^{1}H Nuclear Magnetic Resonance Spectroscopy for the Analysis of Gas-phase Mixtures at Pressures near 0.1 MPa

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For decades, nuclear magnetic resonance (NMR) spectroscopy has been used as powerful tool for the analysis of liquid-phase mixtures. Mole fractions of mixture components can be determined without calibration, and with relative uncertainties of 1 % or less. On the other hand, the use of NMR spectroscopy for the analysis of gas-phase mixtures is remarkably rare. This seems to be due in part to a commonly held, but erroneous, notion that NMR spectroscopy does not work on gases. In fact, NMR spectroscopy is just as sensitive to nuclei in the gas phase as it is to nuclei in any other phase. However, compared to the analysis of liquid-phase samples, the analysis of gas-phase mixtures by NMR spectroscopy does present significant challenges. First, sample concentration is inherently low in the gas phase. Second, sample preparation and storage are more complicated for gas-phase samples. Third, the lack of a deuterated solvent complicates spectral optimization. Fourth, spin-lattice relaxation times can be very short in the gas phase, which broadens spectral peaks and can result in significant overlap. Fifth, the adsorption of less volatile components on the walls or cap of the sample tube can cause measurement errors. We will discuss strategies for dealing with these challenges. We will also discuss how parameters for spectral acquisition and spectral analysis affect measurement uncertainty. Finally, we will show analytical results for a test sample—a gravimetrically prepared mixture of methane and propane, which was analyzed by proton NMR spectroscopy over a range of pressures from 0.02 MPa to 0.5 MPa. Results with the test sample, along with a detailed uncertainty budget, indicate that a measurement uncertainty comparable to liquid-phase NMR analysis was achieved.