

Speaker

SPEX DOUBLE SPECTROMETER — PROGRESS REPORT #2

TOGETHER with each spectrometer we pack an inspection report filled with key data to satisfy us that the instrument met specifications when it left the factory and assure the customer that it will once again meet those specs after our serviceman finishes correcting the abuses of the shipping interests. Specifications are not easy to arrive at or meet; yet progress and competition force a constant tightening of tolerances. We'd like to give you some insight into that part of our operations aimed simply at making each new instrument better than the one released prior to it.

A good place to start is with wavelength accuracy and precision (Fig. 1). Each of our 3/4-meter instruments—the evacuable and non-evacuatable single spectrometers, the double spectrometer and the spectrograph—bears the same deceptively trivial guarantee normalized to a 1200 groove/mm grating in the first order:

Wavelength accuracy	$\pm 1\text{A}$ over 6000A
Wavelength resettability	$\pm 0.3\text{A}$

Put in a more familiar setting, this is like measuring a mile straightaway to within a foot and duplicating such readings within a few inches. To achieve this degree of reliability in an optical spectrometer requires a leadscrew finished within a hairsbreadth of those controlling the finest grating-ruling engine. The leadscrew must be straight and round, its grooves evenly spaced, of uniform diameter and positionally exact; it must rotate on its concentric shoulders with a minimum of end-play; it must turn in coaxially-aligned, truly circular bearings that barely clear the leadscrew shoulders. All mechanical linkages must be loose enough to turn or slide yet tight enough so there is no play between them—a feat not unlike that of the irresistible force meeting an impenetrable wall. Add one more intrepid likelihood—mechanical creepage of metal due to buildup of internal stresses during machining—and you will have some idea why Michelson suggested, early in the century, that it was easy to construct a ruling engine. All one had to do was to think of each of the components as being made of rubber! To not much less degree does this advice apply to the drive mechanism of a precision spectrometer.

Constantly alert to that admonishment, we have been able to construct spectrometers which usually meet our stringent wavelength requirements with a healthy margin of safety to spare. Table 1, data from a Model 1400-II double spectrometer, recently delivered, is typical of wavelength figures actually attained. The $\pm 1\text{A}$ error is confined over more than twice the specified wavelength interval.

On the same instrument, the standard deviation of eleven measurements of resettability of the mercury green line was calculated as $\pm 0.13\text{A}$. Maximum deviation was $\pm 0.15\text{A}$.

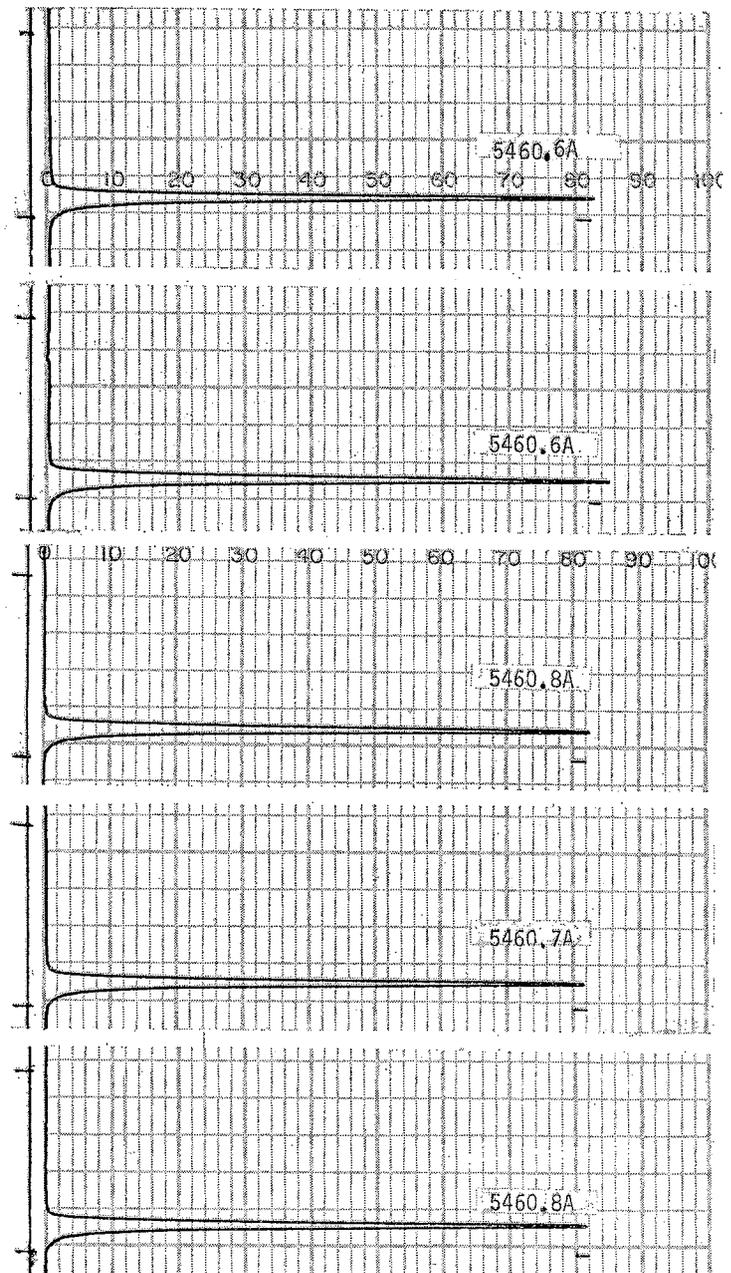


Figure 1: Wavelength reproducibility can be measured in two ways: by reading the vernier on the counter and by interpolating between the fiducial spikes made by the event marker at 5A intervals.

WAVELENGTH ACCURACY

Wavelength Data			
WL, A	Reading, A	Error, A	Tracking
2536.5	2536.8	+0.3	ok
4358.37	4358.3	0	ok
5460.75	5460.5	-0.2	ok
8716.70 (4358 II)	8715.6	-1.1	
10921.48 (5460 II)	10922.1	+0.7	
13074.9 (4358 III)	13075.8	+0.9	

TABLE 1: This data is taken from one of the inspection reports furnished with each spectrometer. Over a span of 10,500A the total wavelength runout is $\pm 0.6A$. Specification is $\pm 1A$ over 6000A.

/i & A

New precision tools in our shop have contributed to this progressive upgrading of performance. Especially responsible is a numerically-controlled hybrid milling machine and drill press installed about six months ago. Directed by typewriter punched paper tape, this Cincinnati Milling Machine Acracenter routinely turns out work with a positional accuracy of a few tenths (in shop jargon, a tenth is 0.0001"). Never losing its patience, never daydreaming, never dragging its feet in fatigue—never erring—the computerized machine drills, reams, taps, and counterbores a Swiss cheese of holes and mills dozens of slots in our spectrometer parts. Piloted by a top-notch, experienced machinist, it speedily turns out parts that are more alike from one to the next than he could hope to accomplish manually, given unlimited time.

ALTHOUGH quality of gratings has improved strikingly and steadily, individual differences between them will often contribute to someone's panacea and another's poison. In astronomy, for example, a ghost line is rarely meddlesome. Lines are so weak to begin with that the persevering astronomer finds it hard enough to see parent lines let alone offspring. Similarly, resolution is not of major concern to the astronomer whose studies are usually limited by the coarse grains in high speed photographic emulsions. He willingly accepts a few ghosts—even intense ones—and a loss of resolution in trade for his paramount objective, high efficiency. On the other hand, the Raman spectroscopist struggles to minimize instrumental stray light and to gather every last vestige of the feeble molecular scatter evoked by an intense beam of light. Since gratings establish the lower scatter limit in a spectrometer, they must have the lowest possible scattered light and ghost intensities to avoid interference with Raman lines.

Examining scattered light and ghost intensity data for gratings applicable to laser-Raman spectroscopy with our Model 1400-II Double Spectrometer often reveals its most valuable attributes. Fig. 2a and 2b are curves of a 600 groove/mm grating blazed at 1μ in the first and second orders. In Order 1 it is suitable for work with the YAG laser emitting at 1.06μ ; in Order II it is excellent with a He-Ne laser where in many respects it is the equal of a good 5000A blaze grating in Order I.

For similar dual application is a grating (Fig. 3a) compatible with Ar⁺ excitation at 4880A in the second order and with He-Ne 6328A in the first order.

The Fig. 3b curve is from a grating intended for third order work with a He-Ne laser. Dr. R. A. Gee of the University of Bradford, England, who requested it, realistically expects to achieve a resolution 1-1/2 times that of a 1200 groove/mm grating in the first order and at a saving of close to \$1000. for the grating pair.

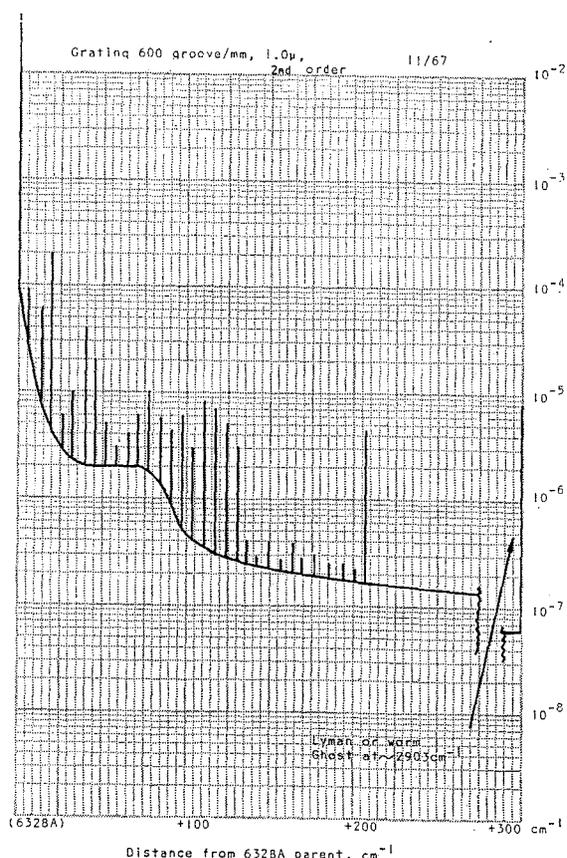
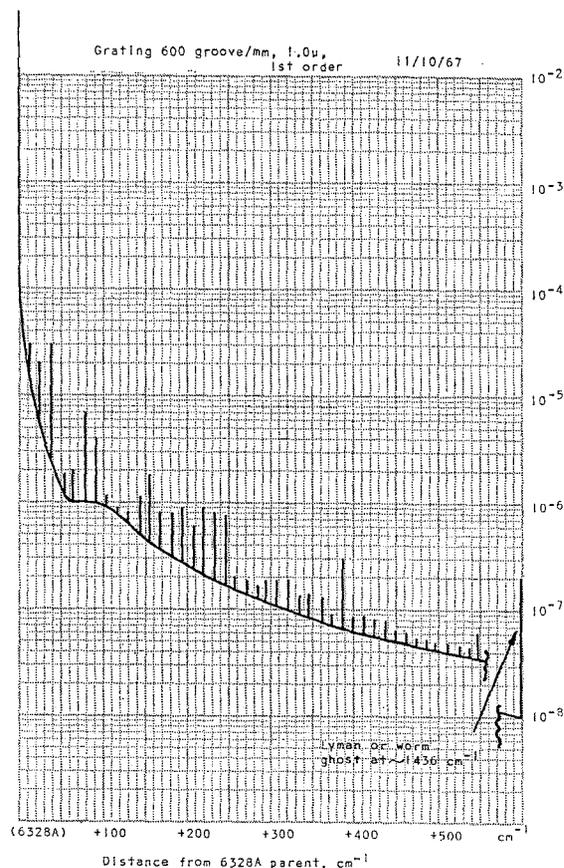
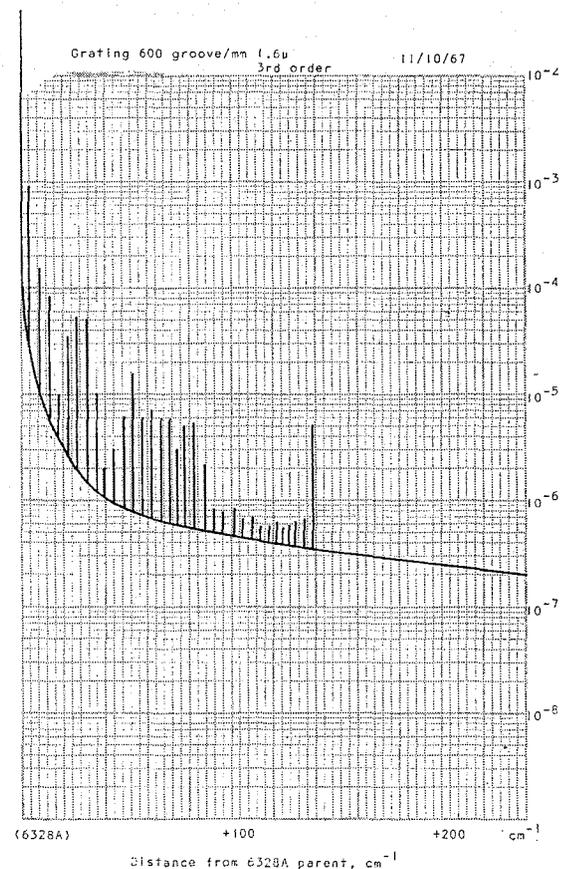
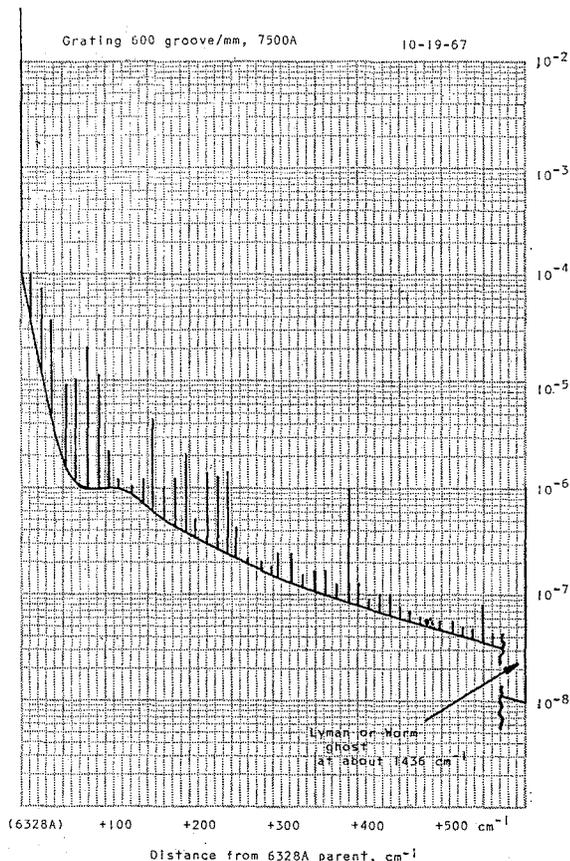


Figure 2: Scattered light and ghost intensity values are compared with the exciting laser line for a grating in Order 1 (top) and in Order 2 (bottom) with a 1700 (single) spectrometer.



GRATING PERFORMANCE AT 6328A

Grooves	Grating Blaze	Order	Efficiency, %		Relative Luminosity
			A	B	
600	7500A	1	65	68	26
600	1 μ	1	41	19	15
600	1 μ	2	32	64	15
600	1.6 μ	2	35	14	7
600	1.6 μ	3	43	60	50
600	1.6 μ	4	<1	<1	<0.01
1200	7500A	1	87	30	42
1200	5000A	1	55	84	60

TABLE 2: Data on gratings recommended for laser-Raman spectroscopy with a He-Ne laser. Of these, the 1200 groove/mm grating blazed at 5000A is most commonly specified because of its high luminosity over the entire 0-4000 cm^{-1} range of usual Raman interest. For a limited wavenumber range, the 600 groove/mm grating blazed at 1.6 microns set to the third order makes a good choice. At higher wavenumber shifts, however, it must be set to the second order. Efficiency A is with parallel polarization; B, perpendicular.

In an exacting, thorough presentation, R. L. Christiansen and R. J. Potter (1) have analyzed two distinct types of double spectrometers. To distinguish between these, one will be referred to as a **double** spectrometer, the other a **dual** spectrometer. Both employ a common system of driving two gratings through the same angular rotation so that the light is first dispersed by one grating and then the other. In the double spectrometer, there is also a lens effect: a reversal of image. The second dispersion is in the same direction as that of the first dispersion and double dispersion is achieved. In the dual spectrometer no such reversal occurs. Instead of double dispersion, spectral homogeneity results.

Mandelberg (2) proposed a dual spectrometer which, by rotating the two gratings one above the other (or preferably a non-existent single tall grating) on a common shaft, would exhibit a minimum tracking error. That is, the two gratings are more readily constrained in his design, now sold commercially, than in our side-to-side arrangement which requires a mechanical linkage like the front wheels of an auto.

Performance differences between the double and dual spectrometers are so marked that it would be well to show why. Exaggerated to emphasize the differences, the spectral results are portrayed in Fig. 4.

As pointed out by the Stokes (3) the advantages of double dispersion are real and significant. Luminosity can be increased by a factor of up to 2 for a given resolution; conversely, by retaining luminosity, resolution can be substantially improved. Fig. 5 demonstrates both; the fourth weak component of the CCl_4 459 cm^{-1} line is a good indicator of the resolution with the slits opened to 50/50/50 μ , even better resolved than for the 25/25 μ setting with the single spectrometer. In other words, for slits opened twice as wide the resolution of the double instrument is as good as or better than the single. The effect is underscored by opening the slits to 100/100 μ in the single where the 459 cm^{-1} isotope structure is completely unresolved. With the same settings note that its structure with 100/100/100 μ slits in the double instrument is still healthily resolved.

Explaining this is straightforward. Double dispersion means that for given slit widths the bandpass of the double instrument is one-half that for the single. All other things being equal, the resolution at 25/25 μ with the single spectrometer should therefore be equivalent to 50/50/50 μ in the double.

Figure 3: Scattered light and ghost intensities of these two gratings, again taken on a single spectrometer, must be squared for reference to the Double Spectrometer (1400) as used for Raman spectroscopy.

What happens when all three slits are set to the same bandpass is depicted in the 50/50/100 μ condition where the luminosity is roughly half of that in the 100/100/100 μ condition. It will be noted that the resolutions of the 459 cm^{-1} lines under the two conditions are essentially identical. By opening the first two slits to a condition of twice the bandpass, luminosity is doubled while resolution is maintained.

Perhaps paradoxically, it is interesting to note that when the absolute efficiency of a grating peaks above 70%, theoretical increase in luminosity offsets the combined reflectivity and diffraction losses and the luminosity actually increases. The blaze of modern gratings at their peak is often between 70 and 80%* so such gains are now realizable. More important from the standpoint of the researcher, an instrument with double dispersion yields twice the intensity for equivalent resolution as compared with a dual spectrometer in which the light is not doubly dispersed. The phenomenon is of particular concern beyond 0.9 μ where mirrors are 99% efficient and gratings often exhibit an absolute efficiency of 80% or greater. In the infrared weak signal levels are so frustratingly commonplace that one tends to distrust the reasoning and must be persuaded that simply doubling dispersion can improve luminosity. The reward appears as unlikely as getting anything else for nothing. But a measurement or two will convince the skeptic that he can reduce his slit widths to achieve better spectral detail than with a single spectrometer.

Admittedly, tracking of a double spectrometer is considerably harder to achieve than of a dual spectrometer. As pointed out by Landon (4) both systems, however, share the common problem of equalizing the focal lengths as well as the angles of incidence and diffraction of the two halves of the instruments. In the double spectrometer, linkages between the gratings have to be so designed and constructed that the gratings present identical angles to the incoming beams. Constant progress has been made in the Spex linkage system; our latest instruments track even at very narrow slit settings, much better than the specification of $\pm 0.1\text{\AA}$ over 5000 \AA .

A convenient way to check tracking is with an incandescent lamp source, scanning the spectrometer over 4000-9000 \AA , the region of concern to most laser-Raman investigators. The slits are first set to 20-20-200 μ and a tracing taken. As shown in Fig. 6a, a peak is reached at around 5000 \AA , the blaze wavelength; beyond 7200 \AA where the first scale change is made, the S-11 photomultiplier detects mostly second order spectra. In Fig. 6b, the tracing is repeated, this time with the exit slit cut down to 20 μ .

When tracking is perfect, the shapes of the two curves are identical, the 0.1 \AA -wide band of light passing with equal ease through each slit. Any mismatch on the other hand, would be evident by a drop in intensity in the 6b tracing as part of the image was obscured by a slit jaw. Small intensity differences may, in fact, be noted by superimposing the two tracings. This is, however, well within specifications. Failure of this test under such narrow band width conditions would involve a precipitous drop to zero intensity, the narrow beam missing the narrow exit slit target altogether.

Irrespective of the tracking test, what is accomplished by narrowing the three slits to 20 μ ? What happens if the intermediate slit is opened so the band of radiation it directs to

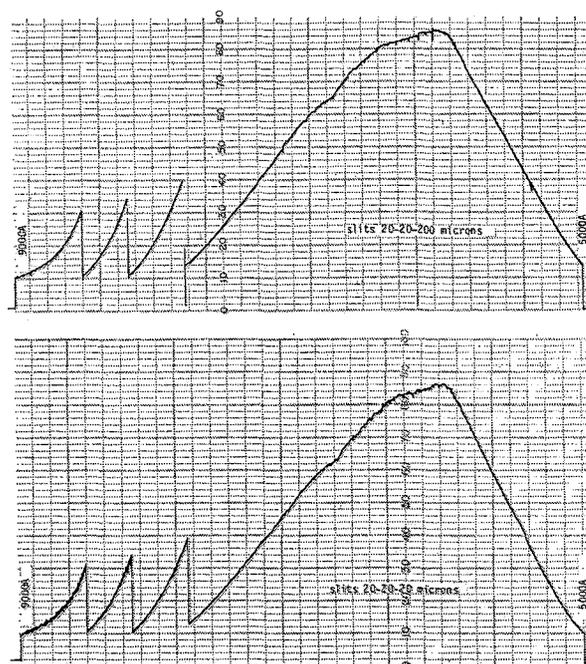


Figure 6: A tracing from 5000 \AA to 9000 \AA with an incandescent lamp source and slits set at 20/20/200 microns is repeated with slits set at 20/20/20 microns, demonstrating accurate tracking.

the final slit is considerably wider than that slit? Under such conditions, small angular shifts in beam direction will not appreciably change the intensity of radiation existing through the spectrometer. At the same time the exit slit can be narrowed down as far as necessary to establish the required resolution. As already explained in Fig. 4, light at the exit slit is dispersed (as contrasted with homogenized in a dual spectrometer) so that it is this slit rather than the intermediate slit which establishes resolution.

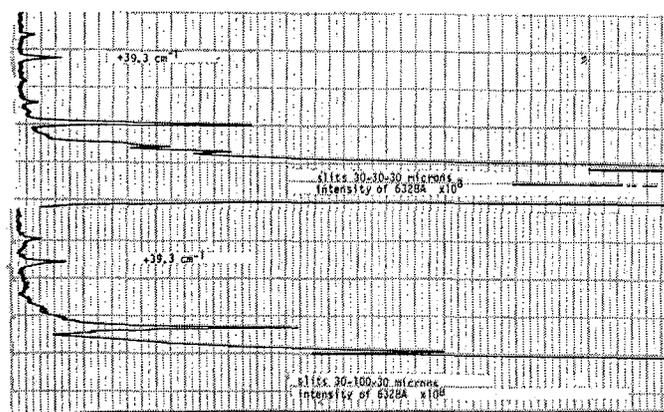


Figure 7: For (a) all three slits are set at 30 microns resulting in a bandpass at the final slit of about 0.38 cm^{-1} at 6328 \AA . In (b) the same bandpass is achieved since the final slit is still set at 30 microns. The intermediate slit is, however, opened to 100 microns. Note that the intensity of the background beyond the 39.3 cm^{-1} ghost is about equal under both conditions. Intensity of the ghost itself is about 7×10^{-10} of the exciting line. Closer to the exciting line the background and ghost intensities rise. For almost all work involving Raman shifts the two slit conditions produce exactly the same results. Incidentally, the sample was a disc of pressed graphite roughened to increase its scatter. Normally, these lines and scatter are undetected.

*Manufacturers specify blaze efficiency by comparison with the reflectivity of an aluminized surface at that wavelength. A furnished figure of 80% is thus equivalent to an absolute efficiency of around 74%.

An experiment was performed to ascertain what, if any, differences would occur in a typical Raman spectrum if the intermediate slit were opened. Fig. 7 shows the results close to the exciting 6328A line, the only place where any differences were observable. With a narrow intermediate slit, background scatter rises slightly out to about 25 cm^{-1} . Beyond that, in the region where Raman spectra are significant, the two spectra were indistinguishable. Incidentally, the tiny blip just beyond the 39.3 cm^{-1} ghost is a neon line originating in the laser discharge. Often employed as a calibration point, the line can be eliminated only by interposing a narrower bandpass filter in the entrance beam than the 20A one used here.

This work points up the fact that it is rarely, if ever, necessary to work with a narrow intermediate slit thus easing the demand for extreme tracking accuracy in a double spectrometer. Under practical laboratory conditions, where the temperature, barometric pressure and humidity can vary considerably, this becomes an important consideration in the choice of an instrument. By contrast, to attain high resolution in a dual spectrometer, the instrument must track perfectly because it is the intermediate slit which limits the resolution. This slit should be readily accessible for adjustment to permit the investigator to keep the dual instrument properly tuned.

Raman spectroscopists are still seeking a single substance to evaluate incontrovertibly the performance of a spectrometer for their work. Without wishing to enter the controversy we present, as a finale, spectra of ~~two~~ of the forerunners, the 992 cm^{-1} line of benzene (Fig. 8), the second order spectrum of sodium chloride (Fig. 9) and near scatter of cystine (Fig. 10). We are indebted to C. H. Perry and N. E. Tornberg of MIT and G. R. Wilkinson of King's College, London for the specimen of sodium chloride with which they challenged us at our display booth during the 22nd Molecular Structure and Spectroscopy Symposium held at Ohio State University last September. There, as skeptical frowns on faces of a dozen or so sidewalk supervisors gradually blossomed into satisfied

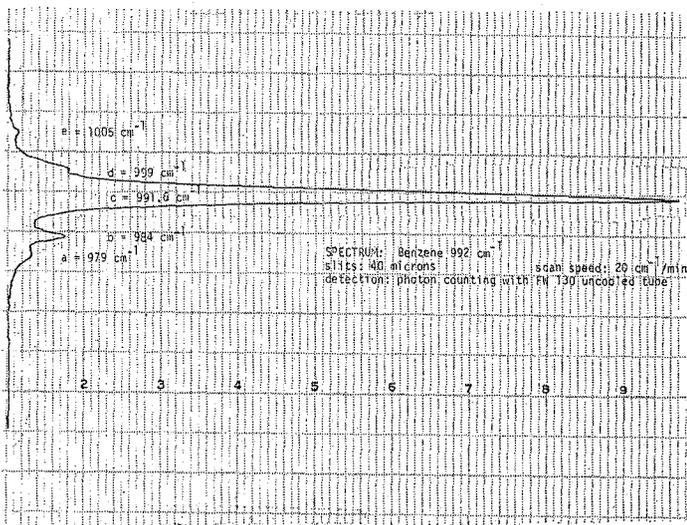


Figure 8: A test combining the resolution and scattered light performance of a spectrometer is provided by the benzene 992 cm^{-1} line. The tiny ledge on the high frequency side near the bottom of the peak is not often seen, requiring a bandpass no greater than 0.8 cm^{-1} . As pointed out by Stamm and Salzman (5) a resolution of better than 1 cm^{-1} cannot be attained for liquids in infrared absorption "because the half-widths of infrared bands are generally greater than those of Raman lines." In certain investigations, this fact may be advantageous, particularly in studying the $\text{C}=\text{C}$ region.

smiles, within about 20 minutes the spectrum below unrolled from the make-shift laser-spectrometer arrangement set up for the exhibit. We later found out why, when Dr. Wilkinson returned with a similar spectrum taken by H. L. Welsh in 1949. That exposure was 48 hours with a Hg arc followed, of course, by an additional half hour of densitometry.

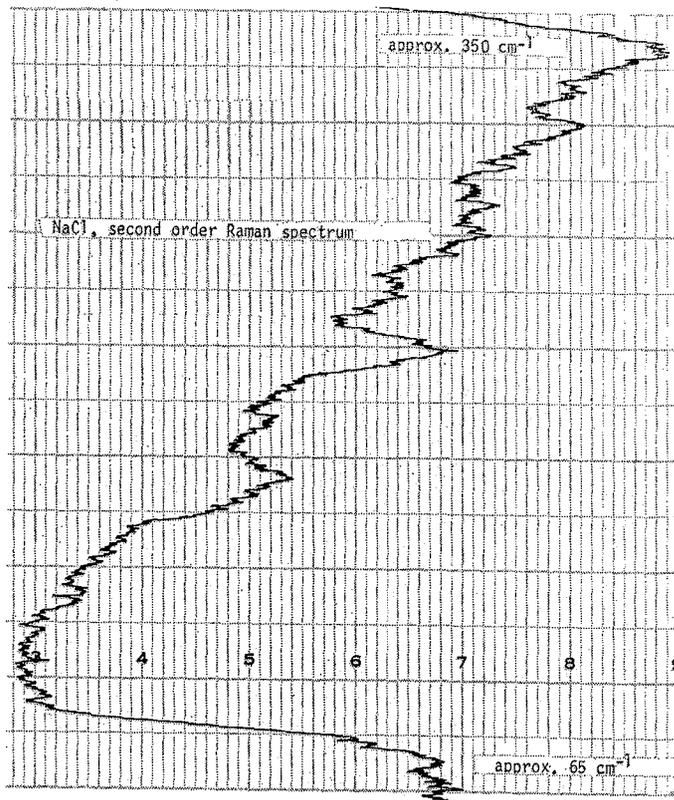


Figure 9: Second Order Raman spectrum of a NaCl crystal approximately 1 cm on edge.

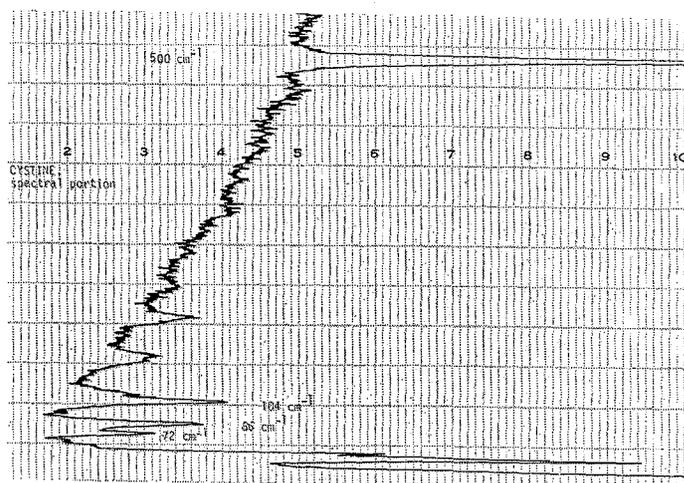


Figure 10: Portion of a Cystine spectrum. Wave numbers given are approximate.

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1. R. L. Christiansen and R. J. Potter, *Appl. Optics*, **2**, 1049, 1963.
2. H. I. Mandelberg, *Appl. Optics*, **5**, 674, 1966.
3. G. W. Stroke and H. H. Stroke, *J. Opt. Soc. Am.*, **53**, 333, 1963.
4. D. O. Landon, *Appl. Optics*, **6**, 346, 1967.
5. R. F. Stamm, C. F. Salzman, Jr., *J. Opt. Soc. Am.*, **43**, 135, 1953.

IT'S NOT

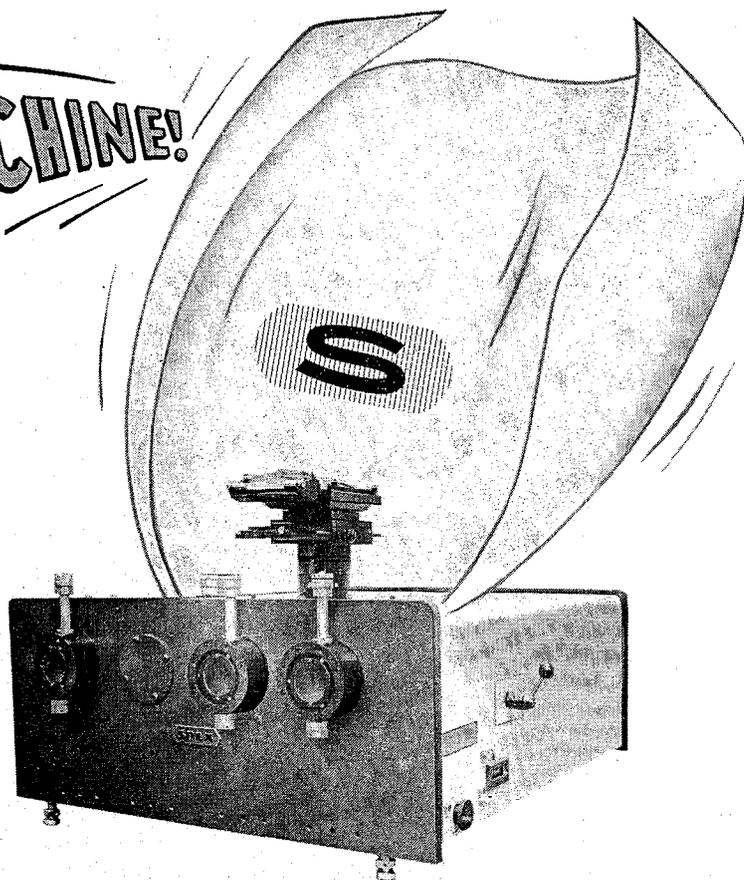
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It's not an all purpose spectrometer that every lab cannot be without...

It's not even the ultimate version of a Raman spectrometer beyond any possible improvements...



It is a relatively new instrumental development (first marketed early in 1966).

It is an instrument that chemists and molecular spectroscopists are fast discovering in neighboring physics labs and adopting for their own.

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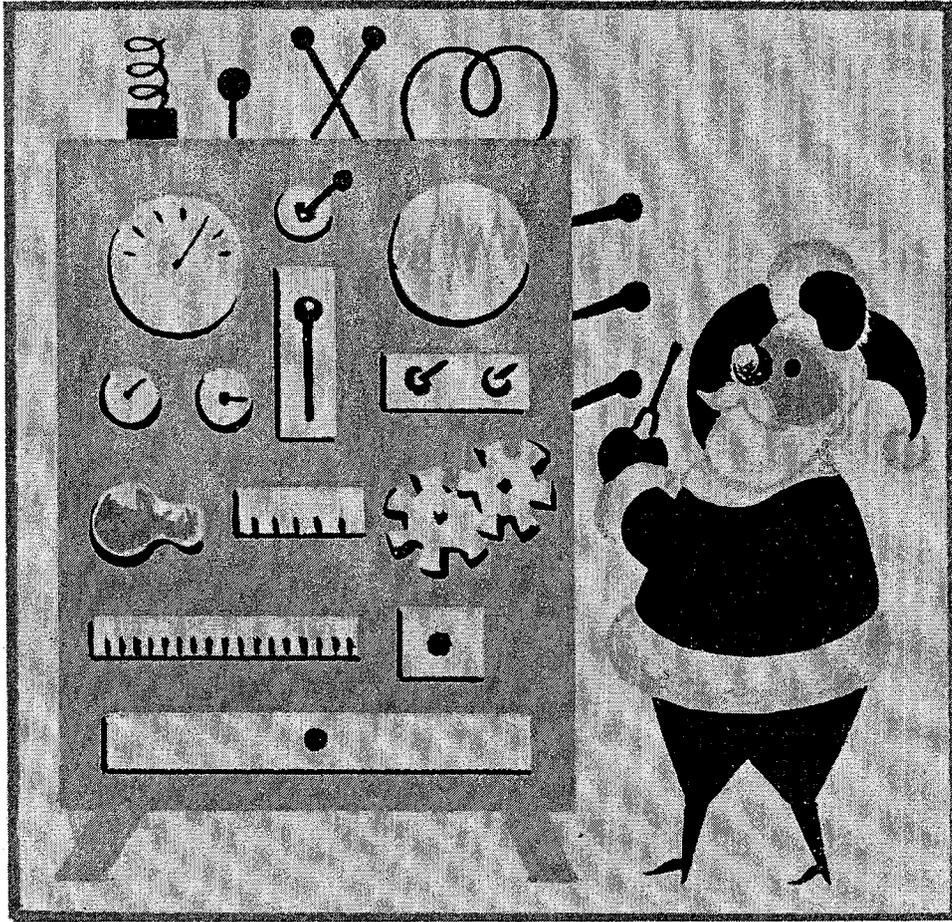
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