MICROSAMPLING TECHNIQUES IN LASER RAMAN SPECTROSCOPY

by

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THE introduction of continuous-wave laser energy as an excitation source for Raman spectroscopy has finally launched this discipline as a practical analytical tool for the organic chemist. Although the powerfully complementary nature of Raman and infrared data in structure elucidation and confirmation studies had been recognized for approximately 40 years (1), the shortcomings of pre-laser excitation sources deterred many investigators from working with Raman apparatus. The principal drawback was the mercury-vapor lamp of which dozens of types had been tried with varying degrees of success. Even the best to evolve, the Toronto arc., left much to be desired. In order to achieve an intensity level sufficient for exciting Raman spectra, it had to be run under conditions which generated a great deal of extraneous heat. The short wavelength of excitation (4358A) caused many samples to fluoresce, often swamping the weaker Raman bands. Molecular decomposition of the sample was a common casualty. Despite its "sledge hammer" approach, the Toronto arc produced much lower intensity Raman spectra than those obtained by the present heat-less 80 mW He-Ne laser whose emission wavelength is so long (6328A) that samples seldom decompose or fluoresce.

Another shortcoming of pre-laser Raman spectroscopy was the necessity for a fairly large sample. Light produced from a source other than the laser is emitted from many points independently so that there is no phase relationship, no directionality, no polarization to the radiation. While the overall light intensity of such a noncoherent source may be high, the out-of-phase transverse waves produced cannot be combined to improve the luminance (brightness or energy per unit area). Despite hundreds of attempts by almost as many scientists over several centuries, the problem of increasing the brightness of a source remained insoluble and almost as classic as that for producing perpetual motion.

In sharp contrast, the brightness of a laser beam may be greatly increased simply by interposing a condensing lens in its optical path. A typical laser beam diameter is about 2 mm and it can be focused down to a diffraction limited point of dimensions comparable to the wavelength emitted. Energy densities in the order of 10^6 W/cm² can be achieved, a figure at least 10,000 times greater than that of the most powerful Toronto arc. Focusing this high density energy permits excitation of an extremely small sample volume without loss of scattering energy. This attribute of the laser, in addition to its high intensity, monochromaticity, and linear polarization makes it the long-awaited "perfect" source for Raman spectroscopy. Furthermore, such devices as the Ar^+ and Kr^+ lasers offer flexibility in the selection of a particular excitation frequency which thwarts the probability of fluorescence, absorption, and photo-decomposition.

One of the greatest assets of laser-Raman spectroscopy is its compatibility with small samples. This was recognized by Lau and Hertz whose first published report (2) pertaining to laser-Raman examination of small samples appeared in 1966. An Ulbricht scattering globe was modified to a cylindrical type device for their purpose (Fig. 1) and with it the authors obtained acceptable spectra on as little as 80 μl of material. Bailey, Kint, and Scherer (3) reduced sample volume still further after adopting an excitation/viewing geometry suggested by Daman, Leite, and Porto (4). As shown in Fig. 2, the focused laser beam is directed down the axis of a cylinder and the scattered radiation is viewed horizontally at 90° from the main axis of the cylinder. Individual capillaries were prepared for each sample by carefully heat-forming a hemispherical lens at one end of a tube, the approximately spherical surface serving as a lens to collimate, rather than to focus, the light. In such capillaries, Raman spectra were recorded on 0.04 μl CCl_4, 0.15 μl indene, and 0.35 μl longifolene. Employing a 0.3 μl capillary cell, the authors measured depolarization ratios for selected CCl_4 bands which compared favorably with those of previous investigators. However, when the cell volume was reduced to 0.04 μl, depolarization data were not in agreement
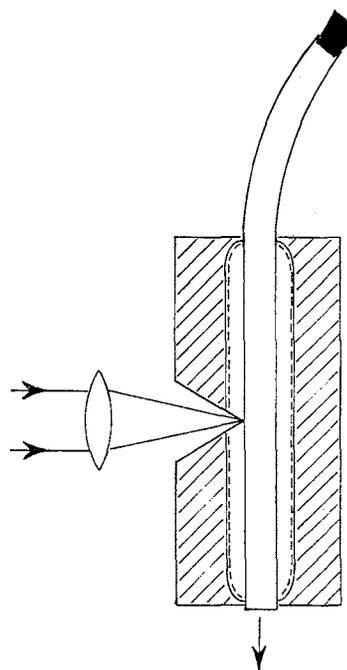

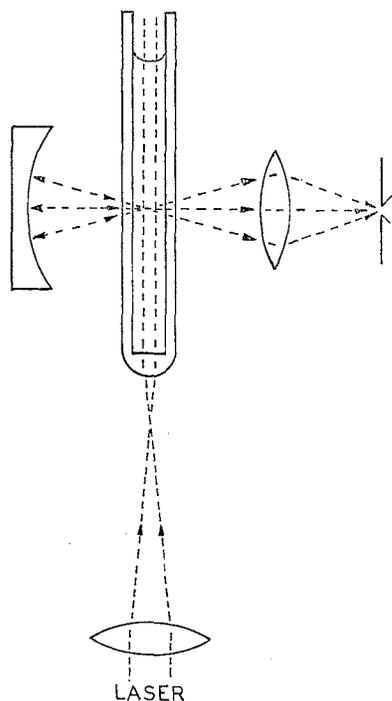Fig. 1 Modified Ulbricht scattering cylinder in which minimum sample size is around 80 μl.

Fig. 2 Axial excitation/transverse viewing cell of Bailey, Kint and Scherer in which minimum sample size is 0.04 μl.
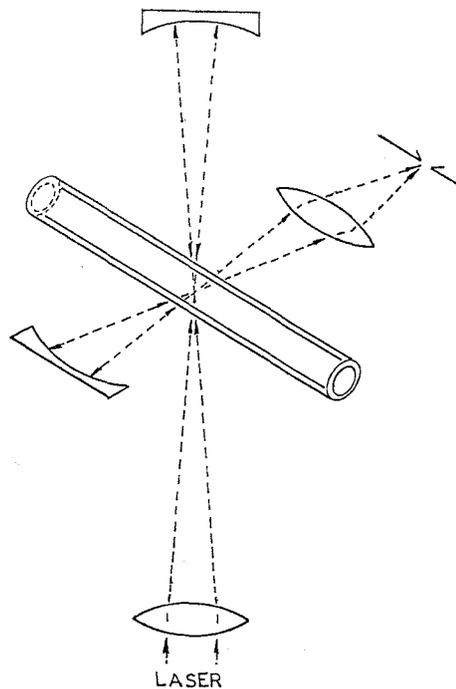

Fig. 3 Transverse excitation/transverse viewing cell of Pez in which minimum sample size is 0.008 μl.

with accepted values.* In addition, cells were awkward to load and, because the geometry of the hemispherical lens could not be controlled, alignment of the cells in the system met with difficulty.

Pez (5) decided to turn the capillary cell through a right angle. Instead of passing the exciting laser beam axially through the cell (like Bailey, Kint, and Scherer) he chose to have the beam enter the cylindrical wall of the capillary transversely, the curved wall helping to refract the beam through the center of the capillary (Fig. 3). Transverse viewing at 90° was similar to that of Bailey, Kint, and Scherer.

The present paper is concerned with an extension of Pez' technique from 1-mm bore capillaries to 0.1-mm bore capillaries. We also show how the technique is conveniently applicable to solids trapped from a gas chromatograph. Raman spectra have been obtained on liquid samples as small as 8 nl, on which measured depolarization ratios are in excellent agreement with those reported in the literature. While an 8 nl sample admittedly is somewhat tricky to run, 30 nl quantities can be routinely examined. Representative spectra have been recorded of liquids and solids. Also, the effects of laser power and irradiating frequencies, as well as other instrumental parameters have been studied and comparisons made between earlier techniques and our adopted Pez technique.

A Spex laser-Raman system was utilized for this investigation. Light from a laser is deviated 90° by a broad-band (4500-6500A) almost totally reflecting dielectric mirror and enters the bottom of a periscope tube. The beam, with its polarization vector properly oriented for ordinary Raman studies, is next deflected upward by a second broad-band dielectric mirror to a microscope objective which focuses the energy to a diffraction limited point within the sample tube. It is often necessary to interpose a narrow-band interference filter (25A half-width, 75% transmittance) in the path of the collimated

beam before the microscope objective in order to suppress contaminating plasma (non-lasing) emission lines. After traversing the material, the diverging beam strikes a concave, broad-band dielectric mirror and returns focused through the sample, thereby multiplying the exciting power. Ideally adjusted, the beam can be multipassed between the laser and mirror M′ with a resulting 10-fold increase in Raman signal as compared with a single passing of the radiation. Realistically, only a doubling of the signal intensity should be expected with capillary tubing cells; the smaller the tube diameter, the more stringent and time-consuming its alignment becomes.

Light scattered by the sample at 90° to the beam direction is collected by an f/1.6 lens and a 5X image is focused on the spectrometer entrance slit. Back-scattered light is collected at the same time by a spherical mirror effectively to double the intensity of the Raman radiation focused on the entrance slit.

Between the lens and entrance slit are placed a polarizing analyzer and an optical scrambler, the latter preventing grating polarization from affecting the measured depolarization ratios. The scrambler is a suitably oriented quartz wedge which converts the received plane polarized light to random, elliptically polarized light before it reaches the grating. Diffraction gratings all behave differently to polarized light, their diffraction intensity being a function of wavelength of the polarized beam. Accurate depolarization measurements thus require some means, like the scrambler, for avoiding this source of error.

The principal component in the laser-Raman system is the spectrometer itself. It is a ¾-meter, f/6.8 Czerny-Turner double spectrometer (Model 1400-II) in which two 1200 groove/mm gratings are constrained to rotate together and so arranged optically that they double the luminosity of the instrument. This so-called additive dispersion permits the slits to be opened to twice the widths of a similar single grating spectrometer. This done, twice the intensity of light is passed for a given resolving power as compared with a single grating spectrometer. In a typical experiment where a spectral slit width of 6 cm⁻¹ is indicated, the spectrometer slits are opened to 450 μ in a double spectrometer compared with 225 μ in a single instrument.

*Dr. Scherer recently advised us that he has improved the system and now obtains good depolarization values on such small sample volumes.
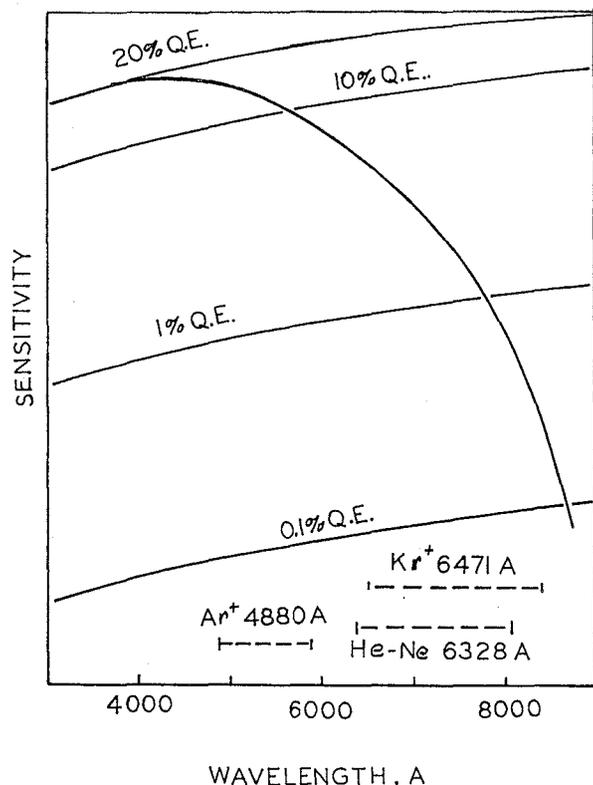
Fig. 4 Response curve of typical FW 130 photomultiplier. Its quantum efficiency extends so far into the red that it is satisfactory out to a 3000 cm⁻¹ shift with Kr 6471A excitation. At the other extreme, it operates optimally with 4880A, the principal blue line emitted by an argon laser.

The photomultiplier, characteristics of which are shown in Fig. 4, is an extremely efficient converter of light to electrical energy, with a peak quantum efficiency of around 25%. Its noise is kept exceedingly low by reducing the effective cathode area to a reasonable minimum (~10 mm²), and further noise reduction may be achieved by thermoelectrically cooling the entire photomultiplier to −30°. The picoammeter dc amplification system includes means to vary the time constant to match that of the scanning speed; the 0.3-second cross-chart strip-chart recorder displays the Raman spectra.

The beam diameter of all laser wavelengths employed in this investigation is approximately 2 mm and, after focusing, it is reduced to approximately 20 μ ($\phi = \lambda f / d$, where ϕ is focused beam diameter, f = focal length of lens, d = laser beam diameter, and λ = wavelength of exciting light). Thus, the focused beam volume is approximately 10^{-2} nl (10 nanograms when density is unity) which theoretically represents the absolute minimum volume of sample that can be expected to yield a measurable spectrum.

Table 1 summarizes the relative powers of each of the three lasers used in this work.

TABLE 1. OUTPUT POWER LEVEL OF THREE LASERS

Type of Laser	Wavelength Emitted, A	Output Power, mW
He-Ne	6328	80
Ar⁺	4880	1100
Ar⁺	5145	1000
Kr⁺	5682	240
Kr⁺	6471	400

TABLE 2. COMPARISON OF DIFFERENT LASER EXCITATION FREQUENCIES

Raman Region (cm⁻¹)	A Molecular Scattering Efficiency	B Relative Laser Power (80mW = 1.0)	C PM Quantum Efficiency [a]	D Grating Efficiency [b]	E Normalizing Factor for Equivalent Bandpass [c]	F [d] Raman Intensity
He-Ne Laser						
0 (6328A)	1.0	1.0	1.0	1.0	1.0	1.0
3000 (7811A)			0.25	0.80	1.6	0.32
Ar⁺ Laser						
0 (4880A)	2.8	14.0	2.3	1.2	0.59	64.
3000 (5717A)			1.5	1.1	0.81	51.
0 (5145A)	2.3	13.	2.2	1.2	0.65	51.
3000 (6084A)			1.2	1.1	0.91	36.
Kr⁺ Laser						
0 (5682A)	1.5	3.0	1.5	1.1	0.80	7.2
3000 (6850A)			0.73	1.0	1.1	3.6
0 (6471A)	0.90	5.0	0.90	1.0	1.0	4.1
3000 (8030A)			0.17	0.75	1.7	1.0

a FW 130 photomultiplier

b 5000A blaze (average of two sets of gratings)

c Constant luminosity conditions

d $A \times B \times C \times D \times E = F$

Table 2 summarizes the relative performance of the three lasers with respect to the signal level at the Rayleigh ($\Delta 0$ cm^{-1}) and at $\Delta 3000$ cm^{-1} Raman shifts. It should be pointed out that the data in Table 2, though representative, are not necessarily accurate for all systems, depending on the specific performance characteristics of each of the components. However, the basic information contained is sound: molecular scattering efficiency is a fourth-power function of frequency; lasers have different power output levels in addition to different output wavelengths; photomultiplier response varies over more than an order of magnitude in the region from 5000-8000A; grating efficiencies, peaked at a particular wavelength, fall off toward lower and higher wavelengths; and dispersion of a grating spectrometer, almost constant with respect to wavelength, varies considerably over the range 5000-8000A requiring the slit to be adjusted if constant spectral slit width is desired.

In the first column of Table 2, the wavelengths at excitation and at a 3000 cm^{-1} wavenumber shift are given. Note that the 3000 cm^{-1} shift extends from 5717A (with Ar$^+$ 4880A excitation) to 8030A (with Kr$^+$ 6471A excitation). In later columns of this table, all values are normalized to the He-He laser to facilitate comparisons.

Column A shows that lasers emitting at shorter wavelengths have considerably greater scattering efficiencies, i.e., proportional to the fourth power of the frequency. By switching to Ar$^+$ 4880A from He-Ne 6328A one obtains a source energy 2.8 times as powerful for Raman studies. Column B indicates that, bolstering the fourth-power law, the actual wattage levels of the ionized lasers are so much higher than He-Ne that still another advantage exists: up to 14 times more power is gained with 4880A excitation at the 1100 mW output level measured. Column C illustrates how the FW 130 photomultiplier fares with various lasers. Because the response of the FW 130 extends beyond 8000A, the need for a second photomultiplier is obviated. (Previously an S-1 cathode, sensitivity 7500-11,000A, was needed when measuring shifts beyond 2500 cm^{-1} with red laser excitation.) Column C demonstrates the effect of the detector fall-off in response at higher wavelengths. At a 3000 cm^{-1} shift from the Kr$^+$ 6471A line, the response of the FW 130 is approximately 1/10 of the counterpart shift from Ar$^+$ 4880A. Despite this, its noise level is sufficiently low so that the photomultiplier is suitable out to 8365A, representing a 3500 cm^{-1} shift from 6471A.

Grating efficiency (Column D) decreases so slowly that even at the longest wavelength of interest, 8030A, representing a 3000 cm^{-1} shift from Kr$^+$ 6471A, the loss is only 25%.

The Spex spectrometer operates at constant **instrumental** slit widths. Column E accounts for the changing instrumental slit width required to give constant **spectral** slit width at different wavelength or frequency settings of the spectrometer. The dispersion at the exit slit of the spectrometer is approximately 5.5 A/mm over the entire Raman range. Since frequency is a reciprocal function of wavelength, the number of wavenumbers per Angstrom changes over the spectral range of general interest. For a slit opened to 1 mm, the spectral bandpass at 4880A will be 4 cm^{-1} while the spectral bandpass at 6328A will be 2.5 cm^{-1}. This permits one to open the slits wider with red excitation than with blue excitation for equivalent bandpass.

Multiplying Columns A through E together gives a final value for Raman signal intensity in Column F, again normalized to an 80 mW He-Ne laser. Even at equal laser power, the Ar$^+$ 4880A generates a Raman signal 4.6 times as great as that from the He-Ne 6328A. Furthermore, the power level at 4880A is 14 times as intense. Even though the instrumental slit is narrower, one can conclude that, whenever applicable, 4880A excitation is to be preferred. At a 3000 cm^{-1} shift, the overall figure of merit, which takes into account both resolving power of the spectrometer and intensity of the laser is unmatched.
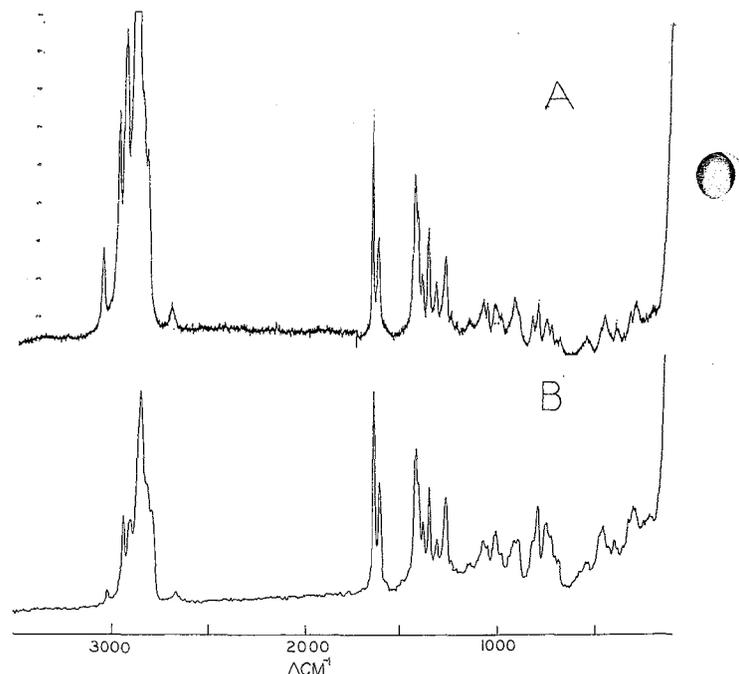

Fig. 5 **Raman spectra of 0.8 μl linalool in a 1-mm bore borosilicate capillary, A) with Ar$^+$ 4880A excitation, B) with He-Ne 6328A excitation. Note how much stronger the bands in the 3000 cm^{-1} region are with 4880A excitation, an effect due mainly to the rapid fall-off of efficiency with wavelength of the FW 130 photomultiplier.**

Fig. 5 illustrates the difference between the spectra of linalool, a terpene alcohol, recorded with He-Ne (Curve B) and Ar$^+$ (Curve A) laser sources. Instrumental conditions were adjusted to give nearly equal intensity C=C stretching bands at ~1640 cm^{-1}. The disparity in relative band intensities points up one of the difficulties entailed in developing retrieval systems for Raman reference spectra.

Given an unlimited budget, the practicing laser-Raman spectroscopist will welcome as many laser lines as he can get. A blue sample can absorb the red He-Ne 6328A line to such an extent that no Raman spectrum is seen; the sample will heat up rapidly, or decompose, or may even explode. On the other hand, photodecomposition of a colorless sample is more likely to occur at shorter excitation frequencies. Shorter wavelengths generally favor the probability of fluorescence; yet we have found that many samples which do fluoresce have their peak fluorescent output in the range 7000-8000A when excited by **any** wavelength below that value. This region of fluorescence is outside the Raman region for 4880A excitation but well within it for 6328A excitation. Paradoxically, fluorescence often results in an interfering background with red excitation while it has no effect with 4880A excitation. We conclude that the many literature comments referring to fluorescence with Hg arc sources (4358A) cannot be applied to blue lasers (4880A). It is our belief that many of the fluorescent problems encountered with the Hg sources are attributable to incomplete and inadequate filtering of all lines except 4358A.

THREE types of sampling were compared. The first two are axial/transverse systems in which the laser beam enters along the axis of a glass cylinder and the scattered radiation is examined at 90° perpendicular to the cylinder wall. For samples in the range 5-20 μl, a glass cell with a flat polished silica window on the bottom was used. For this and smaller size samples, the method of Bailey, Kint, and Scherer was adopted. Although the latter method is still axial/transverse, the actual sample container is a glass capillary with a hemispherical lens.

To differentiate between these methods, the first will be referred to as employing an axial/transverse **cell**; the second as employing an axial/transverse **capillary**.

The third technique, that of Pez, employs a capillary in which excitation and 90° scattering are both in transverse directions. This will be termed transverse/transverse.

In the axial/transverse cell, the quality of spectra from samples in the range 5-20 μl is identical with those from macro samples. In this system, the length and bore of the cell cannot be made smaller than that dictated by the convergence of light from the microscope objective. When the cell diameter is reduced too far, the converging light will impinge on the cell walls and interfere with the spectrum. For example, with a 90 mm fl lens, the beam diameter is approximately 125 μ at each end of a 5 mm long tube.

Bailey, Kint, and Scherer conceived an excellent scheme to overcome this limitation on minimum sample size. Expanding on an idea from telescope technology, they reasoned that a hemispherical lens formed on the bottom of a capillary would recollimate the focused laser beam within the capillary so that the beam would not strike its walls (Fig. 2). This occurs when the distance between the instrument's microscope objective lens and the capillary integral lens is equal to the sum of their focal lengths. These investigators demonstrated spectra of samples down to 0.04 μl.

Some shortcomings of the axial/transverse capillary prompted this investigation. Because the tiny lens is heat-formed, one cannot easily control its effective focal length and quality. The varying focal length required a means to adjust the capillary vertically in order that the beam be properly collimated through the capillary. In our experience, striations, bubbles, and other imperfections in the formed lens disrupted the polarization, and depolarization ratios obtained by us using this technique were not in good agreement with published data. Further, diffraction effects gave rise to a beam that was not truly collimated. A 100 μ diameter beam (6328A) was found to expand about 40% in a 5 mm length.

The relationship between intensity of the Raman line of CCl_4 at 459 cm^{-1} and its depolarization ratio is illustrated in Fig. 6. An increase in the relative line intensity occurs as the capillary is adjusted vertically to bring its lens into prime focus position. As the 459 cm^{-1} line intensity reaches a maximum, the depolarization ratio approaches a minimum of 0.07, still an order of magnitude above the accepted value. What causes this discrepancy is not clear. It can be seen from the figure that glass fluorescence was too weak to affect the depolarization values obtained. Rather, it is our opinion that the optical finish of the hemispherical lens is one determining factor. This would explain why we obtained equally poor depolarization ratios when working with our larger axial/transverse cells and axial/transverse capillaries.

At International Flavors & Fragrances, Inc., spectral information often must be obtained on submicroliter GLC fractions of natural and synthetic substances in order to elucidate their structure. Because of the limitations of the axial/transverse methods we decided to investigate and extend Pez' technique.

For relatively large samples ($\sim$1 μl) we have found standard borosilicate melting point capillary tubes of approximately 1-mm bore to work so satisfactorily that they now have become routine for both liquids and solids. Only with materials boiling below 100° is it necessary to seal the tube. Depolarization ratios for CCl_4 are in excellent agreement with those reported in the literature.

For samples ranging from 8 nl to 1 μl, we have found that we can work satisfactorily with borosilicate capillaries of 0.5 (1.1-mm o.d.), 0.25, and 0.1-mm bore (0.7-mm o.d.), obtained from Wilmad Glass Co., Buena, N. J. The cell holder for the 1-mm melting point tubes can be used for these capillaries without modification.
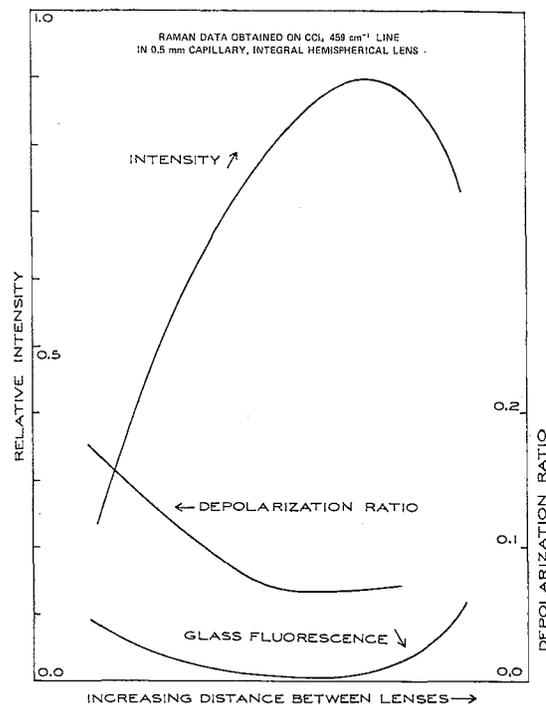

Fig. 6 Relationship between Raman line intensity of the 459 cm^{-1} line of CCl_4 and its measured depolarization ratio.

The 0.5-mm and 0.25-mm bore capillaries are compatible with most gas chromatographs for trapping both liquids and solids. Only an 8% and 12% reduction, respectively, in the flow rate of helium gas occurs (compared to a 4% drop for 1-mm bore tubes) when the capillary is inserted in the exit port of a gas chromatograph equipped with a 1/8" packed column. A negligible flow rate reduction (4%) takes place when a 0.25-mm tube is used for trapping from a support coated open tubular (SCOT) column. These data are important because column resolution is adversely affected by an increase in pressure drop.

An alternative technique of loading small bore capillaries was found to be convenient. When a 0.5-mm bore capillary employed for GLC trapping contains too small a volume of sample for the focused laser beam, the capillary is removed from the gas chromatograph, one end sealed by means of a micro-torch and the material centrifuged down to the closed end. A 0.25 or 0.1-mm bore capillary is then "threaded" into the 0.5-mm capillary and capillary action effects the transfer. Sample quantities of 60 nl and 8 nl occupy a 1-mm long section of 0.25 and 0.1-mm bore capillaries, respectively.

Fig. 7 compares partial spectra of 8 nl (lower curve) and 800 nl (upper curve) linalool samples contained in 0.1 and 1.0-mm bore capillaries. It was necessary to increase the amplification of the former by a factor of 10 to normalize the two curves. The scattering paths of the two samples differ by a factor of 10 which reduces the Raman intensity by this value, but this can be offset by an equivalent increase in amplification. Another way of accomplishing this effect is to increase the signal by employing an Ar$^+$ laser instead of a He-Ne laser.

Fig. 8 shows a spectrum of CCl_4 at a volume of 8 nl excited by He-Ne 6328A laser. Note particularly the virtual absence of the 459 cm^{-1} line when the analyzer was rotated through 90°; the depolarization ratio is 0.007.

That this transverse/transverse capillary technique can be applied equally to solids and liquids is demonstrated in Fig. 9. Here, about 0.1 mg of benzoic acid was isolated by GLC in a 0.5-mm bore capillary. By alternate heating and cooling of the material, it was compacted into a rod about 1-2 mm long within the capillary.
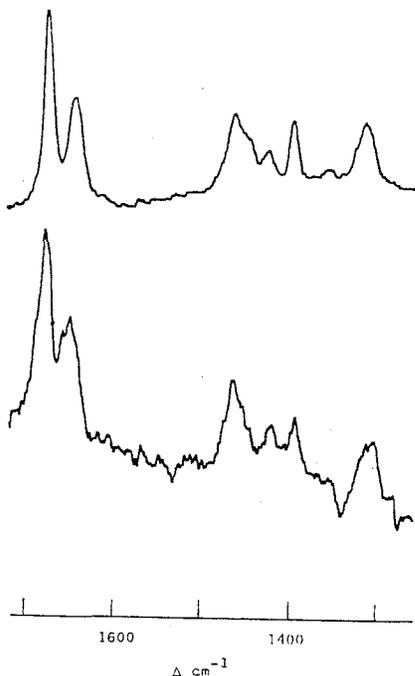
Fig. 7   Comparison between spectra of 800 nl of linalool (upper curve) with 8 nl of the same material (lower curve).
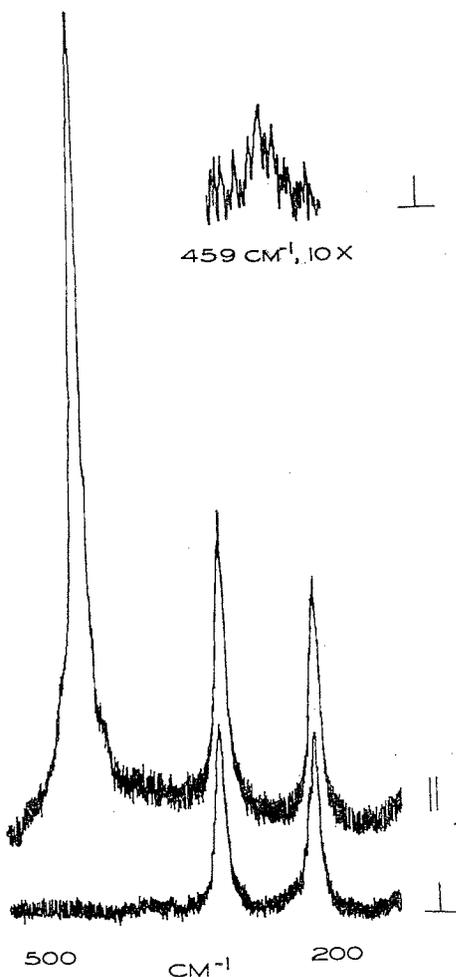
In summary, we have found the following advantages for the transverse/transverse capillary technique:

1) Although a decrease in signal level proportional to tube bore occurs, interpretable spectra on as little as 8 nl can be obtained in capillaries of 0.1-mm bore. This value is significantly below the lowest previously reported volume of 30 nl of CCl_4 (2).

2) Excellent depolarization values are attained readily on 8 nl quantities.

3) Loading and aligning of the samples are accomplished quite easily.

4) Since the sample can be isolated in the center of a comparatively long tube, its ends can be sealed without overheating the sample.

5) Fluorescence of the glass, while noticeable, does not interfere as much as it does in the axial/transverse techniques.

6) Solids can be run as conveniently as liquids with samples as small as 0.1 mg.

7) Once sealed, samples may be retained indefinitely and a "library" built up. Of course, photosensitive samples must be protected from light.

8) Capillaries are relatively inexpensive, require no preparation, and are surprisingly rugged.

9) The technique is amenable to multipassing with a resulting two-fold enhancement of signal level. Signal intensities at least twice as great as those obtained from the axial/transverse techniques are attained routinely.

10) Air-sensitive samples may be loaded in an inert atmosphere glove box.

So satisfactory has the transverse/transverse capillary technique become that in both our laboratories virtually all samples are now run in this manner.

EARLY in our experiments we found that fluorescence of the various glasses available in capillary forms gave some interference with Raman spectra. The amount of such fluorescence is dependent on the length of the laser beam path through the glass. This distance is relatively small with standard Kimax 1-mm melting point capillaries and, fortunately, these glass tubes showed less fluorescence than that from any of the limited number of silica glasses we have examined so far. Fused silica is entirely free of objectionable fluorescence and emits a relatively weak Raman spectrum; however, fused silica capillaries require inconveniently high sealing temperatures and are considerably more expensive.

459 CM⁻¹, 10X

Fig. 8   Depolarization of the 459 cm⁻¹ line of CCl_4 is so complete that it takes a 10X amplification to measure the line in the perpendicular plane.
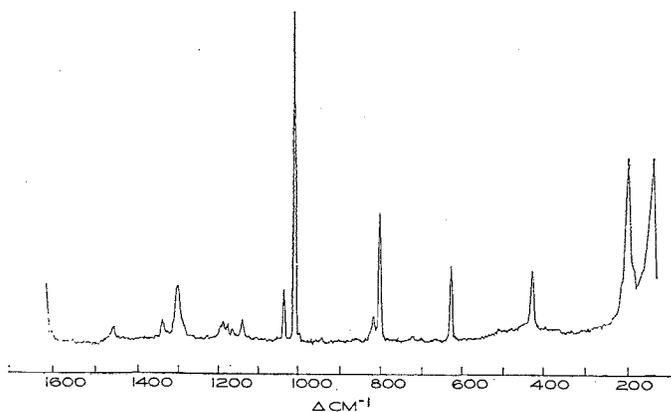

Fig. 9   That the Pez capillary technique is equally at home with solids is shown for a sample of 0.1 mg of benzoic acid GLC trapped in a 0.5-mm bore capillary.
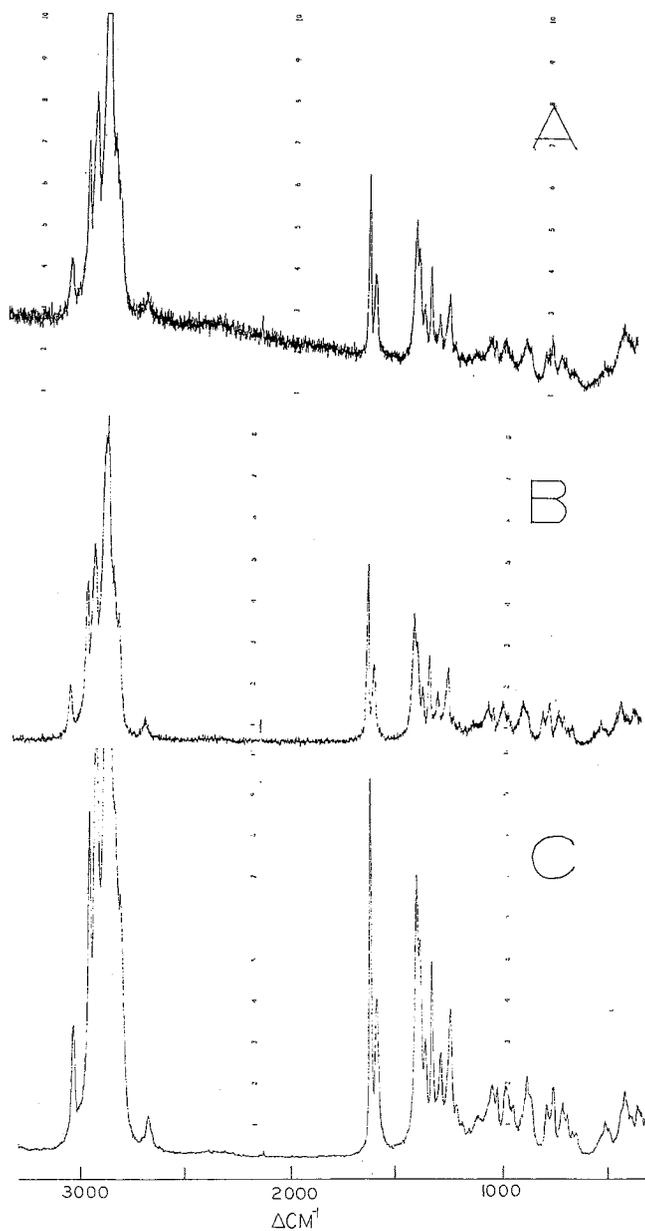
Fig. 10 Fluorescence of the container is eliminated when the material is switched from borosilicate (A) to Lindeman glass (B). Curve (C) shows how the noise in the spectrum can be quieted by boosting laser power six-fold, from 100 mW in the upper curves to 600 mW.

When the o.d. of the capillary is kept constant while the bore is reduced, the observed interference arising from the laser beam's interaction with the glass worsens. This fluorescence effect, while annoying, was insignificant compared to another problem which faced us: linalool was vaporized in a 0.25-mm bore capillary during the course of recording its spectrum utilizing 600 mW of Ar⁺ 4880A excitation. Since no optical mechanism exists whereby linalool can absorb significant amounts of such energy, regardless of power density (a 1-cm path length of linalool shows no absorbance of 4880A radiation), glass absorption of the laser energy was implicated. Illumination of bulk samples of ordinary glasses with the Ar⁺ laser beam enabled us to observe a red halation around the path of the blue laser beam. No such phenomenon occurred in fused silica.

Correlating these visual observations with the spectral measurements, we reasoned that the mechanism of fluorescence in glass was inefficient, and that some of the input laser energy appeared as heat. If this indeed were the case, heating should not occur in fused silica capillaries or in other non-fluorescing glasses. To confirm this hypothesis, samples of linalool were placed in fused silica capillaries and in x-ray diffraction capillaries (both 0.25-mm bore) made from Lindeman glass (lithium borax). Spectra were obtained from the most powerful source then at our disposal, 600 mW at 4880A. In these capillaries, lack of fluorescence went hand in hand with lack of heating to prove to our satisfaction that sample heating was indeed a secondary effect probably due to fluorescence of the borosilicate glass in the infrared as well as the visible. A comparison between borosilicate and Lindeman glass fluorescence is illustrated in Fig. 10. This figure also illustrates how the slightly noisy background observed in the spectrum of linalool at 100 mW excitation is almost entirely eliminated when the power is boosted to 600 mW. In other words the advantage of working with a non-fluorescing glass is threefold: disturbing background is removed, any effects of local heating of the sample are minimized, and greatly increased power may be pumped into the sample to optimize signal-to-noise.

Since the handling of samples even smaller than those reported in this study would necessitate additional laser power; since the higher power densities thus produced would be more likely to result in sample heating; and since the means for dissipating the heat would be poorer the smaller the sample, there must obviously be some reasonable lower limit to Raman sample size with condensed materials. To extend this lower limit, Raman spectroscopy of materials in the vapor phase appears to be an attractive approach. Future work will be directed toward this end as well as toward getting better glasses for conveniently fabricating Raman sample cells. We are certain that the axial/transverse technique of Bailey, Kint, and Scherer, and the transverse/transverse technique of Pez will both benefit by the substitution of glasses which absorb less energy from the laser beam.

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IF YOU DO NOT YET OWN A RAMALOG

About to embark on our fourth year of manufacturing high-speed, low-scattered-light double spectrometers which, along with the latest laser prodigies, have provided latter-day pioneers in Raman Spectroscopy with the signal/noise it takes to keep the frontier on the move, we have a couple of suggestions we hope you will find helpful:
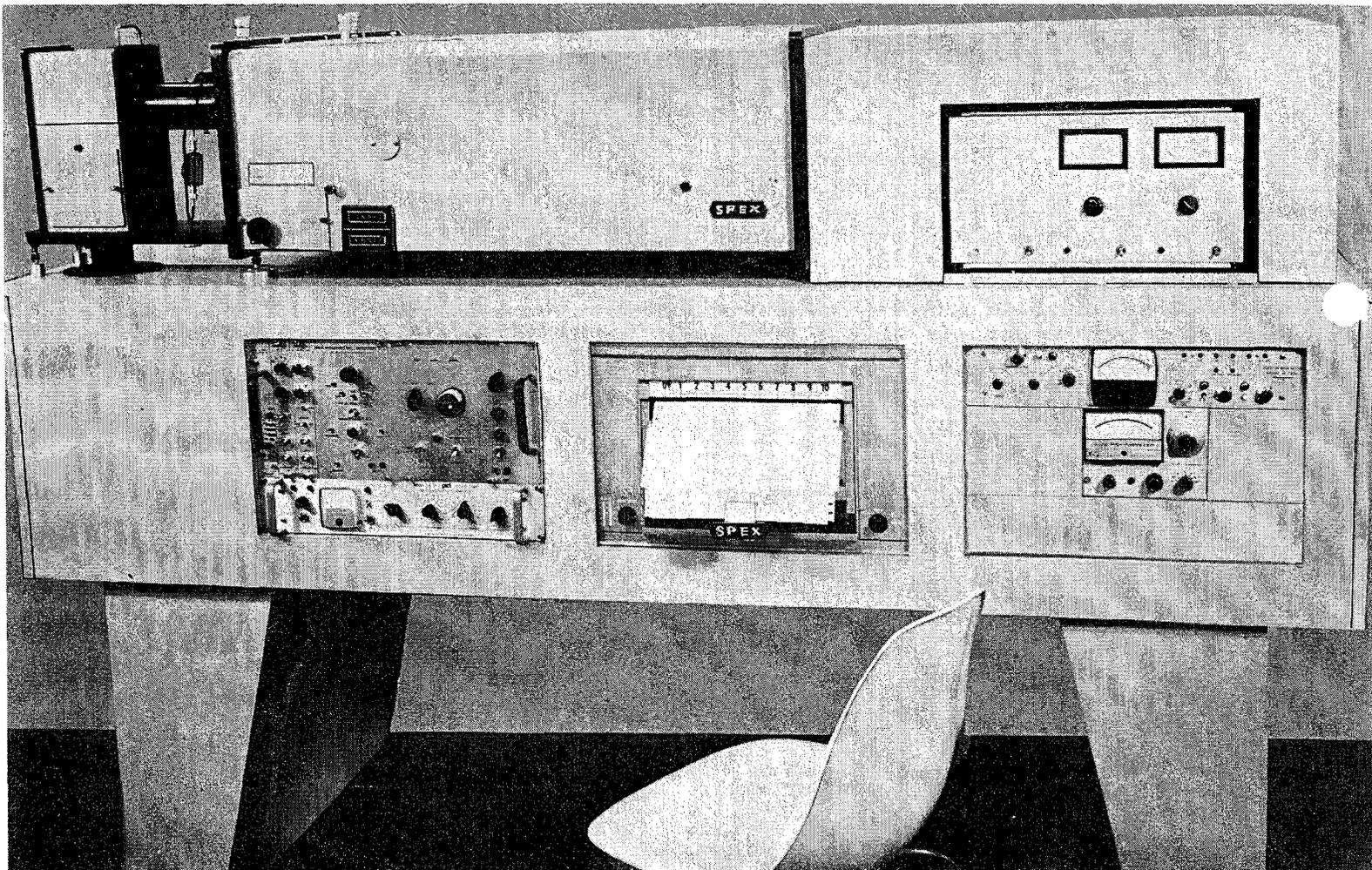
1) BUY A RAMALOG

An oddball in today's spiralling economy, Raman instruments are benefitting from the fall of laser prices, coincidentally paralleling their improvement in spectral (red, yellow, green and blue) output, power level and stability. Today's systems may surprise you with their new-found economy, versatility and (if you have not yet read this issue's article) applicability to daily bread and butter samples. If this raises a question or two, we have sales and laboratory people ready to work hard at getting you the answers.

2) TRY OUR RAMAN LABORATORY SERVICE

We believe we are alone in the world in offering Raman analyses on a commercial basis. That makes it easy to be tops in the field, of course, but despite the lack of a challenger, we envision ours to be a deluxe-class service. Our lab is equipped with the latest model Ramalog including He-Ne and Ar+/Kr+ lasers. Pps. 1-7 herein abound with exemplary data.

Supervising the work is our own Ramalogs newsletter editor, J. R. Allkins, who came to us via London University, England and two years of post-doctoral research under E. R. Lippincott at The University of Maryland. Not surprisingly he has a slew of techniques already worked out for solids, liquids and gases but being of an inquiring nature he might even welcome the rare problem sample and come up with a new convenient method.

For those of you with a sample volume that doesn't yet justify setting up a Raman laboratory we have established a price schedule, necessarily based on the time consumed for each analysis. For $30.00/hour with a minimum charge of $90.00 we will provide a spectral tracing and report, complete with the exception of interpretation.