



Designation: E 1840 – 96

Standard Guide for Raman Shift Standards for Spectrometer Calibration¹

This standard is issued under the fixed designation E 1840; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers Raman shift values for common liquid and solid chemicals that can be used for wavenumber calibration of Raman spectrometers. The guide does not include procedures for calibrating Raman instruments. Instead, this guide provides reliable Raman shift values that can be used as a complement to low-pressure arc lamp emission lines which have been established with a high degree of accuracy and precision.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.4 Some of the chemicals specified in this guide may be hazardous. It is the responsibility of the user of this guide to consult material safety data sheets and other pertinent information to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to their use.

2. Referenced Documents

2.1 ASTM Standards:

E 131 Terminology Relating to Molecular Spectroscopy²

E 1683 Practice for Testing the Performance of Scanning Raman Spectrometers²

3. Terminology

3.1 *Definitions*—Terminology used in this guide conforms to the definitions set forth in Terminology E 131.

4. Significance and Use

4.1 Wavenumber calibration is an important part of Raman analysis. The calibration of a Raman spectrometer is performed or checked frequently in the course of normal operation and even more often when working at high resolution. To date, the most common source of wavenumber values is either emission

lines from low-pressure discharge lamps (for example, mercury, argon, or neon) or from the non-lasing plasma lines of the laser. There are several good compilations of these well-established values (1-8).³ The disadvantages of using emission lines are that it can be difficult to align lamps properly in the sample position and the laser wavelength must be known accurately. With argon, krypton, and other ion lasers commonly used for Raman the latter is not a problem because lasing wavelengths are well known. With the advent of diode lasers and other wavelength-tunable lasers, it is now often the case that the exact laser wavelength is not known and may be difficult or time-consuming to determine. In these situations it is more convenient to use samples of known relative wavenumber shift for calibration. Unfortunately, accurate wavenumber shifts have been established for only a few chemicals. This guide provides the Raman spectroscopist with average shift values determined in seven laboratories for seven pure compounds and one liquid mixture.

5. Raman Shift Standards

5.1 *Reagents and Methodology*—Raman shifts were measured in seven laboratories for the following eight materials:

Compound	Source
Naphthalene	Mallinckrodt ⁴
1,4-Bis(2-methylstyryl)benzene (a laser dye)	Aldrich ⁵
Sulfur	Aldrich ⁵
50/50 (v/v) toluene/acetonitrile	Mallinckrodt ⁴
4-Acetamidophenol ⁶	Aldrich ⁵
Benzonitrile	Aldrich ⁵
Cyclohexane	Mallinckrodt ⁴
Polystyrene	Aldrich ⁵

5.1.1 The eight materials were selected to cover a wide wavenumber range (from 85 to 3327 cm^{-1}) for both solids and liquids. They have no known polymorphs, and several batches were examined. All of the chemicals are readily available at high purity from commercial sources such as Aldrich.⁵ Six of the laboratories in the study used FT-Raman spectrometers; one used a scanning Raman system; and one employed a multichannel spectrometer. The shift values were determined

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² *Annual Book of ASTM Standards*, Vol 03.06.

³ The boldface numbers in parentheses refer to a list of references at the end of the text.

⁴ Available from Mallinckrodt, 16305 Swingley Ridge Dr., Chesterfield, MO 63017.

⁵ Available from Aldrich, 1001 W. St. Paul Ave., Milwaukee, WI 53233.

⁶ The active ingredient of Tylenol, a registered trademark of McNeil-PPC.

independently by each laboratory; only an approximate spectrum without peak frequencies was provided as a guide. No wavenumber calibration procedure was recommended, but each laboratory used their own calibration procedure to obtain the most accurate data possible.

5.2 *Data*—Figs. 1-8 and Tables 1-8 give representative spectra and peak data for the eight standards. Uncorrected, relative peak intensities determined with a SPEX 1403 scanning double monochromator (1200- lines/mm gratings) and RCA 31034A photomultiplier tube with 514.5-nm excitation

are included to help the user match spectral peaks with the tabulated shift values. Average shifts and standard deviations (σ_{N-1}) appear in the tables. With the exception of a few values at low and high Raman shifts, only values with standard deviations less than 1.0 cm^{-1} are reported. Most of the unreported peaks were weak, had poor shape, or overlapped other bands causing unacceptably high uncertainty in the data.

6. Keywords

6.1 Raman spectroscopy; wavenumber calibration

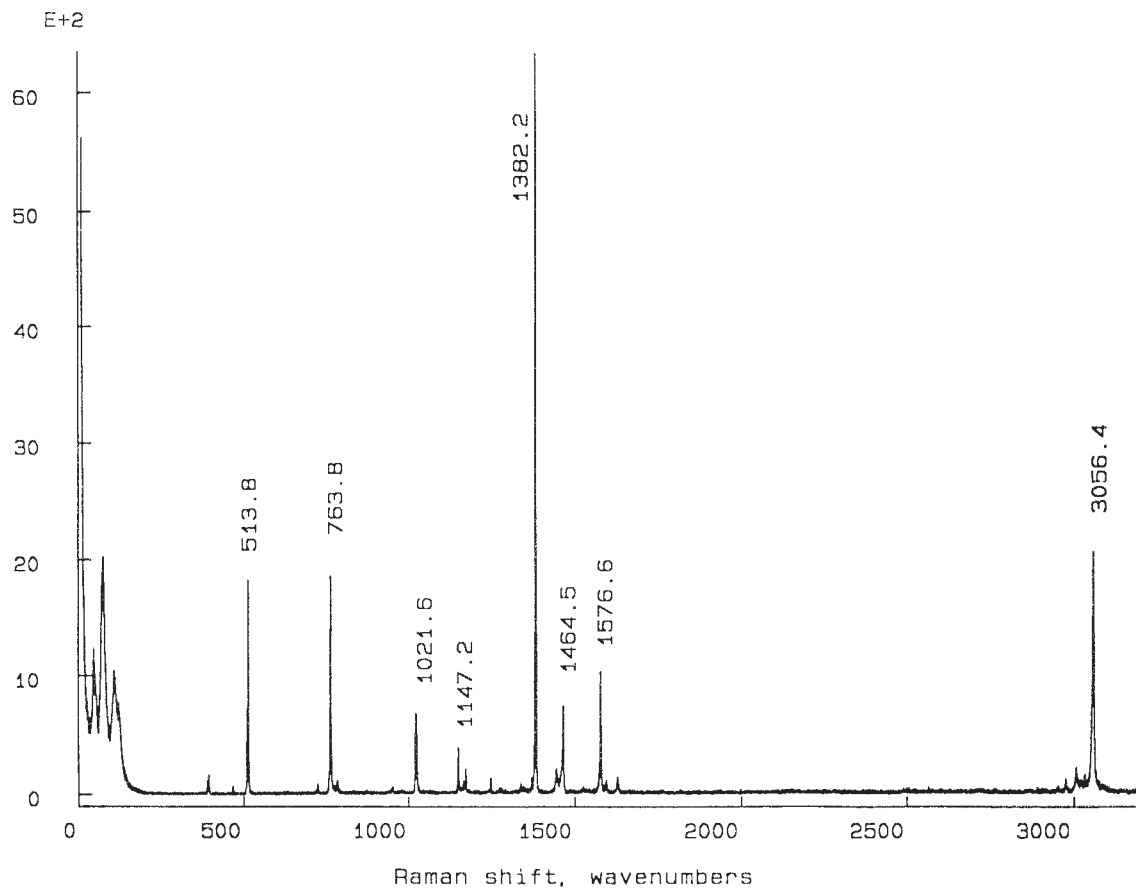
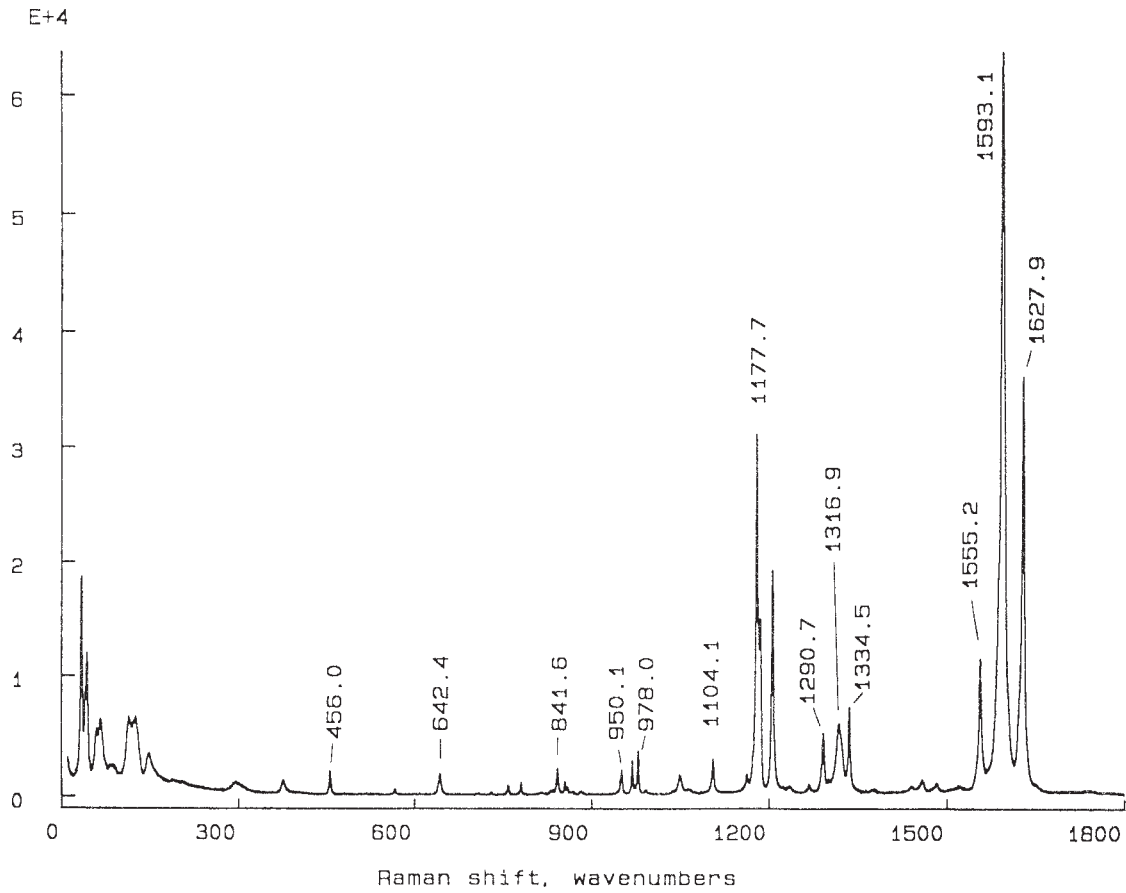
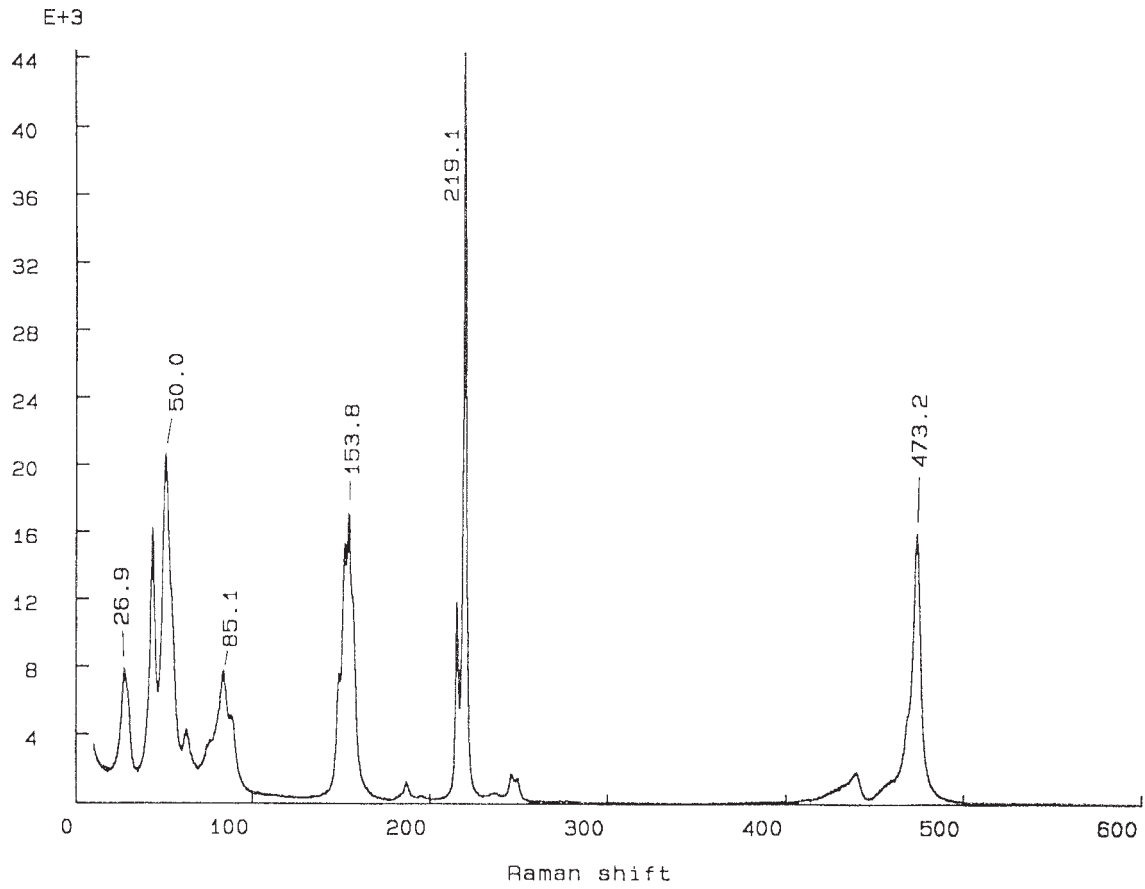


FIG. 1 Naphthalene



Raman shift, wavenumbers
FIG. 2 1,4 bis (2-Methylstyryl) Benzene



NOTE 1—Lower three frequencies are averages of only 1 to 3 values.

FIG. 3 Sulfur

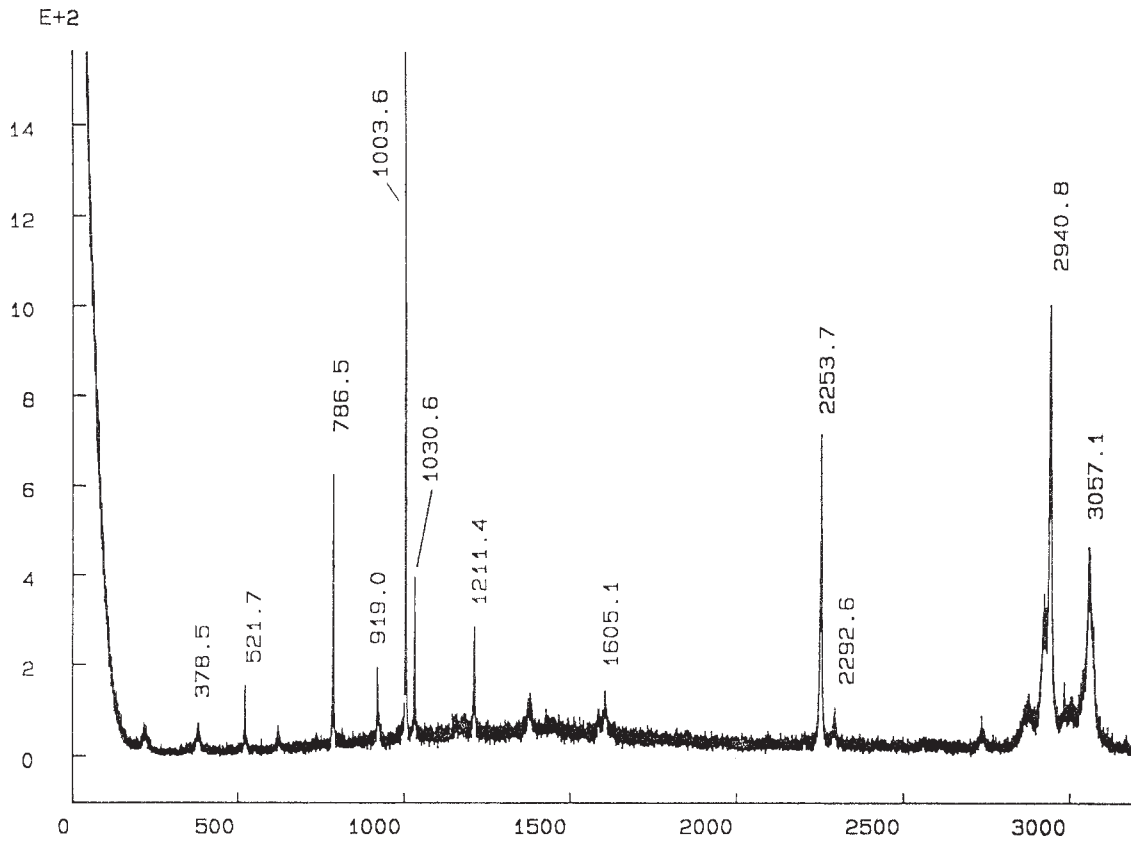


FIG. 4 50/50 Toluene/Acetonitrile

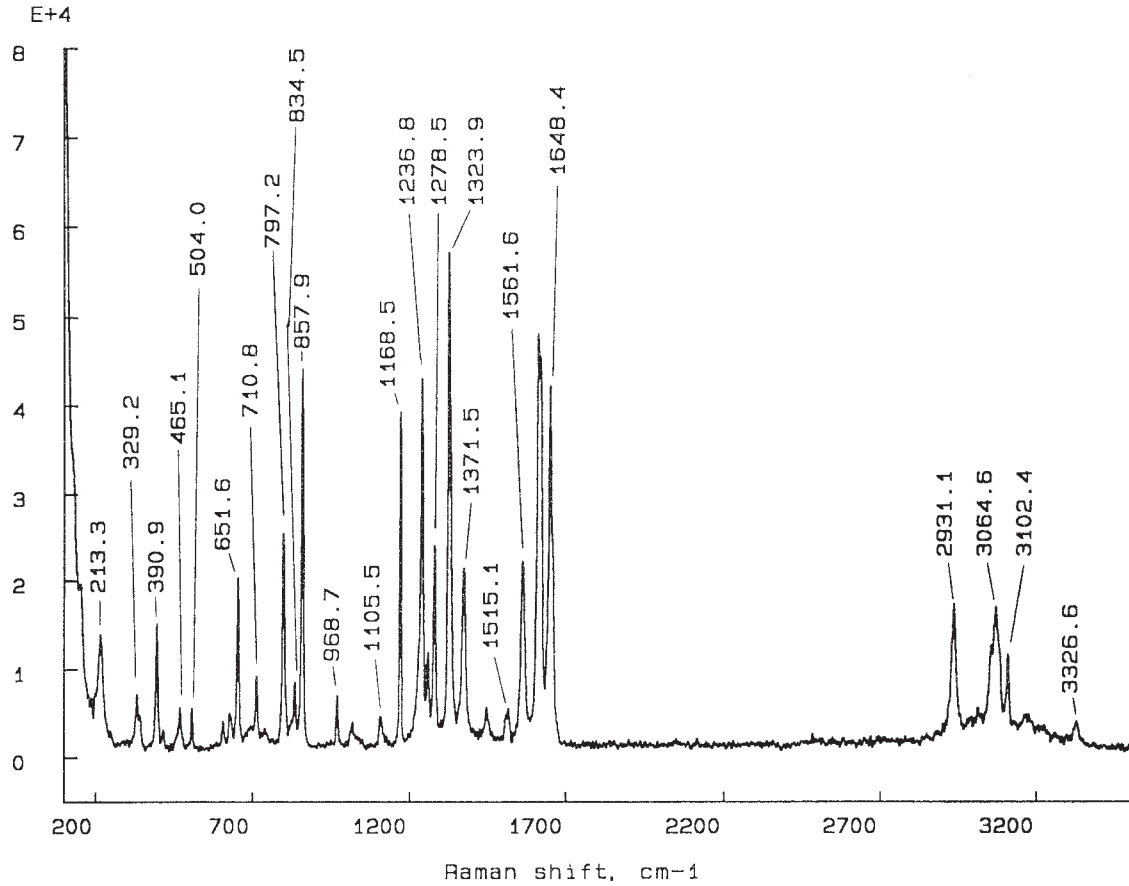


FIG. 5 4-Acetamidophenol (Tylenol)

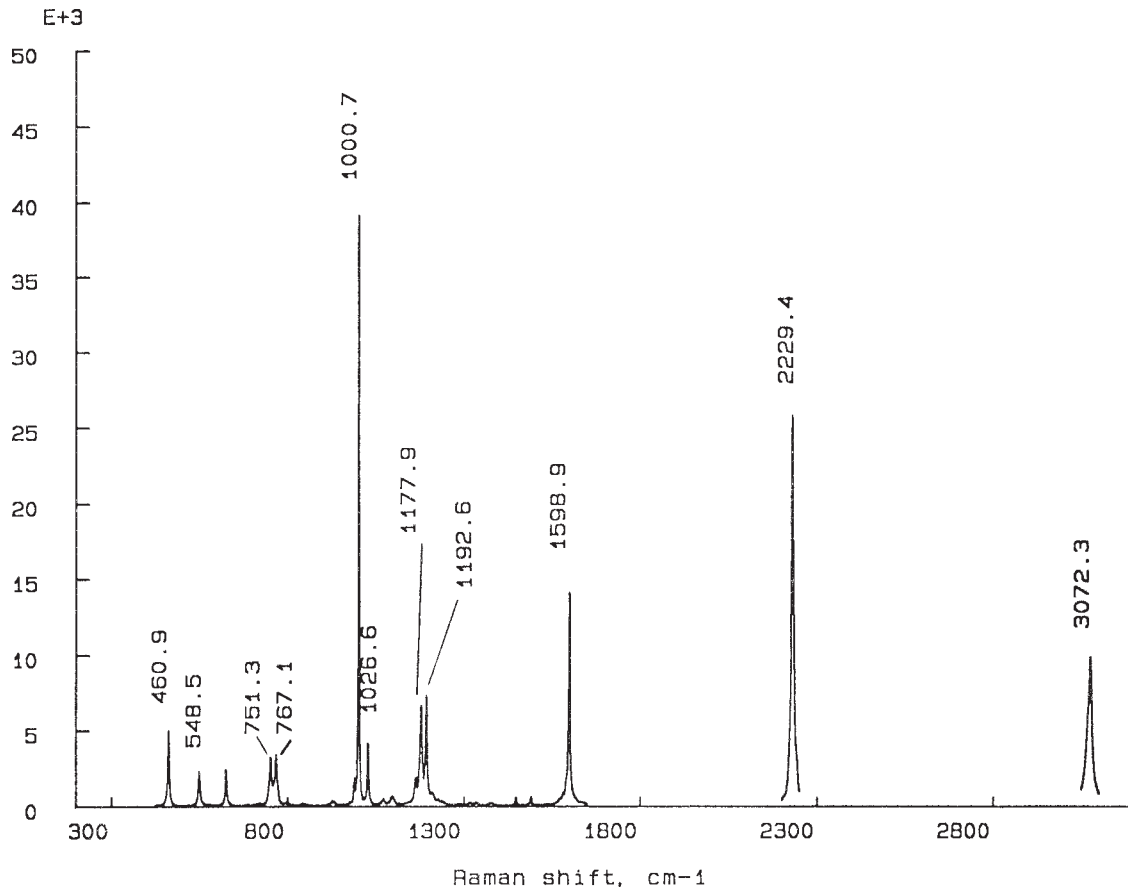


FIG. 6 Benzonitrile

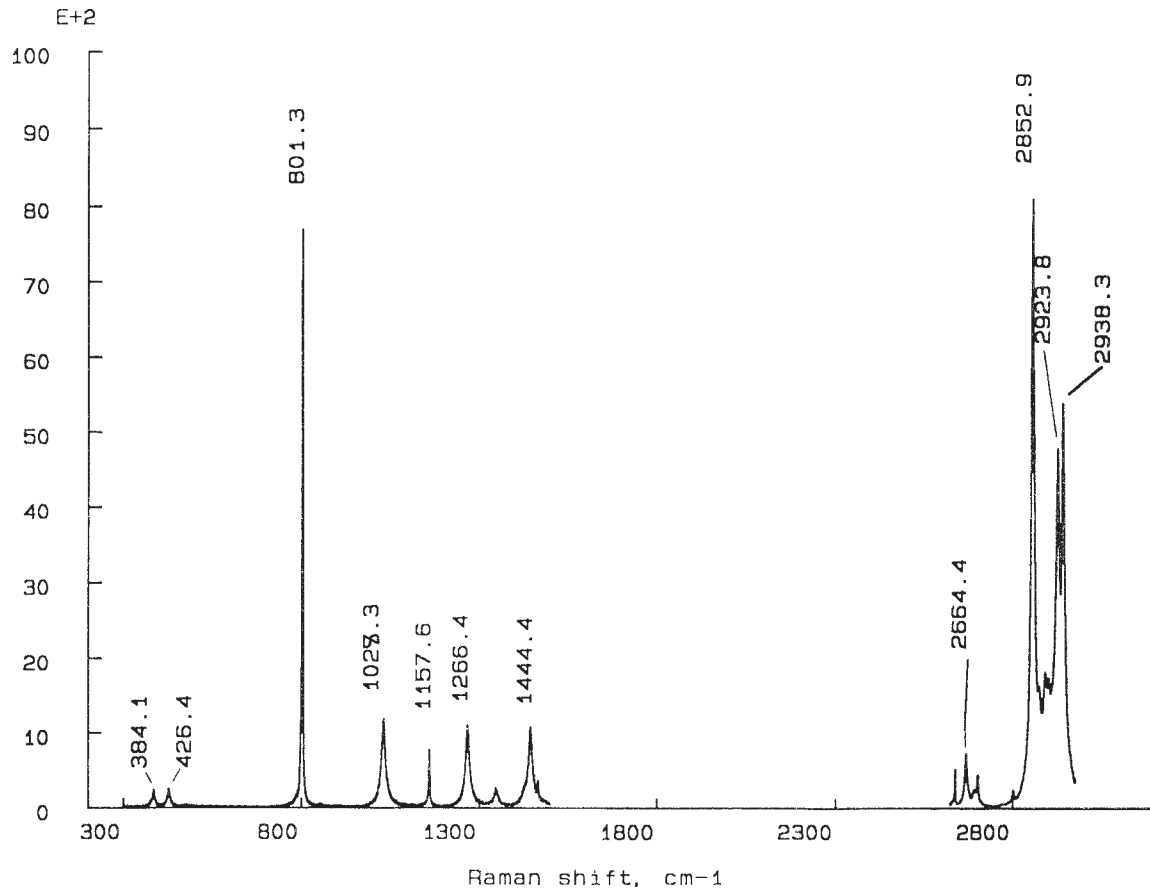


FIG. 7 Cyclohexane

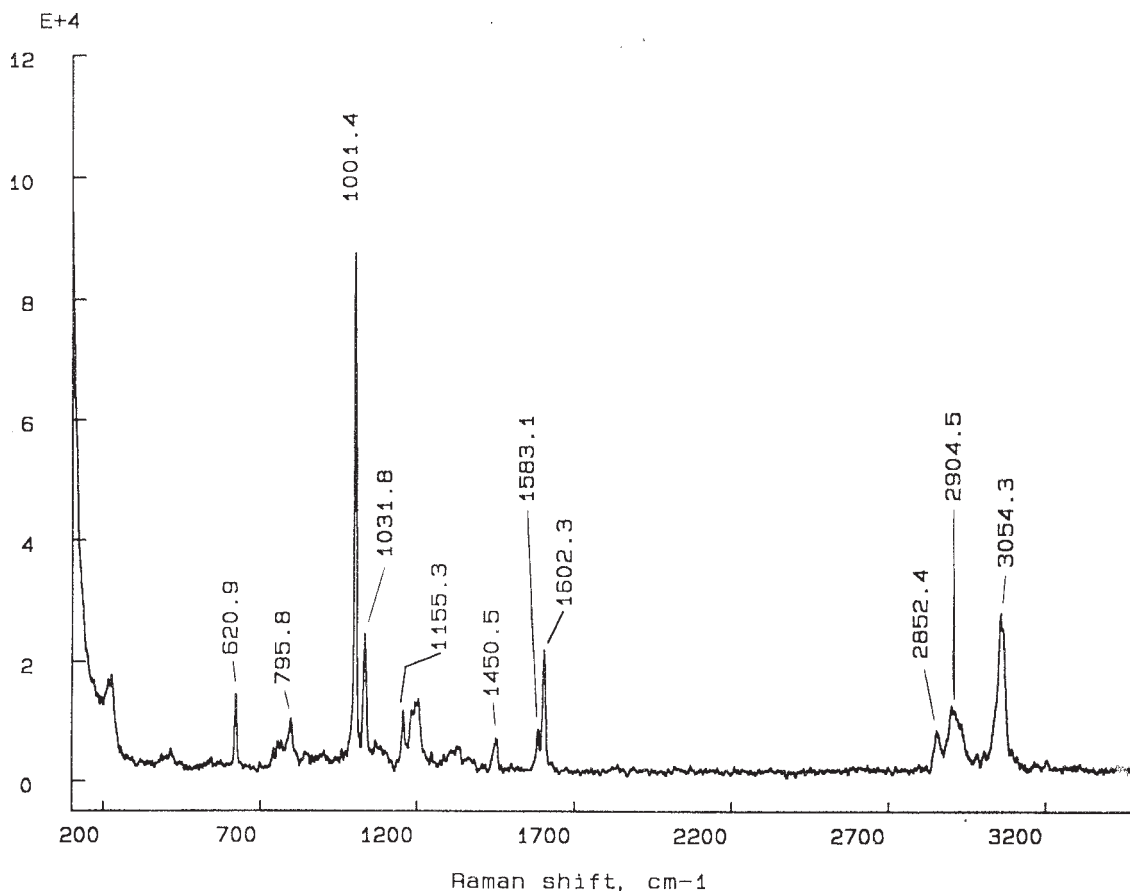


FIG. 8 Polystyrene

TABLE 1 Naphthalene

Average (cm-1) ± Standard Deviation	Relative Intensity
513.8 ± 0.31	29
763.8 ± 0.31	30
1021.6 ± 0.49	11
1147.2 ± 0.34	6
1382.2 ± 0.31	100
1464.5 ± 0.29	12
1576.6 ± 0.29	16
3056.4 ± 0.41	32

TABLE 2 1,4-Bis(2-Methylstyryl)Benzene

Average (cm-1) ± Standard Deviation	Relative Intensity
456.0 ± 0.56	3
642.4 ± 0.12	3
841.6 ± 0.28	4
950.1 ± 0.13	4
978.0 ± 0.16	6
1104.1 ± 0.31	5
1177.7 ± 0.56	49
1290.7 ± 0.28	9
1316.9 ± 0.94	10
1334.5 ± 0.16	12
1555.2 ± 0.19	18
1593.1 ± 0.44	100
1627.9 ± 0.23	56

TABLE 3 Sulfur

Average (cm-1) ± Standard Deviation	Relative Intensity
85.1 ± 2.6	17
153.8 ± 0.50	38
219.1 ± 0.57	100
473.2 ± 0.49	36

TABLE 4 Toluene/Acetonitrile

Average (cm-1) ± Standard Deviation	Relative Intensity ^A
378.5 ± 0.92	4 (A)
521.7 ± 0.34	10 (T)
786.5 ± 0.40	39 (T)
919.0 ± 0.40	11 (A)
1003.6 ± 0.37	100 (T)
1030.6 ± 0.36	23 (T)
1211.4 ± 0.32	16 (T)
1605.1 ± 0.47	6 (T)
2253.7 ± 0.42	44 (A)
2292.6 ± 0.89	5 (A)
2940.8 ± 0.25	64 (A)
3057.1 ± 0.63	30 (T)

^A (T = toluene, A = acetonitrile).

TABLE 5 4-Acetamidophenol^A

Average (cm-1) ± Standard Deviation	Relative Intensity
213.3 ± 1.77	17
329.2 ± 0.52	11
390.9 ± 0.76	25
465.1 ± 0.30	11
504.0 ± 0.60	11
651.6 ± 0.50	33
710.8 ± 0.68	17
797.2 ± 0.48	45
834.5 ± 0.46	14
857.9 ± 0.50	82
968.7 ± 0.60	12
1105.5 ± 0.27	7
1168.5 ± 0.65	70
1236.8 ± 0.46	75
1278.5 ± 0.45	42
1323.9 ± 0.46	100
1371.5 ± 0.11	38
1515.1 ± 0.70	9
1561.5 ± 0.52	37
1648.4 ± 0.50	73
2931.1 ± 0.63	29
3064.6 ± 0.31	26
3102.4 ± 0.95	20
3326.6 ± 2.18	7

^A Active ingredient of Tylenol (see Footnote 6).

TABLE 6 Benzonitrile

Average (cm-1) ± Standard Deviation	Relative Intensity
460.9 ± 0.73	15
548.5 ± 0.82	7
751.3 ± 0.74	10
767.1 ± 0.59	10
1000.7 ± 0.98	100
1026.6 ± 0.81	13
1177.9 ± 0.82	20
1192.6 ± 0.56	25
1598.9 ± 0.70	36
2229.4 ± 0.39	67
3072.3 ± 0.41	26

TABLE 7 Cyclohexane

Average (cm-1) ± Standard Deviation	Relative Intensity
384.1 ± 0.78	2
426.3 ± 0.41	3
801.3 ± 0.96	95
1028.3 ± 0.45	15
1157.6 ± 0.94	6
1266.4 ± 0.58	14
1444.4 ± 0.30	12
2664.4 ± 0.42	8
2852.9 ± 0.32	100
2923.8 ± 0.36	58
2938.3 ± 0.51	67

TABLE 8 Polystyrene

Average (cm-1) ± Standard Deviation	Relative Intensity
620.9 ± 0.69	16
795.8 ± 0.78	10
1001.4 ± 0.54	100
1031.8 ± 0.43	27
1155.3 ± 0.56	13
1450.5 ± 0.56	8
1583.1 ± 0.86	12
1602.3 ± 0.73	28
2852.4 ± 0.89	9
2904.5 ± 1.22	13
3054.3 ± 1.36	32

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