Gas Chromatography/Mass Spectrometry of 1,3 Butadiene (99+%)

DATE:	September 27, 2010
Lot #:	Aldrich #13511DH
CAS #:	106-99-0

ANALYST:
Reviewer:

Operating Conditions

Instrument:	Agilent 6890 Gas Chromatograph/MSD 5793		
Inlet:	Split (100:1) at 250° C		
Column:	Agilent J&W DB-5MS 30m L x 250µm ID x 1µm film (nominal)		
Carrier Gas	UHP Helium		
Ionization Mode:	Electron impact		
Scan Range/Rate:	15-400 Da /1 second		
MS Temperature – Quad:	150°C		
MS Temperature – Source:	230°C		
Electron Multiplier:	2388 V		
Temperature Program:	Time (min)	Temperature °C	Rate °C/min
	0.0	35	-
	2.0	35	-
	7.6	175	25
	11.6	175	-

Preparation of the Sample for Analysis

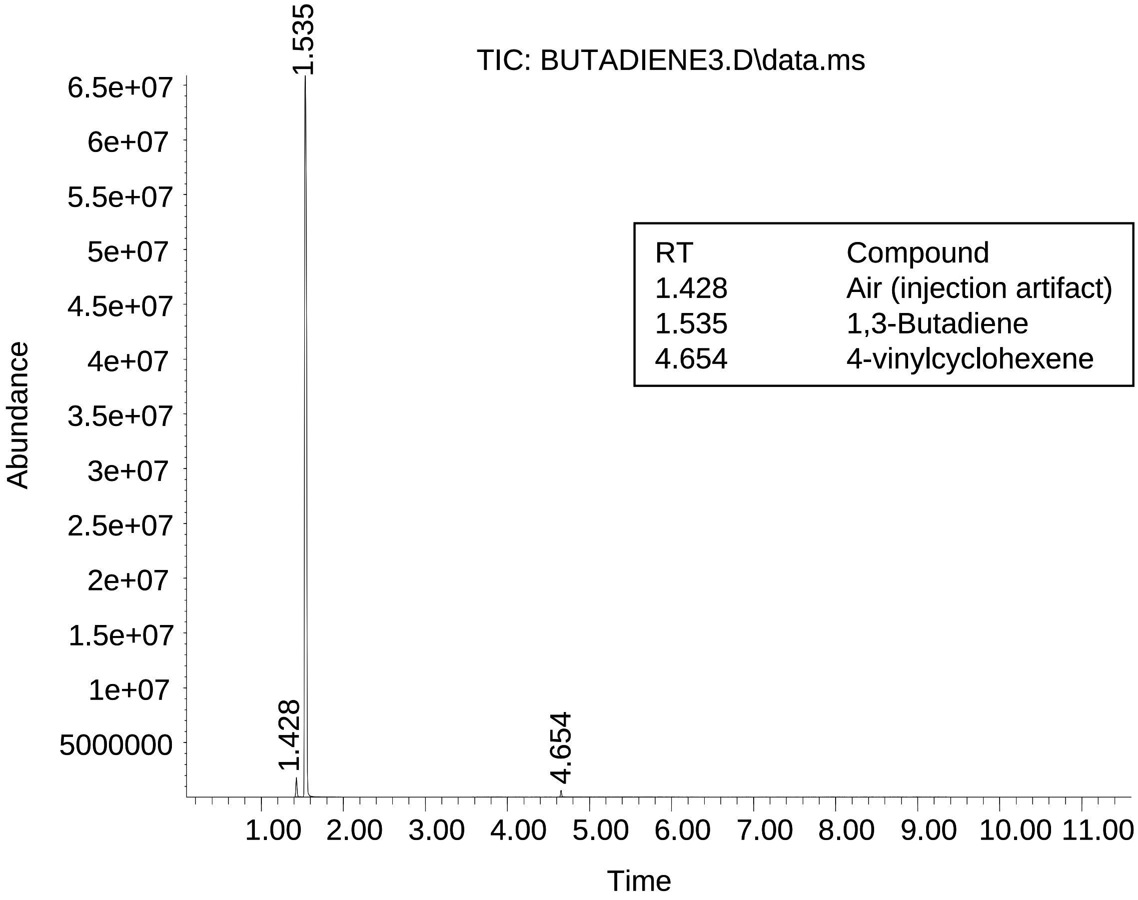
A 2 liter Mylar gas bag was filled with sample directly from the gas cylinder. Fifty microliters of this sample was split injected onto the chromatograph for GC/MS analysis.

Results

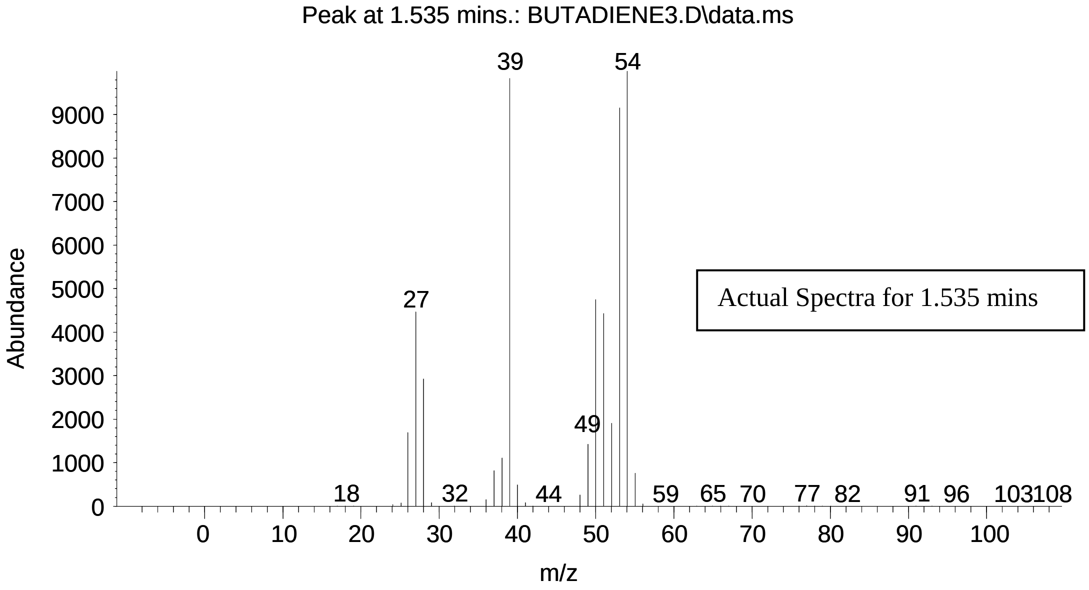
Retention time and area percent for each component in the analyzed sample is given in the table and on the chromatogram below.   The air observed the chromatogram was confirmed to be introduced as an injection artifact. Mass spectra for 1,3 butadiene, its major impurity vinyl cyclohexene along with the corresponding standard mass spectra for each are also included for reference.

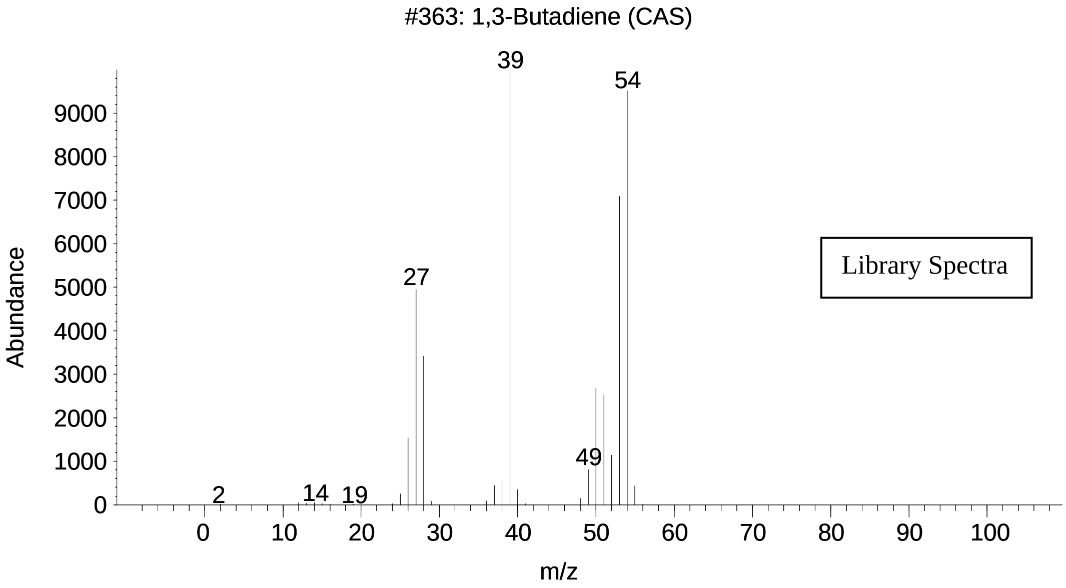
```
Area Percent Report

Data Path
Data File  : BUTADIENE3.D
Acq On     : 23 Sep 2010  13:56
Operator   :
Sample     : 1,3-butadiene
Misc       :   50uL manual injection
ALS Vial   : 1   Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator:   ChemStation

Method:       C:\MSDCHEM\1\METHODS\reach.m
Title:        1,3-Butadiene 99%+

  Signal     : TIC: BUTADIENE3.D\data.ms

 peak    R.T.      peak        corr.       % of        peak            CAS
   #     min      height       area        total      identity        Number

   1    1.535   66041917   1089358811   99.46%   1,3-butadiene       106-99-0
   2    4.654     619128      5883336    0.54%   Vinyl cyclohexene   100-40-3


            Sum of corrected areas:     1095242147

reach.m Mon Sep 27 10:12:04 2010
```

Total ion chromatogram:

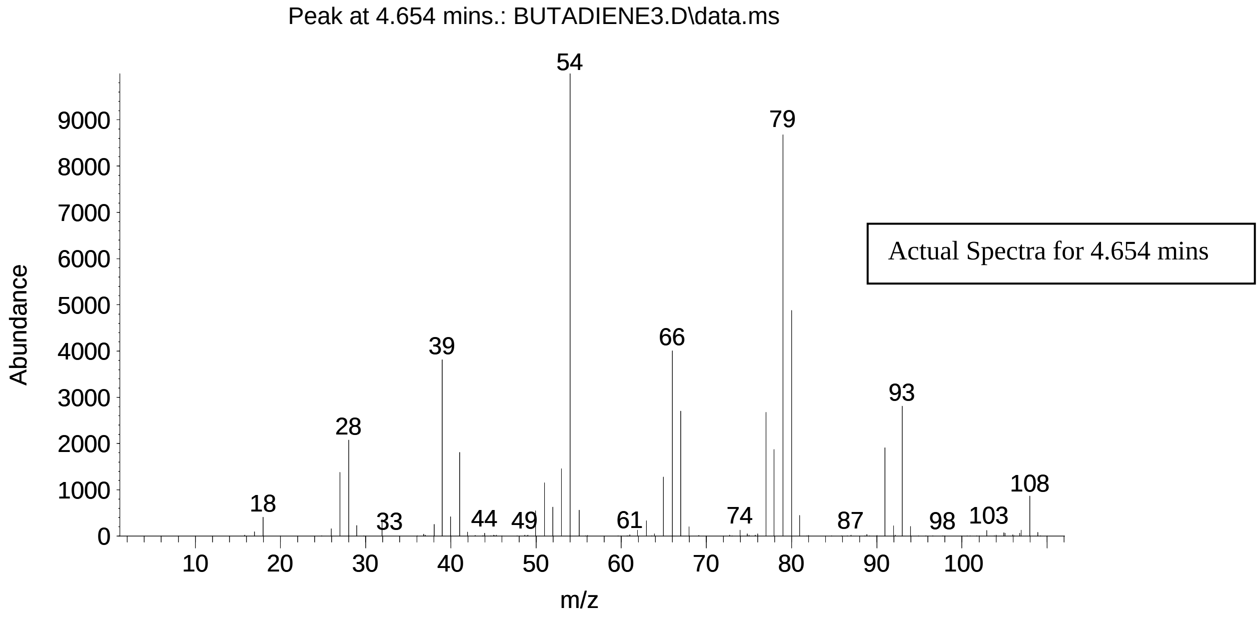


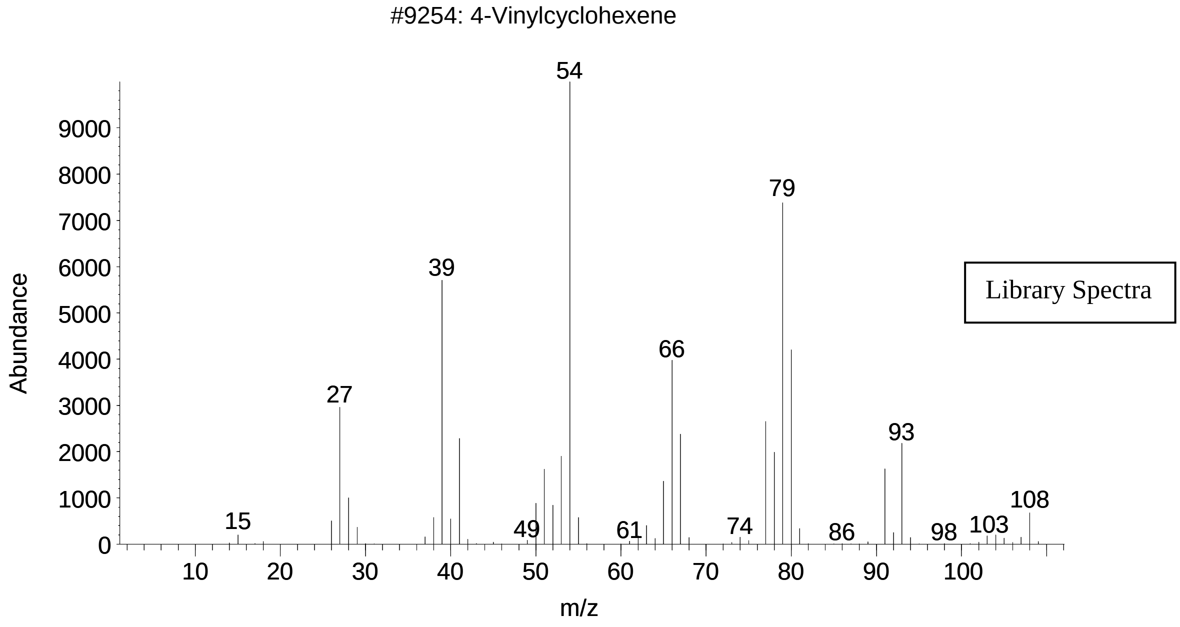
Mass Spectral Confirmation Peak 1:





Mass Spectral Confirmation Peak 2:



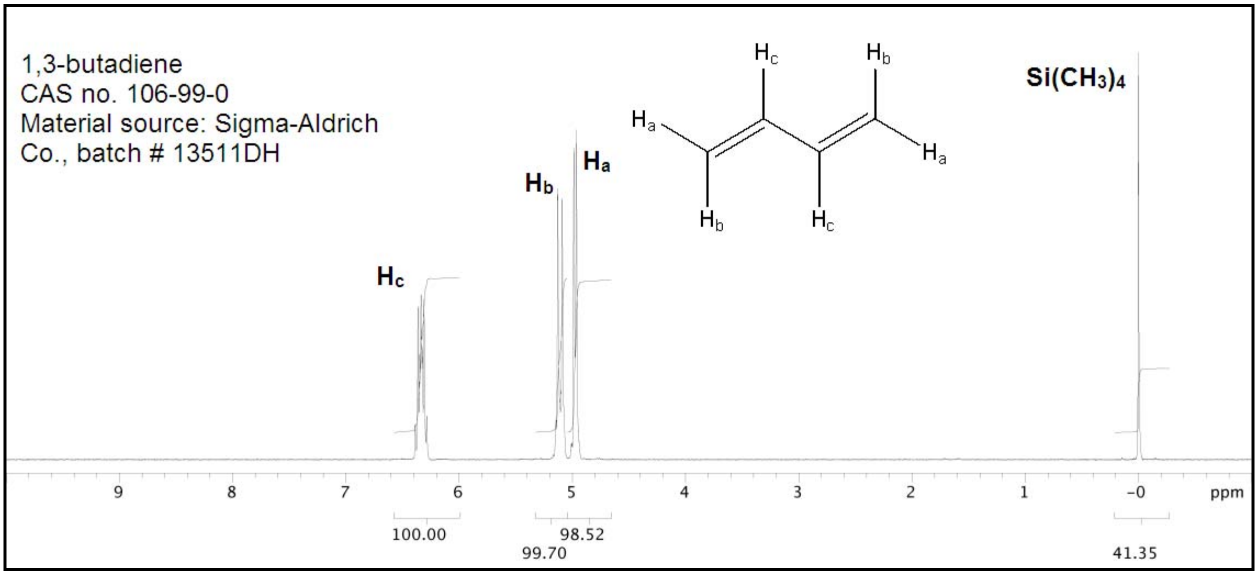


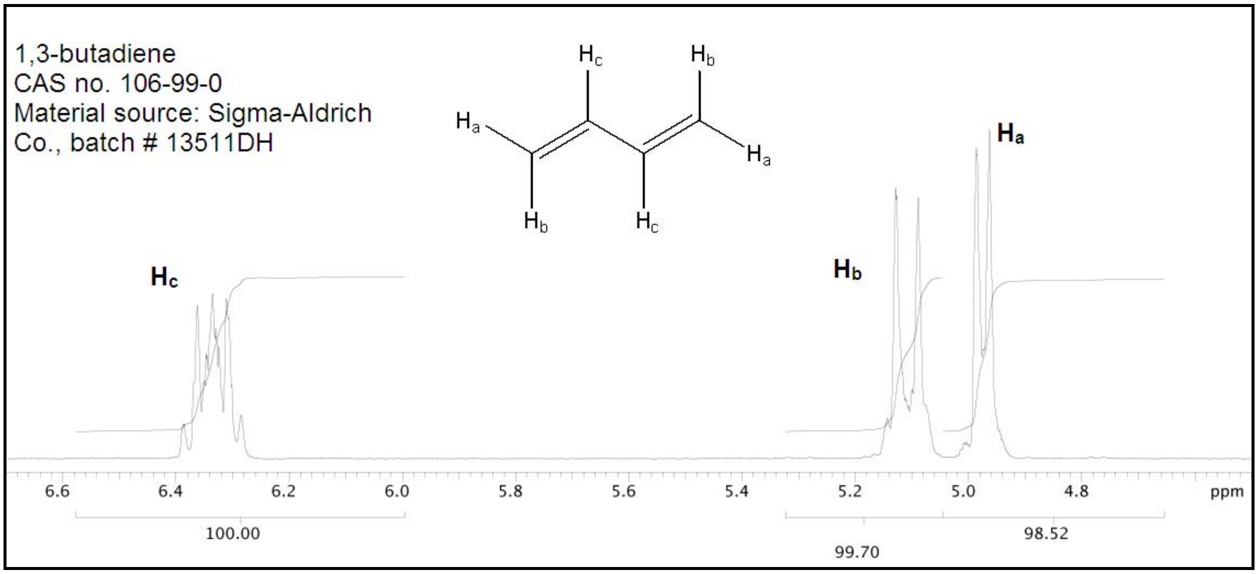
NMR analysis of 1,3-butadiene

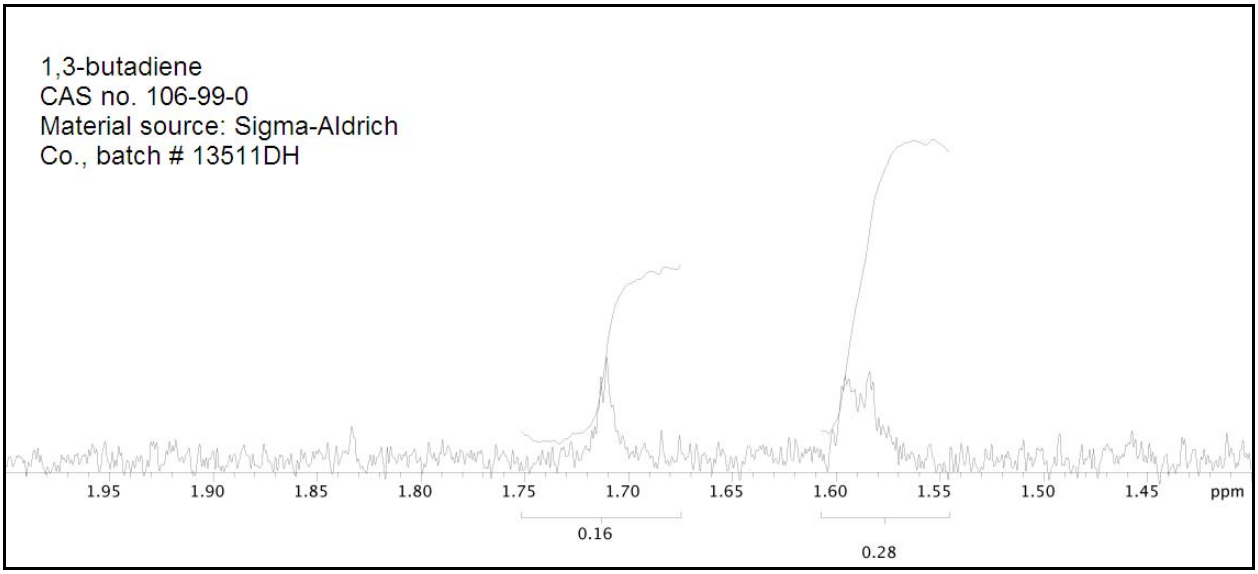
CAS No. 106-99-0

Material source: Sigma-Aldrich Co., batch no. 13511DH

^{1}H NMR spectrum of gaseous 1,3-butadiene with tetramethylsilane standard

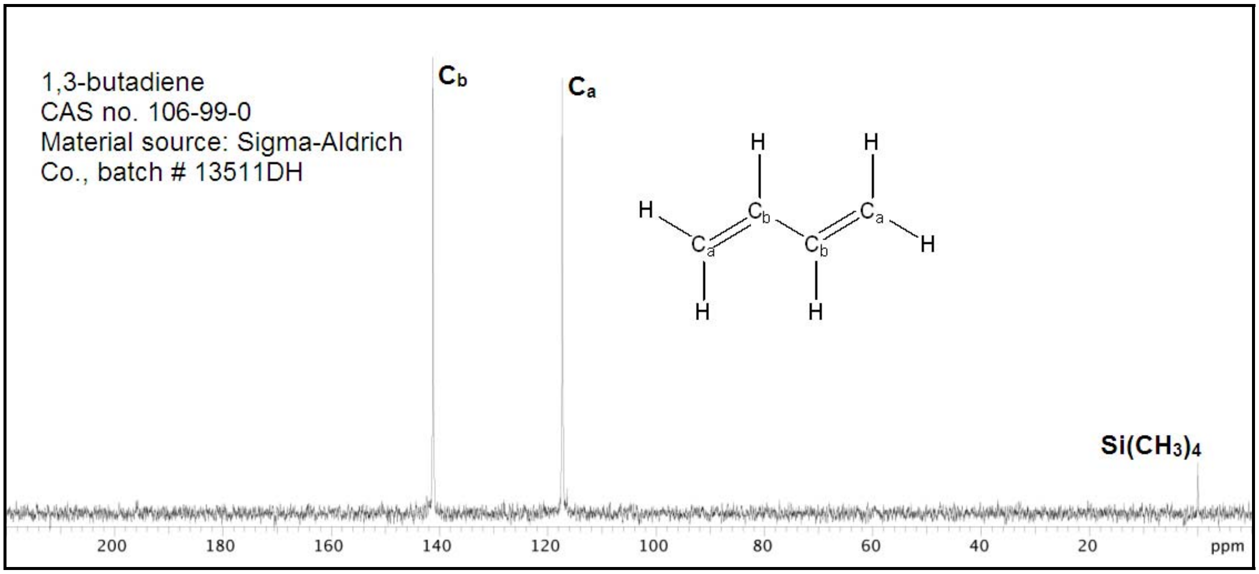






This is a ^{1}H NMR spectrum acquired of neat 1,3-butadiene gas at 2.02×10^5 Pa partial pressure, with trace tetramethylsilane (TMS) added as an internal chemical shift. The top spectrum shows the entire spectral window. The second spectrum shows an expansion with the resonances of interest, also showing integral intensities. The third spectrum shows an expansion of the trace impurities observed in the spectrum. The ^{1}H Larmor frequency was 399.97 MHz. The chief resonances observed in the spectrum were those of TMS at 0.00 ppm and 1,3-butadiene at 4.97, 5.11, and 6.33 ppm. Impurities were observed at 1.59 and 1.71 ppm.

^{13}C NMR spectrum of gaseous 1,3-butadiene with tetramethylsilane standard



This is a ^{13}C NMR spectrum acquired of neat 1,3-butadiene gas at 2.02 x 10^5 Pa partial pressure, with trace tetramethylsilane (TMS) added as an internal chemical shift. The ^{13}C Larmor frequency was 100.58 MHz (400 MHz instrument). The only resonances observed in the spectrum were those of TMS at 0.00 ppm and 1,3-butadiene at 117.36 and 141.24 ppm.

Operating Conditions:

The spectrum was acquired on a Varian INOVA 400 MHz NMR spectrometer equipped with a 5 mm C, P {H,F} probe.

For the ^1H spectrum, 8 transients with a flip angle of 90 °, acquisition time of 2 s, and recycle delay of 28 s were averaged. An exponential line broadening of 0.3 Hz was applied during the Fourier transform. 131,072 points were used in the frequency domain of the transform. The sample temperature was 30 °C.

For the ^{13}C spectrum, 45,752 transients with a flip angle of 73 °, acquisition time of 0.25 s, and recycle delay of 1.0 s were averaged. (Efficient spin-rotation relaxation is observed in ^{13}C NMR in the gas phase, permitting rapid signal-averaging.) Broadband ^1H decoupling was effected by the Waltz-16 sequence during acquisition (inverse-gated decoupling). An exponential line broadening of 4 Hz was applied during the Fourier transform. 65,536 points were used in the frequency domain of the transform. The sample temperature was 30 °C.

Preparation of Sample:

A medium-walled 5 mm o.d. NMR tube was attached *via* adapter to a vacuum manifold equipped with a precision barometer, and was evacuated. The tube was immersed in liquid nitrogen and closed to the manifold. A quantity of 1,3-butadiene was introduced into the manifold, and the stopcock to the NMR tube was opened until the pressure difference corresponded to the proper quantity of gas to yield 2.02 x 10^5 Pa partial pressure of 1,3-butadiene in the tube. In a similar manner, 6.08 x 10^3 Pa partial pressure of tetramethylsilane were introduced. The tube was then flame-sealed.

Results**:**

The chief resonances in the ^1H and ^{13}C NMR spectra are those of 1,3-butadiene and the chemical shift referent. The ^1H chemical shifts of the chief resonances are 4.97, 5.11, and 6.33 ppm. Because of the magnetic nonequivalence of each chemically equivalent pair of the ^1H resonances of 1,3-butadiene in this AA'BB'CC' spin system, the determination of multiplicities and scalar couplings is a complex undertaking, and is not attempted in this report.

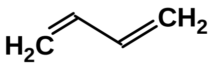
The minor impurity peaks observed at 1.59 and 1.71 ppm are thought to correspond to CH_3 resonances. If this is the case, then proper adjustment of the integral intensity by the number of equivalent nuclei responsible for the signal indicates that these impurities are present at < 0.1 mol% of the 1,3-butadiene.

The only visible resonances in the ^{13}C NMR spectrum are those of 1,3-butadiene and the chemical shift referent. The ^{13}C chemical shifts are 117.36 and 141.24 ppm.

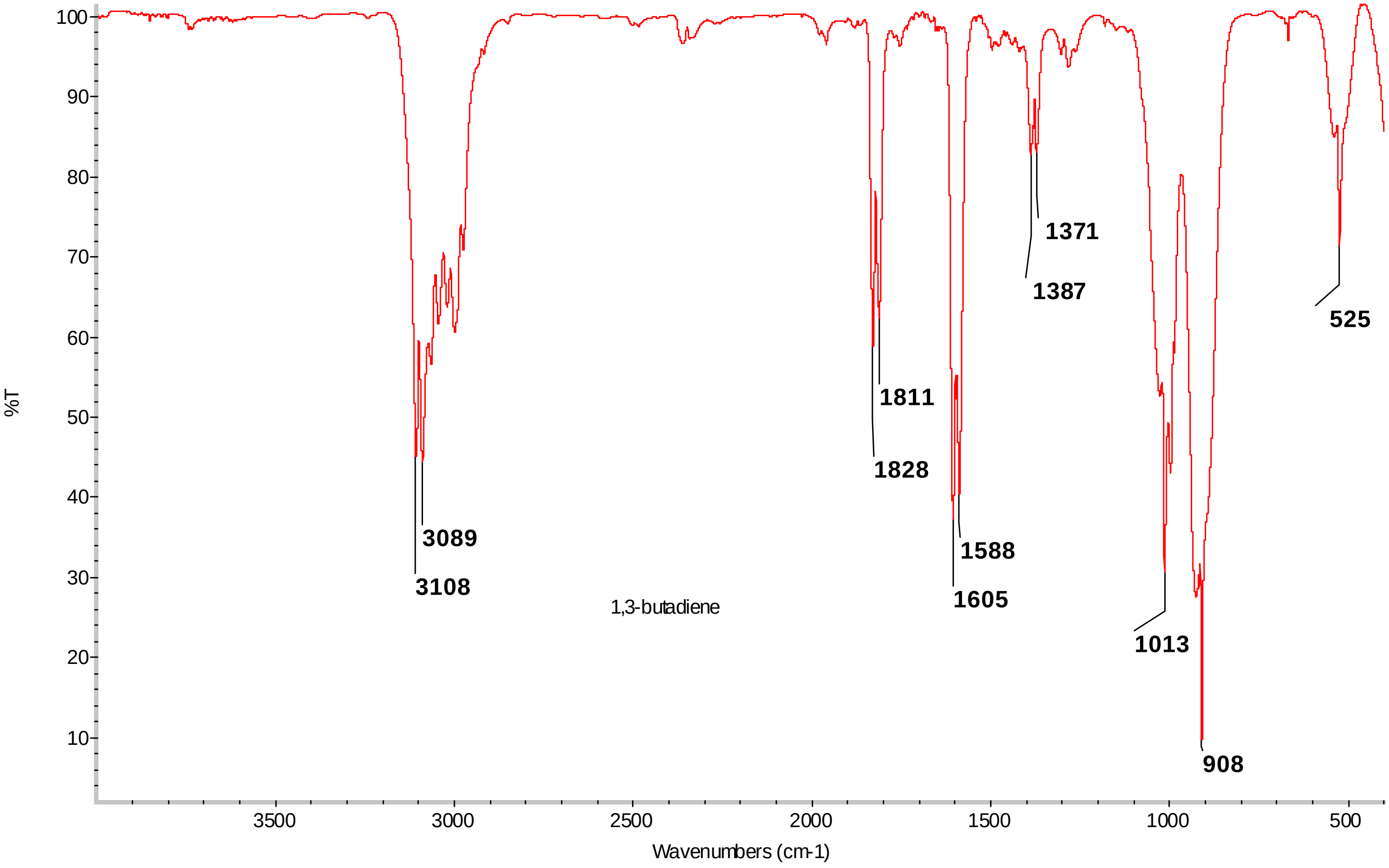
These data are consistent with available spectral data on 1,3-butadiene (see e.g. AIST Spectral Database for Organic Compounds, spectrum # WHPM02426 for ^{1}H; Wiley Subscription Service, spectrum # CNCC-99312-001G for ^{13}C). The assignments given in this report are derived from these literature sources.

Procedure for Generation of an FT-IR Spectrum for

1, 3-butadiene *(CAS 106-99-0)*



(Source: Sigma-Aldrich Co., batch no. 13511DH,)



Operating Conditions

Instrument:	Nicolet Nexus 6700 FTIR
Number of Scans:	128
Resolution:	4 wavenumber
Low Pass Filter:	11,000 kHz
Apodization:	Happ-Genzel
Collection range:	4000-400 wavenumber

Preparation of Sample

Sample was analyzed at 30 torr partial pressure in a 10 cm gas cell. The gas was transferred from a cylinder by use of a vacuum manifold.

Results:

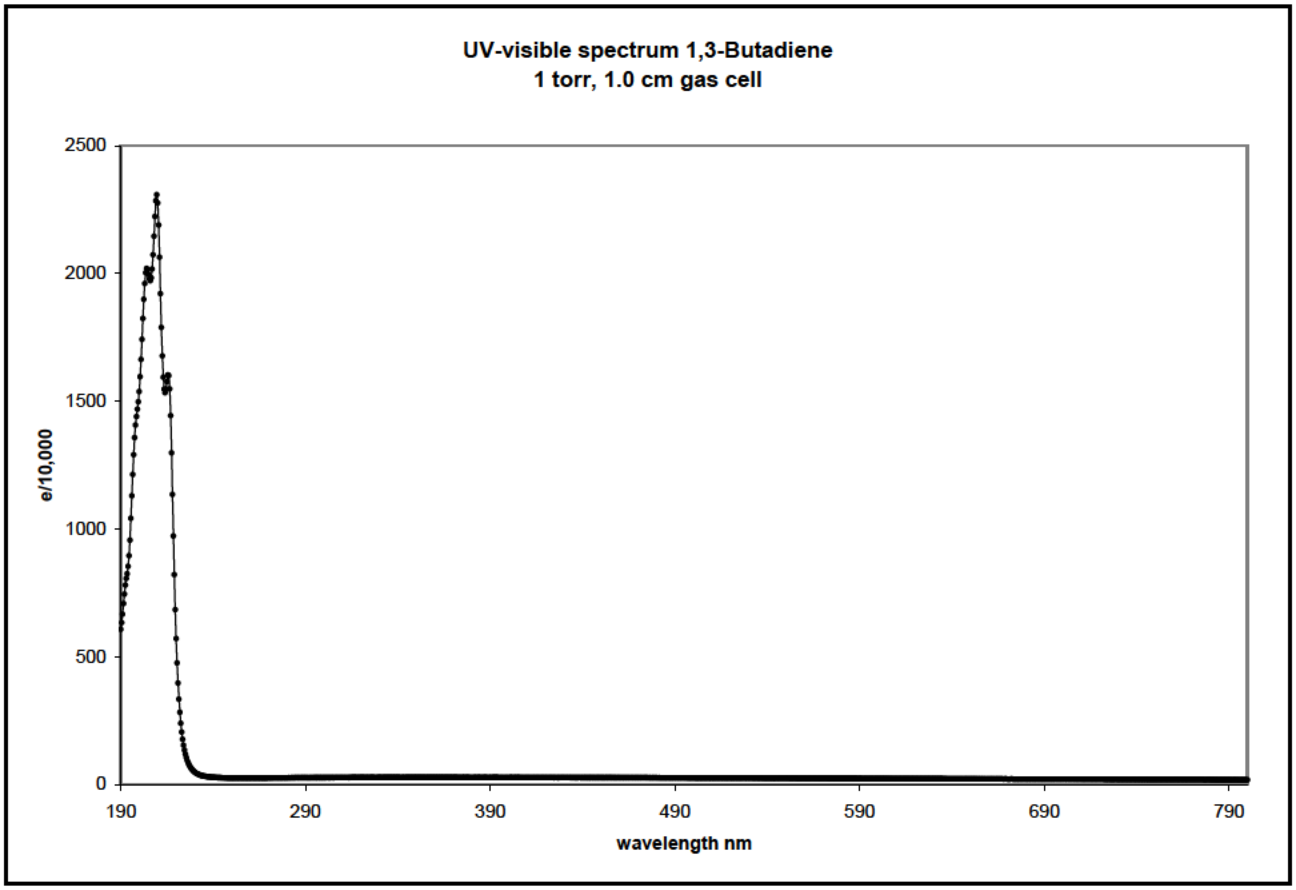
IR Peak assignments:

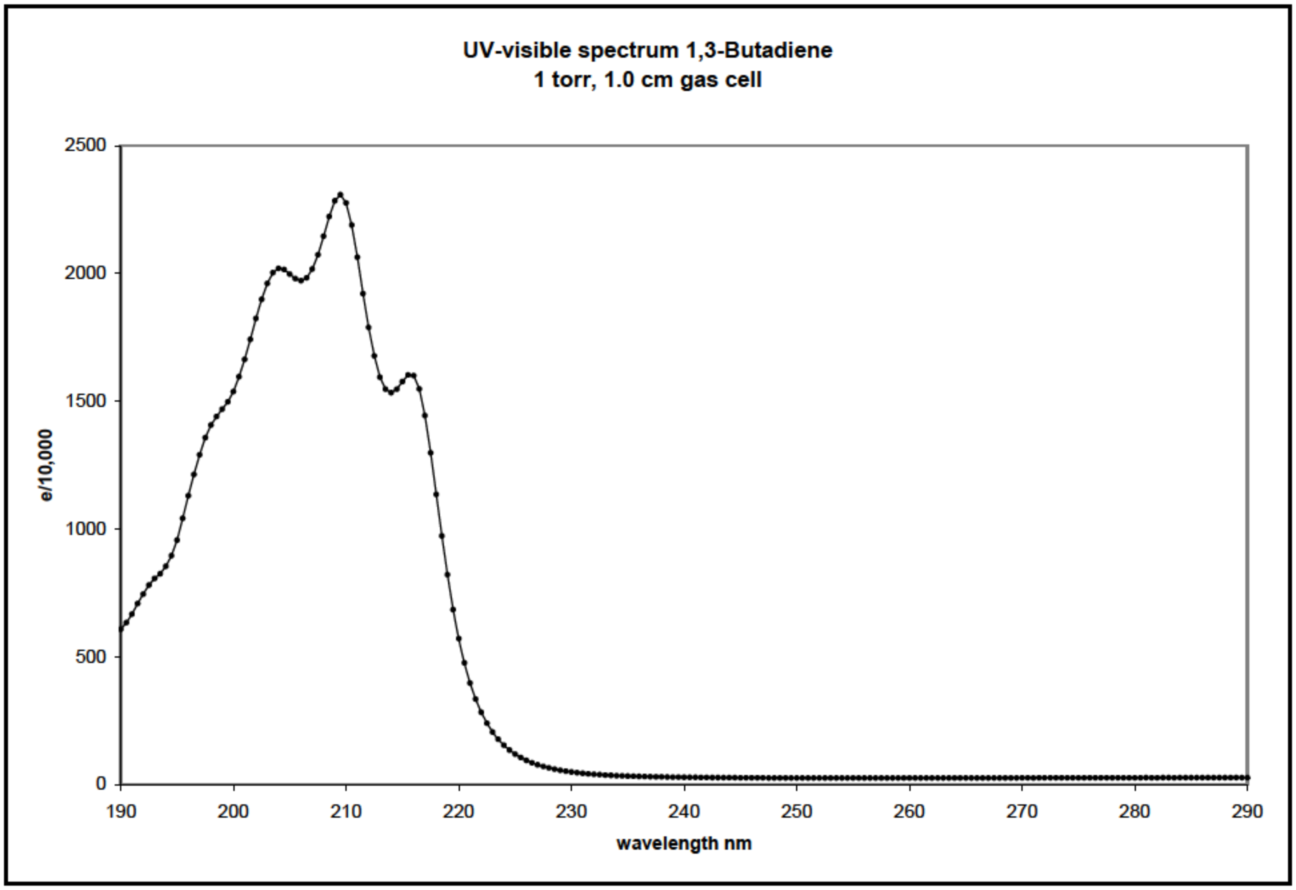
3089, 3108 cm-1	C-H stretch of -HC=CH2
~1600 cm-1	C=C stretch of HC=CH2
908 cm-1	CH2 wag of C=CH2

The gas phase spectrum is consistent with literature spectra of 1,3-butadiene. For example, see ***The Aldrich Library of FT-IR Spectra, Edition I, Volume 3, Vapor Phase, Charles J. Pouchert editor, 1989, p. 38C.***

UV-visible spectrum 1,3-Butadiene, CAS # 106-99-0,

Source: Aldrich 99%+,





Preparation:

A 1.0 cm quartz cell with a gas-tight stopcock was backflushed and emptied with the 1.3-butadiene four times. The final fill, at 1 torr pressure, was used as the sample.

Operating Conditions

Instrument:	Varian Cary 5000
Range:	800 nm – 190 nm
Scan Rate:	150 nm/minute
Data Interval:	0.5 nm
Averaging Time:	0.2
Slit Height:	Full
Beam Mode:	Double
Source Changeover:	340 nm
Baseline Correction:	On
Sample Concentration	1 torr 100% 1,3-butadiene

Spectra Collection

A baseline was collected with empty sample and reference beam. A spectrum of the empty cell is collected versus an empty reference beam. The spectrum of the sample is then collected. by filling the cell with 1,3-Butadiene (100%, 1 torr). The empty cell reference is subtracted from the sample spectrum.

Results:

λ (nm)	**ε cm2/mol**
190	6070000
193.5	8240000
198.5	14400000
204	20190000
209.5	23080000
215.5	16030000
230	490000
500	260000
800	180000