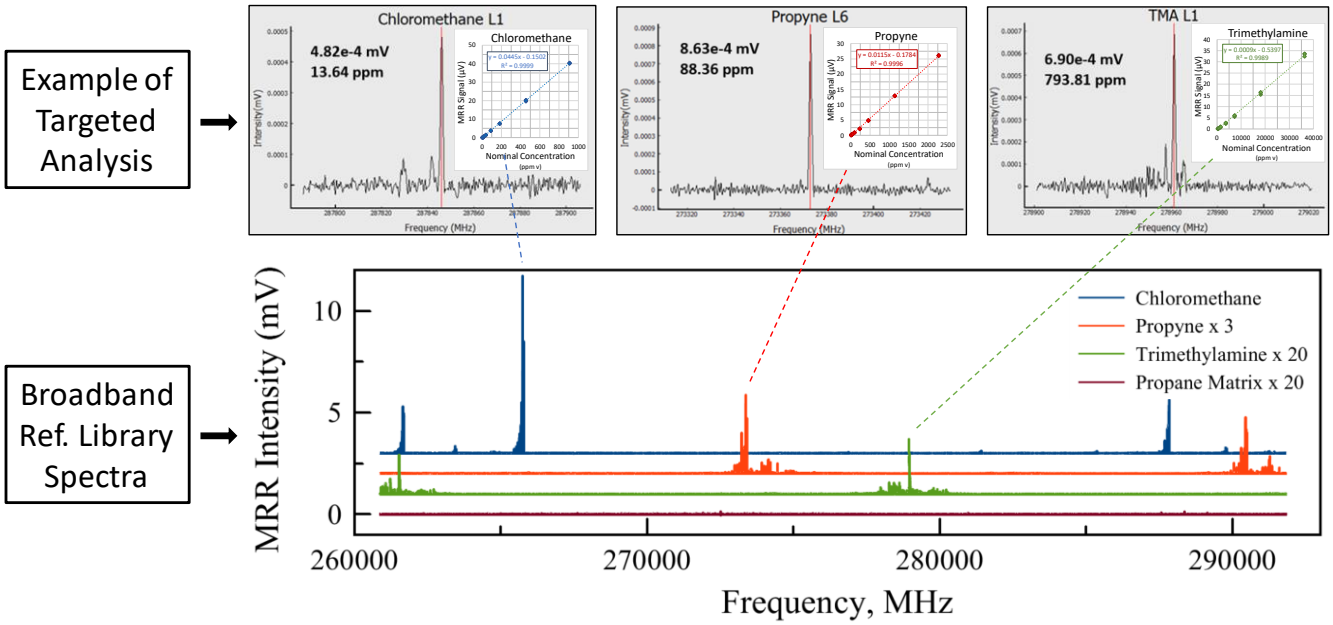

Figure 2. Simultaneous measurements of chloromethane, propyne, and trimethylamine in propane (C3) matrix using MRR. Broadband spectra (bottom plot) from the BrightSpec Spectral Library are used to select overlap-free analyte peaks for fast and highly sensitive targeted analysis (three top plots).

Table 1. MRR linearity, low detection limits (LODs), and repeatability.

Analyte	MRR Linearity (R^2)	2 s LOD (ppm v)	2 s Repeatability at ~100 ppm v (n=3)
Chloromethane	0.9999	0.8	1%
Propyne	0.9996	2	5%
Trimethylamine	0.9989	28	16%

It should be noted that even at only 2 seconds per analyte measurements, the MRR method demonstrates excellent linearity, sub-ppm to low-ppm LODs, and good analysis repeatability for all analytes. Longer MRR measurements will significantly improve the method validation metrics.

Results

Table 2 shows the results of targeted DIP-MRR analysis of the pre-made gas mixtures containing the specified concentrations of chloromethane, propyne, and trimethylamine in propane matrix. As can be noticed from this table, there is a good agreement between the nominal and measured values for these three analytes.

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 demonstrated a rapid, highly selective, easy-to-use, and consumable-free MRR method that is capable of simultaneous quantitation of multiple polar impurities in light hydrocarbon streams without any chemical separation or chemometrics. The developed method shows analytical validation metrics comparable to or exceeding that of conventional gas analysis methods even for challenging analytes such as volatile amines and chlorocarbons, and with analysis cycle time of 2 minutes. With the gas-flow inlet sampling, the presented analysis can be performed as frequently as every 10 seconds.

In addition to fast analysis times and extraordinary resolving power, key MRR advantages include online capability, ease of routine operation, and fast and straightforward method development. As a result, MRR can solve common analytical challenges of conventional gas analysis techniques such as analysis cycle and method development times, analyte coelutions, tailing peaks, reactivity, low-mass analytes, isomers, high vapor pressure analytes, and others.

A major benefit of MRR implementation is the significantly improved analysis throughput. In addition, MRR can also serve as an orthogonal method for analysis verification or certification purpose; or as a fast and convenient screening tool for identification and quantitation of unexpected analytes in process gas streams.

References

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