tion of the hydrocarbon concentrations in air for safety research and operations. In composition determinations, a sample is typically withdrawn from a container, is vaporized if liquid, and is analyzed with a suitable instrument, such as a gas chromatograph. There are many situations, however, in which an *in situ* determination would be advantageous. An *in situ* method can provide assurance that the composition measured is representative, and it can be used to monitor concentration changes in time and space, and under extreme conditions.

The Raman spectrometric method was selected because it was expected that all of the natural gas components, including nitrogen, could be clearly identified in the mixture spectrum, and that with reasonable calibration effort, the concentrations of the components could be determined with sufficient precision for many technical applications. Previous work[1-9] tended to support this expectation.

I. EXPERIMENTAL

The apparatus assembled for this work was typical of

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double monochromator equipped with a photomultiplier and photon counting system.

A computer was used to automate the data acquisition system to operate the monochromator drive through stepping motors. All data were obtained in digital form using photon counting techniques. The data acquisition system was under complete computer program control.

During an experimental run, each intensity reading of a spectral profile was taken at a frequency step of 0.15 cm^{-1} and the photocount at each frequency was collected for a time interval of 1 s after the grating drive had come to a full stop after each step. Data were displayed on a

TABLE I. Compositions of the binary and ternary mixtures used in this work.[a]

Mixture	Isobutane	Nitrogen	Methane
1		0.7502	0.2498
2		0.597	0.403
3		0.50115	0.49985
4		0.4007	0.5993
5	0.03856		0.9604
6	0.08110		0.91880
7	0.1130		0.8860
8	0.08108	0.9188	
9	0.079	0.120	0.800
10	0.081	0.590	0.328

[a] Concentrations are mole fractions.

TABLE II. Composition of the gravimetrically prepared, eight component, natural gas type mixture used in this work.[a]

Component	Concentrations
Nitrogen	0.00859
Methane	0.75713
Ethane	0.13585
Propane	0.06742
Isobutane	0.01336
Normal butane	0.01326
Isopentane	0.00223
Normal pentane	0.00216

[a] Concentrations are mole fractions.

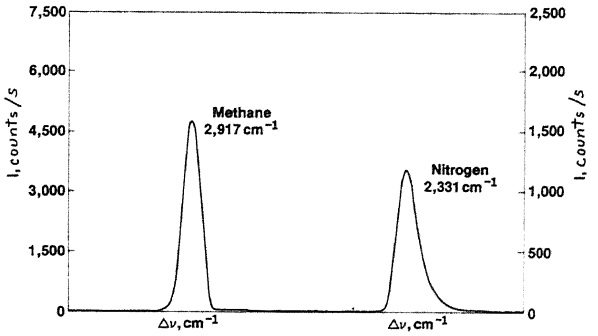

FIG. 1. Raman spectrum of 0.403 methane-0.507 nitrogen mixture.

cathode ray tube (CRT) and traced on an X-Y recorder as each point was collected.

Although the laser power was held constant to within 0.5%, the residual variation still degraded the precision of the measurements. In order to improve the precision, we monitored a small portion of the laser light with a photomultiplier tube and its output was recorded in the computer memory along with the spectra as the readings of the incident laser light. During data analyses, each photocount reading of the spectral profiles was normalized with respect to the incident laser power.

II. PROCEDURES

In a determination of the composition of a ternary mixture containing isobutane, nitrogen, and methane, there were four Raman spectral lines involved. They are the C—C stretch mode and the C—H stretch mode of isobutane at 800 and 2917 cm^{-1}, respectively, the Q-branch of nitrogen at 2331 cm^{-1}, and the Q-branch of methane at 2917 cm^{-1} (also a C—H stretch mode).

As an illustration, we show in Fig. 1 a typical Raman spectrum of a binary mixture of nitrogen and methane (mixture 2). Notice that the spectral line is well defined for each species with a simple profile. However, for isobutane, the vibrational Raman spectrum is more complex as one can see in Fig. 2. There is a simple line at 800 cm^{-1} but a complex structure at 2917 cm^{-1}, one component of which coincides with the methane line. The interference of the isobutane lines with that of methane at 2917 cm^{-1} is a problem to be dealt with and will be discussed later. These spectra were obtained with an instrumental width of 3.3 cm^{-1} at full width at half maximum. The scanning range is 25, 31, and 42 cm^{-1} for methane, nitrogen, and isobutane (C—C stretch mode only), respectively.

The spectra line intensities were evaluated from the integrated area under individual spectra lines. The limits of integration were about 15 cm^{-1} for methane and isobutane lines at 2917 cm^{-1} and 20 cm^{-1} for isobutane (C—C stretch) and nitrogen lines. The limits were always defined from the peak of a spectral line in units of scanning frequency step so that there was no need to rely on the exact positioning of the monochromator. Because the profile of a spectrum was measured at equally spaced frequencies, the integrations for the intensities were carried out using the modified trapezoidal rule. The frequency step size was chosen to be sufficiently small so that the numerical integration of the spectral profile introduced an error that was smaller than the statistical error. A small contribution from dark noise photocount (~5 counts/s) was subtracted to render the true net signal.

The procedure for determining the composition of a ternary mixture began with a series of calibration measurements, which consisted of measuring intensities of three pairs of spectral lines so as to yield three molar intensity ratios (MIR), which were defined for a binary mixture as $(I_2/y_2)/(I_1/y_1)$, where I and y are the intensity and mole fraction concentration, respectively, with the subscripts designating the two components in the mixture. Operationally the MIR is the same as the relative scattering cross section, although we are reluctant to use the latter term for reasons discussed later.

For the purpose of calibration, we chose to measure the following three MIRs: the isobutane line at 2917 cm^{-1} relative to that at 800 cm^{-1}, designated by C_{ii} from a pure isobutane gas sample, the isobutane line at 800 cm^{-1} relative to nitrogen Q-branch at 2331 cm^{-1} designated by C_{in} from a nitrogen-isobutane binary mixture, and the methane Q-branch at 2917 cm^{-1} relative to the nitrogen Q-branch at 2331 cm^{-1} designated by C_{mn}, from a nitrogen-methane binary mixture. The measurements on the ternary mixture then cover the same three spectral regions.

For a gas mixture in which the Raman spectral lines of constituent species do not interfere, the relation between the mole fractions of each species and the spectral intensities is simply $(I_j/C_{jx})/\sum_k I_k/C_{kx})$ where I_j is the integrated intensity of jth component and C_{jx} is the MIR of jth component with respect to xth component which is chosen to be the common reference for all components. By definition, the MIR of the reference itself is equal to unity.

Designate the spectral line intensities of a spectrum of a ternary mixture of isobutane, nitrogen, and methane at 800, 2331, and 2917 cm^{-1}, respectively, as I_1, I_2, and I_3.

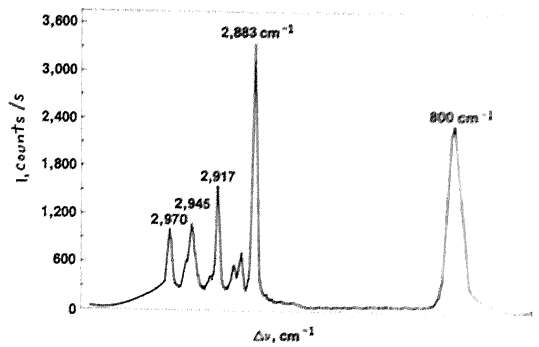

FIG. 2. Raman spectrum of isobutane gas at ambient temperature and 0.27 MPa (24.3 psig).

Then I_1 and I_2 are representative of isobutane and nitrogen, respectively. However, I_3 is a sum of the contributions from methane and isobutane since the spectra of methane and isobutane interfere at 2917 cm^{-1}. In order to obtain the spectral line intensity of methane alone, the amount of I_3 contributed by isobutane must be subtracted. One can measure from a pure isobutane sample the intensity at 2917 cm^{-1} with respect to that at 800 cm^{-1}; therefore, one can also determine for the ternary mixture the amount contributed by isobutane at 2917 cm^{-1} from the intensity at 800 cm^{-1}. Accordingly, subtracting the isobutane contribution at 2917 cm^{-1} from the total intensity gives the amount contributed by methane alone. Therefore, we have

$$y_1 = (I_1/C_{in})/I_0,$$

$$y_2 = I_2/I_0,$$

and

$$y_3 = [(I_3 - C_{ii}I_1)/C_{mn}]/I_0,$$

where y_1, y_2, and y_3 are the mole fractions of isobutane, nitrogen, and methane, respectively, and

$$I_0 \equiv I_1/C_{in} + I_2 + (I_3 - C_{ii}I_1)/C_{mn}.$$

III. RESULTS

Vibrational Raman spectra were obtained for methane, nitrogen, and isobutane and for eight binary mixtures containing these constituents. The mixture compositions are given in Table I. For the mixtures of methane and nitrogen we found that the molar intensity ratios were independent of concentration and pressure within the statistical uncertainties in the ranges examined.

Two ternary mixtures, one methane-rich (mixture 9) and the other nitrogen-rich (mixture 10), were analyzed using the Raman spectrometric method. A spectrum for the methane-rich ternary mixture is shown in Fig. 3. The analytical results are presented in Tables III and IV. The estimated uncertainties given are 1 standard deviation. Only the statistical uncertainties associated with the intensities, including those of the calibration measurements, are propagated and accumulated to yield the final uncertainties which turn out to be about 0.001 in the mole fraction for all components. One must note that because of the round-off errors, the three mole fractions do not always add up to unity. Agreement between the gravimetrically determined values and the spectrometrically determined values is very good, typically less than 0.002 in the mole fraction.

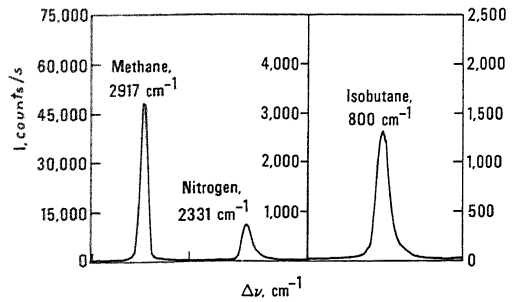

FIG. 3. Raman spectrum of 0.800 methane-0.120 nitrogen-0.079 isobutane mixture.

TABLE III. Isobutane, nitrogen, and methane concentrations in mixture 9 and related binary calibration data.[a]

Mixture concentrations	Spectrometric		Gravimetric
	Run 1	Run 2	
Isobutane	0.080	0.079	0.079
Nitrogen	0.122	0.122	0.120
Methane	0.798	0.799	0.800
Binary calibration data	Run 1		Run 2
C_{ii}	1.1606 ± 0.0032		0.8969 ± 0.0024
C_{in}	3.203 ± 0.008		3.768 ± 0.015
C_{mn}	7.256 ± 0.021		6.612 ± 0.019

[a] Concentrations are mole fractions.

TABLE IV. Isobutane, nitrogen, and methane concentrations in mixture 10 and related binary calibration data.

Mixture concentrations	Spectrometric	Gravimetric
Isobutane	0.083	0.081
Nitrogen	0.590	0.590
Methane	0.328	0.328
Binary calibration data		
C_{ii}	1.1606 ± 0.0032	
C_{in}	3.203 ± 0.008	
C_{mn}	7.256 ± 0.021	

[a] Concentrations are mole fractions.

It appears that the calibration parameters C_{ii}, C_{in}, and C_{mn}, determined from two different runs on different days, which are shown in Table III, are in disagreement, although the concentrations determined from these parameters are in good agreement. The differences in the calibration data could be attributed to the fact that each of the spectral lines at two frequencies of a spectrum were affected to a different extent when the optical alignment of the apparatus was not reproduced exactly. This behavior may be caused by chromatic dispersion of light in the cylindrical cell as well as in the collecting optics. For our purpose, as long as the calibration parameters (or the optical alignment) remained unchanged during the course of a complete set of measurements, the analytical results were not affected. The internal consistency of the calibration parameters obtained on two different experimental runs can be tested by examining the ratio of the molar intensity of C—H stretch mode of methane relative to that of isobutane. The ratio obtained for the two runs should be free from chromatic effect because both spectral lines are at the same frequency. The ratio is simply given by $C_{mn}/(C_{in}C_{ii})$. The values determined for the two runs, 1.952 ± 0.010 and 1.956 ± 0.011, respectively, are in excellent agreement. It should also be mentioned that the depolarization effect in the scattering process was not a major concern because the depolarization ratios of nitrogen, methane, and isobutane were small, and because they did not depend strongly on temperature and density in the ranges investigated.

A vibrational Raman spectrum, obtained for a gravimetrically prepared eight component natural gas type mixture, is shown in Fig. 4, a, b, and c. The gravimetric composition is given in Table II. Spectral lines associated with all of the components except the pentanes, which are present in low concentrations (<0.25%), are clearly identified. The interferences among spectral lines occur only at 2917 cm^{-1}. For a natural gas type mixture, the

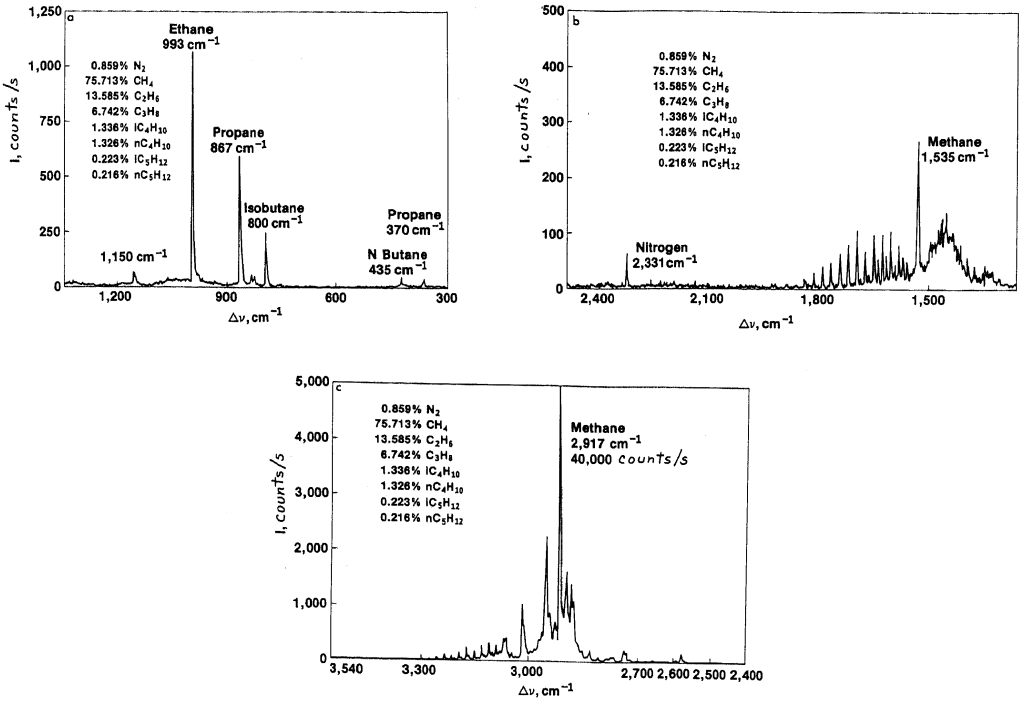

FIG. 4. Raman spectrum of a gravimetrically prepared, eight component, natural gas type mixture. The peak counting rate for methane Q-branch at 2917 cm^{-1} is 40,000 counts/s.

spectral line of methane is the dominant one at 2917 cm^{-1}, and the small contributions from other components can be dealt with by making use of the pure component spectra, as demonstrated by the analyses of the two ternary mixtures.

IV. CONCLUSIONS

The Raman spectrometric method has been successfully used for *in situ* determinations of the compositions of two ternary mixtures of natural gas components at ambient temperature and at pressures to 0.8 MPa. The imprecision of such determinations is estimated to be about 0.001 in the mole fraction. Differences between spectrometrically and gravimetrically determined concentrations did not exceed 0.002. We believe that the technique used here for the ternary mixtures can be generalized and applied to multicomponent natural gas type mixtures. The best results are obtained when calibration mixtures and unknowns are measured with the optical alignment undisturbed. Any refocusing of the lenses or repositioning of the sample cell between runs may disturb the alignment sufficiently that the previous calibrations may not be consistent with the measurements that follow. For applications where high precision is not required, one might consider the alternative of utilizing the published values of relative scattering cross sections instead of calibration measurements of MIRs to determine the compositions.

In conclusion, we suggest that more systematic work on the dependences of the molar intensity ratios on concentration and density, as well as depolarization effect, be carried out to cover a larger range in density and temperature, and to include liquid phase densities where we anticipate greater difficulties.

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1. D. H. Rank and R. V. Wiegand, J. Opt. Soc. Am. **36,** 325 (1946).
2. D. D. Tunnicliff and A. C. Jones, Spectrochim. Acta **18,** 579 (1962).
3. T. T. Wall and D. F. Hornig, J. Chem. Phys. **45,** 3424 (1966).
4. D. E. Irish and H. Chen, Appl. Spectrosc. **25,** 1 (1971).
5. D. A. Long, in *The Characterization of Chemical Purity Organic Compounds*, ed. by L. A. K. Staveley (Butterworths, London, 1971), p. 149.
6. D. J. Lockwood, J. Scott, W. L. Elsdon, and D. E. Irish, J. Raman Spectrosc. **2,** 593 (1974).
7. C. H. Warren and L. Ramaley, Appl. Oct. **12,** 1976 (1973).
8. H. W. Schröter and H. W. Klöckner, in *Raman Spectroscopy of Gases and Liquids*, ed. by A. Weber (Springer-Verlag, Berlin Heidelberg, 1979), p. 123.
9. T. Schimanouchi, *Tables of Molecular Vibrational Frequencies, Consolidated Volume I,* NSRDS-NBS 39 (National Standards Reference Data Service, National Bureau of Standards, Washington, DC, June 1972).